

Department of Chemical Engineering
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**SIMULTANEOUS EXTRACTION OF
HYDROCARBONS AND HEAVY METALS
FROM CONTAMINATED SOILS**

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To my wife, Tess, and my parents
With all my love

Xu Han

ABSTRACT

Soil Washing is a promising alternative treatment method for contaminated site remediation. An industry contaminated site – the OMEX site was selected for the study, and several extraction additives (chelating agent and surfactant) were used to investigate the application of soil washing for the removal of heavy metals and hydrocarbons. The interactions and transport of the contaminants were studied by bench-scale experiments for both heavy metals and hydrocarbons. Soil characterization was performed before the experiments.

The soil characterization indicated that the OMEX soil contained large amounts of Pb, Zn (heavy metal) and total petroleum hydrocarbons (TPH). The contaminant concentrations were 986 mg/kg of Pb, 284 mg/kg of Zn, and 29000 mg/kg of TPH. The contaminated soil was also high in moisture content, organic content and total organic carbon (TOC). From soil analyses on different particle size fractions, most contaminants were concentrated in the fine soil fraction, below 150 μ m, which constituted about 35% by weight of the contaminated soil.

Heavy metal removal by chelating agents was conducted first. The results showed that 3% EDTA solution offered the highest removal efficiency for both Pb and Zn. About 90% of Pb and 65% of Zn were removed by using 3% EDTA solution for 29 hours. The extraction kinetics proved to be slow, reaching equilibrium in a relatively long time (more than 10 hours). In soil washing the solution pH had some effect on the removal of both Pb and Zn, with marginally better removals observed at a lower pH. The experimental study indicated that the ratio of washing solution volume to soil weight (L/S) had little effect on the percentage removal of both Pb and Zn.

In hydrocarbons removal tests, experiments verified that surfactant solutions can be effective in removing organics from coarse soil fraction, while some amount of surfactants were adsorbed by fine soil particles. Anionic

surfactants such as SDS exhibited less sorption capacity than nonionic surfactants due to the electrostatic repulsion of the former. 4% SDS solution had the highest TPH removal efficiency for OMEX soil, but the 2% SDS solution was used as it produced only marginally lower results than the 4%. The percentage removal of TPH was about 78% by using 2% SDS solution. The TPH removal by SDS solution was observed to be a slow and non-equilibrium process. Higher solution temperature can improve removal efficiency of TPH from OMEX soil. Combined washing with a chelating agent and a surfactant was effective in removing both heavy metals and hydrocarbons. Removals of 78% Pb, 82% Zn and 81% TPH were obtained from OMEX soil in the combination test. However, the TPH concentration in fine soil was still very high after washing and would need further treatment.

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NOTATION

AAS	=	Atomic absorption spectroscopy
CEC	=	Cation exchange capacity
CMC	=	Critical micelle concentration
DEP	=	Department of Environmental Protection
EDTA	=	Ethylenediaminetetraacetic acid
GC	=	Gas chromatography
HOC	=	Hydrophobic organic compound
K_{oc}	=	Carbon normalized sorption coefficient
K_{ow}	=	Octanol – water partition coefficient
K_p	=	Partition coefficient
L/S	=	Liquid to solid ratio
MSWS	=	Mobile soil washing system
NTA	=	Nitrilotriacetic acid
NAPL	=	Nonaqueous phase liquid
PAH	=	Polycyclic aromatic hydrocarbon
SDS	=	Sodium dodecyl sulfate
S/S	=	Solidification/stabilization
SVE	=	Soil vapour extraction
SVOC	=	Semi-volatile organic compound
TCE	=	Trichloroethylene
TOC	=	Total organic carbon
TPH	=	Total petroleum hydrocarbon
USEPA	=	United State Environmental Protection Agency
VOC	=	volatile organic compound
VRU	=	Volume reduction unit
θ_{ww}	=	Moisture content

CHAPTER ONE

INTRODUCTION

1.1 SOIL CONTAMINATION

1.1.1 Source of Contamination

Soil Contamination can be defined as the introduction of hazardous foreign materials into the ground by human activities such as accidental spills of chemicals or waste materials, leakage of septic tank or buried storage tanks, improper injection of liquid wastes, unmanaged dump sites, land application of agricultural pesticides, operation of municipal landfills and industrial or residential disposal. Soil contamination produced by these various human activities is one of the most serious problems occurring in industrial countries because it can be directly related to the contamination of local groundwater, which is often the source of drinking water. Soil contamination can affect groundwater quality and cause long term environmental and health damage unless it is detected and treated properly (Fetter 1993).

1.1.2 Types of Contamination

The types of soil contaminants include organic compounds, inorganic compounds, pathogens, and radioactive materials. Organic compounds are those carbon-containing compounds such as aromatic hydrocarbons (benzene, toluene, ethylbenzene, xylene, aniline, nitrobenzene); oxygenated hydrocarbons (phenol, 2-naphol, acetone); and hydrocarbons with specific elements such as N, P, S, Cl, Br, I, F (quinoline, chloroform). Inorganic

compounds are obtained from mineral sources such as arsenic, nitrate, and copper. Pathogens are microorganisms such as bacteria or fungi, that have the capacity to cause diseases under normal conditions. Radioactive materials such as radium, radon, or uranium are unstable atoms that undergo spontaneous decay, releasing ionizing radiation. Over exposure to the ionizing radiation can cause acute adverse health effects (Stevenson 1991).

In this dissertation, only organic compounds and inorganic compounds will be considered as targets for treatment for soil contamination because they are the most common health-threatening materials detected in soil in Western Australia.

Generally, when a soil contaminant is first introduced into the soil, it will infiltrate downward through the vadose zone by gravity, encounter the water table, move along with the groundwater flow, migrate by a physico-chemical transport process, and eventually form a contaminant plume in the groundwater. Once the plume has developed, and contaminant transport becomes a time-dependent process, it is very difficult to restore the groundwater to a specified water quality standard. An effective strategy is to clean up sites before significant ground water contamination can occur (Mackay 1989).

1.2 SOIL REMEDIATION TECHNOLOGIES

Soil contaminants can be adsorbed into the soil matrix as they migrate with pore fluid flow and are deposited at the soil-water interface, depending upon the specific physico-chemical properties of the contaminants and the soil (O'Neill 1993). Deposition of a soil contaminant in the soil matrix frequently causes the degradation of the groundwater quality and can eventually be associated with adverse health, social, environmental and economic impacts.

There are two broad categories of the cleanup process: The first is source control; if there is an ongoing source of contamination, the source should be controlled immediately to prevent any further spread before any soil remediation is attempted. The second part of the cleanup process is applying remediation techniques to remove the contamination.

1.2.1 Source Control

In most of the cases, physical removal of the contamination source should be done first to prevent further contamination. This includes enacting the related legislation against the illegal disposal of hazardous waste. Effective source controls are cutoff and repair of leakage from infrastructure elements such as septic tanks, buried pipes, and underground storage tanks; excavation of the contaminated soil and transportation to a safe landfill or treatment plant; construction of barriers such as slurry walls, grout curtains, clay liners or sheet piles to contain the leachate or groundwater plume, thus isolating the source of the contamination; coverage over the contaminated area to prevent the infiltration of hazardous waste; diverting groundwater flow away from the contaminated region by hydraulic controls. These source controls can effectively prevent any further increase of the contamination concentration of the soil and serve as the starting point for the remediation process of the contaminated area.

1.2.2 Remediation Techniques

Once the contamination source is successfully controlled, the second part of the cleanup process is to remediate the contamination plume to remove or reduce the concentration of the contaminants. Various methods of remediating contaminated soil by implementing various types of remediation techniques are available. Three primary strategies used separately or in conjunction to remediate most sites are:

- ◆ Destruction or alteration of contaminants;
- ◆ Extraction or separation of contaminants from environmental media;

◆ Immobilization of contaminants.

Several techniques are discussed briefly here.

1.2.2.1 Biodegradation

Biodegradation technique can be used for both in-situ and ex-situ. It is a process in which indigenous or inoculated microorganisms (i.e., fungi, bacteria, and other microbes) degrade (metabolize) organic contaminants found in soil and/or groundwater. In the presence of sufficient oxygen (aerobic conditions), microorganisms will ultimately convert many organic contaminants to carbon dioxide, water and microbial cell mass. In the absence of oxygen (anaerobic conditions), the contaminants will be ultimately metabolized to methane, limited amount of carbon dioxide, and trace amounts of hydrogen gas. Sometimes contaminants may be degraded to intermediate products that may be less, equally or more hazardous than the original contaminant. For example, trichloroethylene (TCE) anaerobically biodegrades to the persistent and more toxic vinyl chloride. To avoid such problems, most biodegradation projects are conducted in-situ.

The in-situ bioremediation of soil typically involves the percolation or injection of groundwater or uncontaminated water mixed with nutrients and saturated with dissolved oxygen. Sometimes acclimatized microorganisms and/or other oxygen source such as hydrogen peroxide are also added. An infiltration gallery or spray irrigation is typically used for deep contaminated soils.

1.2.2.2 Soil Flushing

In-situ soil flushing is the extraction of contaminants from the soil with water or other suitable aqueous solutions. Soil flushing is accomplished by passing the extraction fluid through in-place soils using an injection or

infiltration process. Extraction fluids must be recovered from the underlying aquifer and, when possible, they are recycled.

Recovered groundwater and flushing fluids with the desorbed contaminants may need treatment to meet appropriate discharge standards prior to recycle or release to local, publicly owned wastewater treatment works or receiving streams. To the maximum extent practical, recovered fluids should be reused in the flushing process. The separation of surfactants from recovered flushing fluid, for reuse in the process, is a major factor in the cost of soil flushing. Treatment of the recovered fluids results in process sludges and residual solids, such as spent carbon and spent ion exchange resin, which must be appropriately treated before disposal. Air emissions of volatile contaminants from recovered flushing fluids should be collected and treated, as appropriate, to meet applicable regulatory standards. Residual flushing additives in the soil may be a concern and should be evaluated on a site-specific basis (USEPA 1994).

1.2.2.3 Soil Vapour Extraction

Soil vapour extraction (SVE) is an in-situ unsaturated (vadose) zone soil remediation technology in which a vacuum is applied to the soil to induce the controlled flow of air and remove volatile and some semivolatile contaminants from the soil. The gas leaving the soil may be treated to recover or destroy the contaminants, depending on local and state air discharge regulations. Vertical extraction vents are typically used at depths of 1.5 meters or greater and have been successfully applied as deep as 91 meters. Horizontal extraction vents (installed in trenches or horizontal borings) can be used as warranted by contaminant zone geometry, drill rig access, or other site-specific factors.

Groundwater depression pumps may be used to reduce groundwater upwelling induced by the vacuum or to increase the depth of the vadose zone. Air injection is effective for facilitating extraction of deep contamination, contamination in low permeability soils, and contamination in

the saturated zone. In addition, steam/hot-air injection or electric/radio frequency heating can be used to increase the mobility of semivolatiles and facilitate extraction (USEPA, 1994).

1.2.2.4 Solidification/Stabilization

Solidification/stabilization (S/S) reduces the mobility of hazardous substances and contaminants in the environment through both physical and chemical means. Unlike other remedial technologies, S/S seeks to trap or immobilize contaminants within their "host" medium (i.e., the soil, sand, and/or building materials that contain them), instead of removing them through chemical or physical treatment. Leachability testing is typically performed to measure the immobilization of contaminants. In-situ S/S techniques use auger/caisson systems and injector head systems to apply S/S agents to in-situ soils.

S/S techniques can be used alone or combined with other treatment and disposal methods to yield a product of material suitable for land disposal or, in other cases, that can be applied to beneficial use. These techniques have been used as both final and interim remedial measures (USEPA, 1994).

1.2.2.5 Vitrification

In-situ vitrification (ISV) uses an electric current to melt soil or other earthen materials at extremely high temperatures (1,600 to 2,000°C) and thereby immobilize most inorganics and destroy organic pollutants by pyrolysis. Inorganic pollutants are incorporated within the vitrified glass and crystalline mass. Water vapour and organic pyrolysis combustion products are captured in a hood, which draws the contaminants into off-gas treatment system that removes particulates and other pollutants from the gas (USEPA, 1994).

1.2.2.6 Soil Washing

Soil washing is a water-based process for scrubbing soils ex-situ to remove contaminants. Soil washing systems incorporating most of the removal techniques offer the greatest promise for application to soils contaminated with a wide variety of heavy metal, radionuclides, and organic contaminants. The concept of reducing soil contamination through the use of particle size separation is based on the finding that most organic and inorganic contaminants tend to bind, either chemically or physically, to clay, silt, and organic soil particles. The silt and clay, in turn, are attached to sand and gravel particles by physical processes, primarily compaction and adhesion. Washing processes that separate the fine (small) clay and silt particles from the coarser sand and gravel soil particles effectively separate and concentrate the contaminants into a smaller volume of soil that can be further treated or disposed of. Gravity separation is effective for removing high or low specific gravity particles such as heavy metal-containing compounds (lead, radium oxide, etc.). Attrition scrubbing removes adherent contaminant films from coarser particles. The clean larger fraction can be returned to the site for continued use (USEPA, 1994).

1.2.2.7 Chemical Reduction/Oxidation

Reduction/oxidation (Redox) reactions chemically convert hazardous contaminants to nonhazardous or less toxic compounds that are more stable, less mobile, and/or inert. Redox reactions involve the transfer of electrons from one compound to another. Specifically, one reactant is oxidized (loses electrons) and one is reduced (gains electrons). The oxidizing agents most commonly used for treatment of hazardous contaminants are ozone, hydrogen peroxide, hypochlorites, chlorine, and chlorine dioxide. Chemical redox is a full-scale, well-established technology used for disinfection of drinking water and wastewater, and it is a common treatment for cyanide wastes. Enhanced systems are now being used more frequently to treat contaminants in soils. The target contaminant group for chemical redox is inorganics. The technology can be used but may be less

effective against nonhalogenated volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs), fuel hydrocarbons, and pesticides (USPEA, 1994).

1.2.2.8 Incineration

High temperatures, ranging from 870 to 1,200°C, are used to volatilize and burn (in the presence of oxygen) halogenated and other refractory organics in hazardous wastes. The destruction and removal efficiency (DRE) for properly operated incinerators exceeds the 99.99% requirement for hazardous waste and can be operated to meet the 99.9999% requirement for PCBs and dioxins.

Commercial incinerator designs are rotary kilns, equipped with an afterburner, a quench, and an air pollution control system. Incinerator off-gas requires treatment by an air pollution-control system to remove particulates and neutralize and remove acid gases (HCl, NO_x, and SO_x). Baghouses, venturi scrubbers, and wet electrostatic precipitators remove particulates; packed-bed scrubbers and spray driers remove acid gases. Limestone or caustic solution added to the combustor loop removes acid gases in the circulating fluidized bed (USPEA, 1994).

1.3 STATEMENT OF PROBLEM

As contaminated sites can pose a threat to human health and the environment, over the past decade there has been an increasing recognition of the problems associated with contaminated site in Western Australia. The Government of Western Australia uses many government agencies, including the Department of Environmental Protection, the Health Department of Western Australia, the Western Australia Planning Commission and the Ministry for Planning, the Water and Rivers

Commission and Department of Land Administration, to assist in monitoring and regulating environmental standards in the State. The problem is of special importance in Western Australia because of the great reliance on groundwater and the threat posed by land contamination to groundwater quality (DEP 1998).

1.3.1 The Waste Control Pty Ltd Site

The initial focus of this project was to analyse and attempt to remove contaminants from a site located next to Waste Control Pty Ltd in Bellevue, Western Australia. Waste Control Pty Ltd is a solvent recycling company and the business involves the cleaning and decontamination of hazardous waste collected from various companies. Apart from providing suitable solvent treatment for spent solvent for recycling and reuse, the company also provides the service of recycling and disposal of hazardous waste. Due to the nature of the work carried on a day to day basis in the Waste Control site, the spillage and therefore the contamination of the soil around the site is inevitable.

Within the site and near the area from which the recycling process takes place, storm water sumps are used to collect any liquid or water spills. It was believed that these sumps often overflowed, and it was very likely that contaminants had spread to the adjacent property, which is owned by Main Roads Department of WA. On testing the site, the initial trials showed that there was very little contamination, see Chapter Four. This resulted in the need for another source of contaminated soil.

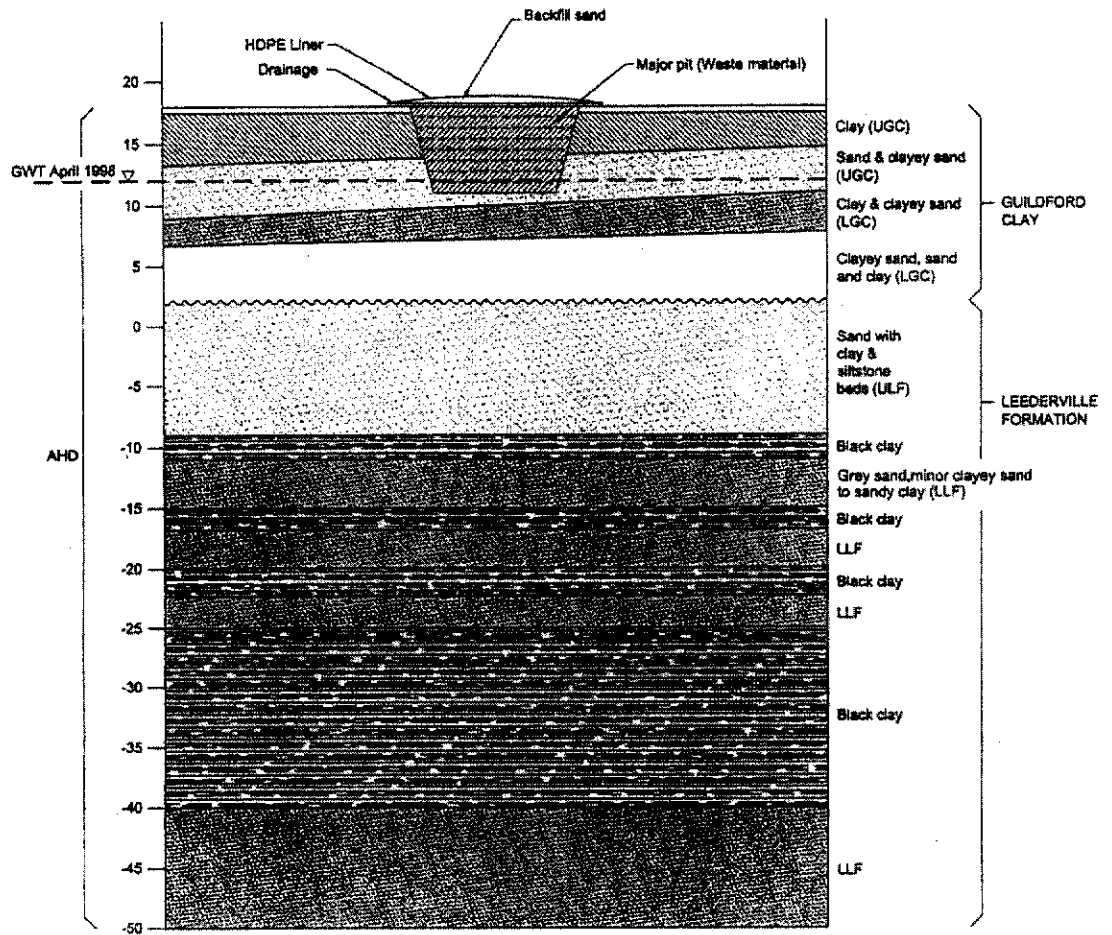
1.3.2 The OMEX Site

In the determination of a suitable source of contaminated soil, samples were obtained from the OMEX site through Department of Environmental Protection.

The OMEX site is located east of the Perth central business district in a mixed residential and commercial area of the suburb at Bellevue. The Western Oil Refining Co. Pty Ltd commenced waste oil recycling operation in 1955 and continued operating on the site up until 1979. The resulting sludge consisted of a bitumen and oil residue, spent fuller earth (used to filter the oil) and acidic wastewater. These waste materials were disposed in a 7m deep clay pit on site, and from 1976 onwards the pit was progressively backfilled with building rubble (clay, sand, brick and concrete), sand, clay, plaster wastes to give a volume of about 13,000m³. Waste oil overflowed from a band surrounding the pit in late 1988/early 1989 and spread onto the adjoining area. Environmental investigations commenced in 1988 following the overflow event, and in October 1997 the Premier of WA initiated a government funded remediation of the site (Egis 1999).

The site is underlaid by interbedded clays and clayey sands of the Guildford Clay to 16m depth and in turn by the Leederville formation (sand and clay beds). The Guildford clay contains minor laterally discontinuous sand aquifers of low to variable transmissivity. The Leederville Formation forms a major confined aquifer beneath the Guildford clay, which at the site consists of a highly transmissive sand bed underlaid by a laterally continuous black clay silt bed at about 25m depth (CMPS&F 1998). A cross sectional representation of the site geology depicting the major pit is shown on Figure 1.1.

TYPICAL CROSS SECTION



Legend

- UGC - Upper Guildford Clay
- LGC - Lower Guildford Clay
- ULF - Upper Leederville Formation
- LLF - Lower Leederville Formation
- GWT - Groundwater Table
- AHD - Australian Height Datum

Figure 1.1 Cross Section View of OMEX Site (Egis, 1999).

1.4 OBJECTIVES OF THE RESEARCH

The major aim of the research was to develop an applicable *ex-situ* soil washing system, which uses a combination of chelating agent(s) and surfactant(s), for the remediation of the OMEX site. To achieve this objective, the scope of work included the following tasks:

(1) Characterize the contaminated soils before extraction.

Prior to the extraction, the physical and chemical properties of selected contaminated soils were studied. The properties included moisture content, particle size distribution, soil pH, type and concentration of contaminants. The selection of extraction agents would be dependent upon the result of the soil analyses.

(2) Identify the removal efficiency of heavy metals and hydrocarbons by individual extracting agents, and optimize process parameters to use.

A laboratory investigation was conducted in which chelating agents and surfactants were used to remove heavy metals and hydrocarbons from contaminated soils. Chelating agents that were selected were citric acid, ethylenediaminetetraacetic acid (EDTA), and Nitrilotriacetic acid (NTA); surfactants included anionic and nonionic surfactants. The relevant process parameters included extractant concentration, ratio of washing solution volume to soil weight, contact time, temperature and pH.

(3) Determine the feasibility of remediating metal/organic contaminated soils by combination of chelating agents and surfactants.

The combination tests were carried out on bench-scale experiment as well. The order of extractants added to the washing solution was studied.

1.5 ORGANIZATION OF THE THESIS

The thesis is arranged into six chapters. The contents of the five chapters are as follows:

Chapter One is an introductory chapter which present soil contamination and types of contaminants, currently available techniques for soil remediation, and the statement of the current problem.

Chapter Two gives a review of soil washing technology and relevant literature pertinent to this study.

Chapter Three provides a description of the experimental methods and materials that were employed in this study.

Chapter Four presents the results and discussion of heavy metals removal studies using various chelating agents:

- (1) presents the results and a brief discussion of the soil properties.
- (2) determine the removal efficiencies of heavy metals by different chelating agents and optimize process parameters for heavy metals removal;
- (3) verify the experiment results through mass balance calculation.

Chapter Five presents the results and discussion of hydrocarbons removal studies using various chelating agents:

- (1) determine the removal efficiency of hydrocarbons by different surfactants and optimize process parameters for hydrocarbons removal;
- (2) determine the removal efficiency of both heavy metals and hydrocarbons by combination test.

Chapter Six contains the concluding remarks, and recommendations for further studies.

CHAPTER TWO

BACKGROUND AND LITERATURE REVIEW

2.1 SOIL PROPERTIES

Contaminants could be adsorbed onto the soil matrix while moving through the pores of the soil. These contaminants are fixed on the soil particles by the specific physico-chemical interaction between the contaminants and the soil. As sorbing sites for the contaminants, soil structure and its environment (soil-fluid interface) are important areas in soil contamination research.

2.1.1 Soil Structures and Environments

Soil is composed of three phases: solid, liquid, and gas. The solid phase is represented by mineral grains, which are the product of rock weathering, and some organic particles. The liquid phase of uncontaminated soil is a solution of various salts in water. The gaseous phase tends toward the composition of air but with a high content of water vapour. The variability of any or all of these three phases together, with corresponding variation in specific interaction of the three phases, provides for nonuniformity in soil composition, characteristics and properties (Yong 1975).

Soils are generally divided into gravel, sand, silt, and clay depending on the size of the particles. By MIT (Massachusetts Institute of Technology), USDA (U.S. Department of Agriculture), and AASHTO (American Association of State Highway and Transportation Officials) Soil classification systems, sand is the size of soil which cannot pass through the #200 sieve (grid size is

about 0.075mm), but is smaller than 2.0mm. Sand particles are made mostly of quartz and feldspar. Silts are the microscopic soil fractions between sands and clays that consist of fine quartz grains and some flake-shaped particles that are fragments of micaceous minerals. Clays are generally defined as particles smaller than 0.002mm. Clay is the most important form of soil in the soil contamination problem because the flake-shaped microscopic particles of clay have electric charges on their faces. Thus, adsorption between polar, nonpolar, or charged organic compounds and the charged sorbing sites is driven by a variety of forces and mechanisms. These include physical adsorption (primarily through London-van der Waal's forces), hydrogen bonding (between H and F, O, and N), ion exchange (mainly cation exchange), coordination (ligand exchange, ion interaction), chemisorption, and hydrophobic sorption (for nonionic organic compounds) (O'Neill 1993).

On the other hand, sand, which is composed of quartz, is a crystal of silica tetrahedra grouped in such a way as to form spirals, with all tetrahedral oxygens bonded to silicon. The tetrahedral structure has a high stability. In addition, the spiral grouping of tetrahedra produces a structure without cleavage planes, sand is already an oxide, there are no weakly bonded ions in the structure, and mineral has a high hardness (Mitchell 1976). Thus, sand has a very stable structure and it does not readily sorb organic compounds dissolved in the groundwater.

2.1.2 Heterogeneity

Soil is a natural mixture of mineral and organic particles and their weathered derivatives. Contaminants may be found in a variety of forms including salts, ionically fixed ions, physi- and chemisorbed compounds, and several organic materials which may be ionic and/or covalent. The idealized soil particle in Figure 2.1 is labelled with six phases: (1) exchangeable ions, (2) precipitated salts, typically carbonates, (3) easily reducible metal oxides such as amorphous manganese oxides, (4) more refractory metal oxides such as

crystalline oxides of iron, (5) organic matter, and (6) unweathered mineral lattice (Dragun 1988).

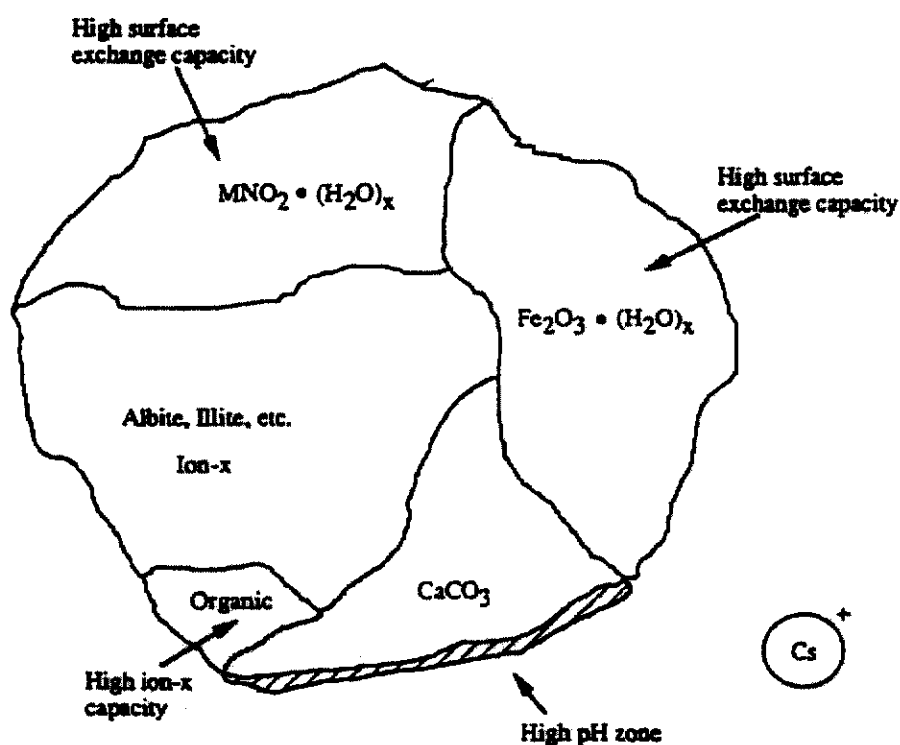


Figure 2.1 Idealized Soil Particle.

As stated above, soil is thus a mixture of particles. It is a heterogeneous matrix of variable size, texture, chemistry, and contamination level. Though contamination generally concentrates in the finer material both due to surface area and the higher cation exchange capacity of fine clay and organic particles, many factors can modify this general effect. Depending on its mode of deposition (alluvial, eolian, etc.), the climatic history, the parent mineralogy, and the contamination pathway, the matrix may range from coarse to fine, include all of the phases described above or be dominated by one or two, and may or may not be uniformly contaminated. Heterogeneity confounds the applicability of results from one location to another, and makes modelling almost impossible. Any testing must account for this variability by

ensuring the sample is well mixed, and performing replicate analyses to check reproducibility.

2.1.3 Fundamental Soil Properties Relevant to Soil Washing

Since soil is in reality a three-phase system comprising solid particles, liquid, and gas, this makes removing contaminants from the soil somewhat different from removing contaminants from purely solid, gaseous, or liquid materials. The three-phase nature of soil could result in contaminants coexisting in multiple phase, such as a volatile chemical being present as both a dissolved species in the fluid phase as well as a vapour. Chemicals can also transfer between phases, such as a constituent of the solid phase dissolving into the soil solution, or charged species being exchanged between the aqueous and solid phase through adsorption/desorption reactions. Contaminants can also be transported in multiple phases either by diffusion, convection, or colloidal transport.

The multiple phases of the soil coexist and in fact interact both chemically and physically. There is a set of fundamental soil properties that generally describe the soil phases individually. These properties are shown in Table 2.1, together with a brief description and a list of soil processes relevant to soil washing that are affected by the property. All of the properties listed in Table 2.1 contribute to the composite behavior of the soil; therefore, they are important to soil washing. Some properties, however, are obviously more important than others, and some groups of properties act collectively to affect specific processes such as water flow or chemical adsorption. For example, in situ soil washing designs must be particularly concerned with soil texture, structure, bulk density, and porosity, which can dramatically affect water-flow patterns that control leaching efficiency. Processes that are designed to remove adsorbed chemicals such as heavy metals will be particularly concerned with chemical properties such as pH, redox potential (Eh), and cation exchange capacity (CEC) (Jones 1994).

Table 2.1 Fundamental Soil Properties Relevant to Soil Washing (Jones 1994).

Phase	Name	Typical units	Description	Soil process affected
Solid	Texture		One of 13 named textural classes representing a designated value of % sand, silt and clay sized particles (see Ref. 20)	Water flow, adsorption, aeration
	Particle-size distribution (PSD)		Curve showing % of particles of an equivalent diameter or less on settling velocity and sieve analysis	Water flow, adsorption, aeration
	Specific surface (s)	m ² /g	Available internal or external mineral surface measured by adsorption of gas or organic material	Adsorption
	Bulk density (ρ_b)	Mg/m ³	Mass of oven-dry soil/volume of soil	Water flow
	Particle Density (ρ_p)	Mg/m ³	Mass of oven-dry soil particle/volume of soil particle (mineral density)	Water flow
	Organic matter	% by mass	Mass of organic matter/mass of oven-dry soil (sometimes expressed as % organic carbon)	Adsorption of organics, biodegradation
	Mineralogy		Crystalline minerals present as determined by XRD	Adsorption
	Structure		Qualitative description following SSSA (Ref. 20)	Water flow
	Cation, anion exchange capacity (CEC, AEC)	cmol(+) /kg	Amount of positive (CEC) or negative (AEC) charge that must be satisfied by ions adsorbed to the soil surface	Adsorption
	pH	pH units		Adsorption, precipitation
Liquid	Electrical conductivity of saturated extract (EC _e)	dS/m	Electrical conductivity of soil solution extracted from soil under saturated conditions. Can be related to osmotic potential and total dissolved solids.	Adsorption, precipitation
	Water content (θ_m, θ_v)	kg/kg, m ³ /m ³	Quantity of water (either mass or volume) per unit quantity (either mass or volume) of oven-dry soil	Water flow, aeration, biodegradation, precipitation
Gas	Water potential (ψ)	J/kg, Pa, m	Measurement of the work that must be done to remove the water from the soil. Potential gradients are the driving force for water flow.	Water flow, aeration
	Porosity (ϕ)	m ³ /m ³	Maximum volume of gas phase (i.e., at zero water content) per volume of soil	Aeration, volatilization
	Pressure	Pa	Barometric pressure of gas phase. Usually assumed to be atmospheric under natural conditions	Vapor diffusion, convection
	Humidity (Rh)	%	Relative saturation of water in soil gas phase. At constant temperature it can be related to water potential	Water vapor diffusion

Treatment is less efficient when the contaminated soil contained large amounts of fine particles, because fine particles provide a large total surface area per unit weight for contaminant adsorption (Bhandari 1994). Fine particles like clays are also known to contain higher amounts of natural organic matter. These factors are responsible for the enhanced surface sorption of hydrophobic contaminants on finer soil particles.

2.2 BASIC CONCEPTS OF CONTAMINANT SORPTION AT SOIL SURFACES.

Processes which influence the behaviour of contaminants in the subsurface must be considered both in evaluating the potential for movement as well as in designing remediation activities at hazardous waste site. Such factors not only tend to regulate the mobility of contaminants, but also their form and stability. Sorption is often the paramount process controlling the behavior of contaminants in the subsurface.

2.2.1 The Adsorption of Metal Ions by Soils and Their Constituents

The most important chemical processes affecting the behaviour and bioavailability of metals in soils are those concerned with the adsorption of metals from the liquid phase on to the solid phase. These processes control the concentrations of metal ions and complexes in the soil solution and thus exert a major influence on their uptake by plant roots (Alloway, 1995). Several different mechanisms can be involved in the adsorption of metal ions, including cation exchange (or non-specific adsorption), specific adsorption, co-precipitation, and organic complexation. In order to provide an introduction to the adsorption mechanisms, the four processes mentioned above will be discussed briefly.

2.2.1.1 Cation Exchange

Most heavy metals (with certain exceptions, including the metalloids As, Sb and Se and the metals Mo and V) exist mainly as cations in the soil solution, and their adsorption therefore depends on the density of negative charges on the surfaces of the soil colloids. In order to maintain electroneutrality, the surface negative charge is balanced by an equal quantity of cations. Ion exchange refers to the exchange between the counter-ions balancing the surface charge on the colloids and the ions in the soil solution. It has the following characteristics: it is reversible, diffusion controlled, stoichiometric and, in most cases, there is some selectivity or preference for one ion over another by the adsorbent (Gast 1979). This selectivity gives rise to a replacing order amongst the cations, determined by their valency and degree of hydration. The higher the valency of an ion, the greater its replacing power; H^+ ions behave like polyvalent ions and the greater the degree of hydration, the lower its replacing power, other things being equal. Adsorption by cation exchange can also be described as the formation of outer-sphere complexes with the surface functional groups to which they are bound electrostatically (Sposito 1985).

2.2.1.2 Specific Adsorption

Specific adsorption involves the exchange of heavy metal cations and most anions with surface ligands to form partly covalent bonds with lattice ions (Keeney 1979). It results in metal ions being adsorbed to a far greater extent than would be expected from the cation exchange capacity (CEC) of a soil. Specific adsorption is strongly pH dependent and is related to the hydrolysis of the heavy metal ions (Brummer 1986). The metals most able to form hydroxy complexes are specifically adsorbed to the greatest extent. The hydrous oxides of Al, Fe, and Mn are thought to be the main soil constituents involved in the specific adsorption reaction.

2.2.1.3 Co-precipitation

Co-precipitation is defined as the simultaneous precipitation of a chemical agent in conjunction with other elements by any mechanism and at any rate (Sposito 1983). The types of mixed solid commonly formed include clay minerals, hydrous Fe and Mn oxides and calcite in which isomorphous substitution has occurred (Table 2.2). In addition to co-precipitation, replacement of Ca^{2+} cations by Cd^{2+} can also occur in the surface layer of calcite when it comes into contact with solutions containing Cd.

Table 2.2 Trace Metals Normally Found Co-Precipitated with Secondary Minerals in Soils.

Mineral	Co-precipitated trace metals
Fe oxides	V, Mn, Ni, Cu, Zn, Mo
Mn oxides	Fe, Co, Ni, Zn, Pb
Ca carbonates	V, Mn, Fe, Co, Cd
Clay minerals	V, Ni, Co, Cr, Zn, Cu, Pb, Ti, Mn, Fe

2.2.1.4 Organic Complexation

In addition to being involved in cation exchange reactions, solid-phase humic substances such as humic acids also adsorb metals by forming chelate complexes. The stability constants of chelates with metals tend to be in the following decreasing order: $\text{Cu} > \text{Fe} = \text{Al} > \text{Mn} = \text{Co} > \text{Zn}$. Low-molecular-weight organic ligands, not necessarily humic in origin, can form soluble complexes with metals and prevent them from being adsorbed or precipitated. Humic compounds with suitable reactive groups, such as hydroxyl, phenoxyl and carboxyl form coordination complexes with metallic ions. Carboxyl groups play a predominant role in metal binding in both humic and fulvic acids. The maximum amount of any given metal that can be bound is found to be approximately equal to the number of carboxyl groups (Chen 1986).

2.2.2 The Adsorption of Organic Contaminants by Soils

The organic chemicals at many contaminated sites are usually nonpolar organics. It was these types of compounds such as DDT and other chlorinated hydrocarbon pesticides that first caused concern on the potential hazards of chemicals in the environment because of their widespread use and their potential toxicity. Many organics of environmental concern have a limited solubility in water because of their nonpolarity and molecular size as the solubility of an organic contaminant generally decreases with decreasing polarity and increasing molecular size. But even with limited solubilities, many hazardous molecules, such as ethanol, are totally miscible in water. Their combination results in a homogeneous solution regardless of the proportions that are mixed.

2.2.2.1 Octanol-Water Partitioning

Nonpolar organic compounds interact with soil organic matter through a process known as “hydrophobic sorption” which can be explained as the affinity of organic compounds for phases other than water. For example, water being a polar molecule is not compatible with other nonpolar molecules, such as DDT, which is immiscible with water. Organic molecules of increasing size, decreasing polarity and therefore water solubility, are said to exhibit increasing “hydrophobicity” which can be quantified by their octanol-water coefficient. It is a measure of the distribution of the chemical between water and an organic (octanol) phase with which it is in contact. The more hydrophobic the contaminant, the more likely it is to partition into the octanol phase. The partition coefficient provides a fairly accurate understanding of the sorptive process occurring between water and the soil, more specifically, the soil organic matter.

The octanol-water partition coefficient, expressed as K_{ow} in equation (2.1), is determined by measuring the concentration of a particular compound in both the water and the octanol phases after a period of mixing.

$$K_{ow} = \frac{\text{Concentration}_{\text{Octanol}}}{\text{Concentration}_{\text{Water}}} \quad (2.1)$$

Since measured K_{ow} values can be millions for important environmental contaminants (PCBs, chlorinated pesticides, dioxins and furans), they are often expressed as the base 10 logarithm, $\text{Log } K_{ow}$.

The K_{ow} has two attributes that make it especially useful in environmental assessments. Firstly, it varies in a predictable way within classes of organic compounds. For example, as shown in Figures 2.2 and 2.3, if K_{ow} is known for one member of a class of compounds it can be used reasonably well to estimate a value for other members of the same family. In the examples shown, the K_{ow} can be correlated to the number of chlorine atoms or the number of aromatic rings in the molecular structure of classes of contaminants.

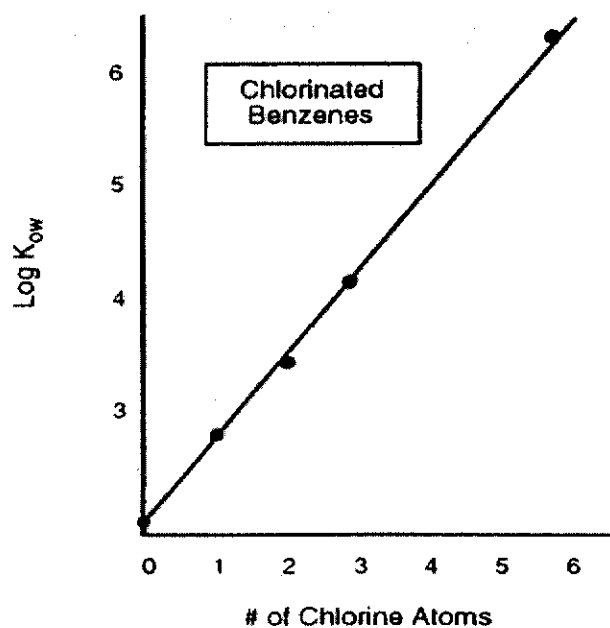


Figure 2.2 Relationship of Molecular Structure to Hydrophobic Character.

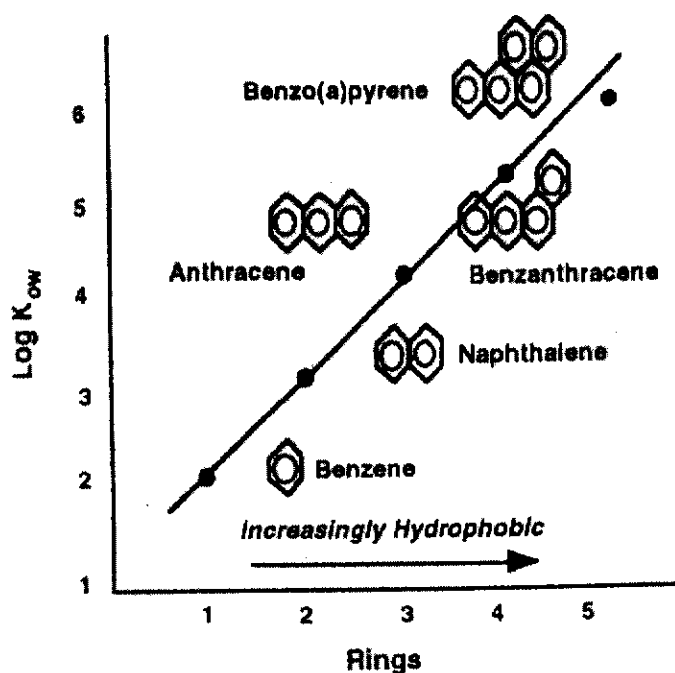


Figure 2.3 Relationship of Molecular Structure to Octanol-Water Partition Coefficient.

Secondly, work of a number of agricultural and environmental researchers have correlated sorption on the organic matter of soils with the K_{ow} of the compounds involved. By using these attributes of the K_{ow} , it is possible to estimate the potential sorption of organic contaminants based on the structure of the compounds and the organic carbon content of the soil or aquifer material.

2.2.2.2 Sorption to Soils

It has been suggested that nonpolar organic compounds are sorbed by soils as a function of their hydrophobicity (K_{ow}) and the organic carbon content of the soil. There has been considerable research which suggested that the slow kinetics of the sorption process may be significant in swiftly moving ground water. Sorption studies using flow-through columns produce results sensitive to the flow rate, and batch tests indicated that increased sorption occurred with longer exposure times.

Sorption is expressed in terms of a partition coefficient K_p , which is defined in equation (2.2) as the ratio of the concentration of contaminants associated with the solid phase to that in solution, and is, therefore, conceptually similar to K_{ow} .

$$K_p = \frac{\text{Concentration}_{\text{Solid Phase}}}{\text{Concentration}_{\text{Solution}}} \quad (2.2)$$

Units are $\frac{\text{mg/kg}}{\text{mg/L}}$, which is L/kg.

The usefulness of K_{ow} in estimating sorption stems from the fact that the soil organic matter serves the same function as octanol in the octanol-water test. As a result, there have been many empirical relationships developed for estimating sorption from the K_{ow} and the soil organic carbon content. One expression, developed in the laboratory by Piwoni and Banerjee (1989), for the sorption of common environmental contaminants which a low aquifer organic carbon is:

$$\text{Log } K_{oc} = 0.69 \text{ Log } K_{ow} + 0.22 \quad (2.3)$$

where K_{oc} is carbon normalized sorption coefficient, defined as

$$K_{oc} = \frac{\text{Sorption Coefficient, } K_p}{\text{Fraction Organic Carbon}} \quad (2.4)$$

When applying such a relationship, it is important to select a study in which the compounds used are similar to those of interest at the site under investigation. These estimates of sorption are based on a good evaluation of the soil organic carbon content at a site which is obtained from the degradation of naturally occurring organic matter.

2.3 SOIL WASHING TECHNOLOGY

2.3.1 Background of Soil Washing Technology

Dennis (Dennis 1994) defined soil washing as a physical/chemical process in which contaminated soil is excavated, screened to remove debris and large objects, and then washed with fluids to remove undesirable contaminants. The process removes contaminants from soils in one of two ways: by dissolving or suspending them in the wash solution (which is later treated by conventional waste water treatment methods) or by concentrating them into a smaller volume of soil through simple particle size separation techniques (similar to those used in sand gravel operation) (USEPA 1991). Generally, but not always, the liquid used is water or an aqueous solution containing chemicals designed to enhance the washing process (Jones 1994).

The fundamental strategy of the first washing mechanism is to extract unwanted contaminants from soil through washing or leaching the soil with liquids. The extraction process includes two primary steps. First, the contaminant must be separated from the soil matrix or pore space and transferred to the washing solution. Second, the washing solution, containing the chemical being extracted, must be extracted from the soil, completing the process of cleaning or washing the soil. The extracted washing solution is either treated to recover the original contaminant or processed for disposal. An additional step may be required to remove any residual chemicals left behind by the washing solution (Jones 1994).

The concept of reducing soil contamination through the use of particle size separation is based on the finding that most organic and inorganic contaminants tend to bind, either chemically or physically, to clay and silt soil particles. The silt and clay, in turn, are attached to sand and gravel particles by physical processes, primarily compaction and adhesion. Washing processes that separate the fine (small) clay and silt particles from the coarser sand and gravel soil particles effectively separate and concentrate

the contaminants into a smaller volume of soil that can be further treated or disposed. The clean, larger fraction can be returned to the site for continued use (USEPA 1989).

2.3.2 Soil Washing Process Applications

Soil washing can be used either to reduce contaminant levels to acceptable ones or to reduce the quantity of material to be processed by another technology such as incineration. Generally speaking, soil washing is effective on coarse sand and gravel contaminated with a wide range of organic, inorganic, and reactive contaminants. Removal efficiencies, however, depend on both the type of contaminant and soil. Ninety to ninety-nine percent of volatile organic contaminants have been easily removed by soil washing. By selecting the proper surfactant, semivolatile organic contaminants can be removed, but to a lesser extent (40 to 90 percent). Metals and pesticides often require acids or chelating agents for successful removal. This is because metals and pesticides are normally insoluble in water. In addition, the soil washing process can be used to treat specific wastes and other hazardous wastes including wood-preserving chemicals, organic solvent, electroplating residues, paint sludges, pesticides and their production residues, and petroleum/oil residues. The applicability of soil washing on general contaminant groups and soil types is shown in Table 2.3.

Table 2.3 Applicability of Soil Washing on General Contaminant Groups for Various Soils (Dennis, 1994)

Contaminant Groups	Matrix	
	Sandy/Gravelly Soils	Silty/Clay Soils
Organic		
Halogenated volatiles	■	◆
Halogenated semivolatiles	◆	◆
Nonhalogenated volatiles	◆	◆
Nonhalogenated semivolatiles	◆	◆
PCBs	◆	◆
Pesticides (halogenated)	◆	◆
Dioxins/furans	◆	◆
Organic cyanides	◆	◆
Organic corrosives	◆	◆
Inorganic		
Volatile metals	■	◆
Nonvolatile metals	■	◆
Asbestos	●	●
Radioactive materials	◆	◆
Inorganic corrosives	◆	◆
Inorganic cyanides	◆	◆
Reactive		
Oxidizers	◆	◆
Reducers	◆	◆

■ Good to excellent applicability: High probability that technology will be successful.

◆ Moderate to marginal applicability: exercise care in choosing technology.

● Not applicable: expert opinion that technology will not work.

Good to excellent applicability in Table 2-3 means that there is a high probability that soil washing will be effective for that particular contaminant and matrix. In addition, moderate to marginal applicability means that caution should be exercised in choosing soil washing. Finally, not applicable means that soil washing will not work for that particular combination of contaminant group and matrix.

The key physical parameter to determine whether a soil washing process is feasible is particle size distribution. Even though it should not be the sole

criterion for selecting or eliminating soil washing as a remedial technology, particle size distribution can be used as a prescreening tool for the potential use of soil washing. Figure 2.4 shows a simplistic particle size distribution range of curves that illustrate a general prescreening definition for soil washing technology.

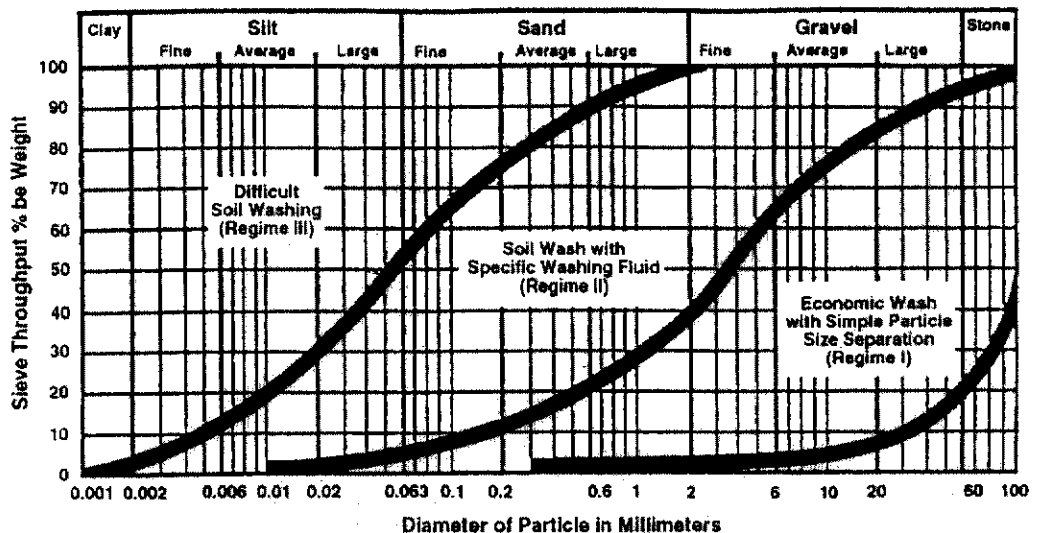


Figure 2.4 Soil Washing Applicable Particle Size Range (Denis, 1994).

In this simplest application, soil washing is a particle size separation process that can be used to segregate the fine fractions from the coarse fractions. In Regime I of figure 2.4, where coarse soils are found, the matrix is very amenable to soil washing using simple particle size separation. Most contaminated soils will have a distribution that falls within Regime II of Figure 2.4. The type of contaminants found in the matrix will govern the composition of the washing fluid and the overall efficiency of the soil washing process. In Regime III of Figure 2.4, soils consisting largely of finer sand, silt, and clay fractions, and those with high humic content, tend to contain strongly adsorbed organics that generally do not respond favorably to systems that work by only dissolving or suspending contaminants in the washing solution. However, they may respond to soil washing systems that also incorporate a

particle size separation step whereby contaminants can be concentrated into a smaller volume. In general, the relative effectiveness of soil washing for various soil types can be seen from the following:

Particle size distribution	Effectiveness
>2mm	Oversize pretreatment requirements
2 – 0.25mm	Effective soil washing
0.25 – 0.063mm	Limited soil washing
<0.063mm	Clay and silt fraction – difficult soil washing

2.3.3 Soil Washing Process Description

Figure 2.5 is a general schematic of the soil washing process. Soil preparation is the first stage of the soil washing process. It includes two procedures: one is to reduce soil aggregate to single grain composition (e.g., gravel, sand, silt, and clay) (Misra 1995), the other is by using screens to remove debris and larger objects of the excavated soil (Dennis 1994). The maximum size of particles in the prepared soil is dependent upon the screening equipment used. In addition, depending upon which soil washing process is used and whether it is semibatch or continuous, the soil may need to be made pumpable by the addition of solvent or water.

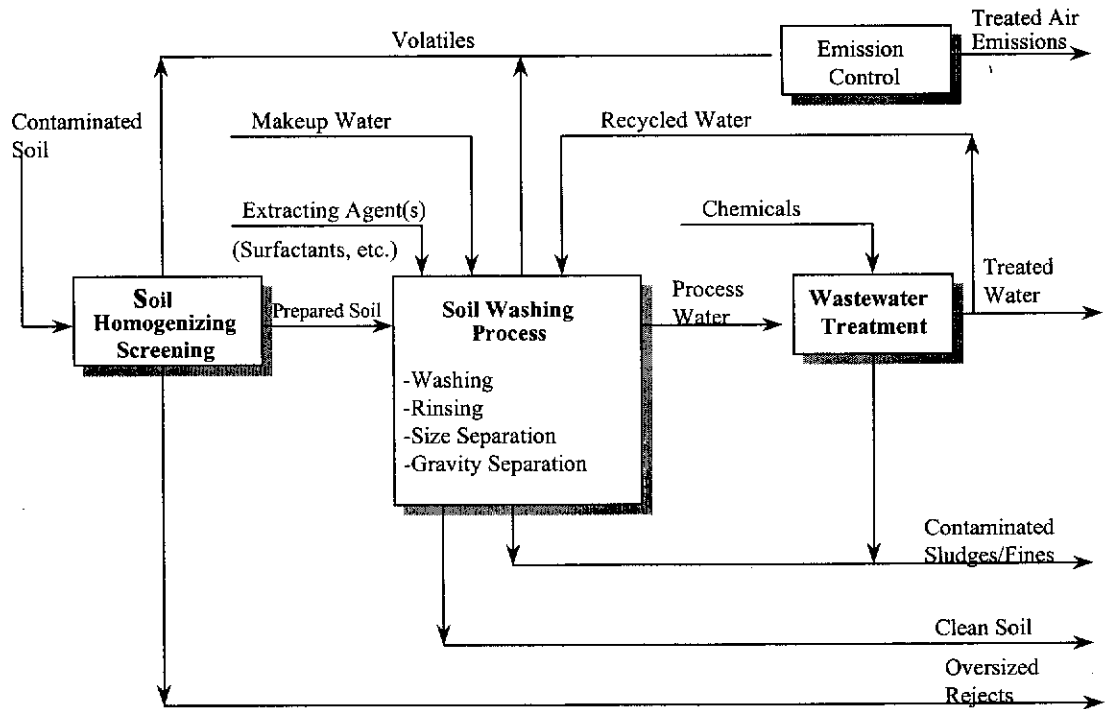


Figure 2.5 Typical Soil Washing Process.

The prepared soil then enters the soil washing process. This process usually consists of mixing, washing, rinsing, and size separation steps. During mixing, the wash fluid is metered to the soil. In the washing step, the wash fluid and soil are intimately mixed to dissolve the soil contaminants and disperse them into the wash fluid.

At the end of the required contact time, the wash fluid and soil are separated. A trommel or vibrating screen device is used to separate the coarse soil particles. They are then rinsed with clean water to remove any remaining contaminants and adhering fine soil particles. The coarse soil particles (sand and gravel) are recovered from the soil washing process as clean soil. In addition, the fine soil particles (silt and clay) are recovered either in a sedimentation tank or in a hydrocyclone or centrifuge.

The contaminated wash fluid and fine soil particles are treated in the final steps of the soil washing process. The metals and fine soil particles in the

contaminated wash fluid may require precipitation and clarification to remove them as a sludge. The fine soil particles normally require either further treatment or secure disposal, because they carry higher levels of contamination than the original soil. If organics are present, the clarifier effluent may require treatment with activated carbon before it can be recycled to the soil washing process. In addition, the presence of volatiles may require either carbon adsorption or incineration to control air emissions.

If the contaminated washing fluid is an organic solvent with organic contaminants, it goes to a separator where the pressure or temperature is changed to separate the organic contaminants from the solvent. The solvent is then recycled to the soil washing process, and the concentrated contaminants are removed from the separator. These contaminants may require analysis to determine whether they are suitable for recycle, reuse, or further treatment before disposal (Dennis 1994).

To illustrate a typical process, the following sections will examine two soil washing systems developed by the U. S. Environmental Protection Agency and will examine alternative components representative of the variety of hardware available for soil washing/volume reduction.

2.3.3.1 The Mobile Soil Washing System

The mobile soil washing system (MSWS) was developed during the early 1980s. Scholz and Milanowske (Scholz 1983) described the system in detail. Figure 2.6 shows the major unit processes in the system.

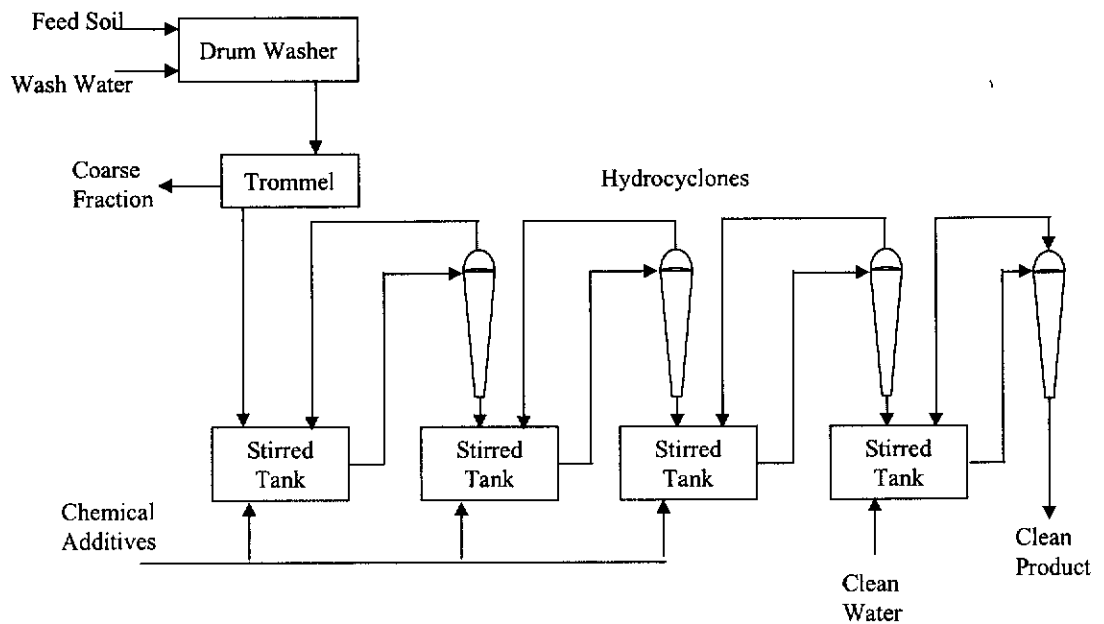


Figure 2.6 The EPA Mobile Soil Washing System.

The drum washer and trommel are a combined unit in which soil is contacted with washing water, which may have chemical additives, and an initial particle size separation is performed. The drum section contains water knives to promote breakup of soil lumps, and it provides time for the soil to soak in the washing water. The trommel separates particles larger than 2mm from the rest of the mixture. Ideally, this +2mm gravel/sand fraction is clean.

The -2mm mixture is fed to a four-stage, counter-current extractor. The soil becomes progressively cleaner as it flows from left to right, and it contacts progressively clean water in each tank.

For most soils, this design obtains minimal benefit from volume reduction. It relies primarily on chemical extraction. Only the trommel is operated under conditions that affect particle size separation. The hydrocyclones are operated primarily for separation of solids from water and not as a particle size separator.

2.3.3.2 The Volume Reduction Unit

The volume reduction unit (VRU) was developed during the late 1980s. Masters et al. (Masters 1991) described the system in detail. Figure 2.7 shows the major unit processes in the system. The VRU is a versatile design for performing experiments to learn more about soil washing.

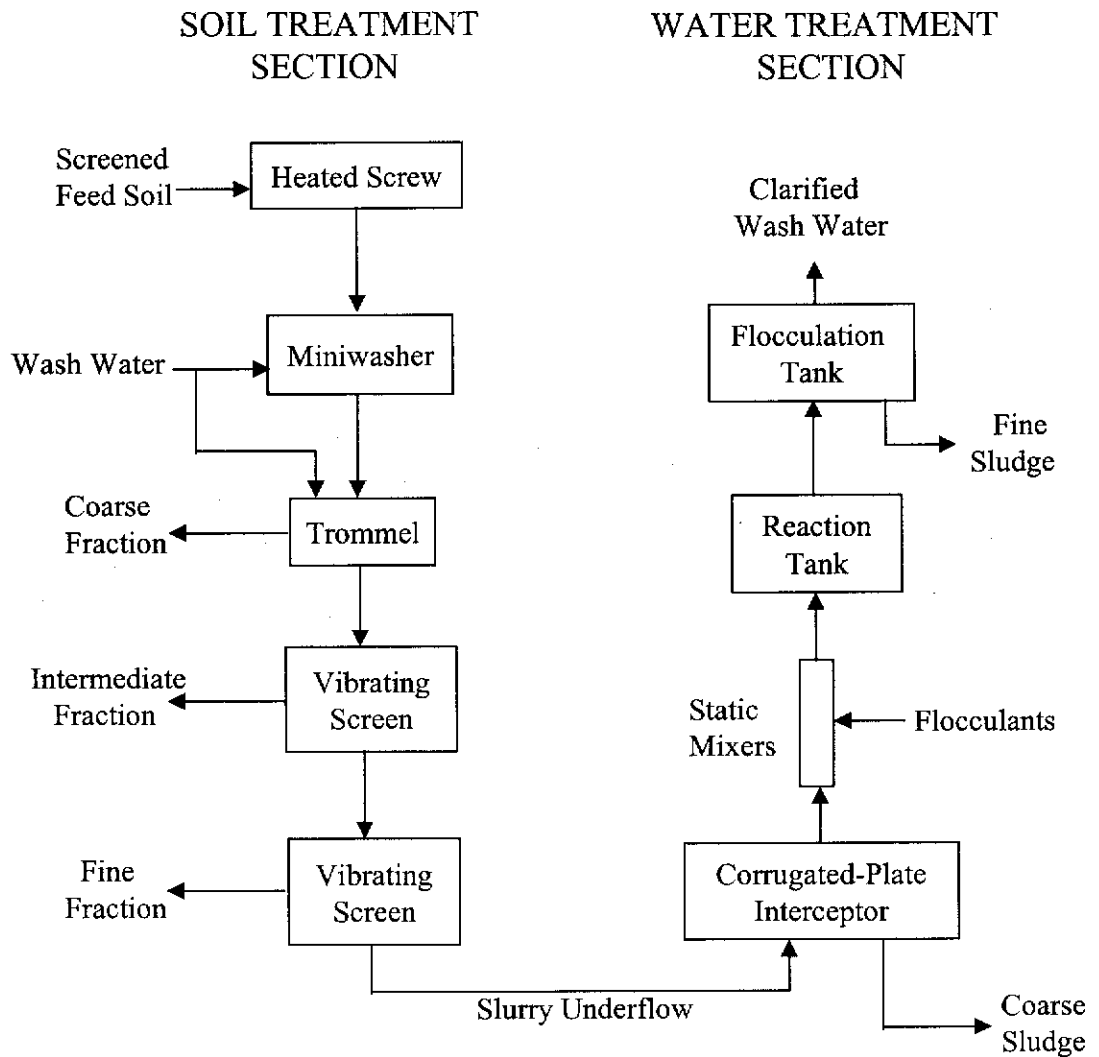


Figure 2.7 The EPA Volume Reduction Unit.

The heated screw is a jacketed screw feeder capable of warming soil to approximately 200°F for low temperature desorption tests. The miniwasher

uses a small quantity of water and concentrated surfactant, caustic, or other washing additive. High attrition is achieved in this mixture.

A small feed screw on the axle of a ribbon blender pushes the washed mixture from the miniwasher into the adjacent trommel. Soil in the trommel is sprayed with additional wash water, and a particle size cut is made at 2mm. Coarse soil overflow from the trommel is usually collected in a drum. Ideally, this fraction is clean.

Underflow from the trommel falls to a series of two vibrating screens that have replaceable inserts. Typically, a particle size cut is made at 40 to 60 mesh (420-250 μ m) in the first screen and 100 to 200 mesh (149-74 μ m) in the second screen. The overflows from these two screens are also collected in drums. Ideally, they are both clean.

Some of the remaining suspended fines are removed in a conventional lamella-type parallel-plate separator, which is also capable of removing any floatable material that make it to this point. More thorough removal of fines is achieved by adding flocculation agents such as alum and a polyelectrolyte. The dosed wash water is passed through two static mixers and a small tank that allows time for the floccing reactions to begin. The growing floc is then allowed to precipitate in the large floc-clarifier tank.

The design capitalizes heavily on volume reduction. The replaceable inserts in the vibrating screens allow for adjusting the particles size cuts to optimize the volume reduction for a specific soil. Solubilizing the contaminants may occur, but this is not highly desirable, because additional wash water treatment would be needed.

2.3.3.3 Alternative Apparatus

Numerous other materials handling and mineral processing devices will perform the unit functions that comprise the MSWS and VRU. Hydrocyclones can be effective substitutes for screens. In the MSWS, the

hydrocyclones are used only to separate soil from wash water to maintain the countercurrent flows. Hydrocyclones can also perform particle size classification. Under the right operating conditions, a hydrocyclone will pass water and small particles of a desired size out from the top (or the vortex finder) and will drop larger particles out from the bottom.

Spiral classifiers and elutriators (upflow classifiers) are also effective in volume reduction processes, particularly where the contaminants exhibit a significant density difference from the soil. Froth flotation is frequently used for separating fines. Jigs and shaker tables, though they are effective devices for mineral processing, are not in wide use for soil washing (USEPA 1993).

Other mineral processing apparatus in common use for soil washing include devices for scrubbing (e.g., attrition mills) and high-performance dewatering devices (e.g., belt or plate-and-frame filter presses).

2.4 CHELATING AGENTS ENHANCED SOIL WASHING

In order to improve the extraction efficiency of contaminants from soil, some extractive agents can be added to the washing solution. In soil washing with extractive agents, the washing solution can be basic aqueous solutions; acidic aqueous solutions; or solutions with surfactants or chelating agents (Raghavan 1991). Acids and chelating agents are generally used to remove heavy metals from soils, but the particular reagent needed depends not only on the heavy metal involved but also on the specific metal compound or species involved. Pickering (Pickering 1986) identified four ways in which metals are mobilized in soils: (1) changes in the acidity; (2) changes in solution ionic strength; (3) changes in the REDOX potential; and (4) formation of complexes. In practice, acid washing and chelating agent soil washing are the two most prevalent removal methods (Rampley 1996).

2.4.1 The Nature of Chelation

A complex has been defined as “a species formed by the association of two or more simpler species each capable of independent existence” (Rossotti 1961). One of the simpler species is a metal ion; the resulting entity formed by its interaction with another species is known as a metal *complex*. One such interaction, the coordinate bond, is established by the donation of an electron pair to a metal cation by either an anion or a polar molecule. The electron donor is often referred to as a *ligand* (L) and resulting association between metal and the ligand is referred to as a metal complex. The formation of the coordinate bond is referred to as either *complexation* or *coordination* (Dwyer 1964).

In many complexes there are other factors which contribute to metal-ligand (M-L) bonding. One of these factors is the electrostatic attraction between the metal ions and the anionic or polar ligand. Another is the formation of π -bonds, which occurs when d-shell electrons interact with vacant ligand orbitals (Bell 1977).

Ligands can vary from being simple to complex. Ligands such as chloride and ammonia are simple since they can only donate one pair of electrons to the metal cation, and are therefore referred to as unidentate. More complex molecules or ions, however, contain several atoms capable of donating electron pairs to the metal, and are therefore referred to as multidentate. Multidentate ligands include bidentate, tridentate, quadridentate, quinquedenate, sexadenate, and octadenate. Ethylenediaminetetraacetic acid (EDTA) is an example of multidentate ligands containing six donor atoms.

The nature of the metal complex formed by coordination may be better understood by reference to the two valance states that describe the metal cation-namely the oxidation state and the coordination number. The **oxidation state** refers to the charge on the metal caused by loss of electrons

from the outer shells of a neutral metal atom. The **coordination number** refers to the number of coordinate bonds that form about a particular metal cation and reflects the size of the cation and steric interferences between ligands competing for association with the metal cation. While coordination numbers of 4 and 6 are common, numbers from 2 to 10 have been observed with particular metal-ligand associations (Bell 1977).

When coordination of a metal with a ligand establishes a heteroaromatic ring, the process is referred to as a chelation. Ligands such as EDTA which act in this way are called chelating agents and the complexes they form are metal chelates. Typically, the more donor atoms involved in the chelation of a metal cation by a single ligand, the higher the stability of the resulting complex. Figures 2.8a and 2.8b show examples of unidentate and bidentate coordination, respectively.

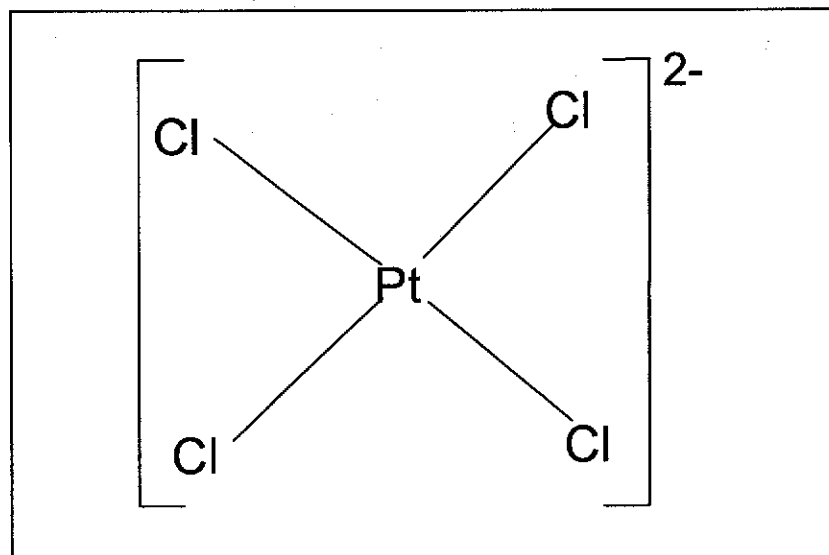


Figure 2.8a Unidentate Tetrachloroplatinate (II).

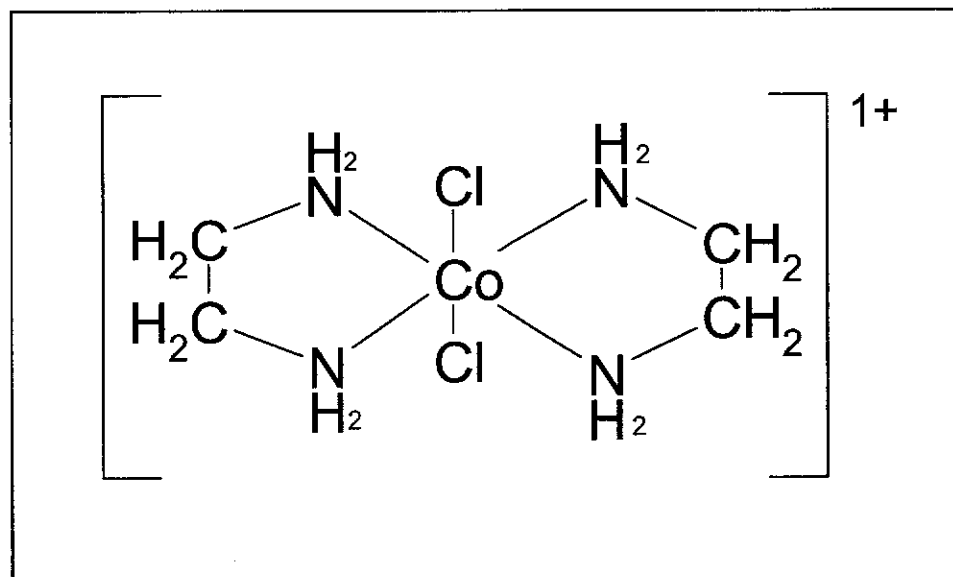


Figure 2.8b Bidentate Trans-dichlorobis (ethylenediamine) Cobalt (III).

2.4.2 Classification and Properties of Chelating Agents

Chelating agents by definition must have at least two donor atoms capable of binding to the same metal cation. A chelating agent with Z donor atoms is therefore capable of forming $Z-1$ chelating rings. Donor atoms are electronegative and usually come from Group V (e.g., N, P, As, Sb) and Group VI (e.g., O, S, Se, Te) elements. The ability to act as donor atom tends to decrease as the atomic number increases and complex stabilities using Group VI elements follows the order $N > P > As > Sb$ (Dwyer 1964). It should be noted that while Group VII elements (e.g., Cl, F, Br, I) are quite electronegative, they typically behave either as unidentate ligands in molecular complexes or bridging atoms in polynuclear complexes. In chelating agents, Group VII elements do not act as donor atoms (Dwyer 1964).

Donor atoms in chelating agents are often part of functional groups that may be classified as either acidic or basic. Acidic groups include carboxylic ($-CO_2H$), phenolic ($-OH$), sulphonic ($-SO_3H$), phosphoric ($-PO(OH)_2$), oxime

(=N-OH), and thiophenolic (-SH). It should be noted that the presence of donor atoms is not sufficient to make a molecule a functional chelating agent (Bell 1977). Donor atoms must be properly located on the structure of the chelating agent, and molecular bonds must be sufficiently flexible to allow adaptation of the chelating agent to the metal cation. In addition, functional groups on the chelating agent must not sterically hinder the metal atom from reaching the chelating site.

As noted above, chelating agents may be classified as bidentate, tridentate, tetradentate, and so forth. Bidentate chelating agents can be classified as those with two basic groups, those with two acidic groups, and those with one acidic and one basic group.

Multidentate chelating agents (e.g., EDTA, NTA) usually contain N and O as donor atoms. Figure 2.9a and 2.9b show the structure of EDTA and NTA. The increased stability that is associated with metal chelates formed with these chelating agents are attributed to the donor atom linkage in the aliphatic structure which gives it increased structural flexibility (Dwyer 1964). While aliphatic structures with more than three nitrogen donors could be synthesized, the resulting basic structure would promote competitive protonation, increase the pH, and promote the formation of metal hydroxides (Bell 1997). The problem can however be alleviated by incorporating acidic and basic groups in the molecular structure as in the case of sexadentate EDTA and other aminopolycarboxylic acids.

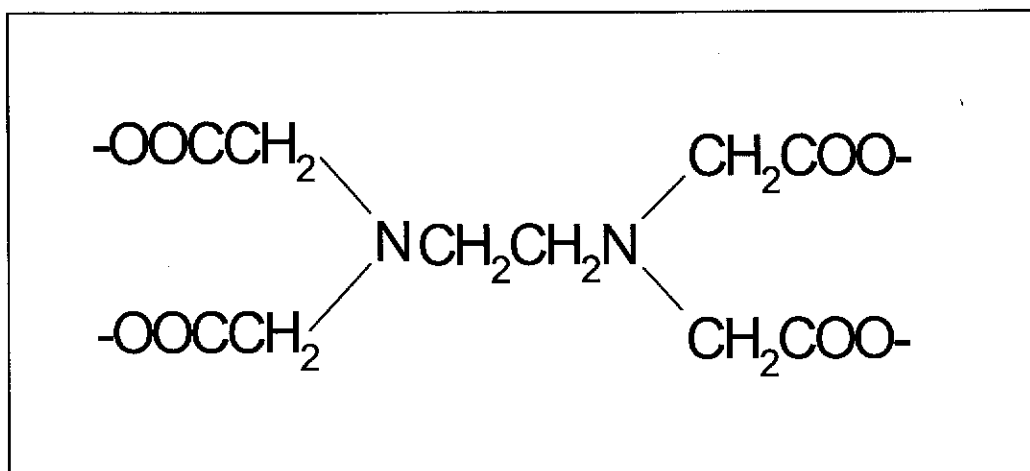


Figure 2.9a Structure of EDTA

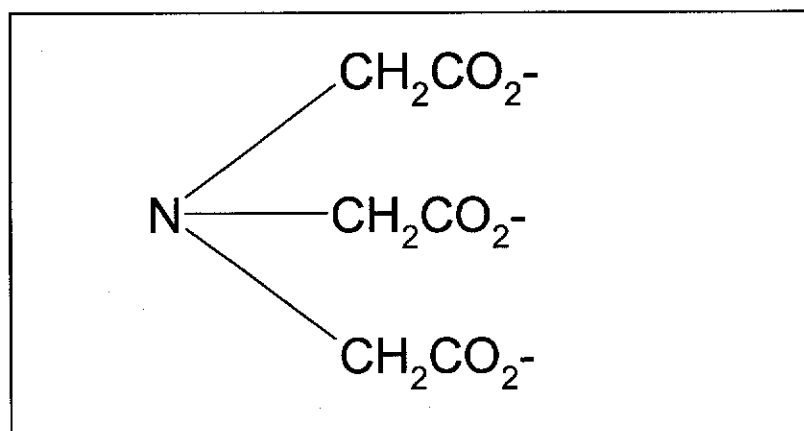


Figure 2.9b Structure of NTA

Aminopolycarboxylic acids are highly effective chelating agents that contain several carboxylalkyl groups bound to one or more nitrogen atoms. Table 2.4 provides a short list of aminopolycarboxylic acids that have been evaluated as chelating agents including the more popular ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA).

Table 2.4 Aminopolycarboxylic Acids (Bell, 1977)

Name	Acronym
Ethylenediaminetetraacetic acid	EDTA
Nitrilotriacetic acid	NTA
1,2-Cyclohexylenedinitrilo-tetraacetic acid	CDTA
Ethylene glycolbis(2-aminoethylether) tetraacetic acid	EGTA
Diethylenetriaminepentaacetic acid	DTPA
Ethylenediaminedi(o-hydroxyphenylacetic acid)	EDDHA
Hydroxyethylethlenediaminetriacetic acid	HEEDTA

2.4.3 Chelating Agents' Selectivity

For target heavy metals extraction application, the chelating agents should satisfy the following criteria.

- (1) The chelating agents (with and without the chelated metal) will be compatible with the foam and will display no adverse effects on the stability of the foam.
- (2) The ligands possess high metal complexing abilities toward heavy and transition metals as opposed to hard sphere cations such as Ca or Mg. The relative magnitudes of the equilibrium complexation constants toward heavy metals and toward alkali metals are an indicator.
- (3) The ligands containing sulfur and nitrogen as donor atoms are generally preferred for higher selectivity toward metals of interest, which are transition metals (e.g., Cu^{2+} , Ni^{2+}) and B-type (soft sphere) cations (e.g., Zn^{2+} , Cd^{2+} , Pb^{2+} , Hg^{2+}). Ligands containing sulfur or nitrogen as donor atoms generally form more stable complexes with soft sphere metals, whereas ligands containing oxygen as the donor atom prefer hard sphere cations.
- (4) Multidentate ligands are preferable because they contain multiple coordinating sites capable of forming more stable complexes with metals.

The selectivity of chelating agents toward heavy metals can be quantitatively computed on the basis of a 'selectivity ratio (SR)' which is defined as ML_{Tot}/FeL_{Tot} or ML_{Tot}/CaL_{Tot} , i.e. the ratio of the solubility of heavy metal (e.g., Pb, Cd) to that of ambient cations (e.g., Fe, Ca, Al) for a given set of metal and chelator concentrations in the system. A high selectivity ratio (SR) for the heavy metals indicates a strong preference of the heavy metals by the chelator. The selectivity ratios will be computed for DOE contaminant metals and for a large number of chelating agents (several hundreds) before a list of choice chelators can be decided (Peters 1999).

2.4.4 Related Studies on Chelating Agent Assisted Soil Washing

Pichtel (1997) investigated the ability of EDTA, NTA, sodium dodecyl sulfate (SDS), and hydrochloric acid (HCl) to solubilize chromium (Cr) and lead (Pb) from a contaminated soil ($Cr_{tot} \sim 4940$ mg/kg; $Pb_{tot} \sim 1300$ mg/kg; pH ~ 10.3) from an abandoned industrial facility. EDTA, NTA, and SDS were contacted with the soil over a wide pH range (~ 2 to 11). The extent of Cr and Pb solubilization was strongly influenced by both solution pH and the chelant-metal chemistry. Increasing the chelant concentration generally resulted in enhanced recovery of Cr from the soil. Cr and Pb recovery increased with higher EDTA concentrations, with maximum recoveries occurring at greater than 1:1 molar ratios of chelant:metal. The 0.1 M EDTA solution removed $\sim 100\%$ of the lead up to pH ~ 4.3 , and 54% of the chromium and 96% of the lead were recovered at pH ~ 12 . The NTA was less effective: $\sim 33-48\%$ removal of Cr (pH 8.9-11.0) and maximum of 38% lead removal was achieved at pH 4.5. The SDS removed 30-40.5% of the lead for pH ranging from 4.4 to 10.9, and 29-35% of the chromium for a pH range of 2.2 to 3.2. SDS was not effective at removing both Cr and Pb, even at molar ratios of greater than 1:1. The author speculated that the anionic surfactant may be precipitated with soil Ca and Mg, as well as bound to positively charged metal oxides and hydroxides. The acid wash using HCl concentrations ranging from 2% to 8% removed 100% of the Cr and Pb; however, 49-51% of the matrix solids were also dissolved, which creates a potential loading

problem in wastewater treatment plant operations. High acid strength destroyed the soil structure and dissolved much of the soil solids. A 1% acid solution was much less effective in metal removal (15.7% and 3.8% removal of Cr and Pb, respectively).

2.5 THE USAGE OF SURFACTANT IN SOIL WASHING

The removal of certain types of organic compounds from contaminated soil is handicapped by the very low solubilities of these compounds in water. These hydrophobic compounds include many common solvents (the chlorinated ethylenes and ethanes, carbon tetrachloride and chloroform, benzene, toluene, ethylbenzene, the aliphatic hydrocarbons) (Clarke 1991). They also include PCBs, polycyclic aromatic hydrocarbons chlorinated pesticides, etc. Surfactants may be beneficial for use in soil washing or soil flushing pump-and-treat technologies by assisting solubilization of sorbed hydrophobic contaminants (Edwards 1991). Surfactants may also impact microbial remediation of hydrophobic organic contaminants in soils by affecting the accessibility of the organic compound to microorganisms. Some surfactants that are suitable for soil washing are listed in Table 2.5.

Table 2.5 Surfactants for Soil Washing (Dennis et al., 1994)

Type	Examples
Anionic	Carboxylic acid salts, sulfuric acid ester salts, phosphoric and polyphosphoric acid esters, perfluorinated anionics, and sulfonic acid salts
Nonionic	Polyoxyethylenated alkylphenols and alkylphenol ethoxylates, polyethylenated mercaptans, long-chain carboxylic acid esters, alkylolamines, and alkanolamides

2.5.1 Surfactant Properties

A surfactant is a substance that, when present at low concentrations in a system, has the ability of adsorbing onto the surfaces or interfaces of the system and could alter the surface properties significantly, i.e. the interfacial free energies of those surfaces (or interfaces) (Rosen 1989).

Surfactants are amphiphilic molecules consisting of two distinct structural moieties: a hydrophilic head and a hydrophobic tail (Rosen 1989). Surfactant molecules migrate to interfaces (air-water, oil-water, and water-solid) where both structural components may reside in their preferred phases minimizing the free energy of the system; i.e., the hydrophilic head moiety resides in water and the hydrophobic tail moiety resides in oil (Shiau 1994).

Synthetic surfactants are categorized according to the electrostatic charge of the hydrophilic portion of the molecule (West 1992). The head group may possess: (1) a positive charge (cation), (2) a negative charge (anionic), (3) both cationic and anionic charges (amphoteric) or (4) zero charge (nonionic) (West 1992). Cationic surfactant head groups are usually comprised of an amino or quaternary nitrogen group and do not perform well in soils possessing a negative surface charge due to strong adsorption of the surfactant to soil particles. The hydrophobic portion of cationic surfactant is attached to a basic group (Rosen, 1989). Anionic surfactants are used in petroleum recovery due to their high aqueous solubility and repulsion from soils that possess a negative surface charge. Head groups of anionic surfactants include sulfonates, sulfates, and phosphates (Ouyang 1995). Hydrophobic portions of anionic surfactants are attached to an acid group. Both anionic and cationic surfactants are dissolved as ions and are influenced by solution pH. Nonionic surfactants are uncharged and soluble through hydrogen bonding at oxygen or hydroxyl groups (Ouyang 1995). Nonionic surfactants contain a polyoxyethylene group. The water solubility of nonionic surfactants is contingent upon the length of the ethoxylated chain; i.e., the longer it is, the greater its solubility (Rosen 1989). Amphoteric

surfactants combine both a basic and an acid group in the same molecule. They behave as anionic surfactants when the solution is acidic and as cationic surfactants when the solution is basic (Rosen 1989).

The hydrophile/lipophile balance (HLB) value, which quantifies the relative dominance of the hydrophilic group over the lipophilic group of the surfactant molecule, is a useful parameter to characterize the emulsification behavior of surfactants (Rosen 1989). The HLB number is calculated for nonionic surfactants as the weight percent of ethoxylate groups ($\text{EO}=\text{OCH}_2\text{CH}_2$) divided by 5 (Currie 1992). Surfactants possessing a strong hydrophobic portion relative to the hydrophilic portion will have a low HLB value (Grimberg 1995). Surfactants with HLB values of 8-18 are categorized as oil in water emulsifiers, and surfactants with lower HLB values are termed water in oil emulsifiers. Attempts at soil remediation typically utilize oil in water emulsifiers.

2.5.2 Surfactant Mechanisms

2.5.2.1 Micellar Solubilization

Surfactant molecules have the capacity to self-assemble into dynamic aggregates termed micelles once a particular aqueous concentration of surfactant monomers has been reached (see Figure 2.10) (Sabatini 1995). This concentration is referred to as the critical micelle concentration, or CMC. Critical micelle concentration values are a function of both system conditions (e.g. water hardness, temperature) and surfactant type. Nonionic surfactants generally have lower CMC than anionic surfactant (Rosen 1989). Typical CMC values range from 0.1 to 10 mM (West and Harwell 1992). The number of surfactant molecules that form each micelle is referred to as the coordination number (Grimberg 1995). Micelles have characteristic sizes within the low nanometer range (Attwood 1983).

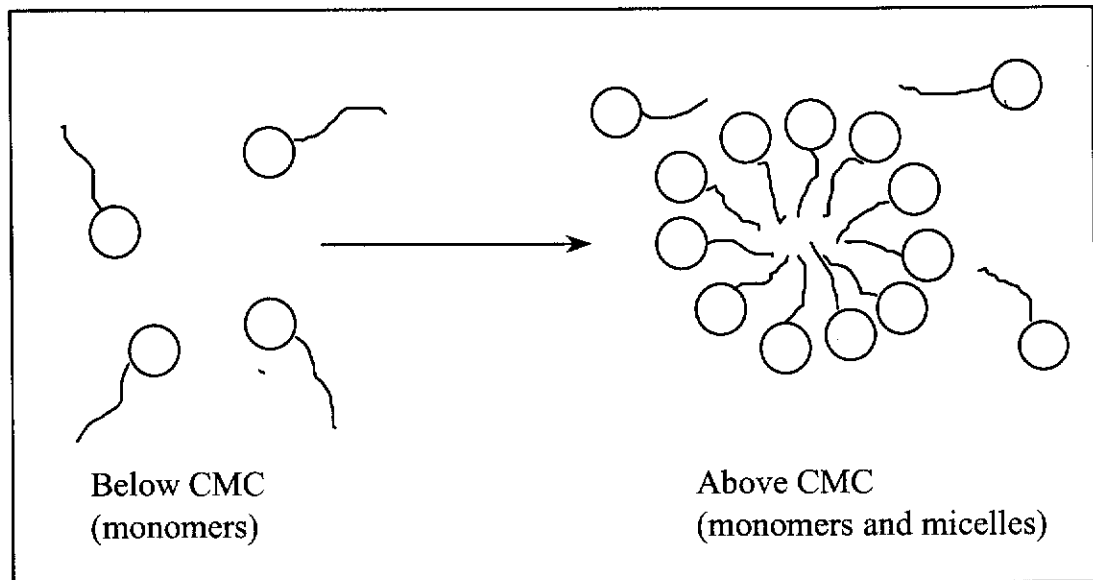


Figure 2.10 Example of Surfactant Micellization.

Micelles contain the hydrophobic tail portions of surfactant molecules within their interior while the hydrophilic portions of the surfactant molecules comprise the micelle exterior (Sabatini 1995). The polar exterior of the micelle imparts high aqueous solubility while the nonpolar interior functions as a pseudo-oil phase into which nonpolar organic compounds may partition (Shiau 1994). The resulting enhanced aqueous solubility of organic compounds through partitioning into the hydrophobic core of the micelle at supra-CMC surfactant concentrations is termed solubilization (see Figure 2.11) (Sabatini 1995). Hydrophobic compounds, including PAHs, partition into the hydrophobic core of micelles. When the hydrophobic solute is present in excess, the apparent solubility (total solute in the aqueous and micelle phases) increases linearly with an increase in surfactant concentration above the CMC. The slope of this increase is defined as the solubilization capacity (Grimberg 1995).

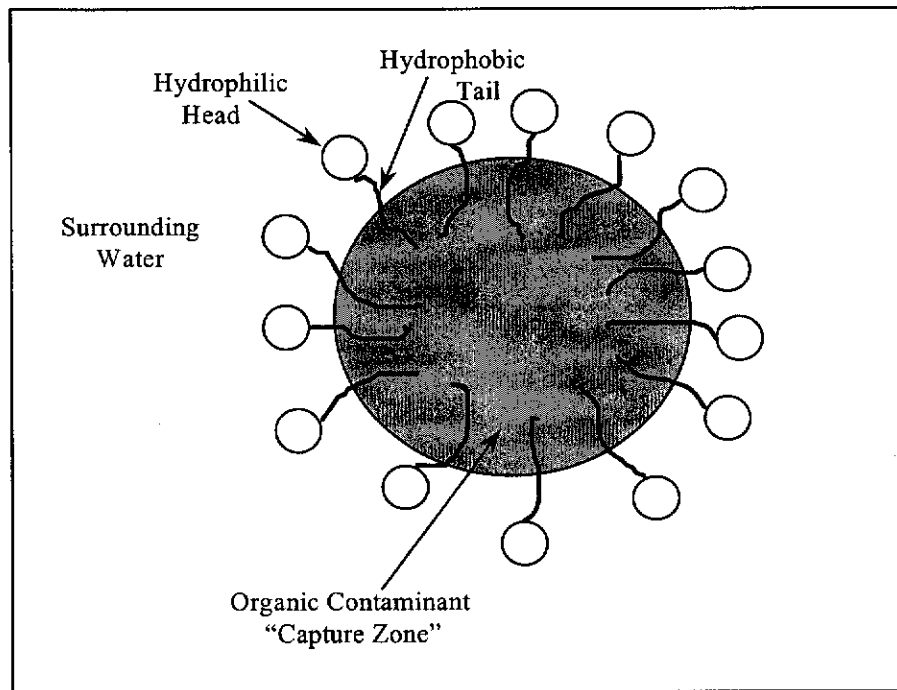


Figure 2.11 Cross-Sectional View of Surfactant Solubilization.

Solubilization has been defined as the spontaneous dissolution of a substance (solid, liquid, or gas) by reversible interaction with surfactant micelles in a solvent to produce a thermodynamically stable isotropic solution (Rosen 1989). Solubilization is believed to occur at a number of sites: (1) at the micelle-solvent interface on the micelle surface; (2) between the hydrophilic head groups (in polyethylenated materials); (3) in the palisade layer of the micelle between the hydrophilic head group and the hydrophobic tail; and (4) in the micellar core. Thus polar molecules are solubilized in the outer regions of micellar structures whereas nonpolar solubilizates are contained within inner portions (Rosen 1989).

2.5.2.2 Mobilization

In addition to solubilization, aqueous surfactant solutions also have the capacity to displace or mobilize residual NAPLs (nonaqueous-phase liquids) from porous media. NAPL movement through the subsurface is governed by capillary forces (Hunt 1989). In order to enter a water filled pore, the NAPL must overcome a capillary displacement pressure (Fountain 1995). Capillary

pressure is generally greater in fine-grained material which function as barriers to vertical migration until sufficient NAPL head pressure develops to overcome the displacement pressure. NAPL will generally exist as residual saturation along its flow path and as pools upon relatively impermeable layers.

Surfactants reduce interfacial tensions between NAPLs and water. Depending on the surfactant employed, the reduction in interfacial tension may range up to four orders of magnitude (Fountain 1995). Capillary pressures are known to decrease directly with reductions in interfacial tension. Mobilization occurs once viscous and/or gravitational forces acting on the NAPL exceed those capillary forces that are responsible for its immobilization. Once mobilization occurs, NAPL is removed from the soil/sediment as a discrete phase. Residual NAPL mobilization continues until a mechanical equilibrium governed by the Young-Laplace equation is reached. To produce substantial mobilization, interfacial tension must be reduced to near 10^{-3} mN/m (Fountain 1995).

2.5.2.3 Emulsification

Water/NAPL/surfactant systems exhibit complex behavior and mechanisms of contaminant removal cannot be attributed solely to solubilization and/or mobilization. An additional mechanism for facilitating NAPL removal is through the process of emulsification. When two immiscible liquids of different densities such as oil and water are mechanically shaken together, two distinct layers commonly form. Surfactant may be added to lower the interfacial tension between the liquids. If the resulting mixture is shaken, the milling together of constituents forces one of the liquids to become dispersed in the other, forming an emulsion (Rosen 1989). An emulsion is defined as a dispersion of droplets of one liquid into another with which it is completely immiscible (Ouyang 1995).

At the CMC, solution interfacial tension is minimized and remains constant as surfactant concentration increases. The retention of oil and other

contaminants present as NAPL within a porous medium is function of viscous, capillary and gravitational forces. The mobility of trapped oil increases at the CMC where the ability of viscous forces to overcome capillary forces is elevated due to the reduction in interfacial tension (Ang 1991). Once mobilized the contaminant can be suspended in the surfactant solution as an emulsion or be displaced and remain as a distinct NAPL. Two types of emulsions can be formed depending on system conditions: (1) macroemulsions with droplets having diameters greater than $1\mu\text{m}$ and (2) microemulsions with droplets of $0.01 - 0.1\mu\text{m}$. Oil in water microemulsions are transparent, isotropic, clear, and thermodynamically stable (Shaw 1980). Conversely, macroemulsions are opaque and thermodynamically unstable, although they are classified as kinetically stable (Fortin 1997). Surfactant solutions rarely reduce interfacial tensions below the 0.1 dyne/cm requirement to induce microemulsion formation.

2.5.3 Surfactant-Assisted NAPL Removal from Contaminated Soils

Surfactants can remove a portion of the NAPL mass rapidly and cost effectively but the ultimate remediation level is based on site conditions. Surfactants increase the mobility of contaminants by combination of the following three mechanisms: (1) increasing contaminant solubilization, (2) reducing contaminant sorption, and (3) lowering interfacial tension between water and NAPLs (Fountain 1995).

Numerous studies have demonstrated the ability of surfactants in facilitating the solubilization of a variety of hydrophobic organic compounds from spiked soil samples (Deitsch and Smith 1995; Di Cesare 1994). Abdul et al. (1992) examined the efficiency of surfactants in removing automatic transmission fluid from batch samples of a sandy textured soil. Results demonstrated that surfactant removed between 56 and 84% of the contaminant whereas, washing with water alone removed only 23% of contamination.

Studies by Tobia (1994) and Ganeshalingam (1994) demonstrated that a high sand and low silt plus fines content make ex situ soil washing with surfactants a promising remediation. Deschenes et al. (1996) found that anionic SDS (Sodium Dodecyl Sulfate) enhanced the ex situ solubilization of sorbed PAHs from aged creosote-contaminated soils. The sandy loam soil contained 13% clay, 16% silt and 71% sand. At supra-CMC concentrations, increases in the solubilization of fluorene, phenanthrene, anthracene, fluoranthene and pyrene were witnessed. Pennell et al (1993) studied the solubilization of dodecane by a nonionic surfactant (polyoxyethylene (20) sorbitan monooleate) as a means for recovering NAPLs from contaminated aquifers. In batch experiments, application of surfactant at supra-CMC doses resulted in the linear enhancement of the apparent solubility of dodecane.

The solubility enhancement provided by surfactants for a given contaminant is a function of the aqueous solubility of the compound; i.e. the greater the aqueous solubility or lower the K_{ow} , the lower the solubilization increase (Fountain 1995). The presence of multi-component NAPLs imposes certain limitations on surfactant performance. NAPLs are comprised of chemicals that possess different polarities, as assessed through their aqueous solubilities (Fountain 1995). While data on the dissolution of PAHs from weathered NAPL-contaminated soils is sparse, the remediation of these soils appears to be limited primarily by the slow rate of contaminant mass transfer to the aqueous phase (Yeom 1996). Surfactant micelles greatly enhance the solubility of individual PAHs, however their utility in enhancing the rate of release of PAHs from NAPL contaminated soils has yet to be thoroughly studied.

2.5.4 Surfactant Selection

Surfactants should be selected to (1) remove the contaminant and (2) minimize environmental damage. The impacts which surfactants have upon the environment can be minimized through proper surfactant selection. The surfactant itself should be non-toxic and relatively easy to remove from the

subsurface by anthropogenic or natural means. Although most surfactants are water soluble and can be easily washed from the sand, it is unlikely that complete removal could ever be accomplished; absolute removal of the surfactant is neither practical nor cost-effective. It is for this reason that the surfactant should be biodegradable.

Cationic surfactants are potent germicides and are toxic to many aquatic organisms at mg/L concentration; the toxicity is moderated by their reactivity to solids (West 1992). Furthermore, most soils are negatively charged and would attract cationic surfactants to their surfaces (Ganeshalingam 1994). This reduces the amount of surfactant available in solution with the consequent reduction in the level of contaminant removal. Moreover, the adsorbed surfactant molecule acts as an organic carbon source on which more contaminants could be partitioned, thereby further reducing their mobilities.

2.5.5 Potential Limitations of Surfactants within Contaminated Soils

Since surfactants are organic compounds, sorption onto soil may be significant (Liu 1991; Rouse 1993). At very low concentration, adsorbed surfactant monomers begin to aggregate and form micelle-like structures called admicelles or hemimicelles, depending on whether the aggregates have one or two surfactant layers (Figure 2.12). Once these structures form on the solid surface, sorption of additional surfactant may rapidly increase until a complete bilayer of surfactant covers the solid surface. The tendency of the surfactant to form admicelles or hemimicelles is dependent on interactions between the hydrophilic moiety of the surfactant and solid surface. The higher the water solubility of the surfactant, the lower the tendency for adsorption.

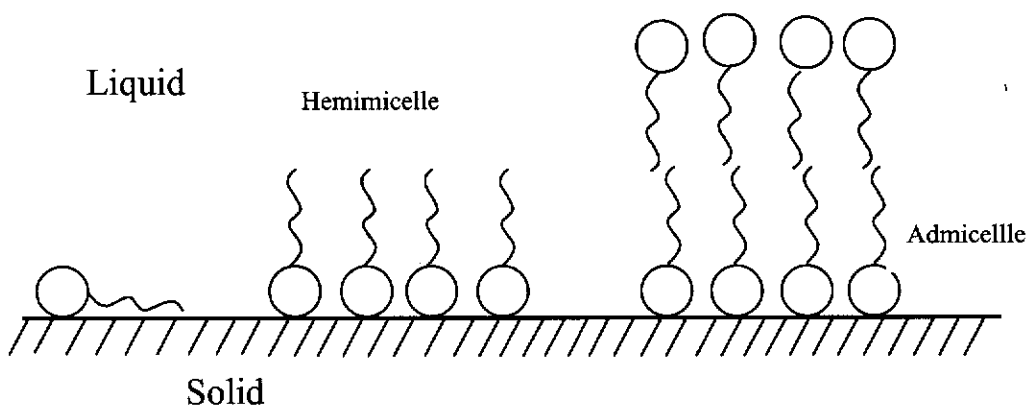


Figure 2.12 Example of Surfactant Sorption.

Sorption reduces the efficiency of the surfactant system and increases costs. Surfactant sorption is a function of total organic carbon content, percentage of clays present in the soil, soil water chemistry and surfactant type (Liu 1992; Rouse 1993). Surfactant sorption typically increases with organic carbon or smectitic clay content (Fountain 1995). Sorption of surfactant onto soil may result in much of the surfactant being unavailable for micellar solubilization (Edwards 1992). Sorption of nonionic surfactant onto soils may elevate the fractional organic carbon of the soil, thus altering its sorptive characteristics (Liu 1992). Thus, sorbed surfactant has the capacity of modifying hydrocarbon sorption behavior, by functioning as an additional sorptive media to which the contaminant may adhere (Liu 1991; Edwards 1992).

The influence of water chemistry on the solubility of surfactants is well documented (Rouse 1993). While surfactants with hydrophile-lipophile balance (HLB) values greater than 12-13 will freely dissolve in distilled water, ionic strengths of as low as a few hundred mg/L may promote surfactant precipitation. Site specific water chemistry must then be used during testing to evaluate whether a given surfactant is effective under given conditions (Fountain 1995). As surface area is a critical factor controlling surfactant sorption, any change in surface area may produce erroneous sorption estimates. Application of distilled water will mobilize clays present in a system producing different sorption characteristics, emphasizing the need for

using water chemistry similar to site conditions to avoid changing clay surface properties.

Surfactant sorption is generally greater for nonionic than for anionic surfactants, but nonionics tend to have greater solubilization capacities (Rouse 1993; Allred 1994). Surfactant adsorption reduces the aqueous concentration of surfactant, thus increasing the concentration of surfactant that must be added in order to reach CMC. This new CMC that incorporates sorption to the soil matrix is termed the effective CMC (Liu 1992). Surfactant sorption must be determined for individual soil systems due to its dependence on contaminated soil characteristics and surfactant type (Rouse 1993).

Nonionic surfactants may partition into trapped residual phases if their solubilities in the NAPL are high; i.e. they possess lower HLBs (West 1992). Further, nonionic surfactants are subject to coacervation, the formation of a separate aqueous phase at a high critical temperature termed the cloud point. This point is noted by solution turbidity. Ionic surfactants are usually insoluble in NAPLs, however their divalent salts may have appreciable solubility in the nonaqueous phase.

2.6 SUMMARY

Due to the mineral composition and chemistry of the clay particles, inorganic and organic contaminants can be adsorbed onto clay particles by a variety of forces and mechanisms; including hydrogen bonding, ion exchange, hydrophobic sorption, coordination bonding, and chemisorption.

Soil washing is effective in removing a variety of contaminants from contaminated soil. The removal efficiency depends on the properties of soil and contaminants. Research has been performed on the desorption of individually adsorbed heavy metals and hydrocarbons on soil particles with various desorbing solution such as chelating agents and surfactants. Each

solution shows a potential for desorbing heavy metals and hydrocarbons. However, systematic studies of these extractants on the remediation of contaminated site with both heavy metals and hydrocarbons have not been conducted.

CHAPTER THREE

EXPERIMENTAL: MATERIALS, EQUIPMENT SETUP AND ANALYTICAL PROCEDURE

3.1 SOIL PROPERTIES DETERMINATION

3.1.1 Test Soils

Soil is a sorbing site for organic compounds. It is a chemically and biologically complex porous medium consisting of weathered mineral fragments, organic matter, microorganisms, water, and air. The fate and transport of contaminant compounds in the soil-water environment depends on physical, chemical and biological interactions between soil and the organic compounds. Therefore, the properties of the test soil that may affect these interactions were studied.

The primary test soil was purchased from W.A. Department of Environmental Protection. The soil samples were collected from the OMEX contaminated site. In March 1998, CMPS&F, an environmental consultant company, performed soil investigation at the contaminated site for the Department of Environmental Protection. Three bores were constructed within the pit wastes intersecting several metres of oil contaminated fill soil. After collection, the soil samples were kept in 2 litre sealed plastic bottles.

Besides the OMEX soil sample, another soil sample was collected from Main Roads Department (MRD) property which was adjacent to Waste Control Pty. Ltd. In April 1998, total 11 soil samples were collected on-site from the

suspected contaminated MRD site. The samples were collected 0.5 m below the ground level. After collection, samples were also preserved in sealed plastic bottles. Once the soil was collected from the ground, roots of the plants, debris, and stones were removed.

3.1.2 Experimental Procedure

All samples were subjected to a variety of physical and chemical tests, such as soil appearance, soil pH measurement, moisture content, particle size distribution, total organic carbon (TOC), organic content, contaminant types and concentrations.

In order to obtain a homogeneous soil sample, the collected soil bought from DEP was poured out from the bottles, but into a 9-litre bucket, and stirred for 15 minutes by a mechanical agitator. The soil sample was then backfilled into the bottles and sealed for future experiment. In addition, all tests were performed with duplicate samples.

3.1.2.1 Soil Appearance

It was determined by visible observation for colour, smell, and status of soil samples.

3.1.2.2 Moisture Content

The moisture content was measured by drying a weighed sample in an oven, according to the procedure described by Gardner (1986). 100 g of soil sample was weighed and placed onto a metal plate. The sample was placed in an oven at a temperature of between 100 and 110°C and was removed from the oven and placed in a desiccator containing active desiccant before each weighing. This was repeated until the sample attained a constant weight (at least 12 hours). The water content was computed by following formula (3.1):

$$\theta_{ww} = \left(1 - \frac{\text{weight of dry soil}}{\text{wet soil}} \right) \times 100\% \quad (3.1)$$

3.1.2.3 Soil pH

Soil pH was measured by Method 9045, which was developed by Office of Solid Waste, U.S. Environmental Protection Agency.

- 1) To 20 g of soil in a 50-mL beaker, 20 mL of distilled water was added, and continuously stirred the suspension for 5 minutes.
- 2) After allowing the soil suspension to stand for about 15 minutes, most of the suspended waste settled out from the suspension. The suspension was then filtered or centrifuged to obtain an aqueous phase for pH measurement.
- 3) The glass pH electrode was immersed just deep enough into the clear supernatant to establish good electrical contact through the ground-glass joint or the fiber-capillary hole.
- 4) The pH reading was recorded.

3.1.2.4 Particle Size Distribution

The particle size distribution for the soil sampled from the MRD site was based on dry sieving. Five different size sieves, from >2 mm to < 0.063 mm, were used in conjunction with a mechanical sieve shaker.

200 g of dried soil sample was placed on the top sieve, with the other four sieves placed below the first. The assembly was covered at the top and a receiver placed below the last sieve and the whole set-up was placed on the sieve shaker. The weight of the soil that remained in each sieve was taken and the size distribution calculated.

As the OMEX soil contained a lot of oily liquid and after drying the soil stuck together, the particle size analysis was conducted by wet sieving.

200 g of soil sample was placed in a 2-L beaker and 1 litre distilled water was added. The mixture was stirred for 15 minutes to reduce soil aggregate to single grain composition. The mixture was then poured out of the bottle onto the top sieve. Additional water may be added to make the smaller particles pass through the sieve. The finest particle contained in water was obtained by filtration. The soil was dried, weighed and the percentage of each fraction was computed.

3.1.2.5 TOC/Organic Content

Total organic carbon (TOC) was analysed by the Western Australian Chemistry Centre, a government owned analytical laboratory. Organic content was measured by putting 50 g dry soil sample into a furnace at 550°C for 12 hours, and computing the difference of soil weight.

3.1.2.6 Contaminant Analysis

Two general types of contaminants were identified for the project: heavy metals and hydrocarbons. Atomic absorption spectroscopy and gas chromatography were used to analyse heavy metals and hydrocarbons respectively. The analysis of hydrocarbons was performed commercially by Analytical Reference Laboratory as well as other professional testing laboratories. Procedure for AAS analysis is described in section 3.4.

3.2 BATCH EXTRACTION TEST USING CHELATING AGENTS

Three separate chelating agents were evaluated for use as possible extractants for contaminated soil containing heavy metals. Tests were conducted with the following three chelating agents: tetrasodium ethylenediaminetetraacetic acid (EDTA), trisodium nitrilotriacetic acid (NTA), and citric acid. All extractants were bought from SIGMA Chemical Company

as reagent grade chemical. The known physical and chemical properties of all three chelating agents are presented in Table 3.1.

Table 3.1 Chelating Agent Properties

Properties	EDTA-Na ₄	NTA-Na ₃	Citric acid
Appearance & Odor	Odorless, white powder	Odorless white crystalline powder	Odorless white crystals
Formula Wt.	416.21	257.1	210.1
Solubility (H ₂ O)	10 g/100 mL	66 g/100 mL	>50%

Chelating agent solutions with specific concentrations were prepared by adding appropriate amounts of the chemicals to distilled water. This procedure was performed before each experiment and repeated as required throughout the experimental phase of this study.

The basic experimental procedure for heavy metals removal consisted of the following steps. The experimental set-up is illustrated in Figure 3-1.

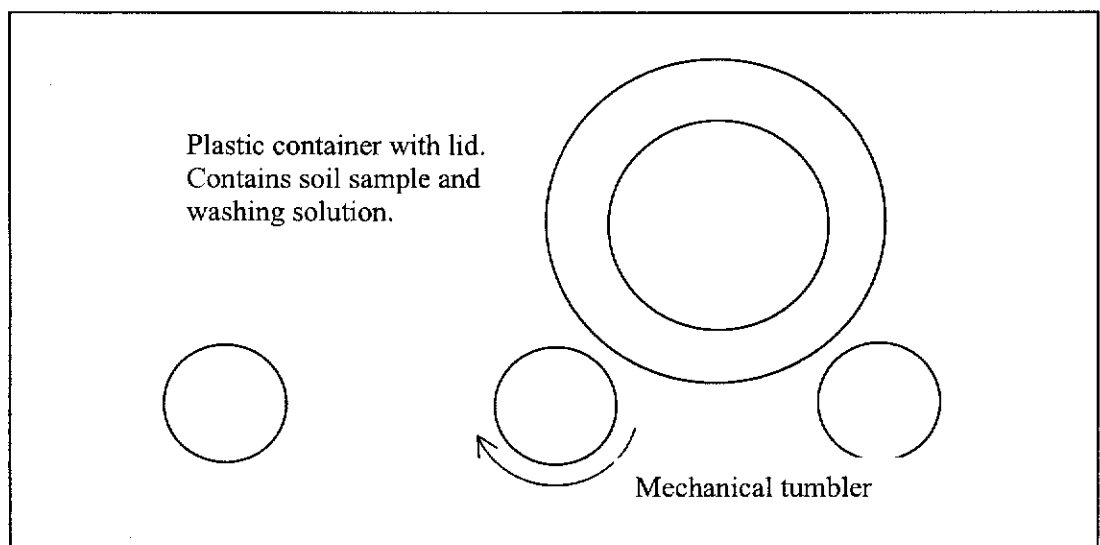


Figure 3.1 Diagram of Experimental Setup.

1. 100 g portion soil sample with 1000 mL extractant solution were placed in a 2 litre screw cap jar.
2. The soil and washing agent were intensively mixed on a rolling table for a fixed period at room temperature ($21 \pm 1^\circ\text{C}$).
3. The soil-solution mixture was withdrawn every 1 hour and then centrifuged at 3000rpm for 10 minutes to separate the aqueous and soil phases.
4. The supernatant was withdrawn with a syringe and filtered with a 0.45 micron filter disk. This sample was ready for analysis of heavy metal concentration by AAS.
5. After washing, the soil-solution mixture was passed through a 0.150 mm sieves to separate coarse and fine soil. Fine soil contained in the liquid was collected using a filter paper and a vacuum pump. Both soils were put into the oven to dry.
6. The dry soil sample was digested by acids according to USEPA Method 3050 before analysed by AAS.

The above procedure consisted of the general steps for a soil washing trial. The concentration of washing solution, contact time, pH and other washing conditions were changed in a suitable range in order to optimize the process parameters of soil washing. A three wheels rolling table was used for most of the experiments because it could load about four bottles in one go. In solution temperature optimization trial, a water bath with temperature regulator was used. In this experiment, the mixture of soil sample and washing solution was placed in the same size plastic bottle which was used in other experimental work. The bottle was put into the water bath and the heavy metals extraction was achieved by propeller agitator with adjustable speed. Before the temperature optimization experiment, the removal efficiency of heavy metal by rolling table and agitation was compared to ensure that they were equivalent.

The effects of the following variables on the extraction of heavy metals were studied: extractant type and concentration, extraction time, liquid to soil ratio (L/S), temperature, rotation speed, and pH (see Table 3.2).

Table 3.2 Experimental Soil Washing Operating Conditions.

Variable	Range
Extractants	EDTA, NTA, Citric acid
Concentrations (% w/w)	0.5, 1, 2, 3, 4, 5, 10
Extraction Time	Up to 29 hours
L/S Ratio	5, 10, 15, 20
Temperature (°C)	20, 40, 60
pH	3, 5, 8

3.3 EXTRACTION TEST USING SURFACTANTS

Five different types of surfactants were used in this study, consisting of one anionic and four nonionic surfactants. They are selected on the basis of a literature survey of surfactant-aided soil washing and biodegradation studies in order to provide a range of surfactant types for the solubilization tests. The anionic surfactant is sodium dodecyl sulfate (SDS), which is widely applied in many areas. The other four nonionic surfactants are Triton X-100, Tween 80, Brij 35 and Tergitol 40. All nonionic surfactants contain different numbers of oxyethylene (OE) group. All surfactants were bought from SIGMA Chemical Company as reagent grade. The known physical and chemical properties of all five surfactants are presented in Table 3.3.

Table 3.3 Surfactants Properties

Properties	SDS	Triton X-100	Tween 80	Brij 35	Tergitol NP-10
Type	Anionic	Nonionic	Nonionic	Nonionic	Nonionic
Name	Sodium dodecyl Sulfate	Octylphenol ethylene oxide condensate	Polyoxyethylene sorbitol ester	Polyoxyethylene 23 lauryl ether	Tergitol NP-10 nonionic
Structure	$\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$	$\text{C}_8\text{H}_{17}\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{O})_{9.5}\text{H}$	$\text{C}_{64}\text{H}_{124}\text{O}_{26}$	$\text{C}_{12}\text{H}_{25}(\text{CH}_2\text{CH}_2)\text{OH}$	$\text{C}_9\text{H}_{19}\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{O})_{9.8}\text{H}$
Formula Wt.	288.38	625	1310	1198	652
Appearance & odor	White powder with slight odor	Clear to slightly hazy, colorless liquid	Viscous liquid, clear yellow	White solid	Light yellow liquid
Solubility (H ₂ O)	10 g/100 mL	Soluble	Soluble	Soluble	Soluble
CMC	1.2×10^{-2} (25°C)	0.22 to 0.24 mM	13-15 mg/L	0.06 mM	0.004 % wt.

The experimental procedure for hydrocarbon removal consisted of the following steps:

1. 100 g portion soil sample with 1000 mL extractant solution were placed in a 2 litre screw cap jar.
2. The soil and washing agent were intensively mixed on a rolling table for a fixed period at room temperature ($21\pm 1^\circ\text{C}$).
3. After the washing, the solid was allowed to settle down and the liquid was decanted, the soil sample was placed back on the rolling table, and 1000 mL distilled water was added for a period of half an hour to remove the residue surfactant.
4. After that, the soil and solution mixture was passed through a 0.150 mm sieves to separate coarse and fine soil. Fine soil contained in liquid is collected using filter paper and vacuums pump. Both soils are put into the oven to dry.
5. The dried soil sample is ready for total organic carbon (TOC) analysis and gas chromatography (GC) analysis.

The effects of the following variables on the extraction of TPH were studied: extractant type and concentration, extraction time, and temperature.

3.4 ANALYTICAL METHODS

3.4.1 Heavy Metal Analysis

Atomic absorption spectroscopy (AAS) was applied to analyse the concentration of heavy metals. To perform atomic absorption spectroscopy, the heavy metal contaminants must be in an aqueous form. Liquid samples collected from the experiment can be directly analysed by AAS. However, heavy metals in solid samples needed to be extracted into the aqueous solvent. Thus, EPA Method 3050 was chosen to digest the soil samples. The digestion procedure is as follows:

1. A 1 g sample (dry weight) was weighed into a digestion vessel. Add 10 mL 1:1 nitric acid, then the mixture slurry was mixed and covered with a watch glass. The sample was heated to $95^{\circ}\text{C}\pm 5^{\circ}\text{C}$ and refluxed for 10 to 15 minutes without boiling. The sample was cooled, and 5 mL of concentrated HNO_3 was added. The cover was replaced and refluxed for 30 minutes. If brown fumes were generated, this step was repeated (addition of 5 mL of conc. HNO_3). The solution was heated at $95\pm 5^{\circ}\text{C}$ without boiling for two hours.
2. To the cooled sample, 2 mL of water and 3 mL of 30% H_2O_2 was added. The vessel was covered with a watch glass and the covered vessel was returned to the heat source for warming.
3. 30% H_2O_2 in 1-mL aliquots was added with warming until the effervescence is minimal or until the general sample appearance was unchanged.
4. The sample was covered with a watch glass and continued heating the acid-peroxide digestate at $95\pm 5^{\circ}\text{C}$ without boiling for two hours.
5. 10 mL conc. HCl was added to the sample and covered with a watch glass. The sample was placed on the heating source and refluxed at $95\pm 5^{\circ}\text{C}$ for 15 minutes.
6. The digestate was filtered through Whatman No. 41 filter paper (or equivalent) and the filtrate was collected in a 100-mL volumetric flask and analysed subsequently by an AAS.

The AAS used was a Varian SpectrAA 10 Atomic Absorption Spectrometer. The metal ions, which were measured were Cd, Cr, Cu, Mn, Ni, Pb, and Zn. The analysis of any metal ion by AAS requires the preparation of standards for the construction of calibration curves. All samples were tested in the most sensitive wavelength for the particular metal. Table 3.4 shows the working conditions of the AAS instrument for the metal ions tested.

Table 3.4 Analysis Condition of AAS.

Element	Fuel	Support	Wave Length (nm)	Spectral Band Pass (nm)	Optimum Working Range (µg/mL)
Cd	Acetylene	Air	228.8	0.5	0.5-2.0
Cr	Acetylene	Nitrous Oxide	357.9	0.2	2.0-8.0
Cu	Acetylene	Air	324.7	0.5	2.0-8.0
Mn	Acetylene	Air	279.5	0.2	1.0-4.0
Ni	Acetylene	Air	232	0.2	3.0-12.0
Pb	Acetylene	Air	217	1.0	5.0-20.0
Zn	Acetylene	Air	213.9	1.0	0.4-1.6

The operation procedure is summarized in the following. In general, after choosing the proper lamp for the analysis, the lamp was allowed to warm up for a minimum of 15 minutes. During this period, the instrument was aligned, the monochromator was set at the correct wavelength. The proper monochromator slit width was selected, and the current was adjusted according to the manufacturer's recommendation. Subsequently, the flame was lighted and the flow of fuel and oxidant was regulated. The burner and the nebulizer flow rate were manipulated for maximum percent absorption and stability. The photometer was balanced and a series of standards of the element of interest was made. A calibration curve was obtained by plotting the concentrations of the standards against absorbances. The test samples were then aspirated and the concentrations determined directly.

For determination of metal concentration in solid samples, it was calculated by the following equation:

$$\text{mg metal/kg sample} = \frac{A \times V}{W} \quad (3.2)$$

where:

A = mg/L of metal in processed sample from calibration curve,

V = Final volume of the processed sample, mL.

W = Weight of sample, grams.

3.4.2 Hydrocarbon Analysis

3.4.2.1 Total Organic Carbon (TOC)

To obtain a rough estimate of organic material after the washing, soil samples were analysed for total organic carbon (TOC) first after soil washing experiment. The TOC analysis was performed by Chemistry Centre using Walkley and Black method S09.

3.4.2.2 Total Petroleum Hydrocarbon (TPH) & Polycyclic Aromatic Hydrocarbon (PAH)

Such analysis was performed by Analytical Reference Laboratory (ARL), a commercial analytical laboratory.

CHAPTER FOUR

WASHING OF HEAVY METALS FROM CONTAMINATED SOIL WITH CHELATING AGENTS

4.1 SOIL CHARACTERIZATION

Selected physical and chemical properties of MRD and OMEX soil samples are presented in Table 4.1.

Table 4.1 Selected Properties of MRD and OMEX Soil Samples.

	MRD Soil	OMEX Soil
Appearance	Brown-yellow colour, dry and loose structure, without smell.	Dark-black colour, little fluidity and pungent smell.
Moisture Content	1.4%	23.9%
pH	6.6	3.5
Organic Content	NA*	15.4%
TOC	NA	7.04%

* NA: Not available.

The sample collected from MRD site is yellow-brown in colour, with a dry and loose structure, and without smell. The sample collected from OMEX site is dark-black colour, containing free liquid on the top of the sample, with little fluidity, and with pungent smell. From the observation of these two samples, the OMEX soil sample was apparently contaminated and saturated by waste liquid.

The moisture content for the MRD sample is 1.4% in wet weight, and for the OMEX sample is 23.9% in wet weight. Moisture in MRD sample was much less than that of OMEX sample. MRD sample was collected 0.5m below the ground level, so the soil was still dry due to the dry weather in Perth. As the OMEX site was used for the disposal of liquid waste including acid, oil and grease, the moisture in the soil is abundant. As the OMEX site was used for dumping organic liquid waste, the problem of defining "dry conditions" is difficult. Volatile liquids other than water may also be present. If subjected to too high temperatures, organic materials are oxidized or decomposed and lost from the sample. The temperature used here was 100-110°C, whether the moisture content represents water loss or oxidation and decomposition is difficult to tell. Further investigation by using lower temperature may be required.

The pH of the MRD soil sample was 6.6, quite close to neutral; while the OMEX soil sample was acidic with a pH value of 3.8. The OMEX soil was acidic because liquid wastes disposed at the site included sulphuric acid. The organic content and total organic carbon (TOC) were also high in OMEX soil sample.

Both MRD and OMEX soil samples were sieved using mesh No. 10, 16, 40, 100, and 230 standard sieves. This provided nominal particle size cuts of 2mm, 1.18mm, 0.450mm, 0.150mm, 0.063mm and fines respectively. The resultant distribution is given by weight fraction in Table 4.2 and Figure 4.1.

According to U.S. Department of Agriculture Classification System, the MRD soil is classified as loamy sand, and the OMEX is sandy loam. Figures 4.1 and 4.2 show the critical difference between these two types of soil is the percentage of silt and clay (<0.063mm). The percentage of silt clay in OMEX soil is about four times that in MRD soil. The high percentage of silt and clay indicated the soil had a large total surface area per unit weight and also had more affinity to adsorb contaminants, both hydrocarbons and heavy metals. The high percentage of fine soil increase the difficulty of washing process to

achieve desirable outcome and further treatment for those fine soils may be required.

Table 4.2 Soil Size Distribution

Sieve Size	Size Range (mm)	MRD sample (w/w)	OMEX sample (w/w)
+10	>2	5.1%	6.7%
+16	2 – 1.18	2.7%	3.7%
+40	1.18 – 0.425	26.2%	27.6%
+100	0.425 – 0.150	40.7%	27.7%
+230	0.150 – 0.063	19.5%	11.8%
-230	<0.063	5.8%	22.5%

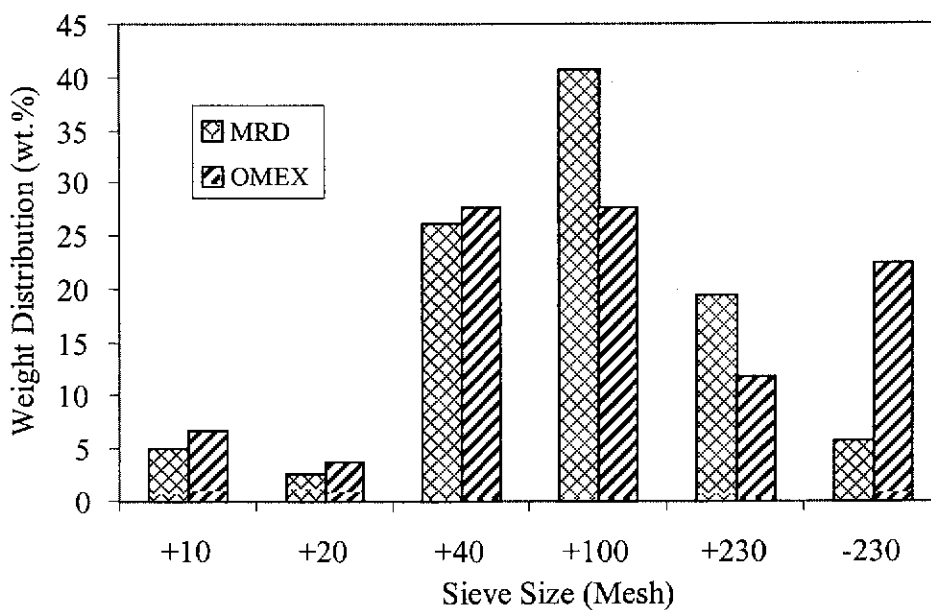


Figure 4.1 Weight Percent by Size Fraction.

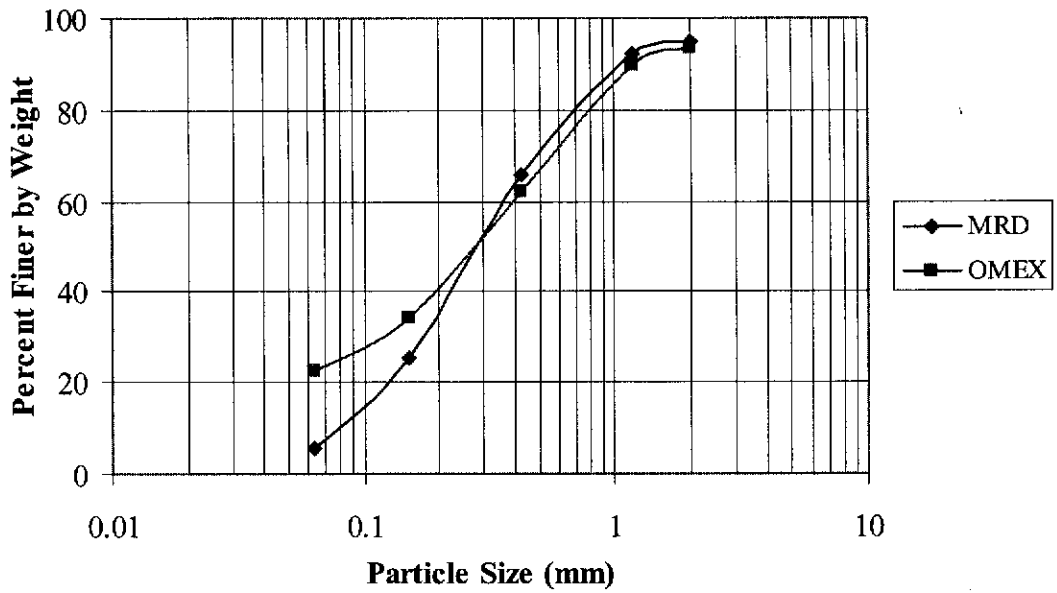


Figure 4.2 Particle Size Distribution (% finer than).

The results of contaminant analyses for the MRD soil samples are listed in Table 4.3. A total of 11 samples were collected from the MRD site and sent for analyses. The results show that the MRD site is not greatly affected by hydrocarbon contaminants. The soil was also not significantly contaminated by some selected heavy metals.

Table 4.3 Result of Contaminant Analysis for MRD Soil Samples. (Unit: mg/kg)

Sample	1	2	3	4	5	6	7	8	9	10	11
As	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Cd	0.8	0.8	1.6	1.2	<0.1	1.7	0.4	0.1	0.2	0.6	4.3
Cr	28	25	94	16	4	22	16	4	4	35	55
Cu	39	4	27	66	2	8	4	2	1	9	33
Pb	4	5	15	6	8	10	6	6	35	5	12
Mn	6	8	9	6	8	5	8	11	10	6	22
Zn	<1	<1	2	2	1	2	<1	<1	<1	1	3
C10-14	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0	<0.2
C15-28	<0.4	<0.4	15	1.3	<0.4	14	20	<0.4	<0.4	22	25
C29-36	<0.4	<0.4	38	3.1	<0.4	30	17	<0.4	<0.4	28	48
BTEX	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
PAH	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2

Compared with Landfill Waste Classification and Waste Definitions issued by the Department of Environmental Protection Western Australia (see Appendix 1), the MRD soil can be classified as Class II Putrescible Landfill and can be landfilled safely.

The results of contaminant levels for the OMEX soil samples are listed in Table 4.4 which shows that the soil was severely contaminated by both hydrocarbons and heavy metals.

Table 4.4 Result of Contaminant Analysis for OMEX Soil Samples. (Unit: mg/kg)

Contaminant	OMEX Sample	Disposal Criteria
Arsenic (As)	2.8	NA
Cadmium (Cd)	1.5	5
Chromium (Cr)	34.5	250
Copper (Cu)	7	100
Lead (Pb)	986	300
Nickel (Ni)	2	100
Zinc (Zn)	284	500
Total Petroleum Hydrocarbon (TPH)	29000	1000
Polycyclic Aromatic Hydrocarbon (PAH)	56	20

For instance, compared with landfill regulation, the concentration of TPH should be no more than 1000mg/kg; and for lead, should be no more than 300mg/kg. TPH, due to its high toxic and cumulative effect to induce cancer and mutations, must be treated to meet the criteria before landfill. The heavy metal contamination is mainly caused by lead and zinc. Further research of heavy metals removal will focus on these two elements. To improve the information on the distribution of contaminants in different size fractions, four size fractions, <0.063mm, 0.063-0.150mm, 0.150-0.425mm and 0.425-

1.18mm, were analysed for the concentration of heavy metals. The results are summarized in Figure 4.3.

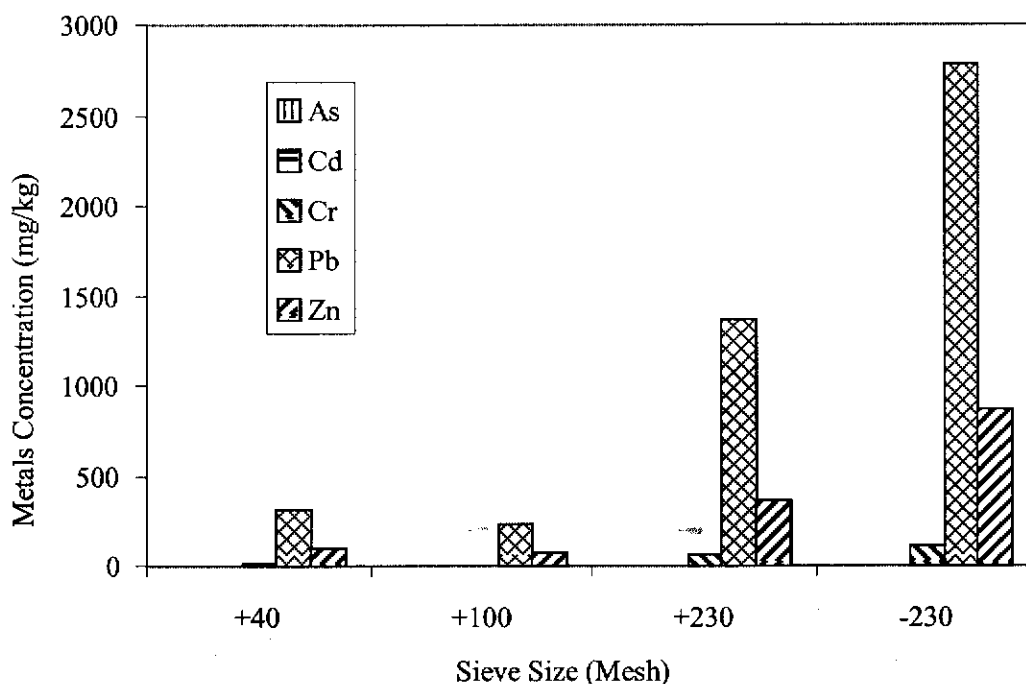


Figure 4.3 Metal Incidence by Size Fraction.

These four particle size fractions were selected as they represented most part of the soil (about 90%). The fraction >2mm mainly contained wood chip and fine gravel, so it should be removed before the process. As can be seen, metals concentration increase with decreasing particle size except the first fraction. This demonstrates that the small particle soil has a higher affinity to adsorb contaminants. The fractions below 0.150mm contained much more contaminants than coarse soil fraction. The soil after washing should be separated in this size to check out whether the fine soil needed further treatment. The concentration of As, Cr, and Cd is not apparent in the figure due to the magnitude of Pb and Zn. Numerical values are listed Table 4.5.

Table 4.5 Heavy Metal Distribution in OMEX Soil.

Sieve Size (mesh)	As	Cd	Cr	Pb	Zn
+40	3.2	0.2	8.8	315	97
+100	0.7	0.1	2.0	226	68
+230	5.1	2.2	57.8	1357	358
-230	5.7	5.0	106.7	2783	862

(Unit: mg/kg)

The distribution of TPH in coarse soil (>150 μ m) and fine soil (<150 μ m) is shown in Table 4.6.

Table 4.6 TPH Distribution in OMEX Soil.

	C ₆₋₉	C ₁₀₋₁₄	C ₁₅₋₂₈	C ₂₉₋₃₆
Coarse Soil (>150 μ m)	<0.2	3.6	590	860
Fine Soil (<150 μ m)	<0.2	490	27000	50000

(Unit: mg/kg)

The results showed that most TPH found in the OMEX soil were long chain hydrocarbons, ranging from C₁₅ to C₃₆. The TPH concentration in fine soil fraction is much higher than coarse soil due to its high affinity to adsorb organic matter.

4.2 EXTRACTION STUDY USING CHELATING AGENTS

4.2.1 Selection of Chelating Agents

As the concentration of heavy metals in MRD soil samples is below the regulation levels, it does not need any further treatment. Therefore, only OMEX soil was chosen as the target in this study. Three chelating agents, EDTA, NTA, and citric acid were selected for heavy metals removal. At first, experiments were performed to determine the removal efficiency of each extractant. Two different concentrations (5% and 10% w/w) and three hours

extraction time were employed in the experiment. Results of the percentage removal determined by atomic absorption spectrometer (AAS) analyses for the OMEX soil after washing are shown in Figure 4.4 for both Pb and Zn.

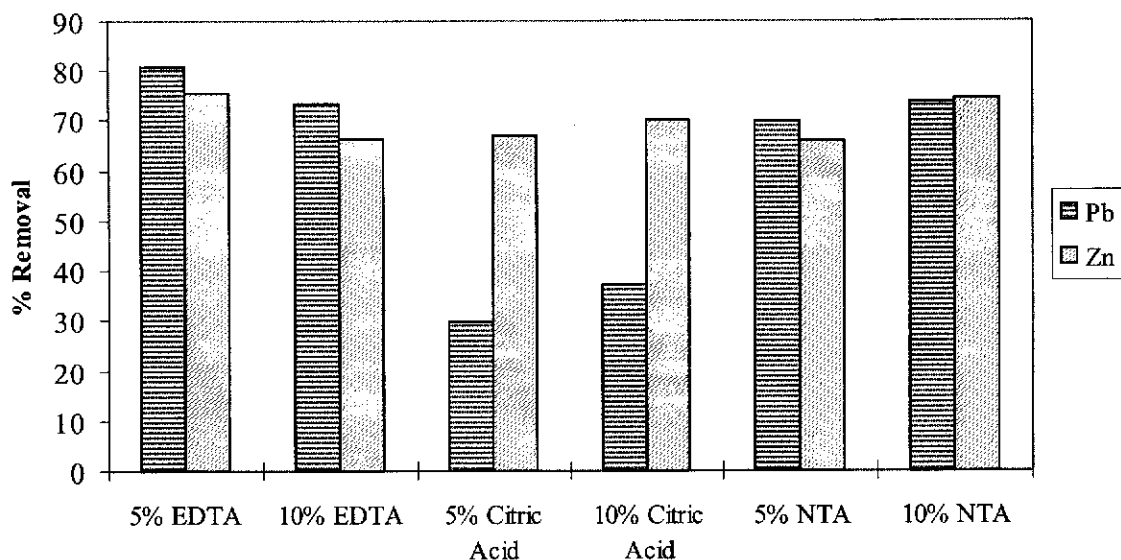


Figure 4.4 Removal Efficiency of Pb and Zn by Different Extractants.

As can be seen from the figure, EDTA produced the highest heavy metal removal for both Pb and Zn. The higher concentration (10%) of EDTA was less efficient than at a lower concentration (5%). NTA and citric acid washes yielded removals less than those obtained by EDTA. However, the differences of Pb and Zn removal efficiencies obtained by EDTA and NTA is not significant, because both EDTA and NTA can form strong water soluble complexes with Pb and Zn. The logarithmic stability constants are 18.3 and 11.8 for the formation of PbEDTA^{2-} and PbNTA^- , and 16.26 and 10.45 for the formation of ZnEDTA^{2-} , and ZnNTA^- .

Considerations of chelate chemistry indicate that five or six-membered rings, such as EDTA, are most stable. Thus it is apparent that the most useful chelating agents are those which favour the formation of the maximum number of such rings and fully saturate the coordination requirements of the ions in a one-step reaction. As a hexadentate ligand, EDTA binds divalent cations, like Pb, very strongly. The complexing power of EDTA lies in the

ligand forming nitrogen atoms and the carbonyl oxygens of the acetic acid groups (West 1969). Structurally, all six ligand groups of the EDTA fill all the available coordination sites of the Pb ion. Furthermore, EDTA is more preferable than NTA because the adsorption of complexation on soil surface. Since all major functional groups of the MeEDTA²⁻ are involved in the complexation, there is little opportunity for bridging to the soil surface. The metal coordination chemistry of NTA complexation is quite different from EDTA. The NTA is quadridentate and metal complexation leaves two metal coordination sites available for interaction with soil surface. Re-adsorption of the MeNTA⁻ could occur through the coordination sphere of the metal, and the adsorption behavior of the complex would be analogous to the free metal (Elliott 1989).

The results also confirm the information presented earlier: EDTA extraction generally performs better than citric acid extraction (Peters 1993). The study indicated that Pb removal using citric acid was much less than those obtained by either EDTA or NTA. Experiments done by Peters (1993) showed that citric acid was favoured to form complex with Zn rather than with Pb in terms of solubilization.

Based on the above experiment results obtained in this study, EDTA was selected for further extraction studies.

4.2.2 EDTA Concentration Selection

As the initial studies showed that 5% EDTA performed better than 10% EDTA, it became necessary to determine the optimum EDTA concentration to use for this study. The range of EDTA concentrations were set between 0.5% to 5% (w/w). Each experiment was conducted for 29 hours at room temperature (21±1°C).

As was stated in the previous section, after washing the soil sample was separated into two fractions: a fine soil fraction below 0.150mm and a coarse

soil fraction above 0.150mm. Each fraction was digested and analysed for heavy metal concentration and the overall concentration of the soil was calculated from the percentage of each soil fraction and its concentration. From the analytical results, it indicated that the heavy metal concentration in the coarse soil fraction was below the detection limit of AAS. The detection limit of AAS is 2 mg/L. The result at the end of 29 hours for each of the washing experiments are shown in Figure 4.5a and 4.6b for Pb and Zn removals respectively.

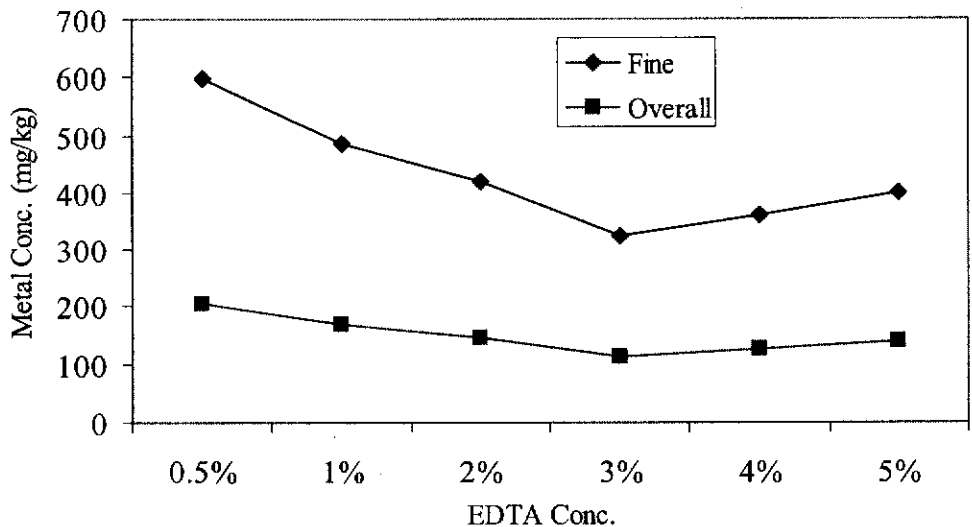


Figure 4.5a Effect of EDTA Concentration on Pb Removal.

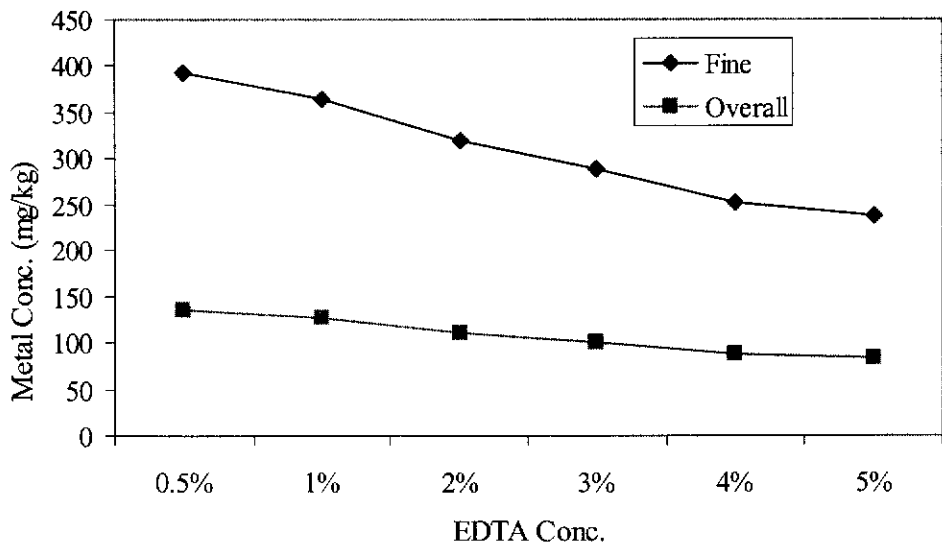


Figure 4.5b Effect of EDTA Concentration on Zn Removal.

Figure 4.5a shows that after washing by 0.5% EDTA solution, approximately 590 mg/kg of Pb was left in the fine soil, and around 210 mg/kg for the whole soil. The concentration of Pb in the fine soil decreased for higher EDTA concentration up to a maximum at 3% with about 320 mg/kg of Pb in fine soil and 110 mg/kg of Pb for the composite soil. Thereafter the concentration of Pb contained in the fine soil increased with higher EDTA concentration. This phenomenon is rather unexpected, that is the Pb concentration in the fine soil decreased with higher than 3% EDTA concentration.

The EDTA used in this study is tetrasodium salt due to its good solubility. The final slurry pH values of the samples were about 10 for the 5% washes and 7 for the 3% washes. The EDTA ligand is generally most effective in chelating heavy metals from an aqueous system in the pH range of 3-6 (Bell 1977). At these pH conditions, $H_2[EDTA]^{2-}$ is often the dominant form in which the metal ions that are present generally form 1:1 stoichiometric complexes. Therefore, the lower performance of higher EDTA concentration could be attributed to the alkaline conditions which prevail in the leaching solution. The decrease of Pb solubilization at alkaline pHs has been reported in the literature (Peter 1992). Furthermore, Ragahavan (Raghavan 1991) discussed that the presence of large concentrations of ions not participating in chelation (such as the large quantity of Na^+ ions present in the EDTA solutions) can also lower the stability of Pb chelant complexes. The factor may also account for the low recovery of Pb in high EDTA concentration because Na was derived from the EDTA tetra sodium salt which was used in the study.

The removal of Zn from the soil is a bit different with that for the removal of Pb, where Zn concentration in the soil continued to decrease with higher EDTA concentrations from 0.5% to 5%. When EDTA concentration was 4% or higher, the drop of residual Zn in the soil levelled off.

Figure 4.6 illustrates the percentage removal of Pb and Zn for different concentrations of EDTA solution used. As can be seen from the figure, the percentage removal of Pb is always higher than that of Zn. The percentage

removal of Pb increased from 79% up to the maximum of 89% at 3% EDTA concentration, thereafter the removal percentage dropped to 86% at 5% of EDTA concentration. The percentage removal of Zn continued to increase from 52% to 71% for EDTA concentrations ranging from 0.5% to 5%. The initial concentrations of Pb and Zn in the untreated soil samples were 986 mg/kg and 284 mg/kg respectively.

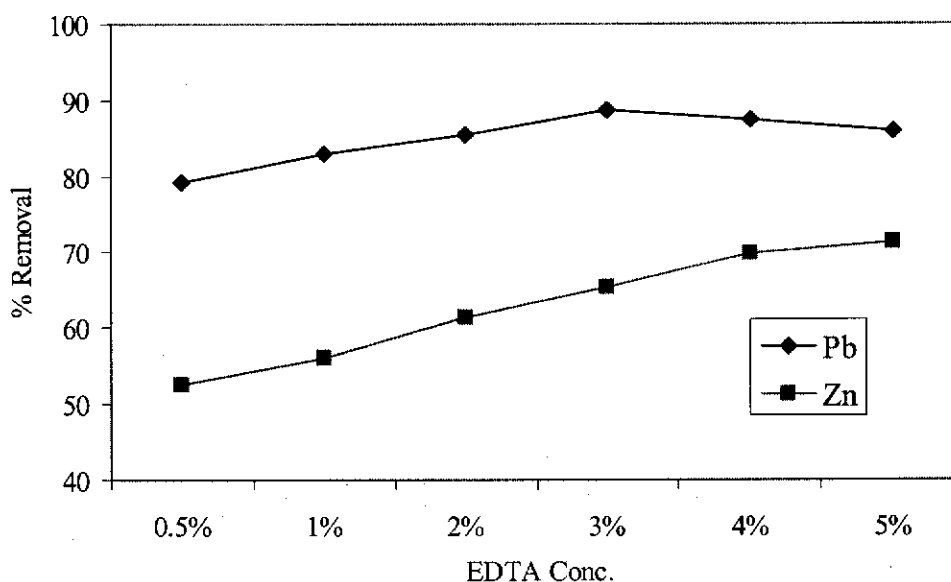


Figure 4.6 Removal Efficiency of EDTA for Pb and Zn Removal.

Usually the metals found in soils with smaller total concentrations may be more tightly bound in the soil, because metals bind tightly to a soil's energy surface sites at low adsorption densities (Cline 1993). Therefore, it is more difficult to extract metals with low initial concentration from soil. A number of other authors distinguished that Zn extraction percentages depended more on the initial concentration than that of Pb (Tuin 1990).

They discovered that greater proportions of Zn are bound stronger to the clay soils than of Pb. From literature review, the unhydrated Pb ion has greatest ionic radius of the heavy metals in environmental study (Weast 1982):

Metal ion	Cd ²⁺	Cr ³⁺	Cu ²⁺	Ni ²⁺	Pb ²⁺	Zn ²⁺
Crystal ionic radius (A)	0.97	0.63	0.72	0.69	1.20	0.74

Helios-Rybicka and Forstner (1986) reported the possible adsorption of metals with an appropriate ionic diameter to more interior sites of three-layer clay minerals. Cu, Ni, and Zn could be bound to interlayer sites or substitute Fe or Mg ions which are of similar size. The high Pb extraction percentages might also be explained by its ionic radius. The Pb ion is probably bound to more exterior sites and can be reached by EDTA more easily.

Finally, based on the experimental findings, a EDTA concentration of 3% (w/w) was selected for all further washing experiments. At this concentration, Pb has maximum percentage removal, and Zn removal could meet the clean-up criteria. Furthermore, the contamination level of Pb was much higher than Zn in the original soil.

4.2.3 Release Kinetics of Heavy Metals

In determining the optimum EDTA concentration for soil washing, samples of the solution were also collected at regular intervals for determination of metals release kinetics. Liquid samples were collected at every hour for each of the experiment. The solution Pb and Zn concentrations were analysed by AAS and the results are shown in Figure 4.7a and 4.7b, where 6 curves are presented, one for each EDTA concentration used.

For Pb release kinetics, it can be seen from the figure that apart from the low Pb concentration with 0.5% EDTA, other EDTA concentrations tended to cluster together with 3% EDTA giving the highest Pb concentration. In the case of Zn release, 4% and 5% EDTA had higher Zn recovery than the other 4 lower concentrations. The difference of Zn release by using 4% and 5% EDTA is not significant.

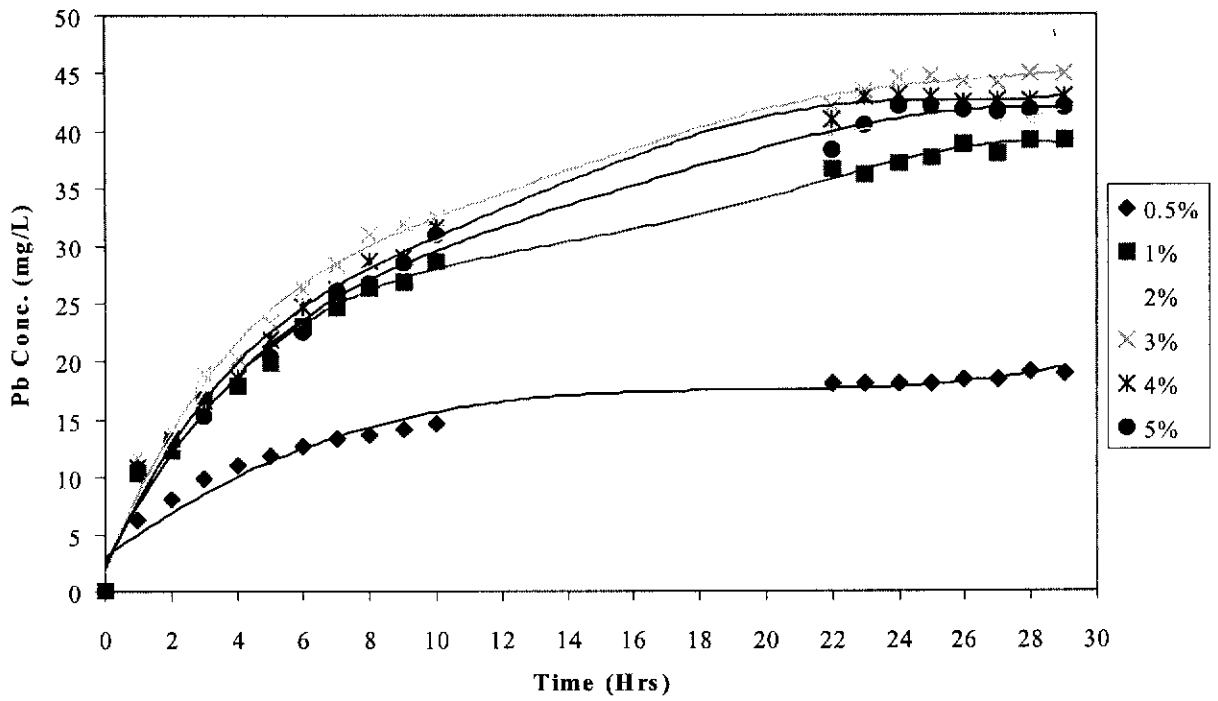


Figure 4.7a Kinetics of Pb Removal Using EDTA.

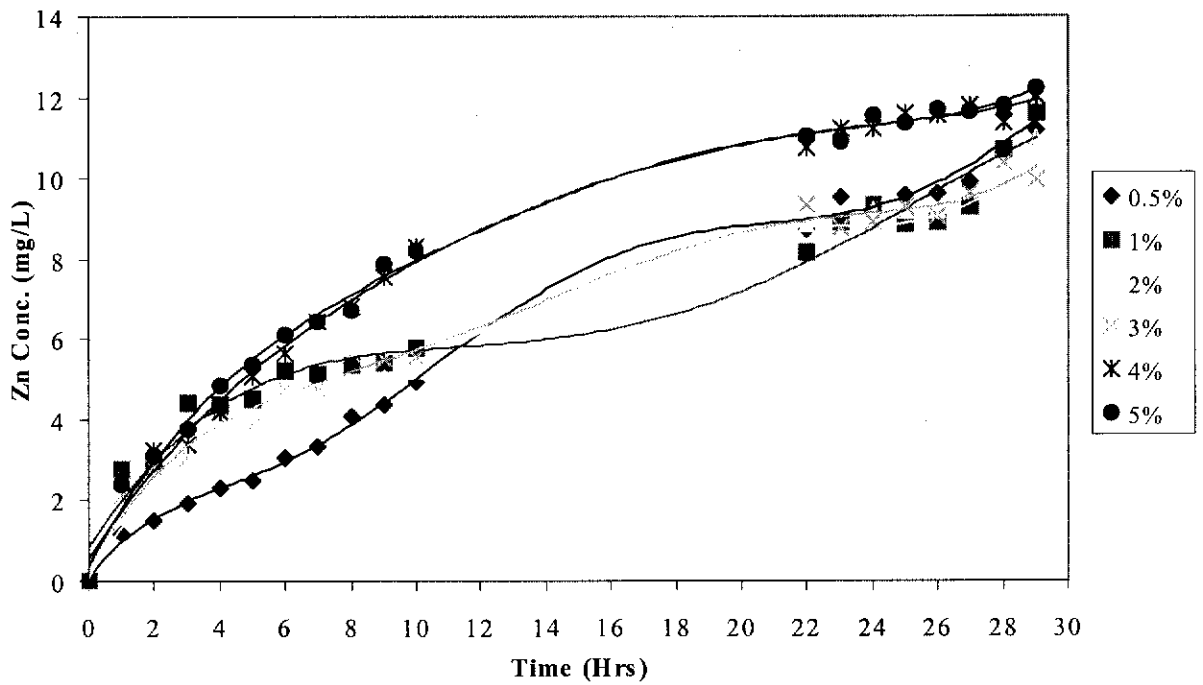


Figure 4.7b Kinetics of Zn Removal Using EDTA.

In general, both figures show that Pb and Zn removal is very slow requiring more than 10 hours to approach equilibrium condition. This finding is in contrast to results reported by other workers (Tuin 1990, Cline 1995, Lo 1999) who found that heavy metal removal was rapid and reached equilibrium within 3 hours. Those researchers found a two-step kinetic process in metal desorption. First, metals release was initially rapid, with the majority of the metal removal occurring within the first few hours; then followed by a second slower, more gradual step of metal removal. The low rate of metal removal found in this study could possibly be explained by the different type of soil used and the high hydrocarbon contamination. Most contaminated soils used in those research mentioned above were artificially spiked with metal solution, while OMEX soil was an industrial waste site and has been contaminated for more than 20 years. In the real waste site soils, metals might reach more interior binding sites of minerals and can be covered by surface coatings or they may exchange with ions in the primary mineral lattice (Helios-Rybicka 1986). Metals may also form less soluble oxide or hydroxylic complexes due to aging (Larkworthy 1987). Therefore, the metals in the freshly spiked soil had been afforded little opportunity to weather and mineralize and were easily removed from the soil. Furthermore, OMEX soil not only contained significant quantities of Pb and Zn, but also up to 15% organic content including hydrocarbons. The organic content would limit the removal of metals from soil as well.

4.2.4 Heavy Metal Removal at Different Time Interval

A series of experiments was carried out to investigate the heavy metal removal at different time interval with a 3% EDTA solution. A total of 7 bottles containing the mixture of OMEX soil and EDTA solution (in L/S ratio of 10) were loaded onto the rolling table. One bottle was taken away for analysis at every hour and the solid was separated from the mixture for metal concentration analysis. The washing time chosen was for 7 hours as it was convenient for the experimental operation. The heavy metal concentration left in the soil after washing was illustrated in Figure 4.8a and 4.8b for both Pb and Zn, respectively.

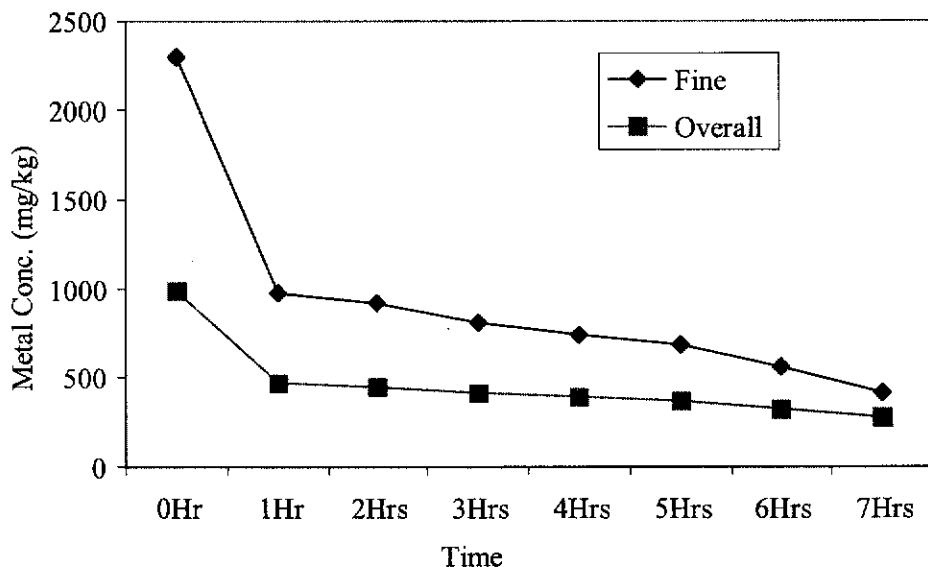


Figure 4.8a Pb concentration in Soil.

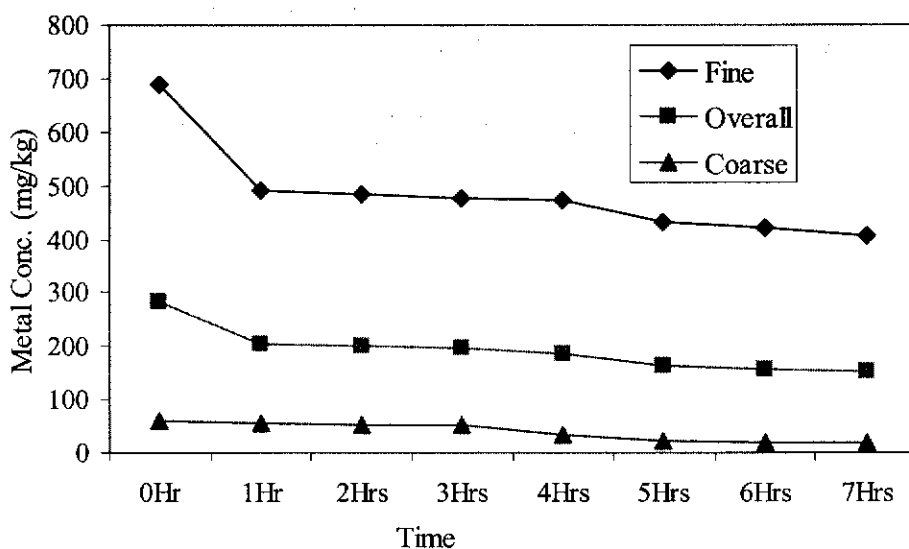


Figure 4.8b Zn Concentration in Soil.

It can be seen from the figures that Pb removal from fine soils is more rapid than Zn removal. Initially, the Pb concentration was 2294 mg/kg in the fine soil and 986 mg/kg in the whole soil. After one hour washing, the concentration of Pb was 975 mg/kg in the fine soil and 460 mg/kg in the whole soil. About 66% Pb was removed from the soil in the first hour. In the

following 6 hours, Pb removal became more gradual. At the end of 7 hours washing, 407 mg/kg Pb was found in the fine soil and 271 mg/kg Pb was left in the whole soil. As can be seen from the Figure 4.8a, Pb concentration in the soil still tended to decrease for longer washing time than 7 hours. Meanwhile, Pb removal in the first hour was much faster compared with subsequent hours.

In the case of Zn removal, the rate of removal in the first hour was also faster than subsequent hours. For instance, the initial concentration of Zn in the fine soil was 689 mg/kg and it dropped to 492 mg/kg after the first hour washing. The final concentration of Zn in the fine soil after 7 hours washing was 406 mg/kg. Zn removal from the coarse soil, however, was pretty slow, and the difference before and after the first hour was not significant. This is probably due to the low initial concentration of Zn and making it difficult to be removed from the soil.

The removal efficiency of 3% EDTA solution at each washing hour was shown in Figure 4.9.

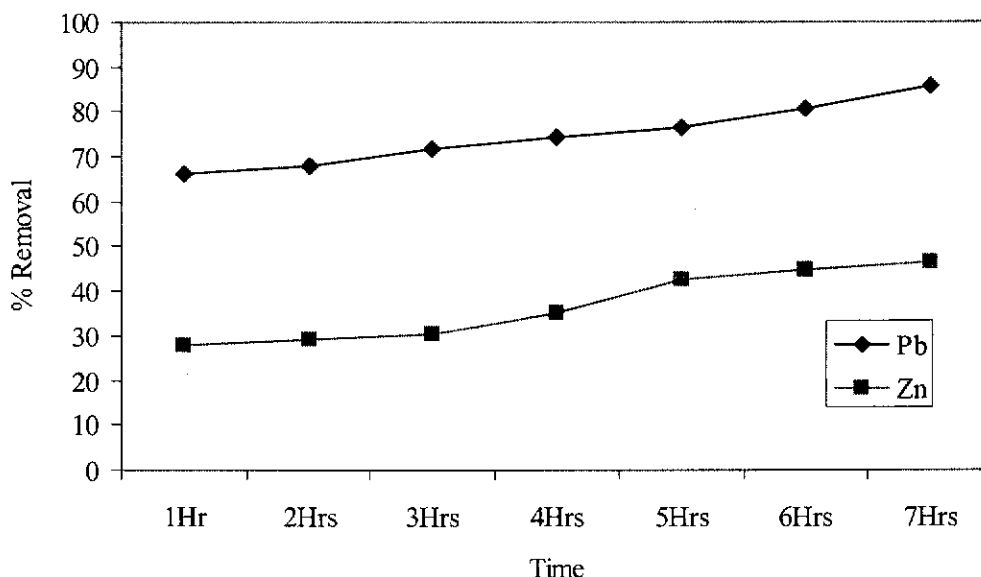


Figure 4.9 Removal Efficiency of 3% EDTA Solution for both Pb and Zn removed from OMEX soil at 7 Hours.

4.2.5 Effect of Solution pH.

All experiments performed above in the earlier section were without adjusting the solution pH value. The washing solution was not buffered and its pH was altered by the natural neutralizing capacity of the soil. The pH value of 3% EDTA solution was about 10, and after mixing with soil sample it dropped to about 8. In this experiment, pH value of the mixture of soil and EDTA solution was adjusted by concentrated HCl before washing. Initially, the pH value was set on 1, 3, and 5. But in the experiment, when pH of EDTA solution dropped below 2, a white cloudy precipitate was formed and therefore it was not suitable for the experiment. At last, only pH3 and pH5 were investigated in the study. The washing condition for this experiment is room temperature, rolling at 67 rpm, and washing for 3 hours. Figure 4.10a and 4.10b show the metal analysis of OMEX soil after washing for different pH values.

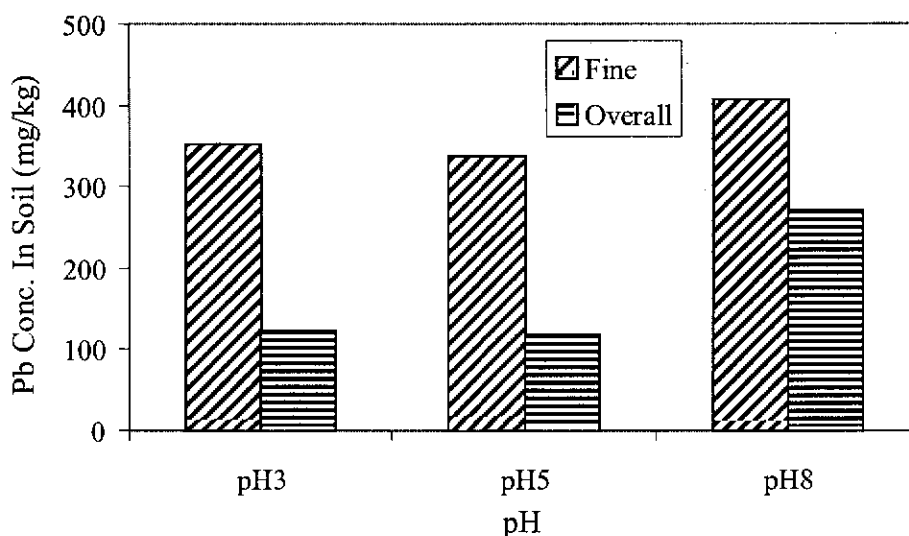


Figure 4.10a Effect of Solution pH on Pb Removal from OMEX Soil.

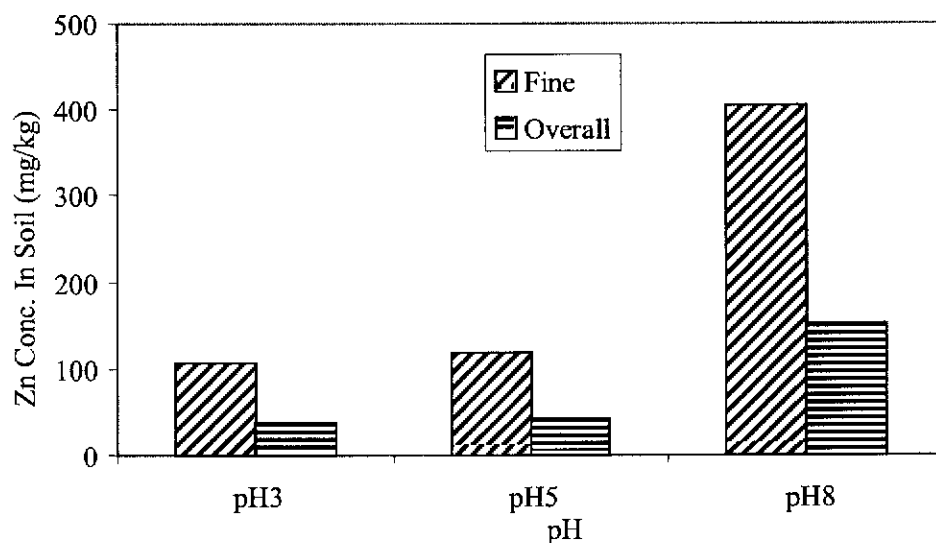


Figure 4.10b Effect of Solution pH on Zn Removal from the OMEX Soil.

Figure 4.10a and 4.10b illustrate that when the pH value dropped, the concentration of both Pb and Zn in the soil decreased. Particularly for Zn removal, significant amount of Zn was removed from the soil with decreasing pH values. When the pH dropped from 8 to 3, the Zn concentration in the fine soil decreased from 406 mg/kg to 107 mg/kg.

As mentioned in the section 4.2.2, the optimal pH value for EDTA complexation is in the range of 3-6, where $H_2[EDTA]^{2-}$ is often the dominant form in which the metal ions that are present generally form 1:1 stoichiometric complex. From this experiment, it is evident that acidic to neutral washing condition can improve heavy metals removal from soil. During the optimum pH range, the difference of metal removal between pH3 and pH5 is not significantly different. In fact, EDTA begins to protonate at pH values less than 4. Protonation reduces EDTA solubility thereby reducing the effectiveness of the ligand to chelate metals. Using EDTA at lower pH value, the dissolution effects of the acid apparently dominate over those of the ligand. Although both proton- and ligand-enhanced dissolution mechanisms can be simultaneously operative, it is likely that the enhancement of the EDTA is minimal (Davis 1995). When the pH value drops below 2, EDTA will be fully protonated as the form of H_4EDTA and precipitate out of solution.

The removal efficiency of EDTA solution at different pH values for the removal of both Pb and Zn is illustrated in Figure 4.11.

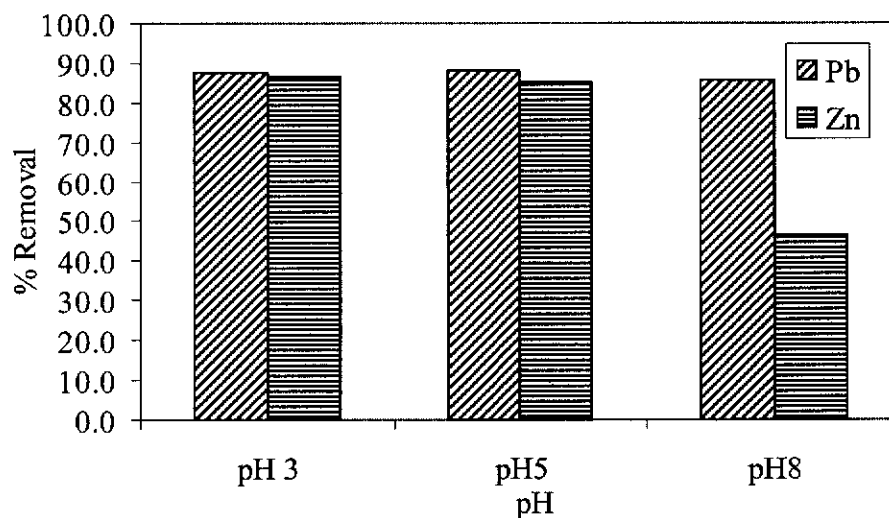


Figure 4.11 Removal Efficiency of EDTA Solution at Different pH Values.

4.2.6 Variation of Liquid to Solid Ratio (L/S)

As all earlier experiments were conducted with a constant liquid to solid ratio (L/S) of 10, it was also essential to find the most economic L/S ratio for the soil washing. A series of experiments were conducted for L/S ratio of 5 to 20. This set of experiments was conducted at room temperature for a constant convenient washing time of 7 hours. The results of both Pb and Zn removals are illustrated in Figure 4.12.

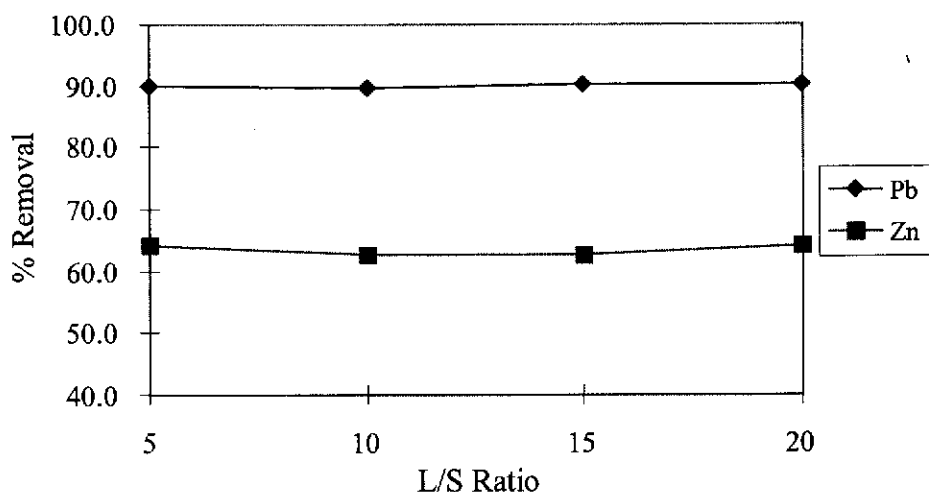


Figure 4.12 Effect of L/S Ratio on Removal Efficiency.

As can be seen from the figure, extractions of both Pb and Zn from the OMEX soil were virtually constant over the whole L/S range studied. This finding shows that using the practical lower limit of L/S=5 is sufficient for both Pb and Zn removal as at this low ratio sufficient ligand sites are available for metal complexation to occur. Therefore, the smaller liquid metal concentrations at higher L/S values cause hardly any shift in the metal distribution between liquid and solid phase. Van Benschoten (1997) also measured that little or no effect of L/S ratio on metals removal when it varied from 5 to 20. Part of the metal pollution is probably bound more strongly to soil components and it is not influenced by the smaller metal concentration in solution. Increasing L/S offers therefore no opportunity to improve the extraction efficiency very much. For economic reasons, it is essential to operate the soil washing at the lowest possible L/S ratio, in this case at L/S=5.

4.2.7 Effect of Solution Temperature

In order to monitor the effect of solution temperature on metal removal, some experiments were conducted by varying the temperature of extractant solution. A two-litre bottle placed in a temperature controlled water bath was

used as the extraction vessel. A constant extractant volume of 1000mL and a liquid to solid (L/S) ratio of 10 were used for each experiment. The soil slurry was mixed vigorously at 400 rpm using standard laboratory mixer with a stainless steel impeller. The temperatures being examined were 20, 40 and 60°C. After 7 hours washing, the soil sample was separated from the mixture and analysed for heavy metal concentrations after digestion. The heavy metal concentrations of soil sample after washing were shown in Figure 4.13 a, b for Pb and Zn respectively.

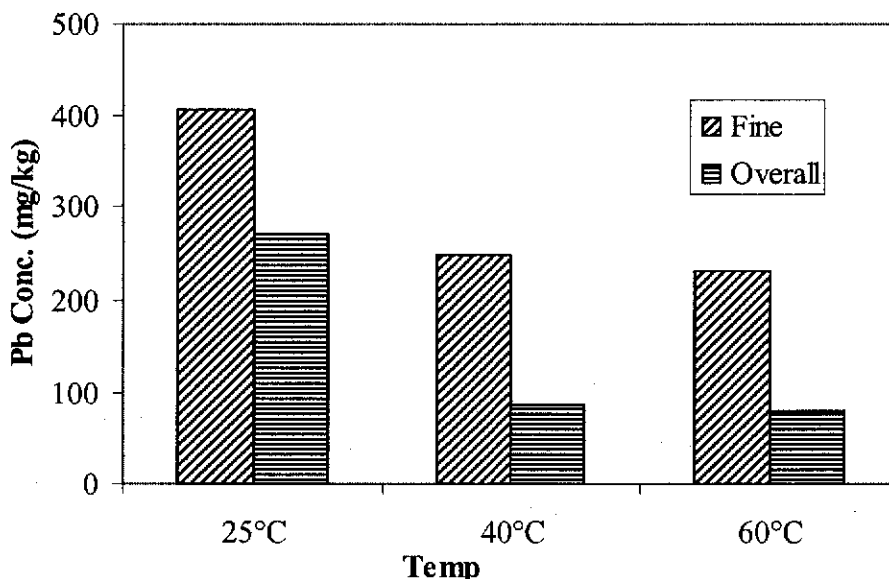


Figure 4.13a Effect of Solution Temperature on Pb Removal.

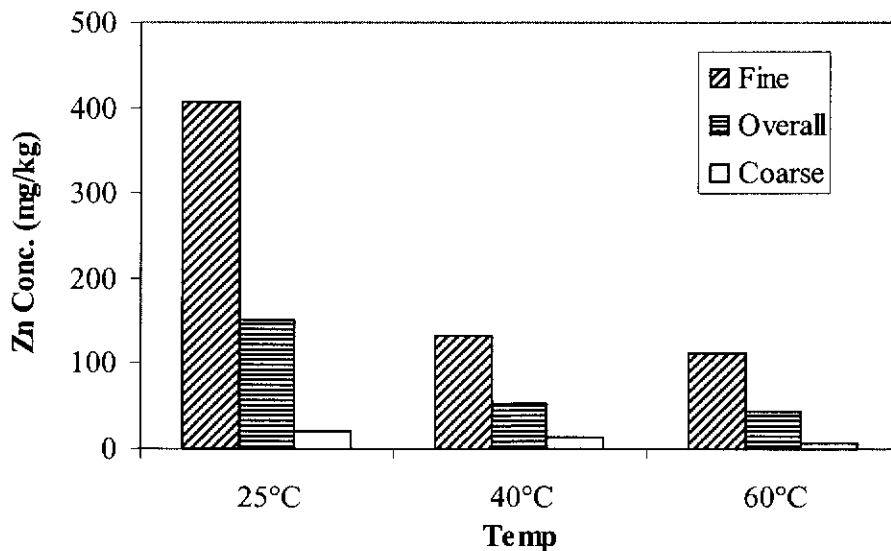


Figure 4.13b Effect of Solution Temperature on Zn Removal.

It can be seen from these figures that the concentration of Pb and Zn of the post-washing soil decreased with increasing temperature of washing solution. The Pb concentration of soil dropped from 140mg/kg to 86.4mg/kg when the solution temperature increased from 20°C to 40°C. The difference between 40°C and 60°C is negligible. The Zn concentration of soil dropped dramatically from 153mg/kg to 53.8mg/kg when the solution temperature increased from 20°C to 40°C. Similar with Pb, the difference between 40°C and 60°C is not significant. The percentage removal of both Pb and Zn is shown in Figure 4.14 from 20°C to 60°C.

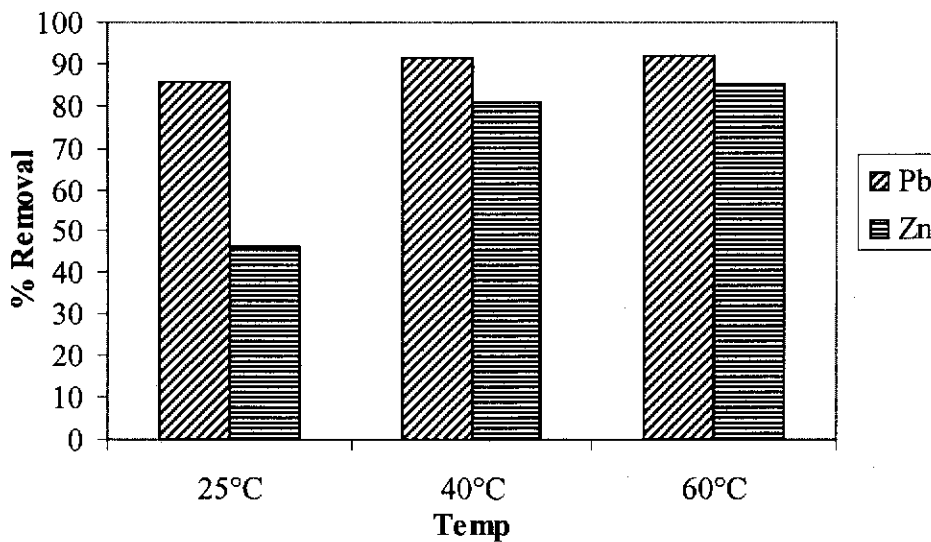


Figure 4.14 Removal Efficiency of EDTA Solution at Different Temperature.

4.2.8 Sequential Extraction Tests

Sequential test was conducted to verify the effectiveness of fresh washing solution on heavy metals removal. In the sequential test, the OMEX soil sample was washed a total of 3 times for 3 hours each time with 3% EDTA solution. The results of sequential extraction test were shown in Figure 4.15 for both Pb and Zn removal.

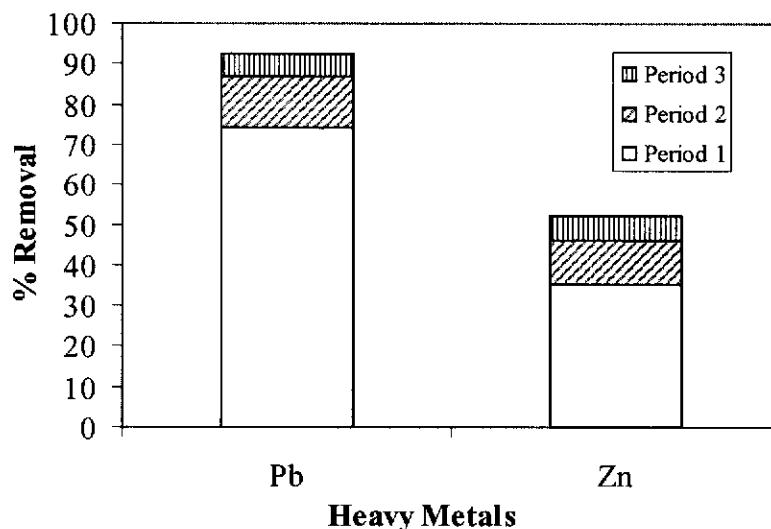


Figure 4.15 Fraction of Heavy Metals Removed in Sequential Extraction Tests.

One can see from the Figure that the first wash was the most effective in removing heavy metals. In general, the second removed less than half of the first. The amount of heavy metals which the third wash removed suggests that third wash removed little additional heavy metals and was unnecessary.

4.3 MASS BALANCE COMPARISONS

Discrepancies between the quantities of heavy metals as determined from the analysis of soil and liquid fractions raised during the mass balance calculation. In EDTA concentration selection and contact time experiments, results of the different calculation methods have been compiled and plotted against each other in Figure 4.16 a and b for both Pb and Zn respectively. Each point represents a single sample, from which the percentage Pb or Zn removal was determined from both the washing solution and the soil after treatment. The nearer the plotted point is to the 1:1 line, the closer the agreement between the determination methods.

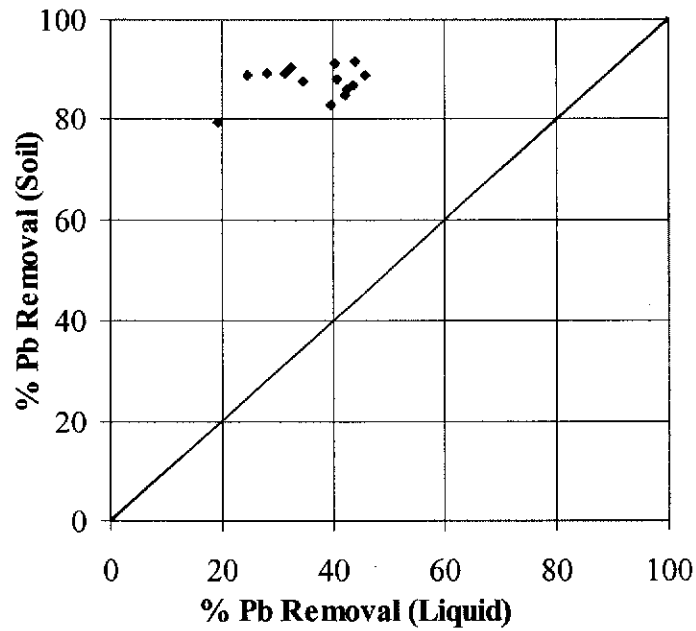


Figure 4.16a Soil vs. Washing Solution Calculations on Pb Removal.

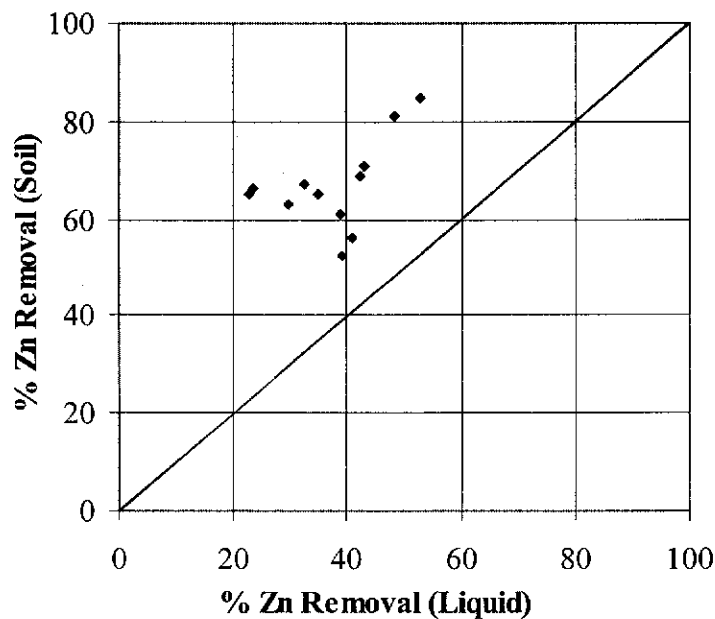


Figure 4.16b Soil vs. Washing Solution Calculations on Zn Removal.

The Figures indicate that the agreement between the two determination methods was poor. The removal percentage gained from the soil is much higher than that gained from the washing solution. In the observation of the experiments, a certain amount of oil was separated from the soil samples. The soil floated on the top of the solution and stuck on the inside wall of

bottle. These oils were removed from the solution during the filtration of sample preparation. It was suspected that the oil may certainly contain some heavy metals.

To prove this hypothesis, a certain amount of oil was taken out from the inside wall of bottle for heavy metal analysis after washing. The oil was digested first using USEPA Method 3031. After digestion, the digestate was analyzed by AAS for concentrations of Pb and Zn. The analytical results showed that the oil contained 1314 mg/kg of Pb and 148 mg/kg of Zn. The result demonstrated that the oil phase contained a high level concentration of heavy metals. As when present in conjunction with organic phase, metal contaminants can partition into the organic phase.

From the oil phase analyses, the more reliable number of metal removal should be the one generated through using the soil since this involves simply measuring the metal concentration before and after the treatment. Using the liquid fraction is less accurate since the heavy metals in oil was not accounted in the analysis and the quantity of oil separated from the soil sample was difficult to determine.

CHAPTER FIVE

INVESTIGATION OF SOIL WASHING WITH SURFACTANTS AND COMBINED EXTRACTANTS

5.1 EXTRACTION STUDY USING SURFACTANTS

Surfactants may be used in soil washing for enhancing the removal of hydrophobic organic contaminants (HOCs) from soils. A surfactant molecule consists of a hydrophobic moiety and a hydrophilic moiety that are referred to as the tail and head groups, respectively. Surfactants are able to form micelle pseudo phases which have a hydrophobic core that can attract HOCs. It is the increase in the apparent solubility of sorbed organics that leads to the use of surfactants in soil remediation.

In order to save the budget of sample analysis, total organic carbon (TOC) was used as the measure of organic contaminants. The analytical work was conducted by Chemistry Centre, a governmental analysis laboratory.

5.1.1 Initial Surfactant Selection

The procedure for soil washing with surfactants followed the method described in Chapter Three. For each surfactant, experiments were carried out to determine the TOC. All experiments were conducted at room temperature ($21 \pm 2^\circ\text{C}$). 100g soil sample and 1000mL 2% surfactant solution (solid:liquid ratio = 1:10) were placed in the glass bottle, and were tumbled on a rotating table for three hours. After washing, soil samples were

separated with a 150 μm sieve into coarse soil (>150 μm) and fine soil (<150 μm). Both soils were analysed for TOC content. Meanwhile, a soil sample was washed by distilled water as blank reference.

Soil washing results for all five surfactants are shown in Figure 5.1a and 5.1b for coarse and fine soil respectively. For coarse soil, the surfactant solutions reduced the TOC content dramatically, while distilled water had no apparent effect on TOC reduction for coarse soil. The SDS produced the best result among all tested surfactants for TOC removal from coarse soil. The effectiveness of surfactants on TOC removal from coarse soil may be attributed to the pollutant binding mechanism and soil surface. Soils with larger average particle size, greater than 63 μm , are usually sandy and have little or no sorption capacity (Van Benschoten 1995). In addition, coarse soil has less surface area than fine soil. Thus, contaminants bind to coarse soils by relatively loose interactions and the quantity adsorbed onto the soil surface is much less than on fine soil. Therefore, washing solutions can remove pollutant easily from coarse soil surface and can achieve high removal efficiencies.

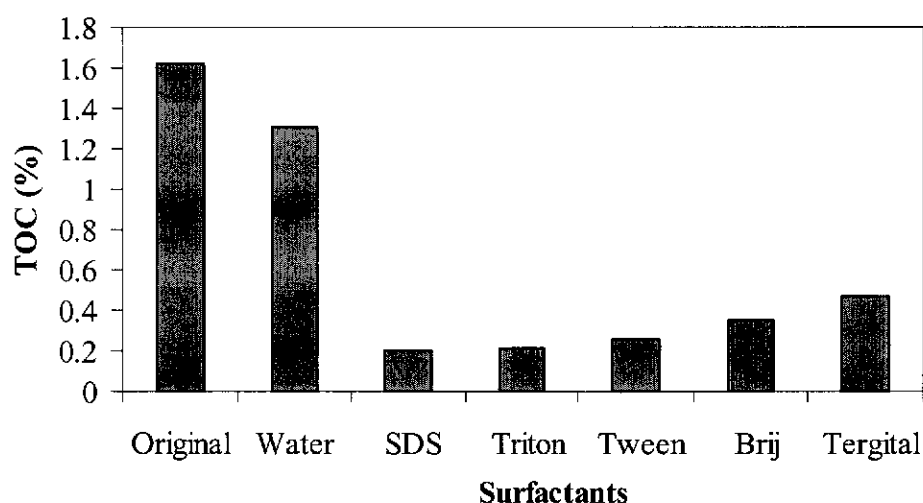


Figure 5.1a TOC Content in Washed Coarse Soil.

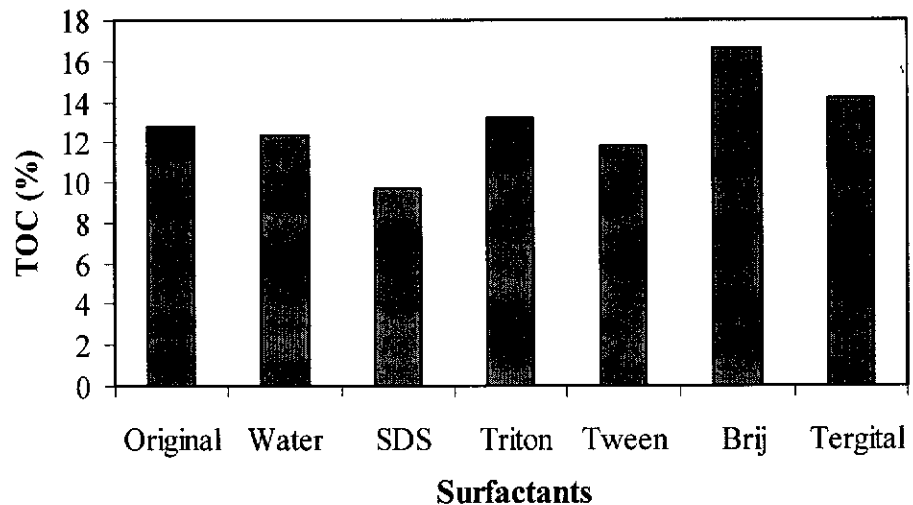


Figure 5.1b TOC Content in Washed Fine Soil.

On the other hand, soil with smaller particles (e.g., average diameters less than $63\mu\text{m}$) usually contain more clay minerals. These clay minerals have large sorptive capacity for contaminants. As fine soils have large specific surface area, it will adsorb more contaminants on its surface. As can be seen from the Figure 5.1a and 5.1b, TOC content in fine soil is much higher than coarse soil. For TOC removal from fine soil, some surfactant solutions had adverse effect, such as Triton, Brij, and Tergitol. The TOC content, after washing by these surfactant solutions, was even higher than that being washed by distilled water and the original soil. SDS had the best performance on TOC removal among all tested surfactants. However, SDS and Tween had no significant difference with distilled water for TOC removal. The high TOC content of washed fine soil may be caused by surfactants sorption on soil surface which is a major problem needing more attention in soil washing technology.

5.1.2 Surfactant Sorption on Soil Surface

One concern in using surfactant in soil remediation is the possible loss of surfactant by sorption to the soil surface. This directly affects the economical use of surfactant in soil remediation, resulting in much surfactant being

unavailable for micellar solubilization of HOCs. In addition, the surfactant adsorbed onto the soil surface will become a new contamination source. As a result of sorption, the amount of surfactant that must be added for the solution concentration to reach the CMC is larger than the amount required in a soil free system.

To quantify the surfactant sorption on soil surface, three surfactants that had the best TOC removal from fine soil were selected for the test. Contaminated soil sample was heated in a furnace at 550°C for 5 hours to strip organic matters so that the soil used in the test has the same structure with other experiment. The cleaned soil was mixed with 2% surfactant and rotated for three hours to establish sorption equilibrium. After washing, soil sample was separated from the mixture and divided into coarse and fine soil fraction. The result of TOC analysis was shown in Figure 5.2 for fine soil only, because from the previous result, coarse soil did not adsorb much surfactant on its surface. It can be seen from Figure 5.2 that all tested surfactants were adsorbed to fine soil surface to a certain level. Among these three systems, anionic surfactant SDS had the least sorption on soil surface. Through calculation, the surfactant loss is in the range of 10% of surfactant used.

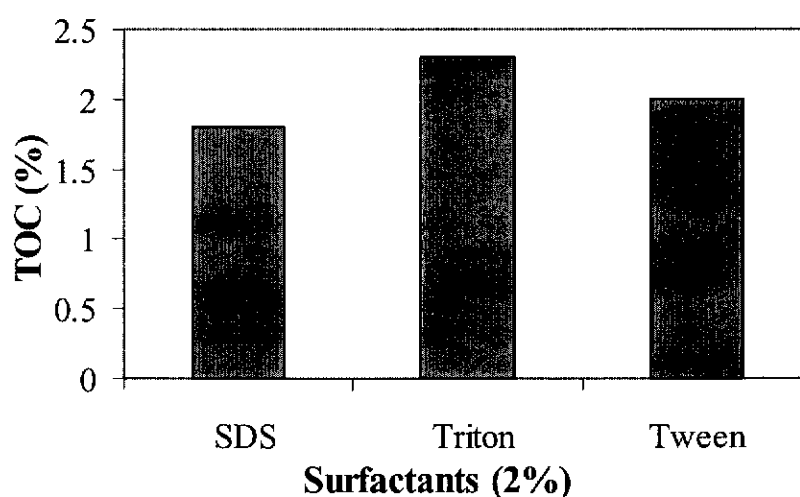


Figure 5.2 Surfactant Sorption Test – Fine Soil.

From Figure 5.2, anionic surfactant SDS was less adsorbed than oxyethylated nonionic surfactants (Triton and Tween) onto the soil surface. This may be due to electrostatic repulsion occurring between the sulfonate group in SDS and the negative charges found on silica surface under natural conditions. This repulsion may lead to less adsorption losses by anionic surfactants in comparison to nonionic surfactants. In addition, the binding characteristics of surfactants may influence the sorption as well. Nonionic surfactant contain oxygen (-O(CH₂CH₂)-) group, which can form chemical bonds with silica, aluminum, magnesium or iron present in the clays, but anionic surfactant can not (Ray 1995).

Anionic surfactant is less adsorbed onto soil surface than does nonionic surfactants under normal conditions. However, high adsorption of anionic surfactant to soil usually is observed at lower pH because the solid/liquid interface is more positively charged at low pH (Huang 1997). At constant monomer concentration, the adsorption of anionic surfactants on mineral oxides increases with decreasing pH due to the increased electrostatic attraction between adsorbate and the soil surface.

Some researchers have observed that sorption equilibrium for surfactant was approached rapidly. As reported in the present paper for several surfactants, the amount of nonionic surfactant that adsorbs onto soil may plateau at a maximum value that occurs concomitantly with attainment at the aqueous phase CMC. Hence, the absolute amount of sorbed nonionic surfactant in a soil/aqueous system may be constant for bulk solution surfactant concentration greater than the CMC, with the result that the fraction of the total surfactant sorbed in the system decreases as a function of surfactant (Liu 1992).

From the experimental results, SDS and Tween were selected for further hydrocarbon removal study. Although nonionic surfactant exhibited more sorption character, it was selected due to its low CMC and good solubilization properties.

5.1.3 Selection of Surfactants

In order to determine the removal efficiency of each surfactant, two different concentrations (0.5% and 2%) and three hours extraction time were employed in the experiments. Results of the TPH concentration analyzed by the Analytical Reference laboratory (ARL) for the OMEX soil after washing are shown in Figure 5.3.

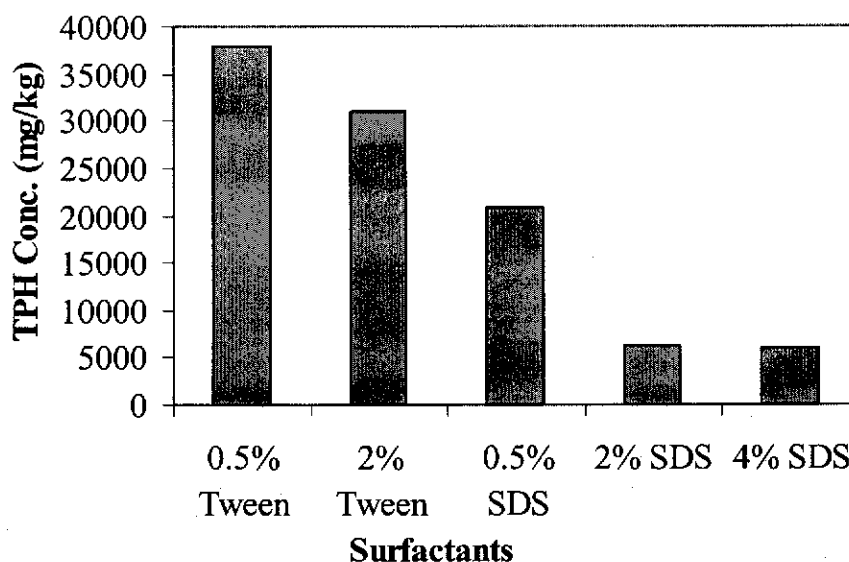


Figure 5.3 TPH Content in Washed Soil.

As can be seen from Figure 5.3, both 2% and 4% SDS produced the highest TPH removal from the OMEX soil. 0.5% Tween solution was the least effective in removing the TPH from the soil particles. In general, SDS was much more effective than Tween in extracting TPH at the same concentration. The removal efficiency of TPH for both surfactant solutions increased with increasing surfactant concentration. As for SDS solution, TPH removal increased dramatically when SDS concentration increased from 0.5% to 2%. The effective washing of TPH from the soil sample can be explained by the increased solubility of TPH in the surfactant micelles. The micellar structure is known to have a hydrocarbon-like core formed by the long hydrocarbon chains. The hydrophobic TPH moves into the hydrophobic

centre of the micelles, which increases the apparent solubility of TPH and enhances its transportation through the soil pores. However, there was little difference between 2% and 4% SDS solution for TPH removal. This may be due to the detergency of SDS character. The detergency of a surfactant is a measure of the surfactant's ability to remove contaminants from surfaces and to keep the contaminants suspended in the aqueous medium. Figure 5.4 shows changes in some physical properties of SDS solution in the neighbourhood of the CMC. Included in this figure is a narrow band of critical concentration with its lower limit being the CMC. Surface tension increases within this band, inter-facial tension approaches a minimum value at the CMC and remains almost constant as concentration increases, detergency increases rapidly through the critical concentration band and remains constant at higher concentration (Abdul 1991).

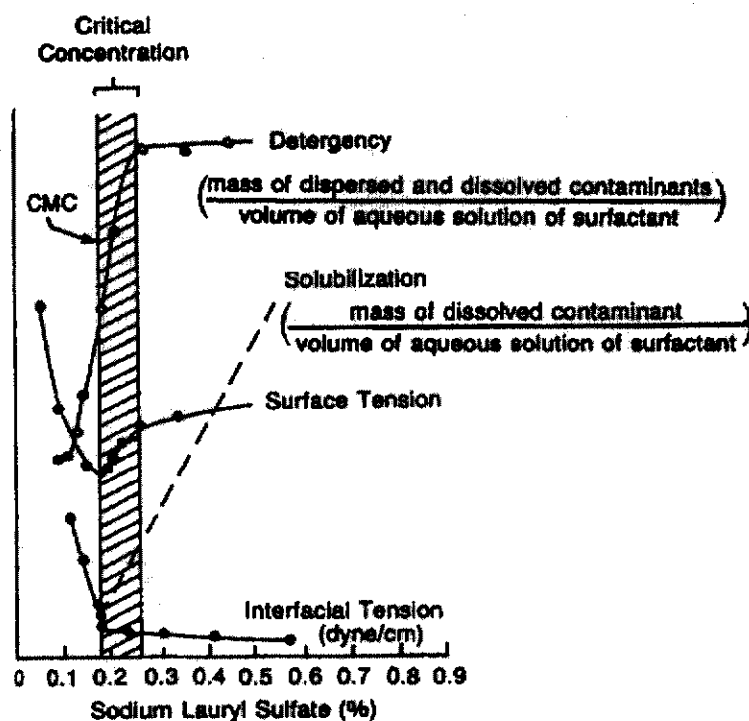


Figure 5.4 Changes in Some Physical Properties of SDS in the Neighborhood of CMC (Abdul, 1991).

5.1.4 Effect of Washing Time

In order to determine the extraction time required to reach the equilibrium status, OMEX soil sample was mixed with 2% SDS solution and washed for nine hours.

The removal percentage of TPH from soil by washing with 2% SDS washing is shown as a function of time in Figure 5.5. As can be seen from the figure, after 3 hours washing, the removal of TPH from soil became very slow. The extent of TPH removal only increased marginally higher than three hours washing. However, after nine hours washing, the TPH removal is still in nonequilibrium status. After nine hours washing, 84% of TPH was extracted from soil sample, while 79% of TPH was extracted within the first three hours.

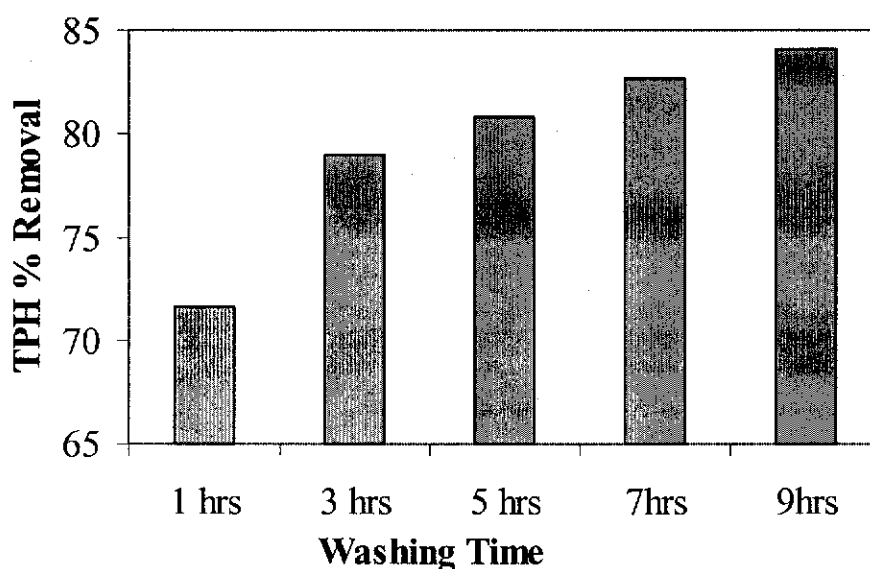


Figure 5.5 Removal Efficiency of 2% SDS Solution for TPH Removal.

Solubilization of soil-bound HOC by micellar surfactant solution involves at least three steps: (1) matrix diffusion of HOC molecules within the soil; (2) mass transfer at the interface (film diffusion); and (3) partitioning into the micellar phase (Yeom 1995). Given that step 3 is extremely fast, step 1 and/or 2 must be rate-limiting. Matrix diffusion of HOCs within the weathered

soil-oil matrix is the most likely rate-limiting step in soil washing. The majority of the residual TPH in OMEX soil was long chain hydrocarbons. The relatively soluble, light-weight TPH molecules trapped within the tar must diffuse through the medium to reach the tar-water interface. It is expected that the rate and the degree of solubilization of higher molecular weight TPHs (long chain hydrocarbon) would be considerably less than those for lower molecular weight TPHs.

5.1.5 Effect of Solution Temperature

Temperature of washing solution is an important parameter in surfactant-aided soil washing process, as some surfactants are sensitive to temperature. Three different temperatures were tested. The temperatures tested were 20°C, 40°C, and 60°C. The mixture of soil sample and SDS solution were agitated in a temperature-controlled water bath for 3 hours. Figure 5.6 shows the TPH removal of OMEX soil after washing plotted against the solution temperature.

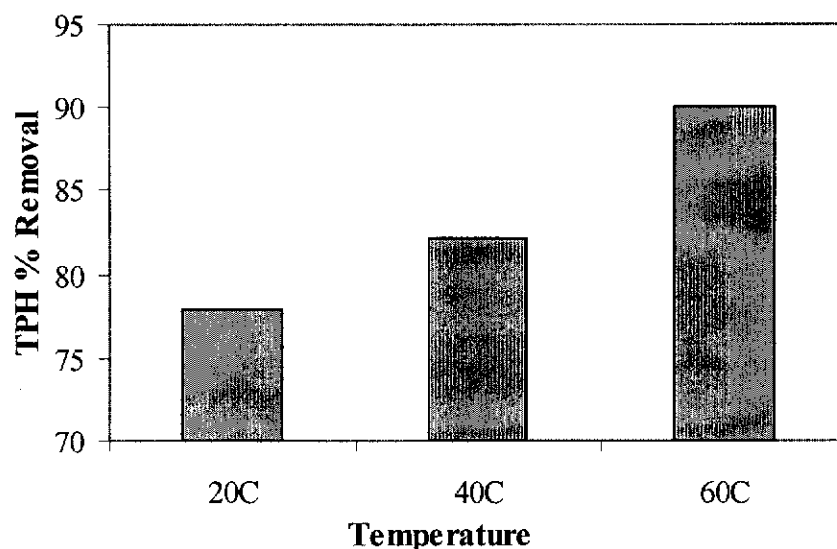


Figure 5.6 Effect of Solution Temperature on TPH Removal.

It can be seen from the figure that TPH removal efficiency improved when solution temperature increased from 20°C to 60°C. The increase of TPH

removal efficiency is due to the properties of ionic surfactant. For ionic surfactants, an increase in temperature generally results in an increase in the extent of solubilization for both polar and non-polar solubilize (Rosen 1989). Therefore, the TPH removal efficiency was improved by more hydrocarbons reacting with surfactant micelle and partitioning into the hydrophobic interior of micelle.

The temperature at which the solubility of an ionic surfactant becomes equal to the CMC of the surfactant is known as the Krafft point. Below the Krafft point, there are very low concentrations of monomers and no micelles are formed. At temperatures higher than the Krafft point, the surfactant's solubility increases dramatically because the monomer concentration is high enough for micelle formation. The micelles act like a separate phase into which the surfactant can partition with little increase of surfactant activity in solution.

For nonionic polyoxyethylenated surfactants, the effect of temperature depends on the nature of the solubilize. Non-polar materials, such as aliphatic hydrocarbons and alkyl halides, which are solubilized in the inner core of the micelle, show increased solubility as the temperature is raised. Aqueous solutions of polyoxyethylenated nonionic surfactants, if the oxyethylene content is below about 80%, become turbid on being heated to a temperature known as the cloud point, following this there is separation of the solution into two phases. The temperature of cloud point depends on the structure of the polyoxyethylenated nonionic surfactant.

5.1.6 Sequential Extraction Tests

Sequential test was conducted to verify the effectiveness of fresh washing solution on TPH removal. In the sequential test, the OMEX soil sample was washed a total of 3 times for 3 hours each time with 2% SDS solution. The results of sequential extraction test were shown in Figure 5.7 for TPH removal.

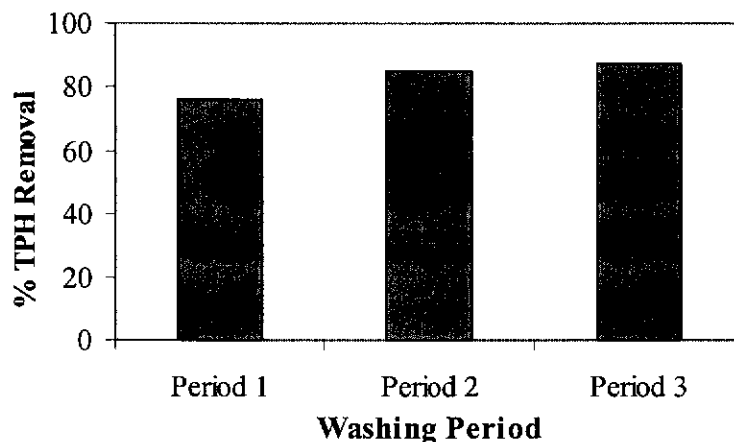


Figure 5.7 Fraction of TPH Removed in Sequential Extraction Tests.

One can see from the Figure that the first wash was the most effective in removing TPH. In general, the second removed less than half of the first. The amount of TPH which the third wash removed suggests that third wash removed little additional TPH and was unnecessary. This result also provides more evidence for Figure 5.5 that after 3 hours washing, the removal of TPH is limited by the slow release of hydrocarbon from the soil matrix.

5.2 COMBINATION TEST

Understanding the difference in soil chemistry between heavy metal and hydrocarbon contaminant groups is important when considering a remedial technology. The fundamental chemistry of a particular remedial technology must be consistent with the combined chemical behaviours for the remediation to be successful.

Heavy metals are not very mobile in the environment and tend to remain relatively close to the point of initial deposition. Heavy metals bind strongly to most soils. The capacity of soil to adsorb (chemically bind) heavy metal generally increases with increasing soil pH, cation exchange capacity,

organic carbon content, iron content, soil/water redox potential, and phosphate levels. These properties are typically high in clay-rich soil. Metal compounds can also be adsorbed onto hydrous oxides of iron and manganese and thus become immobilized in salts containing two or more cations. Heavy metals and their insoluble/precipitated compounds are denser than water and tend to exist in an unbound state in soils. Most metal salts and compounds are highly insoluble in water (McCullough 1993).

Unlike heavy metals, petroleum hydrocarbons can be very mobile in the environment and can travel far from the initial point of release. The capacity of soils to retain hydrocarbons is similar to that of metals for hydrocarbons composed of compounds with longer carbon chains (diesel range and above); however, lighter hydrocarbons can be extremely mobile through diffusive mechanisms (McCullough 1993).

In a combination test using both a chelating agent as well as a surfactant combined test, two washing schemes were designed in order to minimize chemical use and maximize contaminant removal efficiency. The initial soil analysis results showed that heavy metal concentration in OMEX coarse soil was under the regulatory standard level, while TPH concentration was above the standard level. Therefore, both coarse and fine soil needed to be washed by surfactant solution to reduce TPH concentration, but only fine soil needed to be washed by chelating agent solution to reduce heavy metal level. In addition, as the contaminated oil contained large amounts of heavy metals, it is better to remove these organic contents before being washed by chelating agent solution. Since the fine soil is only about one third of whole OMEX soil, reduction in soil volume for treatment will substantially reduce the chemical and water usage in soil washing process.

200g soil sample was used in each experiment to ensure that enough amount of fine soil can be retrieved for analysis. The two alternative washing schemes used in the combination test are described briefly below:

- 1) The original soil sample was divided into coarse and fine soil fractions by wet sieving before conducting experiment. The coarse soil fraction was mixed with 2% SDS solution and tumbled for three hours at room temperature. After washing, the solution was separated from the mixture and fine soil fraction was added into the solution together with EDTA maintained at a concentration is 3%. The mixture was further tumbled for another three hours. The fine soil was then separated from the mixture and both coarse and fine soils were analyzed for heavy metal and TPH concentration.
- 2) The original soil sample was mixed with 2% SDS solution and washed for three hours. After washing, coarse soil was separated from the mixture, and EDTA was added into the mixture to make the EDTA concentration 3%. Then the mixture was washed for another three hours. Finally, both coarse and fine soil fractions were analyzed for heavy metal and TPH concentration.

The results of heavy metals removal by these two washing schemes are shown in Figure 5.8 for both Pb and Zn removals. The figure shows that both washing schemes had good performance on heavy metals removal for Pb and Zn. The removal efficiency is about 80% for both Pb and Zn. After washing the heavy metal concentration in OMEX soil is under the regulatory levels for both Pb and Zn.

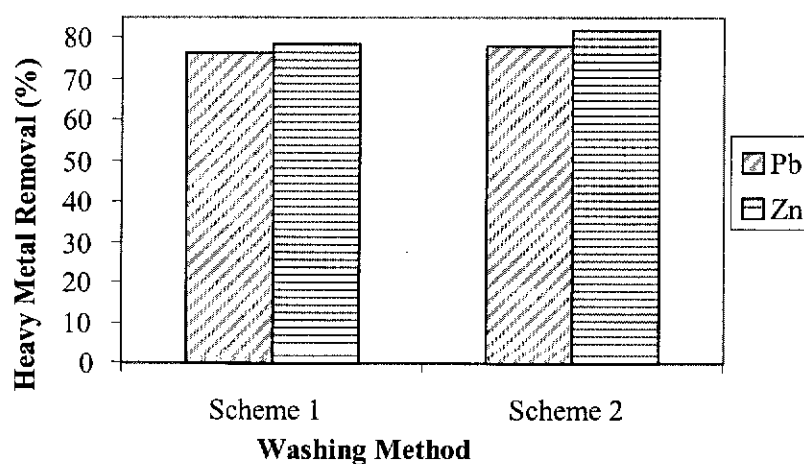


Figure 5.8 Heavy Metal Removal by Two Washing Methods.

The removal efficiency of TPH was shown in Figure 5.9. As for TPH removal, the removal efficiency is also very high for both washing schemes. About 80% of TPH was extracted from the OMEX soil by those two washing schemes. Figure 5.8 and 5.9 show that scheme 2 had better performance than scheme 1 on both heavy metal and TPH removal. As the fine soil was washed together with coarse soil by 2% SDS solution for three hours first in scheme 2, the longer washing period may partly contribute to the better result in scheme 2. In addition, when together with coarse soil, the fine soil is easy to separate into individual particles due to friction and shearing.

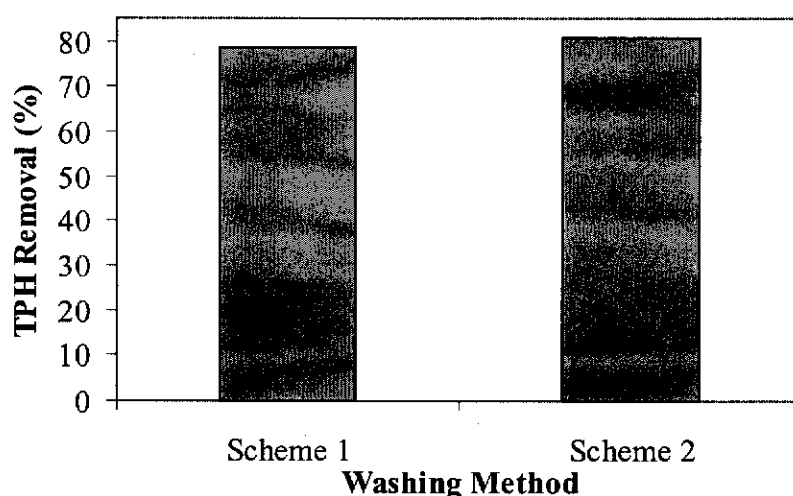


Figure 5.9 TPH Removal by Two Washing Methods.

From the analysis of the washed soil, TPH concentration was still very high after washing, although the percentage removal is near 80%. In particular, the TPH concentration in fine soil is up to 16300 mg/kg after washing. The TPH concentration in coarse soil can meet the regulatory level after washing. The fine soil fraction that contained a high level of TPH after washing will need further treatment such as biodegradation, thermal treatment or landfill. The high level of TPH in fine soil is partly due to the adsorption capacity of fine particles as well as the very high initial concentration (up to 77500 mg/kg). In addition, more than 20 years contamination history makes contaminants adsorb on soil surface more firmly than new by contaminated or artificially spiked contaminated soil.

CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUDING REMARKS

Soil is capable of capturing inorganic and organic compounds in its pore spaces and surface due to the passage of permeant liquids. Depending on the specific physico-chemical properties of the compounds and the soil, compounds dissolved in the fluid may be incorporated into the soil matrix. A considerable amount of research has shown that soil washing is a successful alternative in contaminated soil treatment. However, few studies have addressed the remediation of actual contaminated site containing multiple contaminants (heavy metals and hydrocarbons).

In this study, the remediation of contaminated soil is based on an industry contaminated site – OMEX site, and washing with several extractant additives including chelating agents and surfactants were used. The research was carried out based on laboratory experiments. The principle of the removal technique relies on altering the surface chemistry of the soil particle and/or the nature of the sorbed contaminant compounds. The experiment results showed that 3% EDTA (chelating agent) and 2% SDS (surfactant) solution were effective in removing heavy metals and hydrocarbons from the OMEX soil. In addition, the contaminated OMEX soil was characterized for its physical and chemical properties before commencing the study.

Characterization of contaminated soil is an important and essential procedure before further remedial action should take place. Some soil properties will

directly affect the performance of additives in soil washing and the interactions between soil, contaminants and additives. The extractant selection is also based on the type and quantity of contaminants. Based on the results of the analysis of the OMEX soil, the following specific conclusions can be drawn on the OMEX soil characterization:

1. The OMEX soil was classified as sandy loam, consisting of 77% sand and 23% silt and clay. Particle size distribution is a key factor in soil washing process. Fine particles usually have large surface area per unit volume and high level of organic matter, therefore contaminants are adsorbed on the surface easily and firmly. Due to the high adsorption affinity of fine particles, contaminants are difficult to desorb from fine particle surface. The OMEX soil was high in moisture content, organic content and TOC.
2. The OMEX soil contained appreciable quantities of Pb and Zn at the concentration of 986 mg/kg and 284 mg/kg, respectively. Particle size analysis showed that the contaminants were mainly concentrated in the fine soil fraction (<150 μ m). The Pb and Zn concentration in the fine soil fraction were 2294 mg/kg and 689 mg/kg. The high level concentration in fine soil is due to its high adsorption affinity and large surface area.
3. The OMEX soil also contained large amounts of TPH at concentrations up to 29000 mg/kg. Similar to that for heavy metals, the organic contaminant (TPH) was mainly contained in the fine soil fraction with concentration of 77500 mg/kg.

Chelating agents can convert solid-bound heavy metal ions into soluble metal complexes. Therefore, chelating agent solutions can enhance the mobilization of heavy metals. The following specific conclusions could be drawn basing on the experiments conducted:

1. The experimental results showed that EDTA, at 3% (w/w), is the most effective extractant (chelating agent) for heavy metal removal from contaminated OMEX soil. EDTA is a six-membered ring chelating agent

that can form strong water soluble complexes with most metals. Higher concentrations were less effective than 3% due to the solution pH and large quantity of Na^+ ions.

2. Pb and Zn removal levels were approximately 90% and 65% respectively by using 3% EDTA solution. Washing with other chelating agents was less effective when compared to EDTA.
3. EDTA extractant of heavy metals proved to be slow, requiring more than 10 hours to approach equilibrium. The complexity of the contaminated OMEX soil probably contributed to this case. The OMEX soil was contaminated by industry for more than 20 years and it also contained up to 15% organic content including hydrocarbons.
4. The solution pH had some effect on the removal of Pb and Zn, with better removals observed at a lower pH, in the acidic region. The optimal pH value for EDTA complexation is in the range of 3-6. EDTA begins to protonate at pH values less than 4. Using EDTA at lower pH value, the dissolution effects of the acid apparently dominate over those of the ligand.
5. Liquid to solid ratio (L/S) had no significant effect for the range of conditions studied. A ratio of 5 produced the same result as a ratio of 20. Part of the metal pollution is probably bound more strongly to soil components and it is not influenced by the smaller metal concentration in solution.
6. Increasing solution temperature from 20°C to 60°C slightly improved the removal efficiency of both Pb and Zn.
7. Sequential extraction tests showed that first washing period was the most effective washing while the following washing periods were less effective.

Surfactant solutions can greatly decrease the interfacial tension and increase the solubility of hydrophobic organic compounds (HOCs). Therefore, suitable surfactant solutions can improve the removal of hydrocarbons from contaminated soil. Conclusions that could be drawn from the experimental results include the following:

1. Surfactant solutions were effective in removing hydrocarbons from coarse soil fraction, but surfactants were adsorbed by fine soil particles as clay minerals provide a large surface area for adsorption. Surfactants decrease the surface tension and solubilize the organic compounds by forming micelles; hence, the contaminants are desorbed from soil particles.
2. Anionic surfactant proved to be less adsorbed onto soil surface than nonionic surfactants. This is due to the electrostatic repulsion between the sulfonate group of the anionic surfactant and the negative charges on soil surface under natural conditions. In addition, the binding characteristics of surfactants may influence the sorption as well. Nonionic surfactant contain oxygen (-O(CH₂CH₂-) group, which can form chemical bonds with silica, aluminum, magnesium or iron present in the clays, but anionic surfactant can not.
3. 4% SDS solution was found to be the most effective extractant for TPH removal from OMEX soil. There was no significant difference between 4% and 2% SDS solution on TPH removal efficiency. The detergency of SDS character may contribute to this phenomenon. The SDS detergency increases rapidly through the critical micelle concentration and remains constant at higher concentration.
4. The process of TPH desorption from soil by surfactant is a slow, non-equilibrium and rate-limited process. Most TPH was extracted within the first three hours of washing. Matrix diffusion of HOCs within the soil-oil matrix is the most likely rate-limiting step in soil washing.

5. TPH removal efficiency was improved when the temperature of SDS solution was increased from 20°C to 60°C. For ionic surfactants, an increase in temperature generally results in an increase in the extent of solubilization for both polar and non-polar solubilizate. Therefore, the TPH removal efficiency was improved by more hydrocarbons reacting with surfactant micelle and partitioning into the hydrophobic interior of micelle.
6. Sequential extraction tests showed that first washing period was the most effective washing while the following washing periods were less effective.
7. Combined washing by chelating agent and surfactant was effective in removing both heavy metals and hydrocarbons. TPH concentration in fine soil was still very high after washing and will need further treatment before final disposal.

The task to extracting contaminants from contaminated soil is complex; however, the results of this study provide encouraging visions of how to remediate heavy metal and hydrocarbon contaminated soils by aqueous solution extraction. This method has some limitations and problems. The most serious problem is the high TPH level in the fine soil fractions.

6.2 REMOMMENDATIONS FOR FUTURE WORK

Based on the findings of this study the following recommendations are made for further work to be conducted:

1. As most contaminants are usually concentrated in the fine soil fractions and these contaminants are difficult to remove due to strong adsorption mechanism, it is necessary to study the interactions of soil-contaminant-extractants and the sorption/desorption behaviors of contaminants from small particles. Completion of this study will ensure the performance and

application of the aqueous solution extraction methods for the removal of contaminants from fine soils.

2. One of the major cost of soil washing is that of the extractants. Recovery and reuse of chelating agents and surfactants will strongly help to decrease the cost of soil washing. Soil washing research should be expended to this area to make the whole system more cost-effective.
3. It may be possible to develop a mathematical model to simulate the processes studied here. Such a model would be of value as it could include the effects of sorption/desorption equilibrium, operation conditions, aging, hydraulic conditions and other factors. Such a model would make it possible to conduct "numerical" experiments that could extend the information obtained here to other soils and chemical compounds.
4. Multiple soil washing cycles, such as counter current and cross current, should be utilized to determine if additional contaminants can be removed from the contaminated soils.
5. After soil washing, fine soils are difficult to separate from the washing solution. Different separation methods should be assessed to reduce process period and solution losses. Separation methods may include mechanical methods such as hydrocyclone, and chemical methods such as addition of flocculants or coagulants.

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Appendix A

Appendix A

Western Australian Department of Environmental Protection. Landfill waste classification and waste definitions, 1996.

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Appendix B

Appendix B

Paper for 5th Waste Convention.

Soil washing – a practical method for contaminated soil remediation by Xu Han, H. Ming Ang and Jeff Claflin, School of Chemical Engineering, Curtin University of Technology.

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4.12.02)**

Appendix C

Appendix C

Paper for CHEMECA.

Removal of heavy metals from organically contaminated soil by soil washing by Xu Han, H. Ming Ang and Jeff Claflin, School of Chemical Engineering, Curtin University of Technology.

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