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Foam-Surfactant Technology in Soil Remediation

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A Thesis

in

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Environmental Engineering

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ABSTRACT

Foam Surfactant Technology for In-Situ Soil Remediation

Recently, the use of gas-liquid **foams** as a means of delivering chemicals to the subsurface is being considered as an important to in-situ **soil** remediation. However research in this area has been limited. Column experiments were conducted to investigate the factors that limit the use of foam as an agent for soil flushing. Pressure build up in the soil is an important factor that was studied for foam with different characteristics. In addition, the capability of this technology for the removal of contaminants (Pentachlorophenol, "PCP") from soil and the principal factors that influence the removal efficiency were investigated. The fate and transport of pentachlorophenol, (aromatic pesticide and is mostly used as a wood preservative) was studied in the presence of foam with different properties formed by using two different types of surfactant. TritonX100 and JBR425 were used as representatives of nonionic and anionic surfactants, respectively. The results obtained from this study on a sandy soil showed that foam can be used as a fluid to enhance soil remediation under low pressures compared to other fluids such as liquid surfactant solutions.

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List of Symbols

$\partial h/\partial x$	Hydraulic Gradient in x Direction (m/m)
$\partial h/\partial y$	Hydraulic Gradient in y Direction (m/m)
$\partial V_x/\partial X$	Rate of Change in the Darcy Flux (m/s)
$\partial V_y/\partial Y$	Rate of Change in the Darcy Flux (m/s)
b	Dimensionless Constant
C	Solute Concentration in Aqueous Phase (mg/l)
C_0	Initial Concentration of PCP in the Soil (mg/kg)
C_c	Solute Concentration in the Organic Matter (mg/kg)
C_F	Final PCP Concentration in the Soil (mg/kg)
$C_G(t)$	PCP Concentration in Effluent Gas at Time t (mg/l)
C_I	PCP Concentration in Influent Foam (mg/l)
$C_L(t)$	PCP Concentration in Effluent Liquid at Time t (mg/l)
β	Constant
$C_S(t)$	PCP Concentration in the Soil at Time t (mg/kg)
K_I	First-order Decay Rate Coefficient (mg/mg)
K_b	Linear Distribution Coefficient (mg/mg)
K_d	Distribution Coefficient (mg/mg)
K_{oc}	Organic Carbon Partition Coefficient (mg/mg)
K_x	Hydraulic Conductivity in x Direction (cm/s)
K_y	Hydraulic Conductivity in y Direction (cm/s)
Q_{in}	Influent Flow Rate (m ³ /s)

Q_{out}	Effluent Flow Rate (m^3/s)
S	Amount of Solute Retained by Soil (mg/kg)
S_m	Maximum Sorption Capacity (mg/kg)
S_w	Water Solubility (mg/l)
V_S	Total Volume of Soil in the Column (m^3)

CHAPTER ONE

Introduction

1.1 Background

Excavation of contaminated soil was once the solution for soil remediation. However, because of the high cost of excavation, final disposal to landfills, and due to a lack of available landfill sites, these disposal methods are becoming increasingly less popular (Mann, *et al.* 1993). To decrease the cost, various technologies are being developed and implemented for remediation of soils and sediments. In-situ treatment of the soil typically focused on the removal of pollutants without excavating the soil.

A number of in-situ remedial technologies, including pump and treat, bioremediation and soil flushing have been used to treat contaminated soil and groundwater. Pump and treat, which is mostly used for treatment of contaminated ground water, involves extracting and treating the contaminated ground water on the surface. The treated water is then returned to the ground water aquifer. Bioremediation is an in situ remediation technique that uses microorganisms and bacteria for decomposing contaminants either in the contaminated soil or water. Soil flushing is an in situ soil decontamination technique that mobilizes contaminants trapped in the soil for the purpose of their recovery and treatment. A brief explanation of this technology is in Chapter Two.

However, in many cases, these methods have proven to be ineffective, expensive, unreliable, and often require extended time periods for adequate clean up (Reddy, *et al.* 1995).

Two important characteristics of organic contaminants that are the most common among soil pollutants are low solubility in water and high interfacial tension with water which decrease the efficiency of in-situ soil remediation. For example, in terms of soil bioremediation, organic compounds need to be in a liquid phase to be used by microorganisms and bacteria. Also for soil flushing, these compounds must be transferred to a mobile phase through the subsurface (liquid) before they can be flushed out.

To overcome this problem, different surfactants can be used to enhance remediation rates. Surfactants enhance organic contaminant recovery through two mechanisms. Firstly, surfactants reduce the interfacial tension between water and contaminants and the capillary forces that trap residual organic compounds. Therefore, surfactants are able to transfer the hydrophobic organic compounds (HOCs) to the mobile phase (Cheah, *et al.* 1998). Secondly, surfactants are capable of forming aggregates known as micelles, thus solubilizing HOCs.

Recent efforts (Chowdiah, *et al.* 1997, and Rothmel, *et al.* 1998) using foam (mixture of surfactant and a gas such as air) have shown promising results in in-situ soil remediation and soil flushing. Since foam contains 70-80% air, it provides considerable amounts of

oxygen to the soil, thereby increasing the rate of remediation in soils contaminated with volatile and semi-volatile compounds via to volatilization. In addition, some investigations have been done to study the capability of foam as a carrier of oxygen and nutrients for microorganisms and bacteria in bioremediation (Rothmel, *et al.* 1998).

Numerous studies on foam for the treatment of soil contaminated with aromatic hydrocarbons have been conducted (Chowdiah. *et al.*, 1997; Rothmel. *et al.* 1998). Foam-surfactant technology was found to have some potential for enhanced remediation of contaminated soils, although research in this area has been limited.

Some related areas that need more investigation are:

- Investigation on the behavior of foam inside different types of soil.
- Effectiveness and foamability of different surfactants for the removal of different contaminants.
- Investigation into the compatibility of this technology in combination with other remediation technologies.
- Modeling of the process is necessary in order to evaluate the efficiency of this technology in different cases.
- A field study would provide a better understanding of the process and its limitations and related site problems.

This thesis consists of six chapters as summarized:

- Chapter One gives an introduction to the subject and discusses an overview of research objectives.

- In Chapter Two, the nature of the problem is explained and then the most important areas of investigation are discussed in detail describes most previous attempts that have been done in the same area of investigation.
- In Chapter Three, the process used in the removal of contaminants from the soil is discussed and basic models of contaminant transport in the soil are presented.
- Chapter Four presents all materials and the experimental setup used in this investigation. All processes before and after each test are explained in this chapter.
- Chapter Five summarizes the results obtained in this study. In addition, results are discussed and compared.
- Chapter Six forms the conclusion of this thesis with some important inference made from different stages of this study and obtained results.

An important factor that limits the use of soil flushing as a technology for removal of contaminants is pressure build up in the soil due to the injection of agents during the flushing process. High pressure in the soil causes different problems during the flushing process, such as channeling which results in low removal efficiency. Soil heaving results in the disturbance of the contaminated zone and also requires high energy and power, which results in high cost. The use of surfactants in the form of foams can potentially reduce these problems.

1.2 Objectives

The overall objectives of this research are outlined below:

1. To determine important factors limiting the use of foam as an agent in soil flushing.
2. To evaluate pressure build-up in the soil during the injection of foam for various conditions.
3. To investigate the efficiency of foams in the treatment of soil contaminated with PCP (pentachlorophenol). In this stage of investigation, Triton X100 and JBR425 were used to generate foam.
4. To evaluate the effect of surfactant concentration on the removal rate of PCP from the soil and also to study how different levels of contamination in the soil effect the removal efficiency.
5. To determine, by mass balance calculations, the percentage of PCP recovery by mobilization and volatilization.
6. To determine the overall augmentation and applicability of this technology for in-situ field remediation.

CHAPTER TWO

Literature Review

Introduction

Soil pollution is a serious environmental problem, not only in the highly industrialized Western Countries. Over the last 10 to 15 years, both the awareness of the problem and the policies and strategies developed to solve it have strongly changed, and much has been done to develop remediation technologies. As a result of the international attention paid to the problem, intensive exchange of experiences gained with management and remediation of polluted soils is taking place between the various countries.

A large number of remediation techniques, most of which focus on clean-up, are now available. Most of them are intensively applied in practice. Each case of soil pollution is different and the way to manage it requires, within the limit set by policy and the finances available, careful weighing of all relevant factors (Rulkens, *et al.*, 1998).

2.1 Soil Environment

According to the engineering definition, soil is the loose material that lies between the ground surface and solid rock. According to the soil scientist (Pierzynsku, *et al.*, 1993), the soil is described as the unconsolidated mineral or organic matter at the earth's surface. On the other hand, soil represent all of the unconsolidated sediment or regolith above the competent rock.

Soil contamination results through different sources such as the use of excessive amounts of pesticides and fertilizers that can result in surface water and groundwater contamination, spills of chemicals and the use of landfills as dumping wastes. In the case of low levels of contamination, most soils are able to adsorb and neutralize pollutants to harmless levels through chemical and biochemical processes.

2.1.1 Soil Physical and Chemical Properties

Soils contain solids, liquids, and gases. Composition and arrangement of solids, (which determines the pore volume or pore space in the soil), soil temperature and color are some soil physical properties. Soils, composed of solid particles, range in size from stones to fine clays. Table 2.1 lists different soil compositions and their classifications according to the U.S. Department of Agricultural System (Pierzynsku, *et al.*, 1993).

Soil particles that are held together by physical and chemical forces form aggregates, and soil structure depends on the type of aggregates. Soil structure affects water content in

the soil, gas diffusion at the soil surface, porosity, and also the movement of liquid and gases through the soil.

Particle and bulk density measurements are useful in estimating the type of minerals present in the soil minerals present and the degree of soil compaction, respectively.

Particle density is the mass of a particle per unit volume (g/cm^3).

Table 2.1 Size Classification of Soil Particles (Soils and Environmental Quality, 1994)

	Soil particle	Diameter (mm)	Size Comparison
Coarse fragment	Stones	> 254	> 10 in
	Cobbles	75 – 254	3 – 10 in
	Gravel	2-75	0.09 – 3 in
Sand	Very coarse	2.0 - 1.0	Thickness of a nickel
	Coarse	1.0 – 0.5	Size of a pencil lead
	Medium	0.5 – 0.25	Salt Crystal
	Fine	0.25 – 0.10	Thickness side of a book page
	Very fine	0.1 – 0.05	Nearly invisible to the eye
Silt	Coarse	0.05 – 0.02	Root hair
	Medium	0.02 – 0.01	Nematode
	Fine	0.01 – 0.002	Fungi
Clay	Coarse	0.002- 0.0002	Bacteria
	Fine	< 0.0002	Viruses

Mineral solubility, soil reactions, pH, cation and anion exchange, buffering capability, and nutrient availability are major chemical properties of soils. These are mainly

determined by and depend on the type of clay minerals and organic matter present (Pierzynsku, *et al.*, 1993). Layered aluminosilicate minerals (clay minerals), strongly influence many soil chemical reactions because of their active surface area.

Organic matter plays an important role in the chemistry of soil. Some important properties of soil that are associated with organic matter include soil structure, cation exchange capacity, and pH buffering. This fraction of soil, formed mostly by decomposing plant and animal residues, is a complex mixture of carbon compounds, nitrogen, sulfur and phosphorus (Pierzynsku, *et al.*, 1993).

Concerning the environmental point of view, organic matter can adsorb some pollutants such as Pb, Cd, and Cu that reduce the chance of contamination of surface and groundwater. It should be noted that soils with high organic matter content may require higher pesticide application rates for effective control. Therefore, water contamination is a concern if these pesticides are leached or transported by wind or water erosion (Pierzynsku, *et al.*, 1993).

Another important characteristic of soil that effects some soil functions is its cation exchange capacity (CEC). Cation exchange capacity is the amount of exchange sites that can adsorb and release cations.

2.2 Pollutants Classification

Pollutants are classified according to their general properties in Table 2.2. The nutrient category reflects the negative effect of nitrogen and phosphorus when present in high concentrations. Phosphorous in surface waters and nitrates in surface and groundwater are the main indicators of environmental problems. The pesticides category represents a wide range of organically based chemicals used to control pests such as weeds and insects. Hazardous substances include materials that are toxic to humans or other organisms when improperly used. Most hazardous substances are organic compounds with characteristics comparable to pesticides. Acid precipitation is mainly the end result of the conversion of the oxides of N and S into their respective acids in the atmosphere. Salinity originating from irrigation with water containing high salt concentration, occurs when the concentration of salt and sodium in the soil is high. The primary problem associated with salinity is reduction in plant productivity (Pierzynsku, *et al.*, 1993).

Table 2.2 Pollutants Classification (Soils and Environmental Quality, 1994)

Pollutant Category	Example
Nutrients	Nitrogen and phosphorus in commercial fertilizer, Sewage sludge, Municipal solids waste
Pesticides	Sewage sludge, Municipal solids waste
Hazardous substances	Fuels, Solvents, Volatile organic compounds
Acidification	Acid precipitation, Acid mine drainage
Salinity	Road salt, Saline irrigation water
Trace elements	Cationic metals
Sediments	Soil lost via water erosion, Volcanic dusts

Trace elements are usually present in low concentrations in the soil, although some of them are essential for growth of human and other organisms, many of them are toxic and cause chronic and acute health problems in humans and animals. Sediments represent soil particles that have eroded from the landscape and have been carried to surface water (Pierzynsku, *et al.*, 1993).

2.3 Source of Contamination

Contamination can be defined as the existence of hazardous pollutant either in the ground water or soil, at concentrations above the normal background levels. Substances giving rise to concern include (Smith, 1985):

- Organic chemicals
- Oils and tars
- Toxic and explosive materials
- Combustible materials
- Radioactive materials
- Biologically active materials
- Asbestos and other hazardous minerals

Contamination of the ground itself arises from disposal of wastes, uncontrolled dumps of contaminants, accidental spillage and leakage during plant operation and from the transportation and stockpiling of raw materials, wastes, and finished products (Smith, 1985). It can also happen with overdosing the ground with metal contaminated sewage sludge and other similar wastes. Any former industrial site may be contaminated but some industries have a higher probability of producing contaminated sites such as mining and extractive industries, steel works, wood preservation, metal treating and finishing,

paints, chemical products, oil storage and oil production. Problems arising from a contaminated site depend upon many site factors and how they influence the degree of risk to a set of targets arising from the hazard compounds present in the site (Smith, 1985).

2.4 Pentachlorophenol (PCP)

PCP (Pentachlorophenol), which is a member of the halogenated aromatic family of pesticides, was first used as a wood preservative in 1936 (Richardson, 1978). The biological properties of PCP have resulted in its use as an anti-microbial agent in industrial cooling systems and paper markers, and as a fungicide in protein-based latex paints (Jones, 1981). PCP is prepared by reacting chlorine with phenol in the presence of a catalyst at high temperatures.

2.4.1 Physical and Chemical Properties

PCP is a solid at room temperature. It can be characterized as a stable organic compound, which is poorly soluble in water and highly soluble in organic solvents. It adsorbs strongly to organic solids such as cellulose in wood (Konasewich, *et al.*, 1988). The chemical structure of PCP is shown in Figure 2.1.

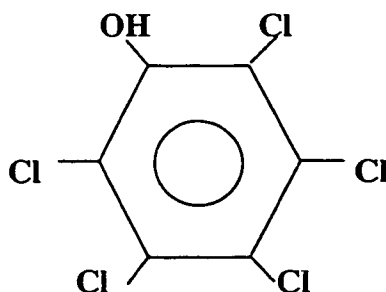


Figure 2.1 Chemical Structure of PCP

PCP is chemically and biologically persistent in high concentrations (e.g., a concentration of 3-6% is used for the treatment of wood). Its persistence in treated wood and its toxicity to wood decay organisms are two major reasons for the use of PCP (Environmental Canada, 1984, and Spenser, 1981). The physical and chemical properties of PCP have been summarized in Table 2.3.

Table 2.3 Physical and Chemical Properties of PCP

Physical State	Solid	Floatability	Sinks in water
Odor	Strong pungent odor when heated	Specific Gravity	1.98 (22°C)
Vapor Pressure	0.00011mmHg (20°C)	Flash Point	Not flammable
Solubility	Freely soluble (oil) Slightly soluble (water) 5 ppm by weight (0°C) 14 ppm (20°C)	Boiling Point	Decomposes at (310°C)
		Melting Point	188 to 191°C
		Appearance	White to light brown solid

2.4.2 Fate of Pentachlorophenol in Soil and Aquatic Ecosystem

2.4.2.1 Fate of PCP in Soil

Pentachlorophenol readily degrades in the environment by chemical, microbiological and photochemical processes. Degradation in soil is affected by numerous chemical and biological factors. The effect of these factors was discussed by Tsunoda (1965), Kuwatsuca (1972) and Sakamoto (1962). The rate of PCP dissipation from soil is closely related to temperature, aeration and organic matter. The degradation of PCP is partially dependent on cation exchange capacity and soil pH, whereas soil texture, clay content,

degree of base saturation, and free iron oxides do not influence the rate of PCP degradation.

2.4.2.2 Fate of PCP in Aquatic Ecosystems

Extensive fish kills occurred in a freshwater lake in December 1974 and again in December 1976 due to the accidental release of wood-treating wastes containing pentachlorophenol (PCP) in fuel oil. Samples of water, sediment, leaf litter, and fish collected from the lake were analyzed to determine the persistence and distribution of PCP in the aquatic environment (Konasewich, *et al.* 1988).

PCP was found to persist in the water and in fish over six months following the spills. Also fish were observed to accumulate PCP rapidly from the water. The concentration in fish decreased as the concentration in the water decreased, but required six to ten months to reach background concentrations. Fish liver tissue had the highest concentration followed by gills and muscles (Konasewich, *et al.* 1988).

2.4.3 Environmental Effects

The exposure of aquatic organisms to PCP could result in both short-term (acute) and long-term (chronic) toxic effects. The environmental effects would be dependent upon a complex array of parameters including concentration, pH, adsorption to suspended solids, temperature, biodegradation rate, and photo decomposition rate (Konasewich, *et al.* 1988).

2.5 Type of Polluted Sites and Remediation Principles

Polluted sites can be categorized into two groups: 1) seriously polluted sites where the pollutants sometimes have penetrated deep into the soil, and 2) sites where the pollution is present mainly at the surface or in the top soil. The remediation techniques to be employed for a contaminated site strongly depend on the nature, concentration and physical state of the pollutant present, and the specific aspects of the site itself (e.g. soil characteristics, site accessibility) (Rulkens, *et al.* 1993).

Pollutants can be divided (according to their physical and chemical properties) into two main groups: heavy metals and organic pollutants. With respect to their physical state, they may be present as separate particles, adsorbed into soil particles, form a liquid or solid film around soil particles, or be present within organic soil substances, and may occur as a solid or liquid in the pores of soil particles.

Pollutants can be removed from the soil according to four different principles: molecular separation (ion exchange), phase separation (desorption), chemical destruction, and biodegradation (bioremediation). Pollutant properties which are most important in terms of remediation include: volatility, solubility in water or an organic solvent, chemical/thermal instability, biodegradability, adsorption/absorption, magnetic or electrical properties, surface properties, size, shape, and density of polluted particles (Pierzynski, 1993).

2.6 Remediation Techniques

2.6.1 Treatment of Excavated Soil (*ex-situ* treatment)

Ex-situ soil treatment focuses on the removal of contaminants from the excavated soil. In this method, contaminated soil is excavated first and then treated by using one or a combination of technologies listed in Table 2.4. Table 2.4 lists important techniques together with their field of application (Kovalik and Kingscott, 1995).

Table 2.4 Treatment of Excavated Soil

Type of technique	Type of soil	Pollutants
Extraction/wet classification	Sandy	All types
Thermal treatment	All types	Organics/Hg
Biological treatment		
• Land farming	Sandy	biodegradable
• Heap pile system	Sandy	biodegradable
• Slurry reactors	All types	biodegradable

Extraction/wet classification or soil washing involves the mixing of contaminated soil with an agent (e.g., water) followed by separation of clean soil particles and treatment of the extracted portion. Soil washing is suitable for the cleaning of sandy soils with a low percentage of clay and humic content (less than 10 to 15%) (Rulkens, *et al.* 1998).

Thermal decontamination of soil is applied in two steps: first, contaminants are evaporated to the gas phase (at a temperature between 150 to 700 °C) and in the second

step, pollutants are removed from the gas phase. Soils contaminated with organic compounds can be treated with this method. High temperature inside the incineration system causes the destruction of the organics present in the soil. Combustible organics are converted to carbon dioxide and water vapor during this process.

Biological treatment involves the degradation of contaminants by microorganisms and bacteria. Creating optimal condition for growing microorganisms in the soil requires the destruction of the contaminants. The most important conditions which affect microbial activity are: temperature, soil moisture content, pH, oxygen concentration, type of electron acceptor, presence of the appropriate micro-organisms, and bioavailability of pollutants to the micro-organisms (Rulkens, 1998).

2.6.2 In-situ Treatment of Soil

Excavation of contaminated soils was once the chosen solution. However, because of the high cost of excavation and final disposal (\$600 to 1000/cubic meter) at hazardous waste landfills, in addition to the lack of available landfill sites, these disposal methods are becoming increasingly less popular. To decrease the cost, various technologies are being developed and implemented for remediation of soils and sediments contaminated with hydrocarbons and heavy metals.

Excavation and transport of contaminated material may also be hazardous and present other environmental hazards. It may not be possible to find a suitable disposal site within an economic distance either because of its toxicity or its bulk, therefore, risk regarding to

long distance transportation comes to the picture. Further, disposal redeposition may simply move the problem elsewhere (Mann, 1993).

In-situ treatment is used to treat the contaminated soil without excavation. Table 2.5 lists the most important *in-situ* treatment techniques together with their field of application and possible modifications (Kovalik and Kingscott, 1995; Martin and Bardos, 1995; Verstraete, 1995).

Table 2.5 In Situ Treatment of Soil (Rulkens, 1998)

Type of technique	Field of Application	
	Type of soil	Pollutants
➤ Soil vapor extraction	Sandy	Volatile
➤ Air sparging	Sandy	Volatile
➤ Bioremediation	Sandy	Microbiological
➤ Electrokinetics	All types	Heavy metal
➤ Solidification/stabilization	All types	Inorganic
➤ Mechanical/physical isolation	All types	All types

Soil vapor extraction (SVE) is a relatively new remedial option utilized to remove volatile organic compounds (VOCs) such as BTEX (Benzene, Toluene, Ethylbenzene, Xylene) from soil in the vadose zone (the unsaturated zone above the ground water table). Extraction wells create pressure gradients in the contaminated zone in which gas flows containing volatile pollutants are withdrawn from the site. On the other hand, the SVE process consists of passing an air stream through the soil, thereby transferring the

contaminants from the soil matrix to the air stream. SVE systems are implemented by installing vapor extraction wells or perforated piping in the zone of contamination and applying a vacuum to induce the movement of soil gases (LaGrega, *et al.*, 1994).

Air sparging (AS) is used for treating contaminated groundwater. Air is injected into the water-saturated soil matrix that causes the stripping of pollutants from the water phase. AS involves injecting atmospheric air into the aquifer to induce mass transfer of volatile organic chemicals to the vapor phase and mass transfer of oxygen to the aqueous phase. The injected air forms channels through the contamination plume as it flows upward through the saturated zone and into the vadose zone. The injected air volatilizes the contaminants in the flow channels and transports them to the vadose zone where they are either biodegraded or removed by SVE (LaGrega, *et al.*, 1994).

Bioremediation or biological treatment refers to degradation of organic compound present in the soil. Nutrients, oxygen and surfactants may be added to the soil to enhance the remediation process. Oxygen can also be supplied by injecting air (bioventing). Sometimes a combination of biodegradation, stripping of volatile pollutants and extraction of water-soluble pollutants is applied. If the proper microbial communities are established and controlled, almost any organic compound can be degraded.

In summary, “microorganisms can metabolize organic compounds via a series of low-temperature (i.e., ambient) enzyme-catalyzed reactions. Metabolism releases energy from the organic compounds and uses the carbon to build new cellular material. As a

side effect, the organic compounds are degraded. Degrading either transforms the waste to simpler organic compounds or mineralizes it to carbon dioxide, water, and cell mass” (LaGrega, 1994).

Electroreclamation or electrokinetics is suitable for the removal of heavy metals especially from clayey and sandy soils. Electrokinetics is based on electrokinetic processes that occur when an electric current is generated between a cathode and an anode in soil. Electrokinetic soil decontamination is a process where electrical, chemical and hydraulic gradients are the driving forces that cause the removal of contaminants. This technique has been demonstrated as being effective in the removal of contaminants (Pamukcu, 1990).

Solidification/stabilization methods are applied for remediation of hazardous waste sites, treatment of residues from other treatment processes, treatment of contaminated land. In solidification/stabilization technology, reagents are mixed with waste to either minimize migration and spreading of contaminants or reduce its toxicity.

There are also large numbers of alternatives and additional techniques that are summarized in Table 2.6. The most appropriate remediation technology depends on a number of factors such as: type and concentration of contaminants, soil structure, and particle size, type of contaminants.

Table 2.6 In Situ Soil Treatment Techniques (Rulkens. *et al.* 1998)

Technique	Principle & Application
Soil flushing	Injection of washing solutions to extract soil contaminants
Steam stripping of the soil	Removal of volatile compounds by steam injection
Electric or radio-frequency heating	Removal of volatile compounds by heating of soil
Extraction with organic surfactants	Increased solubility/mobility of organic compound by surfactants
Hydrofracturing	Increasing soil permeability by injection of pressurized water
Pneumatic fracturing	Increasing soil permeability by injection of pressurized air
In-situ vitrification	Melting of contaminated soil

2.6.2.1 Soil Flushing

Soil flushing is an in situ remediation technique that accelerates the mobilization of contaminants from a contaminated soil for recovery and treatment. In other words, in situ soil flushing is defined as the injection or infiltration of an aqueous solution into a zone of contaminated soil/groundwater, followed by down gradient extraction of ground water and elutriate (flushing solution mixed with the contaminants), and above ground treatment followed by discharge or re-injection (Roote, 1998). Figure 2.2 shows a schematic in situ soil flushing system.

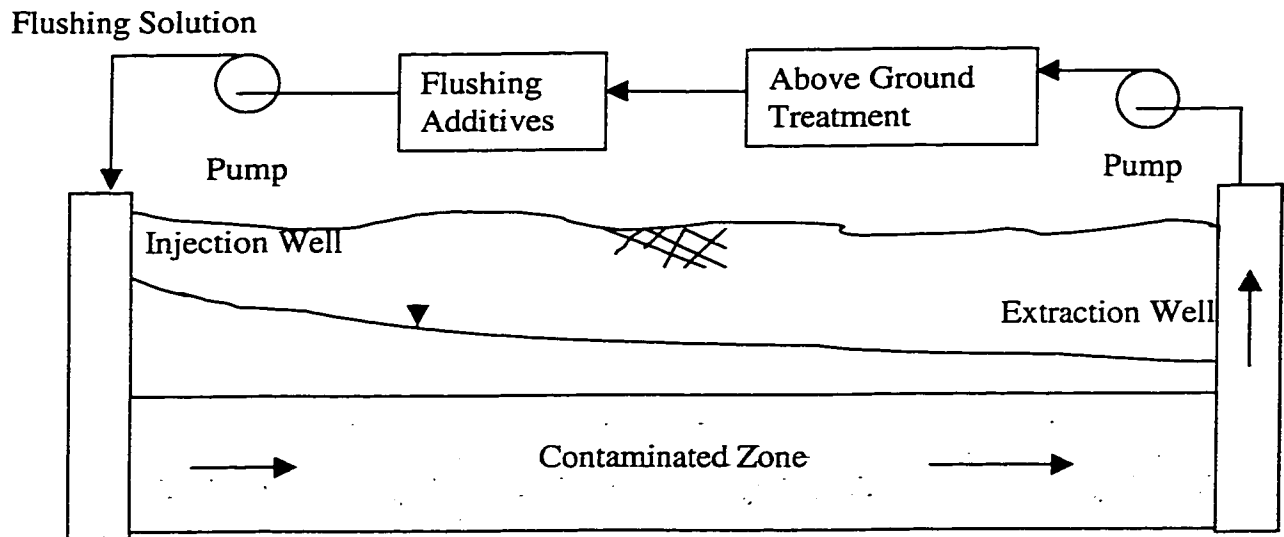


Figure 2.2 Schematic of in situ Flushing System (Roote, 1998)

In this technology, water or other agents are used in the mobilization process. Soil flushing accelerates both geochemical dissolution reactions such as adsorption/desorption, bioremediation, and subsurface contaminant transport mechanisms such as, advection and molecular diffusion (Roote, 1998).

In situ soil flushing can be considered for the removal of hydrocarbons, chlorinated hydrocarbons, metals, salts, pesticides and herbicides. Some advantages of this technique are: no soil displacement and/or disposal cost, minimal disruption of ecosystem, cost advantages at greater depths, and minimized worker exposure to contaminants (Mann, 1993). This technology is most effective in homogeneous, permeable soils. A number of site conditions that limit the effectiveness of this technology are: soil with a low hydraulic conductivity, pipes and underground utilities, and soil contaminated with

insoluble compounds or contaminants that are tightly bound to the soil and the lack of an adequate supply of process water. Effective application of the process requires understanding of groundwater hydrogeologic transport and the way contaminants are bound to the soil. Since soil flushing increases contaminant mobility, there is a possibility of spreading contaminants to clean neighbouring sites (Kommalapati, 1998).

Flushing agents can be water, dilute acid and bases, solvents or surfactants. Acid or bases can be added to improve flushing efficiency. Surfactants can be added to increase the mobility of certain semi-volatile and inorganic contaminants (Mann, 1993). The effectiveness and rate of cleanup depend on the type of soil, contaminant, and flushing solution. In general, soil flushing is most effective in homogeneous, permeable soils (e.g., sands, gravels, and silty sand with permeabilities $> 10^{-4}$ cm/sec). The relationship between capillary processes, water content, and hydraulic conductivity must be understood before a water based flushing technique can be used effectively.

The in situ soil flushing process requires that the flushing fluids be injected into the soil matrix. Using this technology for mobilizing contaminants in the soil can be classified as conventional and unconventional. Conventional soil flushing can be divided into the following processes:

- Natural restoration
- Well capture methods in the vadose zone
- Pump and treat system in the saturated zone

There are many limitations in the use and effectiveness of surfactants. Hard water makes surfactants ineffective. Also soil with high amounts of organic content can cause chemical adsorption of surfactant to the soil besides low permeability that decreases removal efficiency. High rates of surfactant consumption raises the cost of soil flushing (Mann, 1993).

Besides all these remediation techniques, some efforts have been made (Ghowdiah, 1997, Chaphalkar, 1997) using a foam-surfactant agent in soil flushing technology. Some previous studies related to treatment of contaminated soil by injecting of foam-surfactant solutions for removal of organic compounds are described in this chapter. Having a good knowledge of the nature of the surfactant would lead to a better understanding of the process.

2.7 Surfactants

Surface active agents (abbreviated as surfactant) are substances that lower the surface tension of a solvent and form aggregates like micelles in aqueous media. The change of surface tension by dissolution of some compounds originates from concentration of the surfactant at the surface of the solution. A surface active molecule consists of two parts with opposing character. One part is hydrophilic (polar part or water attracting) and the other is hydrophobic (nonpolar or water repelling). A surfactant molecule can be represented as in Figure 2.3.

Hydrophobic portions are usually long chain hydrocarbons. In surfactant solutions, the surfactants tend to concentrate at the air/water interface, where the hydrophilic heads can be hydrated in the water while the hydrophobic tails do not disrupt the hydrogen-bond structure of the water by being immersed in the aqueous phase. By concentrating at the air/water interface of the solution, the surfactant species are able to reduce the free energy of the system, thereby increasing its solubility (Harwell, 1992).

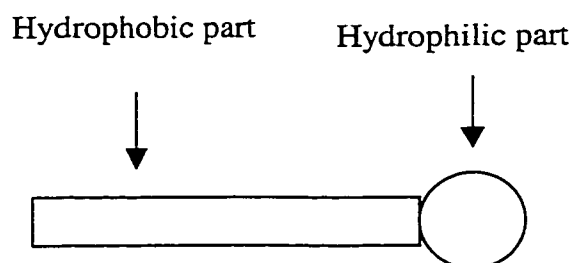
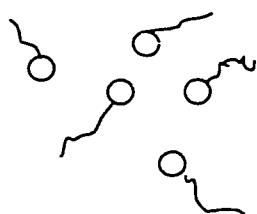


Figure 2.3 Basic components of a surfactant

Surfactants are classified according to their hydrophilic group. Anionic, cationic, amphoteric, and nonionic surfactants contain negative, positive, positive and negative and neutral charges as their hydrophilic group respectively. Anionic surfactants are mainly used as detergents. Cationic surfactants are particularly useful in fabric softeners and hair conditioners. Amphoteric surfactants are usually used as a booster to enhance the detergency. Nonionic surfactants, most popular as emulsifiers, also show strong detergency for oily dirt (Tsuji, 1998).

A phenomenon unique to surfactants is the self-assembly of molecules into dynamic micelles (Figure 2.4). Micelle formation occurs above a critical concentration of surfactant monomers, referred to as the critical micelle concentration (CMC), which is different for every surfactant (Rosen, 1989). The CMC is a function of the surfactant's structure, the temperature of the surfactant solution, the concentration of added electrolytes, and the concentration of solutes (Harwell, 1992). The average number of surfactant molecules in a micelle is called the aggregation number.

Below CMC Concentration (monomers)



Above CMC Concentration (spherical micelles)

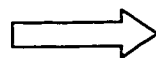
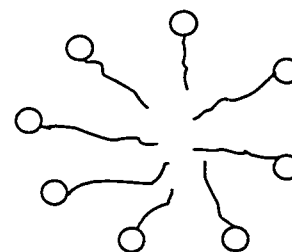


Figure 2.4 Example of surfactant micellization

Surfactants show significant potential for enhancing the remediation of contaminated soil and groundwater with organic compounds (Hiemenz, 1986). Surfactants enhance organic contaminant recovery in soil washing/flushing through two different mechanisms. First, surfactants reduce the oil-water interfacial tension and the capillary forces that trap the residual molecule. Therefore, the residual oil saturation in the presence of the surfactant is appreciably lower and more oil is mobilized than with simple water floods alone. Secondly, surfactants are capable of forming aggregates called micelles. Above the CMC, the hydrophobic end of the surfactant molecule will cluster together inside the micelle structure with the hydrophilic end exposed to the aqueous phase on the exterior. Consequently, the interior of a micelle constitutes a compatible environment for hydrophobic organic molecules.

Below the CMC, according to Hiemenz (1986), no enhancement of organic solubility is generally observed. But it was observed that the aqueous solubility of certain highly hydrophobic organic compounds can be enhanced by certain surfactants even below the CMC (Kile *et al.*, 1989).

Surfactants have also shown some potential for remediation of heavy metals from soil, though research in this area has been limited. The feasibility of using a surfactant for removal of heavy metal from a contaminated soil was evaluated and showed promising results (Mulligan *et al.*, 1999).

2.8 Theory of Foaming

Foams consist of thousands of tiny bubbles that can be generated within a liquid. Foaming occurs when the bubble generation rate is faster than the collapsing rate. Gas makes up the larger volume of such a foam. Therefore, the bulk density of the foam approaches that of the gas rather than the liquid. True foaming only occurs when the intervening liquid between two bubbles thins down to a lamella, instead of rupturing at the point of closest approach.

In foam, the volume of the gas fraction is extremely large and also the distance between individual bubbles is extremely small. The presence of foam represents a balance between the process generating it and the forces causing its destruction. Foams are very unstable because of their high specific surface areas relative to separated gas and liquid phases that have lower surface energy. The characteristics of foam can be classified as shown in Table 2.7.

Table 2.7. Classification of Foams (Ghildyal, *et al.*, 1988)

Type of Foam	Characteristic
True Foam	Predominantly gaseous dispersion
Fluid Foam	Predominantly liquid dispersion
Unstable Foam	Equilibrium state is continuously approached
Metastable Foam	Progress to the equilibrium state is arrested
Transient Foam	Lifetime of seconds
Persistent Foam	Lifetime of hours or days if undisturbed

In summary, processes which take place during foam formation/destruction are: liquid run over from the interfacial films; diffusion of gas from smaller bubbles into larger ones; redistribution of the liquid along the height of the foam column; natural escape of liquid from the foam; destruction of inter bubble films. Foaming behavior is effected by liquid properties such as surface tension, viscosity and ionic strength. Foaming ability of liquids shows an obvious correlation with the surface activity of the solutes. Persistent foams arise only with solutes that severely lower the surface tension with highly surface active substances (Vardar, 1998).

Surface activity in aqueous solutions is associated with molecules having both hydrophobic and hydrophilic properties. At the interface, the hydrophobic end of a surfactant is forced out of solution because the attraction between the water molecules is greater than the combined attraction of water to hydrophilic and hydrophobic parts of the surfactant. This positive adsorption at the vapor-liquid interface lowers the surface tension relative to that of the pure solvent. The “surface activity” of a solute can thus be defined as the ability to lower the tension of a solution by transfer of solute molecules to the surface (Thomas, *et al.*, 1977).

Two important characteristics of foams are stability and quality. By definition quality of foam is the ratio of total gas volume per total volume of the foam (Eq. 2.1). Stability is the time that half of the liquid in the foam needs to drain out (Ghowdiah, *et al.*, 1997). Stability of a foam strongly depends on the film elasticity and the formation of gelatinous surface layers.

In addition, high bulk and surface viscosity enhance the stability of the foam. Among other factors, the presence of volatile compounds, temperature and pH influence foam stability.

$$\text{Foam quality} = \frac{\text{GasVolume}}{\text{TotalFoamVolume}} \quad (\text{Eq. 2.1})$$

Expansion factor which is another parameter for describing a foam defined as below:

$$\text{Expansion Factor} = \frac{\text{FoamVolume}}{\text{LiquidVolume}} \quad (\text{Eq. 2.2})$$

2.9 Surfactant Foam Technology (Background)

As explained previously, a foam is commonly defined as dispersion of gas bubbles in a liquid. The volume fraction (ϕ) of gas in a foam is mostly between 0.50-0.97 (Wilson, 1989). The presence of a surfactant is essential for making and stabilizing a foam. A surfactant adsorbs the air-water interface, thereby lowering the surface tension. Foams, because of their characteristics such as having a large surface area of liquid compared to the air-liquid interface without foam, have been considered as an aid to in-situ soil remediation. Several investigations have been done to find the most important factors related to this process but there is still a long way before the use of foam injection in large scale soil remediation becomes feasible.

An investigation by the Institute of Gas Technology (Ghowdiah, *et al.*, 1997), was done to study the use of gas-liquid foams as a means of delivering chemicals to the subsurface. Experiments were conducted to investigate the physics of foam flow in soil and identify parameters that are important to optimizing foam injection at low pressures so as to avoid

problems due to channeling and soil heaving. Foam was generated by flowing surfactant solution and air simultaneously through a porous disc while the flow rate of surfactant solution and air could be varied independently in order to control the foam quality (87 to 99%) and generation rate (10 to 30 cm³/min). The foam flowed through sand or soil packed in a cylinder 30.5cm long and 7.6cm in diameter. In these experiments silica sand with a porosity of 39% was used. The soil samples were contaminated with polycyclic aromatic hydrocarbons (PAH). The foam was generated by using a 1% solution of an anionic surfactant, Standpol ES-2 (Henkel, Hoboken, NJ).

The foam flow data obtained were analyzed using the single-phase Darcy's equation to calculate an effective viscosity for the foams. Though the mechanism for foam movement actually involves a process of foam breakdown and regeneration throughout the porous medium (Holm, 1968), the effective viscosity is a useful parameter for characterizing foam flow under different conditions. The effective viscosity was calculated as:

$$\mu_{(foam)} = \frac{KAP}{q_{foam}L} \quad (\text{Eq. 2.3})$$

Where μ is viscosity (cp), K is permeability (darcy), q is foam flow rate (cm³/s), A is column cross section (cm²), L is column length (cm), and P is pressure drop in the column (atm).

One important observation was that the effective viscosity of the foam increases with soil permeability (Ghowdiah, *et al.*, 1997). Also it was observed that foam mobility is

relatively independent of soil permeability. This can be useful in preventing fluid leak-off into permeable channels.

Some specific conclusions from this investigation can be summarized below:

- In order to achieve acceptably low pressure gradients (to prevent heaving of soil) there is a need for a foam that has relatively low stability but high foamability
- Delivery of chemicals by foam injection can help reduce leak-off into naturally occurring high-permeability zones.
- During foam flow the soil held significantly more liquid than would be expected from the gas to liquid ratio in the injected foam.
- Higher quality foams exhibited lower pressure gradients during flow, and lower liquid hold-up in the soil.

Another investigation was conducted by *Argonne National laboratory* and *Envirogen Inc.*, (New Jersey, 1998), to study surfactant foam/bioaugmentation technology for in-situ treatment of TCE-DNAPLs (Trichloroethylene, dense nonaqueous-phase liquids). A bench-scale study was conducted to evaluate a remediation technology that utilized surfactant foam for mobilizing and dispersing TCE-DNAPLs combine with a bioaugmentation technology to remediate TCE in-situ.

Foam was generated with a spinning disc generator. This device rapidly and efficiently generates microbubbles (colloidal gas aphrons, CGAs) from low-concentration surfactant solutions. Foams were pumped from the generator to the experimental column at a rate varying between 3.5 to 7 ml of liquid volume per minute.

Glass columns were packed with a uniform washed silica quartz sand with an average diameter of 0.45-0.50 mm. Surfactant solutions employed in these experiments included Tergitol 15-S-12, Steol CS-300, and Biosoft D-40 and an ENV 435 culture was added to the surfactant solution. Six pore volumes of the surfactant/microorganism solution were pumped through the sand column at a flow rate of 5 ml/min.

Some results from this study are summarized below:

- In terms of delivering culture (ENV 435) into the soil, it was observed that the use of the surfactant foam resulted in improved dispersion and survival of the injected TCE-degrading bacteria as compared to the injection of the surfactant solution.
- In terms of remediation of TCE-DNAPLs, foam flushing showed that a significant amount of TCE was mobilized and the TCE concentration was fairly evenly distributed within the first seven core sections. The dispersed TCE was amenable to bacteria degradation as shown by the addition of ENV 435 with foam injection and the observed degradation of TCE was 98%.
- Treatment with foam injection resulted in nearly 70% of the injected TCE being mobilized through the sand column with a total recovery of 89%. Running the column under foam / biotreatment conditions resulted in only a small amount of TCE-DNAPL remaining in the sand column (less than 1.4%) which represents 93% degradation of the residual column TCE.
- Results from this study show that foams can be generated from low concentrations of surfactant solutions (0.1%), but the use of surfactant solutions

for solubilization requires concentration greater than the surfactant's CMC. Thus, high concentration of surfactants solutions (1-10%) are often required to overcome dilution and binding effects in order to be effective. It has also been observed that high surfactant concentrations can result in plugging of injection wells by the dispersion on fine materials or by the formation of viscous emulsions (Nash, 1987).

- Surfactant foams reduce the interfacial tension (IFT) between DNAPLs and the liquid phase, thus capillary forces that trap DNAPLs in pores are reduced, and therefore a lower hydraulic gradient is required to mobilize DNAPLs. The most effective treatment for mobilizing the TCE-DNAPL was a pulsed injection of foam (Nash, 1987).

Another investigation has been done in the Hazardous Waste Research Center (Louisiana State University). The objective of this study was to investigate the suitability of Colloidal Gas Aphron (CGA) suspensions generated from natural surfactant solutions for flushing column containing soil contaminated with Hydrophobic Organics Compounds (HOC). The hypothesis was that CGA suspensions, due to their stability, can be used effectively to remediate contaminated soil and their performance may be superior to conventional surfactant solution due to their small size and the sweep efficiency. An aromatic chlorinated hydrocarbon, hexachlorobenzene (HCB), was selected as the compound for the study (Kommalapati, *et al.*, 1998).

Natural surfactant solutions (1% by weight) were prepared of dry fruit Pericarp powder added to deionized water. Surfactant solutions made from the fruit Pericarps were used to generate colloidal gas aphron suspensions and then injected to soil samples. Soil fraction passing US standard No. 10(2 mm) sieve was contaminated by appropriate amounts of HCB dissolved in petroleum ether. The soil was then dry packed into the column in four layers, each layer was compacted by giving 25 strokes with a compacting rod. The bulk density and the porosity of the packed soil column were about 1.6 g/cm³ and 0.40, respectively.

Some results from this study are described below:

- Natural surfactant solutions increased the solubility of naphthalene and HCB by several hundred-times compared to water. Natural surfactant desorbed as much as 90% of total HCB from soil contaminated with low HCB (2 mg/kg).
- The removal of HCB during the first pore volume was negligible. Surfactant introduced during the initial pore volumes will likely be sorbed onto the soil and not available to solubilize HCB.
- HCB concentration increased steadily after the first pore volume and approached a maximum by the fifth pore volume.

- The removal of HCB appeared to be limited at low contamination levels (2 mg HCB/Kg soil) and the HCB concentration in the effluent was only a small fraction its solubility in such a case.
- For soil contaminated with higher amounts of HCB, effluent HCB concentration approached a constant maximum proportional to the solubility of HCB in the surfactant solution.
- It was observed that pressure increased with an increase in surfactant concentration, but the increase wasn't significant when the concentration increased from 0.5% to 1%.
- The recovery of HCB was lower for low-contamination soils and the recovery increased with increasing contamination on the soil.
- Increasing the natural surfactant concentration increased the recovery of HCB significantly for both conventional solutions and CGA suspensions. The increased solubility of HCB was responsible for the enhanced recovery.

As explained so far, foams (air-liquid) can be used to carry surfactants into the soil as a means of remediation. Due to characteristics, foam may enhance soil remediation in particular cases. More studies, such as examining the removal of other contaminants, investigation of contaminant removal mechanisms, modeling the flow of foam in soil and

modeling of contaminant mobilization in the presence of foam, have to be done in order to use this technique on a larger scale.

CHAPTER THREE

Contaminant Fate and Transport

(Sorption of Organic Compounds in Soils)

Introduction

Subsurface contamination by organic chemicals became a serious and widespread problem for soil and ground water quality in the last few decades. "The most severe contamination problems are due to point sources which frequently involve organic solvents (e.g. aromatic hydrocarbons), gasoline, lubricants in general, as well as coal tars (from manufactured gas plants), wood preservatives (e.g. creosote which may contain **pentachlorophenol**) etc. Non-point sources, which cause usually much lower contaminant concentrations than point sources, result mostly from the application of pesticides in agriculture" (Grathwohl, 1998).

The fate of chemicals in the environment depends on their physico-chemical properties such as vapor pressure and water solubility or the octanol/water partition coefficient that is especially important for hydrophobic organic compounds (HOC). These compounds, once introduced into the subsurface environment, will spread more by transferring mass (advection/diffusion) to the vapor and aqueous phases. In addition, the rate of sorption/desorption is limited by the diffusive transport of the solute to the sorption site. The actual process of adsorption or desorption of a molecule at the sorption site is much faster than transport to the site. In terms of low permeable media (e.g., clay, silt, etc.),

diffusion is the most important transport mechanisms that controls the rate of mass transfer.

3.1 Contaminant Transport Mechanisms

Contaminants that are present in subsurface may appear in different phases. If contaminants are dissolved in water, then, water is the solvent and contaminants are called the solute. When water flows through the soil, contaminant transport along stream lines at the average seepage flow velocity, the contaminant movement is called **advection**.

When water flows in to the soil, another transport mechanism that occurs is **dispersion**. Water flows around the solid particles of porous media, it migrates to the right, left or both sides, and this process repeats millions of times. The result is a mixing of flowing water that causes spreading the contaminant mass.

Contaminants also transport with respect to their chemical kinetic activity. Gradient concentration is the active force in this transportation. In other words, contaminants move from areas with higher concentration to areas with lower concentration. This process is called molecular diffusion or just **diffusion**.

Each one of these transport processes takes precedence depending on the situation. Advective and dispersion processes dominate the contaminant transport system in formations of medium to high hydraulic conductivity. But in cases of low hydraulic conductivity (e.g. clay), diffusive transport is frequently controlling. It should be noted that there are some other mechanical, chemical, and biological processes that participate

in contaminant movement such as ion exchange, precipitation, aerobic degradation, and biological uptake.

The most useful underground water equation that governs ground water flow and contaminants transport is the Laplace equation. Laplace equation illustrates two or three dimension ground water flow and is described below. The Darcy flux into the control volume in the x and y directions are v_x and v_y , respectively. (Fig 3.1)

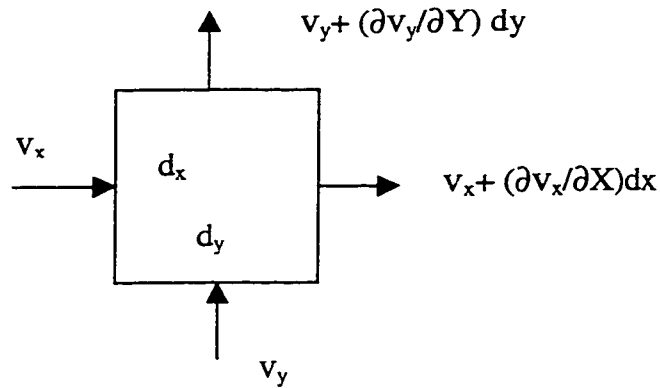


Figure 3.1 Two-dimensional control volume

By assuming no changes in the control volume and according to the equation of continuity,

$$Q_{in} = Q_{out} \quad (\text{Eq. 3.1})$$

Where Q_{in} and Q_{out} are flow rates into and out of control volume respectively. Therefore:

$$Q_{in} = v_x \times dy + v_y \times dx \quad (\text{Eq. 3.2})$$

$$Q_{out} = (v_x + (\partial v_x / \partial X) dx) dy + (v_y + (\partial v_y / \partial Y) dy) dx \quad (\text{Eq. 3.3})$$

Where: $\partial v_x / \partial X$ is the rate of change in the Darcy flux in the x direction

$\partial v_y / \partial Y$ is the rate of change in the Darcy flux in the y direction

Darcy's law can be written for v_x and v_y in both directions as below:

$$v_x = K_x (\partial h / \partial x) \quad (\text{Eq. 3.4})$$

$$v_y = K_y (\partial h / \partial y) \quad (\text{Eq. 3.5})$$

Where K_x and K_y are hydraulic conductivity in x and y direction, and $\partial h / \partial x$ and $\partial h / \partial y$ are hydraulic gradients in the x and y directions.

By combining equations 3.1 to 3.5, the Laplace equation for a two-dimensional flow field can be written for isotropic flow conditions ($K_x = K_y$) as:

$$\partial^2 h / \partial x^2 + \partial^2 h / \partial y^2 = 0 \quad (\text{Eq. 3.6})$$

where h is hydraulic head (cm).

3.2 Sorption Phenomena

Sorption is the process where a component is transferred from one phase to another phase. In soils two sorption phenomena may be distinguished which are *adsorption* and *absorption*. Adsorption describes a process in which the solute accumulation is generally restricted to a surface or interface (e.g. solid/liquid, soil/liquid/gas). In contrast, absorption describes a process in which the solute penetrates into the sorbent. Two terms commonly used in discussing sorption theory are sorbate and sorbent. The sorbate is the contaminant that adheres to the sorbent, or sorbing material.

Sorption of organic chemicals in soils may result from various types of attractive forces between sorbate and sorbent or solute and solvent. In general, chemical, physical, and

electrostatic interactions may contribute to the sorption of organic pollutants in soil. The process of adsorption/desorption is reasonably fast, as Pignatello (1989) concluded from the interactive energies involved in the sorption/desorption process of organic compounds in soils. He stated that "with few exceptions, the micro scale sorption and desorption steps of organic contaminants in soils should be instantaneous on a practical time scale".

3.2.1 Partitioning of Hydrophobic Organic Compounds in Soil

Sorption of hydrophobic organic compounds (e.g. pentachlorophenol) in soils can be attributed to the soil organic matter content (Lambert et al., 1965; Karickhoff, 1984). According to Chiou et al. (1979; 1985) uptake of these compounds by natural organic matter may be interpreted as partitioning of solute between the organic and the aqueous phase, comparable to the dissolution of the compound in a suitable solvent (e.g. octanol) (Chiou, 1989). Sorption may then be quantified by a simple partition coefficient K_{oc} (organic carbon partition coefficient) [L^3M^{-1}]:

$$K_{oc} = C_c / C \quad (\text{Eq. 3.7})$$

Where:

C_c = solute concentration in the organic matter ($\mu\text{g adsorbed/kg organic C}$) [MM^{-1}]

C = solute concentration in aqueous phase [ML^{-3}].

The partition coefficient is inversely proportional to the molar fraction of the solute in the water, (Raoult's law convention. Schwarzenbach et al., 1993), therefore the value of K_{oc} can be estimated based on the water solubility of the compound (Schwarzenbach et al., 1993):

$$\text{Log } K_{oc} = -0.75 \log S_w + 0.44 \quad (\text{Eq. 3.8})$$

Where S denote water solubility [mol/L]. The concept of partitioning predicts a linear relationship between the log of the solute concentration in the organic phase and in the aqueous phase.

3.3 Sorption Models

The sorption process, as explained above, is determined experimentally by measuring how much of a solute can be sorbed by a particular soil. If the sorption process is rapid compared with the flow velocity, the solute will reach an equilibrium condition with the sorbed phase. This process can be described by an equilibrium sorption isotherm. If the sorption process is slow compared with the flow velocity, the solute may not come to equilibrium with the sorbed phase, and a kinetic sorption model will be needed to describe the process. Both equilibrium and kinetic sorption models have been popularly used to describe the sorption or exchange processes.

3.3.1 Equilibrium Sorption Models

Equilibrium distribution of solute among the phases and interfaces of environmental systems typically relates the amount of solute, S , sorbed per unit of sorbing phase to the amount of solute, C , retained in the solvent phase. An expression of this type evaluated at fixed system temperature constitutes a retention or sorption "isotherm". Linear, Freundlich, and Langmuir equations are the most commonly used isotherms to describe equilibrium reactions.

3.3.1.1 Freundlich Isotherm

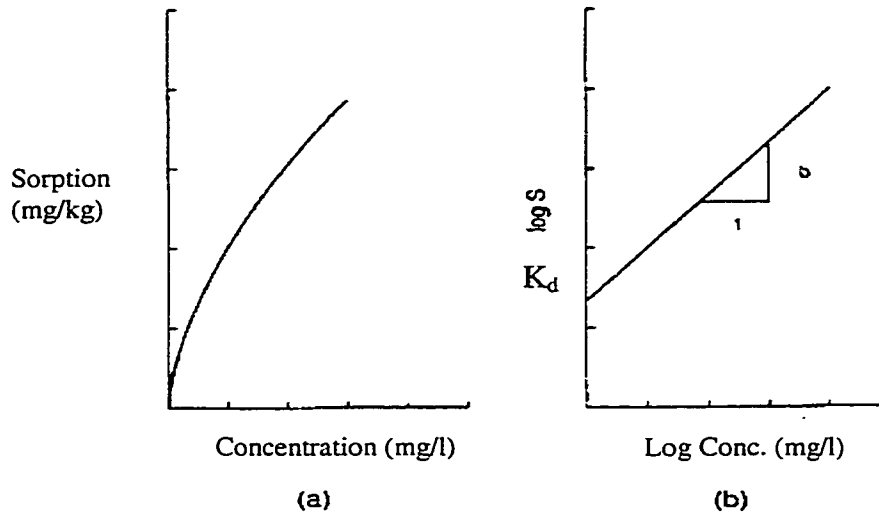
The Freundlich equation is frequently used to describe the sorption reactive solute onto the soil matrix. The Freundlich equation is given by

$$S = K_d C^b \quad [(mg_{pcp}) / (kg_s) = ml/g_s * (mg_s / l)^b] \quad (\text{Eq. 3.9})$$

Where S is the amount of solute retained by soil ($\mu g/g$ or mg/kg), C is the solute concentration in solution (mg/L or $\mu g/ml$), K_d is the distribution coefficient (L/Kg or ml/g), and the parameter b is dimensionless and typically has a value of $b < 1$. A typical Freundlich isotherm is shown in Figure 3.2. The distribution coefficient describes the partitioning as being analogous to the equilibrium constant for a chemical reaction. For $b = 1$, the Freundlich equation is often referred to as the linear reaction equation:

$$S = K_d C \quad (\text{Eq. 3.10})$$

Where K_d is the linear distribution coefficient (L/kg or ml/g)



**Figure 3.2 (a) Freundlich retention isotherm plotted in terms of S versus C
(b) Freundlich retention isotherm plotted in terms of $\log S$ versus $\log C$**

The linear sorption isotherm is shown in Figure 3.3. Selim (1996) described that Freundlich parameters, K_d and b , are best regarded as descriptive parameters in the absence of independent evidence concerning the actual retention mechanisms.

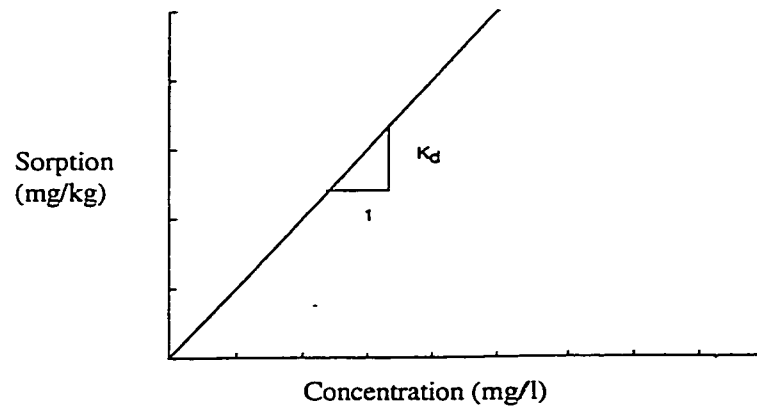


Figure 3.3 Linear retention isotherm, S versus C (Selim, 1996)

A logarithmic representation of the Freundlich equation is frequently used to represent the experimental data. Therefore, the slope of the best-fit curve provides the nonlinear parameter b and the intercept K_d in the equation $\log(S) = K_d + b \log(C)$, when a linear representation of the data in the log form is achieved.

3.3.1.2 Langmuir Isotherm

The Langmuir isotherm (Figure 3.4) is the oldest and most commonly encountered in soil. The major advantage of the Langmuir equation over linear and the Freundlich types is that a maximum sorption capacity is incorporated into the formulation of the model, which maybe a measure of the amount of available retention sites on the solid phase.

The standard form of the Langmuir equation is:

$$\frac{S}{S_m} = \frac{\beta C}{1 + \beta C} \quad (\text{Eq. 3.11})$$

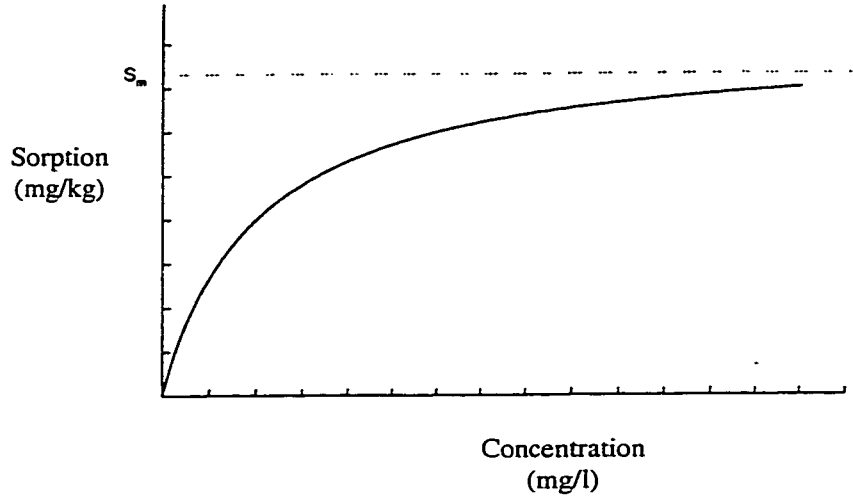


Figure 3.4 Nonlinear Langmuir retention isotherm, S versus C

Where β and S_m are adjustable parameters. Here β (ml/g) is a measure of the bond strength of the molecules on the matrix surface and S_m (μ /g of soil) is the maximum sorption capacity or total amount of available sites per unit soil mass.

3.3.2 Kinetic Sorption Models

All equilibrium models assume that the rate of change in concentration due to sorption is very rapid and that the flow rate is low enough that equilibrium can be reached. If this is not the case a kinetic model is more appropriate. Usually, the kinetic models are related to appropriate solute transport equations to describe the rate that solute is sorbed onto the solid surface and adsorbed from the surface.

3.3.2.1 The Irreversible First-Order Kinetic Sorption Model

The most simple non-equilibrium condition is that the rate of sorption is a function of the concentration of the solute remaining in solution and that once sorbed onto the solid, the solute cannot be desorbed. The irreversible nonlinear first-order kinetic sorption model is given by:

$$\frac{\partial S}{\partial t} = K_1 C \quad (\text{Eq. 3.12})$$

Where S is the amount of solute retained by the soil (mg/kg), C is the solute concentration in solution (mg/L), and K_1 is a first-order decay rate coefficient (L/kg.h), respectively.

3.3.2.2 The Reversible Nonlinear First-Order Kinetic Sorption Model

If the rate of solute sorption is related to the amount that has already been sorbed and the reaction is reversible where the forward (sorption) reaction is nonlinear, whereas the backward (desorption) reaction is linear, then the reversible nonlinear first-order kinetic sorption model can be used. The equation for this model is:

$$\frac{\partial S}{\partial t} = K_d C^b - K_b S \quad (\text{Eq. 3.13})$$

Where K_d (L/kg.h) and K_b (h⁻¹) are forward and reverse reaction rate coefficients. The b is a dimensionless parameter commonly less than unity and represents the order of the nonlinear reaction.

CHAPTER FOUR

Experimental Materials and Methods

Introduction

In this chapter, the material and equipment set up that were used in this study will be described. Materials used include soil (sand and sandy-silt), Triton X100 and JBR425 (representing nonionic and anionic surfactants), and pentachlorophenol as the target contaminant. The experimental set up presented later in this chapter showed better results than other set-ups that were performed with regards to generating uniform foam.

Foam, as explained in Chapter Two, consists of small tiny bubbles which are separated by a thin film of liquid (surfactant solution). Therefore the design of the system for generating and transferring foam had to take this characteristic into account. All characteristics of generated foam are affected by the size of tubing and columns, and connectors.

4.1 Materials

4.1.1 Soil

The soils used in this study were purchased from DAUBOIS Inc., and categorized as fine sand and silt according to the ASTM classification. Results from sieve analyses of two types of soils used in the experiments are summarized in Table 4.1. Type (I) refers to fine sand and type (II) refers to a mixture of fine sand and silt (50% by weight).

Table 4.1 Sieve analyses results

Soil type	Weight retained on sieve (g)			Total weight (g)
	Sieve No: 50	Sieve No: 100	Sieve No: 200	
Fine sand	380.2	107.0	10.2	497.4
Mixture of fine sand and silt	225.1	233.2	39.6	498.1

Total weight of soil used in sieve analysis = 500.0 g

Other characteristics of soils used in this study are listed in Table 4.2. Hydraulic conductivity and specific gravity were measured for the packed column after compaction that will be explained later on in this chapter.

Table 4.2 Soil characteristics

Type of Soil	Classification (ASTM)	Hydraulic Conductivity (cm/s)	Specific Gravity
Soil Type I	Fine Sand	7×10^{-2}	2.547
Soil Type II	Silty-Sandy	6.3×10^{-4}	2.641

4.1.2 Triton X100 & JBR425

Surfactants, Triton X-100 and JBR425, were obtained from SIGMA Chemical Co, and JENEIL Biosurfactant Co, respectively. Triton X-100 and JBR425 were used to represent nonionic and anionic surfactants. Because of its expected strong complexation with the soil matrix (Huang *et al*, 1997), cationic surfactant was not selected.

The Triton X-Series of nonionic surfactants is prepared by the reaction of octylphenol with ethylene oxide. The principle uses of these surfactants are in industrial and household detergent applications and in emulsifying agents. They are employed in almost every type of liquid, paste, and powdered cleaning compound, ranging from heavy-duty industrial products to gentle detergents for fine fabrics. These surfactants are also important ingredients of primary emulsifier mixtures used in the manufacture of emulsion polymers, stabilizers in latex polymers, and emulsifiers for agricultural emulsion concentrates, and wettable powders. (Edward *et al.*, 1994)

The biosurfactant, JBR, has a wide range of uses such as cosmetics, personal care products, detergents, textile manufacturing, industrial laundry supplies and pulp and paper processing and hydrocarbon recovery. In many applications they are expected to be more effective than conventional surfactants in similar concentrations. (Jeneil Biosurfactant Co., 1999)

Several physical and chemical characteristics of these surfactants (Triton X-100 and JBR425) are listed in Table 4.3.

Table 4.3 Physical and Chemical properties of Triton X-100 & JBR425

Surfactant	Type	Chemical formula	M. W. (g/mol)	CMC
Triton X-100	nonionic	$C_8H_{17}C_6H_4(OC_2H_4)_{10}OH$	646.87	$1.8 \times 10^{-4} (mg/l)^{(1)}$
JBR425	anionic	$C_{26}H_{48}O_9$	504 ⁽²⁾	

(1) Edward et al., 1994

(2) Jeneil Bio. Sur.Co., 1999

4.1.3 Pentachlorophenol

PCP (Pentachlorophenol), which is a member of the halogenated aromatic family of pesticides, was purchased from SIGMA Chemical Co., ON, Canada. Exposure to PCP could result in both short-term (acute) and long-term (chronic) toxicity. Some basic information and physical-chemical properties of this compound according to the MSDS (Material Safety Data Sheet) attached to the purchased product is listed in Table 4.4.

Table 4.4 Physical and Chemical properties of PCP ⁽¹⁾

Appearance	White Powder
Boiling Point	310° C
Melting Point	188° C - 191° C
Specific Gravity	1.978
Vapor Pressure	40 mm (211.2° C)

(1) SIGMA-ALDRICH Chemical Co., 2000

4.2 Experiment Method and Setup

Several experiments were run to investigate different parameters involved in the foam-surfactant technology in soil remediation. This investigation was done in two stages. The first stage was related to foam characteristics and pressure build up in the soil. The second stage involved decontamination efficiency of this technology.

4.2.1 Foam parameters and pressure in the soil

Two important characteristics of foams are stability and quality. By definition quality of foam is the ratio of total gas volume per total volume of the foam. Stability is the time that half of the liquid in a specific volume of the needs to drain out. (Ghowdiah, *et al.*, 1997)

$$\text{Foam quality} = \frac{\text{GasVolume}}{\text{TotalFoamVolume}} \quad (\text{Eq. 4.1})$$

The experimental setup for measuring these parameters and foam properties is shown schematically in Figure 4.1. Flow meters A and B control the flow of solution and air, respectively, before injecting into the foam generation column. Surfactant solutions with different surfactant concentrations (0.5%, 1%, 2%) are pumped by pump (I) and the air tubing is connected to a compressed air system in the lab. Range of flow rates (air + surfactant solution) that were used in this stage was between 5 to 30 ml/min. Both surfactant solution and air are injected into a porous stone that is installed in the top of the foam generator column. The porous stone enables foam generation in the presence of surfactant solution and air.

Column (I), (foam generator column), is 3 cm in diameter and 30 cm long and used for monitoring the foam that was generated. Foam exiting this column was taken as samples for quality and stability tests. In each test, samples were collected after foam reached a uniform and steady state in terms of bubble size and appearance that takes 30 to 60 minutes.

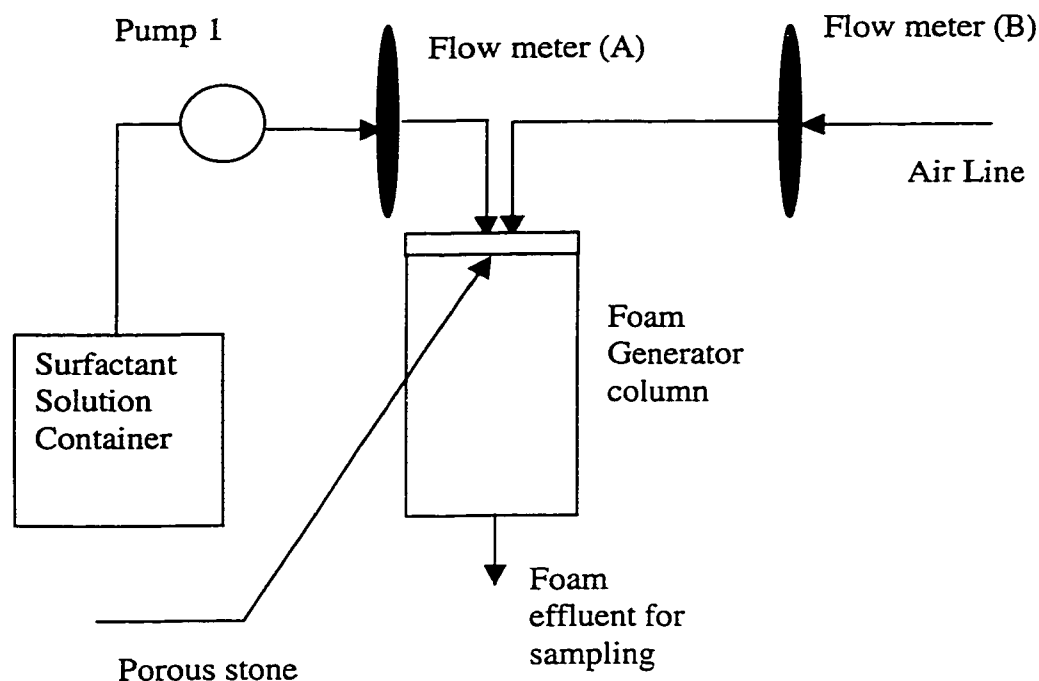


Figure 4.1 Schematic of the foam generator column for evaluating foam quality

Ten different commercial surfactants, (Triton X100, cetyl pyridinium chloride, Pluronic F68, Igepal CA-630, Chaps, Polytergen 305 LP, Surfynol 104 A, Taurodeoxy-Cholic-acid, JBR425, Triyon), were tested for their ability to make foam at low concentrations. Solutions of surfactants in water (distilled water) with three different concentrations

(0.5%, 1%, 2%) (solutions stirred for 10 min) were prepared and foam generated from each was studied for quality and stability.

In each experiment, 50 ml samples of generated foam were taken and left until all the bubbles collapsed. Time required for collapsing half of the foam was used as an indication of stability and the total liquid obtained from the collapsed foam per total volume of the foam sample calculated which indicates the quality of the foam. Only five tested surfactants showed the ability for generating foam at low concentrations. TritonX100 (nonionic) and JBR425 (anionic) gave the best results in terms of quality and stability. Therefore, they were chosen for further investigation.

Because pressure gradient in soil is one of the most important factors in using foams for soil remediation and soil flushing, the effect of foam quality and foam flow rate on the pressure build up in the soil were investigated in this stage.

Solutions of Triton X 100 (1%) and JBR425 (1%) were used to make foam and were injected into the soil sample (packed in four layers) at different flow rates (ranging between 15 ml/min to 35 ml/min) and qualities (ranging between 85% to 98%). In all experiments, foam flowed through the sand until near steady conditions were achieved in terms of exiting foam and pressure measured by the pressure gage, before the pressure gradients were recorded. It usually took a few hours, during which period the pressure gradient increased over time.

4.2.2 Column Test

To study PCP removal efficiency of this technology from the contaminated soil a series of experiments was developed and run. Soil with different hydraulic conductivities, specific gravities and contaminated with different levels of contamination were tested. The experimental setup for this stage of study is shown schematically in Figure 4.2.

4.2.2.1 Soil contamination

Soils which were used in these experiments (fine sand & sandy-silt), were washed for 24 hours with tap water before all experiments and then dried in the oven over night at a temperature of 150°C.

Methanol was used as a solvent for PCP (Pentachlorophenol, C_6Cl_5OH), and a solution of methanol and PCP was added to the soil. To get two different levels of contaminated soils (1000 mg of PCP/ kg of soil & 3000 mg of PCP/ kg of soil), 0.5 g and 1.5 g of pentachlorophenol were dissolved in methanol and added to 500g of washed soil, respectively, and then left over night in the fume hood to evaporate the methanol. Before the contaminated soil was used for decontamination tests, the concentration of PCP was measured.

4.2.2.2 Packing the column & Permeability measurement

Soil was packed in a column with 3.5 cm in diameter and 15 cm long in four layers. Each layer was compacted by stroking the column with a wood bar on four different sides. Permeability of the column after compaction was measured according to ASTM method

and procedure. Also, the specific gravity of the soil was measured. The pore volume of the packed column which is an important parameter for the remainder of the experiments was calculated for the two types of soil and water was pumped into the column at a pressure gradient of close to zero to make it saturated. The volume of water needed to saturate the soil column was used to indicate the pore volume of the column.

Flow rates less than 1 ml/min were used for measuring these properties and to prevent short circuiting which results in inaccurate pore volume results.

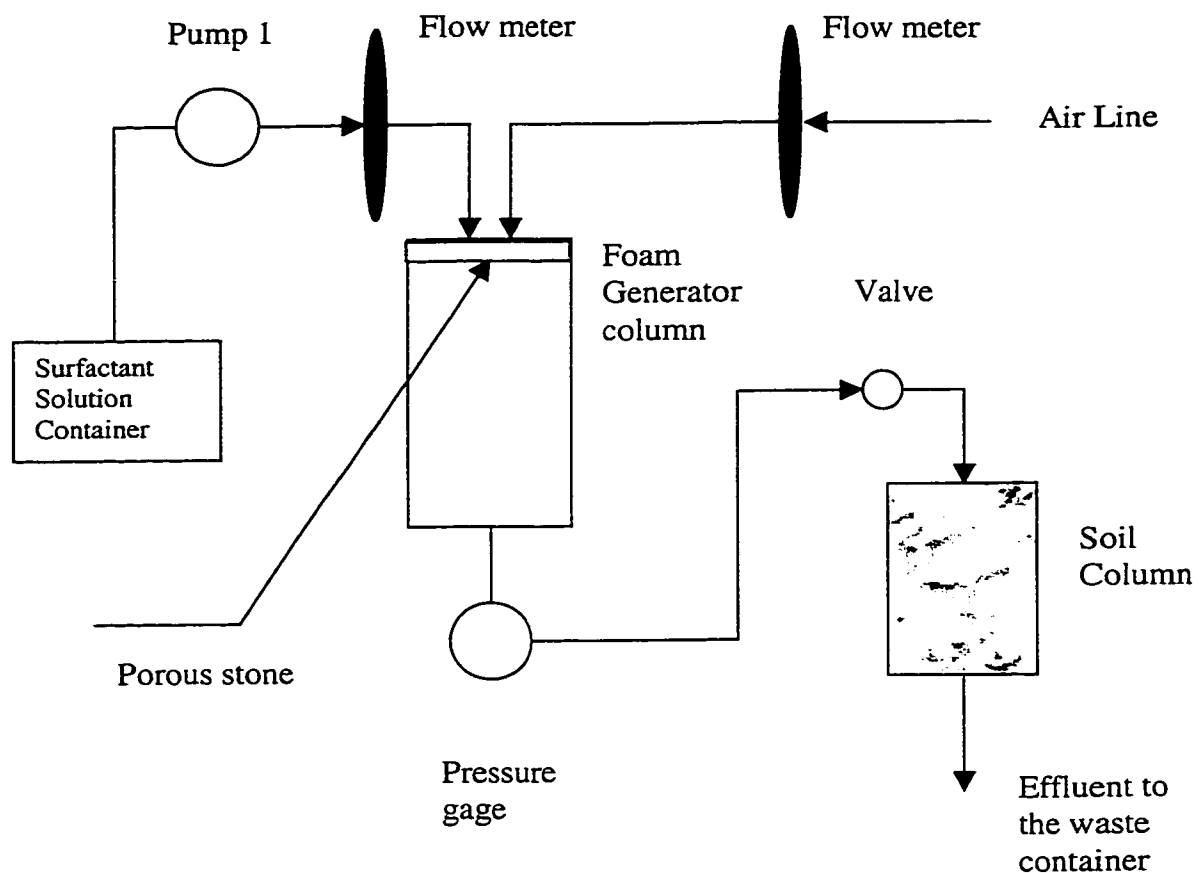


Figure 4.2 Schematic of the Column Test for Removal Experiments

A pressure gage was installed just before the soil column to monitor the change in the pressure build up in the column and a valve was placed before the column to prevent injection of foam into soil before its uniformity and steady-state quality is achieved. It is also used for taking foam samples before injection into the soil. In all the experiments, foam flowed through the sand until near steady conditions were achieved in terms of exiting foam, before the pressure gradients were measured. It usually took several hours, during which period the pressure gradient increased over time.

4.2.2.3 Sampling procedure

Foam exiting the contaminated column was collected for analyzing the PCP concentration. Samples were taken as each pore volumes passed through the contaminated soil (pore volume was measured in the previous stage). Effluent for each sample was collected for 10 minutes in closed containers. Foam samples were left to collapse for 24 hours and then transferred to smaller vials and stored at 4°C.

4.2.2.4 Analyzing of PCP

An UV (Ultraviolet) measuring method was used to analyze the PCP concentration in the samples. Compounds in the effluent foam (Triton X100, PCP) were scanned for different wave lengths to determine their absorbance. A wave length equal to 304 nm shows the best indication for PCP, therefore a standard curve had been constructed to calculate the concentration of PCP in samples. Triton showed an absorbance at less than 220 nm.

Each sample was dried over night and then extracted with methanol (same volume of dried sample) and the UV method was used to calculate the concentration of PCP.

At the end of each experiment samples of soil were taken from the top and the bottom of the washed column to be analyzed for PCP. Soil samples were weighed and methanol was used as a solvent to extract PCP from soil samples which were analyzed for PCP concentration.

CHAPTER FIVE

Results and Discussion

Introduction

The first group of experiments was conducted to study different factors limiting the use of foams as agents in soil flushing. One of the most important limiting factors is pressure build up in the soil during the injection of the washing agent into the soil. This pressure leads to other problems in the process if it exceeds an ultimate pressure. The most common problem is heaving the soil that causes changes in the soil's structure. Also high pressure causes channelling in the soil that reduces the efficiency of soil flushing technology and leads to higher consumption of surfactant in the soil treatment operation.

The ultimate pressure varies for different soils with different characteristics. It depends on the soil's grain size and hydraulic conductivity. The pressure created in the soil must be kept approximately less than ~6 KPa/m to prevent soil heaving and soil channelling that are relevant problems (Ghowdiah, *et al.*, 1997).

The second group of experiments was run to study the efficiency of this technique for removal of contaminants from the soil. The target contaminant was PCP (Pentachlorophenol). Soil was contaminated with pentachlorophenol at two different

levels to represent medium and high levels of contamination. The flushing agent was foam generated by using two different concentrations of surfactants and air.

Generated foam was injected into the contaminated soil packed in the experiment column and samples were taken from the effluent foam to be analysed for PCP concentration. As explained in the previous chapter, samples were taken from each pore volume of surfactant solution passed through the soil. Also contaminated soils were analysed for PCP concentration before packing the column and after the end of the experiment.

5.1 Foam Characteristics Experiments Results & Pressure Build up in the Soil

Various surfactants were used to study their ability for making foam and also to evaluate the stability of generated foam. Results obtained from these experiments are summarized in Table 5.1.

Table 5.1 Quality of foam using different surfactants

Surfactant	Stability (min)	Quality (%)
CHAPS	N/A	N/A
Polytergen 305 LP	N/A	N/A
Surfynol 104 A	N/A	N/A
Triyon	N/A	N/A
Taurodeoxy-cholic Acid	N/A	N/A
Triton X100	6.2	99
Cetyl Pyridinium Chloride	6.0	95
JBR425	6.1	99
Igepal CA-630	4.6	98
Pluronic F68	6.1	95

N/A: foam wasn't generated

As it is shown in Table 5.1, only five surfactants were able to generate foam. TritonX100, Cetyl Pyridinium, JBR425, Igepal CA-630 and Pluronic F68 showed ability for making at low concentrations (0.5 & 1%). Other surfactants either were unable to generate foam or

the stability of generated foam was very low. Consequently, foam production rate was less than foam destruction.

If foam is to be used for remediation purposes, it must have enough stability to provide enough time for injecting. In other words, the rate of bubbles collapsing must be much less than the generation rate. Results in Table 5.1 show that Triton X100 and JBR425 can be used to generate foam with higher quality and higher stability compared to other surfactants. These surfactants (TritonX100 and JBR425) were able to generate foam with a quality of 99%. Both surfactants were characterized by uniform bubble sizes and a strong ability to make foam.

Foams with high quality result in less usage of surfactant and are more cost effective. Also foams with higher quality contain higher volumes of air which is important in remediation of soil contaminated with volatile and semi-volatile compounds.

Based on the results obtained from these experiments (Table 5.1), TritonX100 and JBR425 were chosen for study for the remainder of the investigation.

The next step was to study the relationship between foam flow rate and pressure in the soil. Figure 5.1 shows how pressure build-up in the soil changes with foam flow rate. Pressure recorded in the soil is directly related to foam flow rate. The pressure was determined for foam generated with 1% solutions of TritonX100 and JBR425, with the type I soil (fine sand) at different flow rates.

Pressure in the soil increased from 2.5 kPa/m to 9 kPa/m, as the foam flow rate was increased from 5 ml/min to 35 ml/min (Figure 5.1). Pressure resulted from the injection of foam generated with these two surfactants, showed the same increasing trend with respect to the foam flow rate, although JBR425 showed slightly lower pressures for all flow rates.

According to the literature (Ghowdiah, *et al.*, 1997) this pressure must be less than ~6 kPa/m to prevent related problems regarding to high pressure. It should be noted that this pressure is different for soils with different characteristics. Therefore according to Figure 5.1, foam flow rates must not exceed more than 10-15 ml/min.

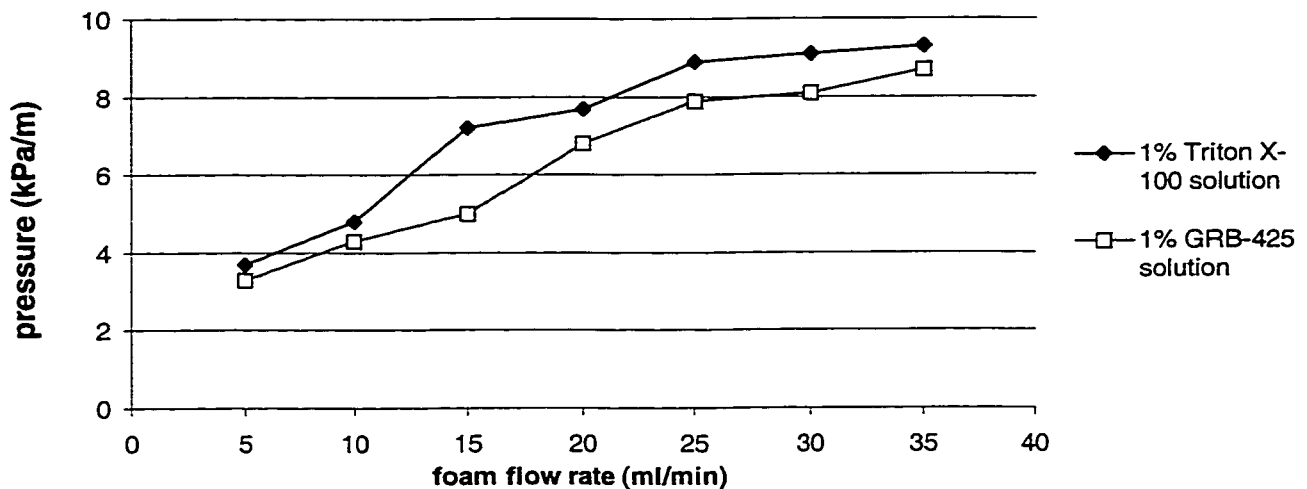


Figure 5.1 Pressure build-up in the soil vs. foam flow rate

Results regarding the effects of foam quality on the pressure in the soil are shown in Figure 5.2. This graph shows that the pressure in the soil drops when the foam quality increases, and also shows higher pressure build up in the soil for higher foam flow rates.

For example, for a foam flow rate equal to 25 ml/min and a foam quality of 92%, the pressure was 9.7 kPa/m. After increasing the quality to 96%, this pressure dropped to around 6.6 kPa/m. It is important to note that by increasing the foam quality from 92 to 96%, usage of surfactant decreases by an order of five which results in lower consumption of surfactants.

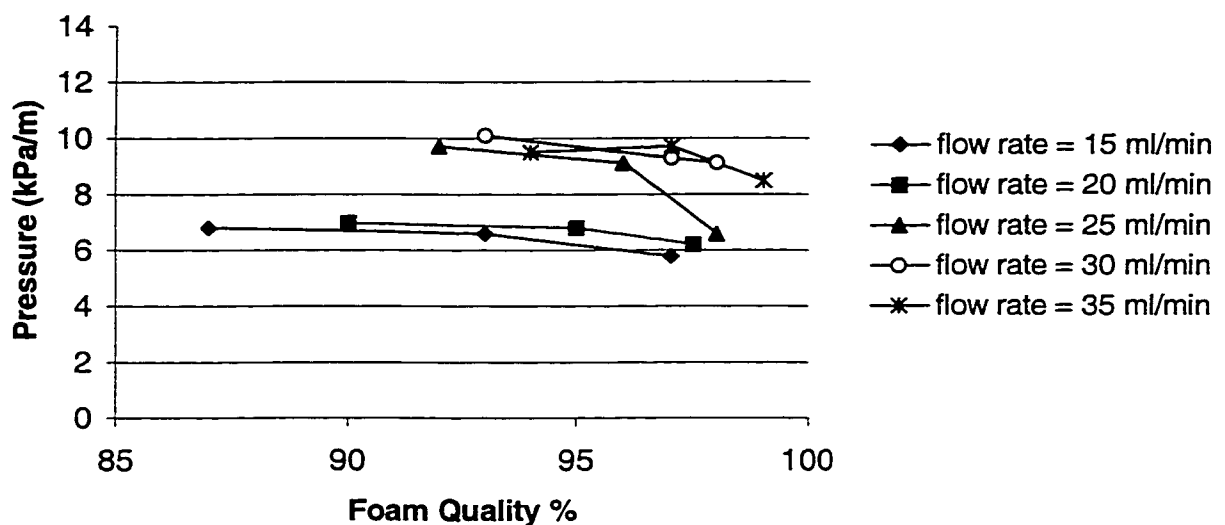


Figure 5.2 Pressure build up vs. foam quality

The reason for obtaining less pressure for foam with high qualities is that foam with a high quality contains a higher amount of air (by definition quality is volume of air in the foam over the total volume of foam), therefore it contains larger bubbles with thinner liquid films. This foam collapses easier and faster when it is injected into the soil compared to foam with low qualities that contains less air and more surfactant solution, consequently the soil shows less resistance against the flow and less pressure.

Destruction and generation of foam was observed through the length of soil column. Exiting foam was observed to be slightly different than the entering foam, since it contained bubbles with larger sizes than the entering foam.

This graph (Figure 5.2) shows that for each individual flow rate, there is a specific foam quality in which pressure in the soil drops rapidly (e.g. for a flow rate equal to 25 ml/min, breakpoint quality is 96%). This certain quality acts like a break point where the soil shows much less resistance against the flow of foam for higher qualities. It may be because of a change in structure of foam with high qualities.

These results suggested that foam must be injected at a very low flow rate and high quality to prevent relevant problems related to high pressure in the soil. Also break quality point is important during the injecting process.

5.2 PCP Removal Efficiency Results

Intensive experiments were conducted to study the effectiveness of foam surfactant technology for the recovery of PCP from contaminated soil. As explained in Chapter Three, foams generated with two types of surfactants (TritonX100, JBR425) were injected into contaminated soil in different level of contamination. Surfactant concentrations were investigated to determine its effects on contaminant removal efficiency.

Figure 5.3 shows the results obtained from flushing Type I (Fine Sand) soil contaminated with 1000 mg/kg of PCP. Solutions of TritonX100 (1% and 0.5% TritonX100 concentration in distilled water) were used to generate foam. The results are shown in Figure 5.3.

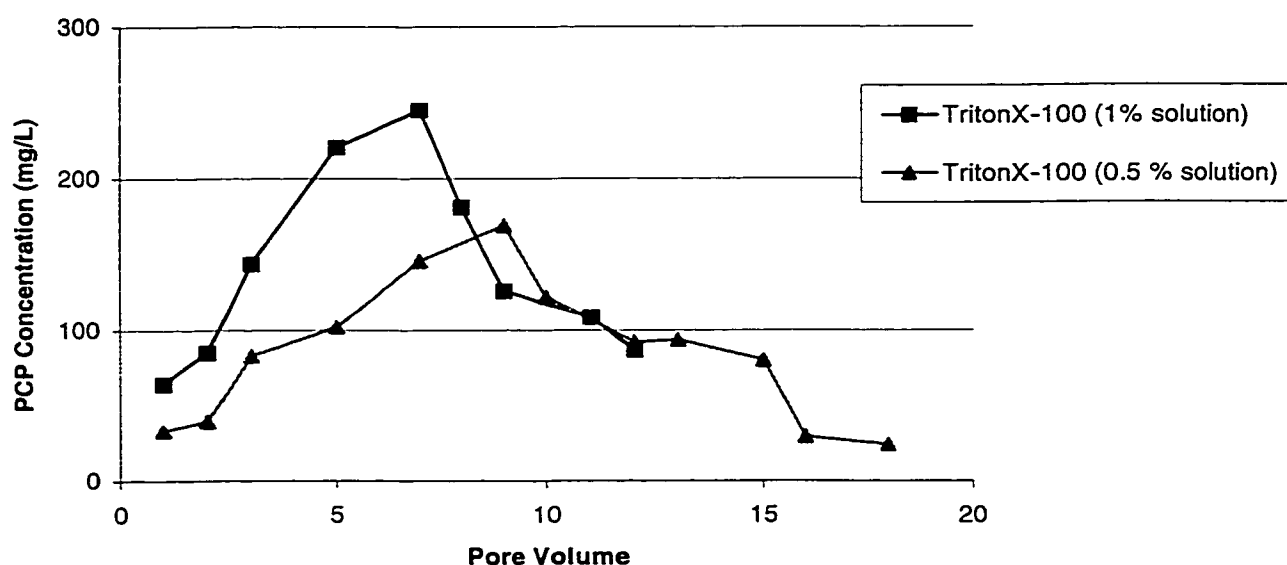


Figure 5.3 Effect of TritonX100 Concentration on PCP removal from fine sand (1000 mg/kg PCP)

As this graph shows, the maximum concentration of PCP in the effluent was observed in the exiting foam after seven pore volumes of surfactant solution with a 1% concentration. When 0.5% of surfactant solution were used, the maximum concentration in the effluent was observed after nine pore volumes when 0.5% of surfactant solution were used.

This maximum PCP concentration was higher for the 1% percent surfactant solution (250 mg/l) than 0.5% solution (180 mg/l). This means that increasing the surfactant concentration in the washing agent by 0.5% increases the maximum PCP concentration in the effluent by 28%. For a better understanding of relationship between foam quality and pressure in the soil more investigations are necessary.

Regarding sorption/desorption processes occurring in the soil throughout the test column, it can be concluded that foam generated with higher concentrations of surfactant, has a greater tendency for extracting contaminants from the soil. The capability of foam for extracting and mobilizing the contaminants from the soil is a function of many parameters such as surfactant concentration, type of soil, and type of contaminant compounds.

Figures 5.4 to 5.6 show results obtained for removal efficiency in different conditions. As these graphs show, in all cases a higher concentration of surfactant in the solution results in a higher PCP concentration in the effluent.

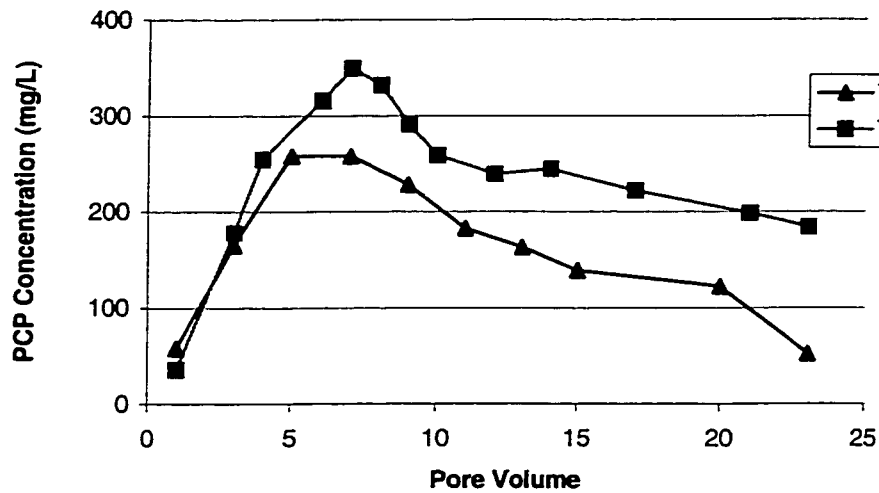


Figure 5.4 Effect of TritonX100 concentration on PCP removal from fine sand (3000 mg/kg PCP)

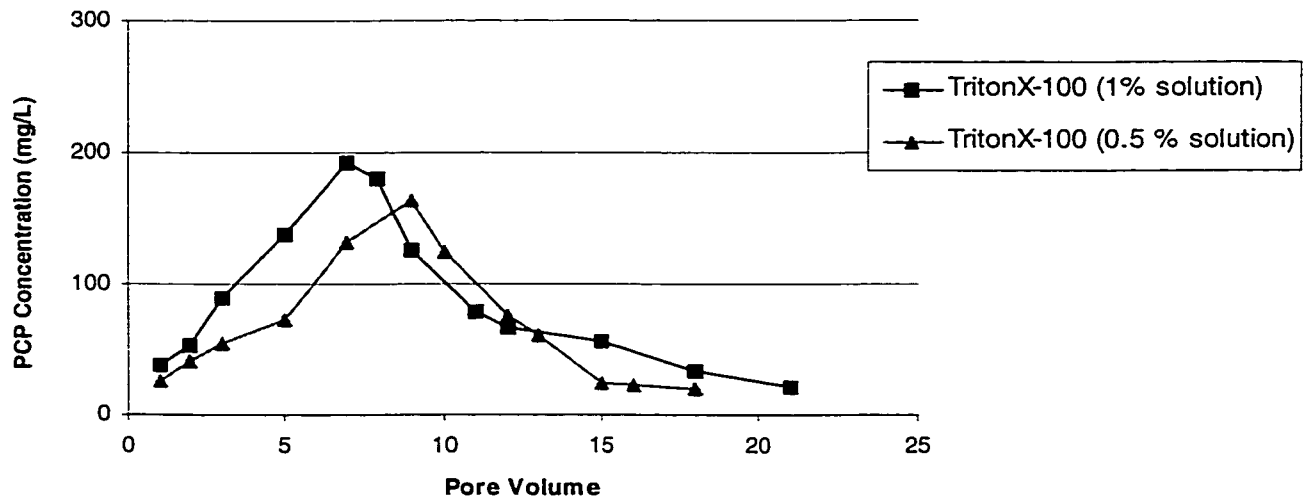


Figure 5.5 Effect of TritonX100 concentration on PCP removal from sandy-silt (1000 mg/kg PCP)

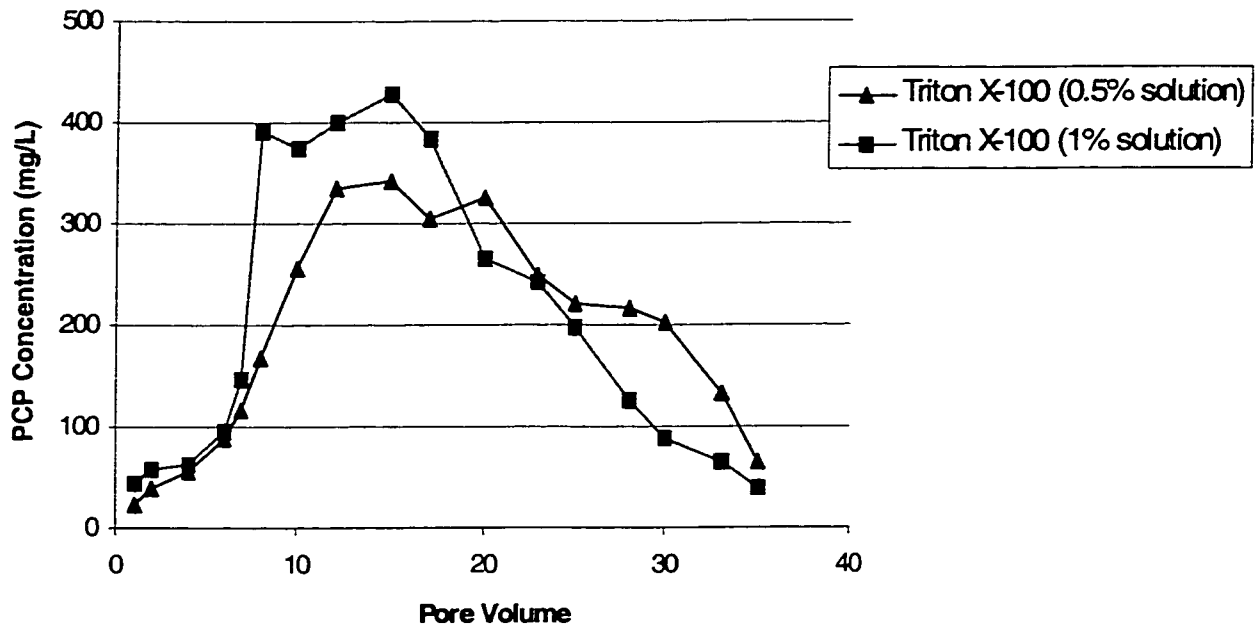


Figure 5.6 Effect of TritonX100 concentration on PCP removal from sandy-silt (3000 mg/kg PCP)

Flushing of foam shows a better result in the sandy soil than for the sandy-silt soil with a lower hydraulic conductivity. It can be seen that sandy-silt soil needs more pore volumes of washing agent to reach the maximum removal.

In Figures 5.7 to 5.10, we can see that the final concentration in the effluent foam increases faster in fine sand soil than sandy-silt soil. It seems this technique is more effective in soil with higher porosity. For example in Figure 5.7, after five pore volumes, the concentration in the effluent is 100 mg/l for fine sand but only 70 mg/l for sandy-silt soil. The reason may be the time necessary for distribution of foam through the soil and the desorption process that is much longer for soil with a low hydraulic conductivity.

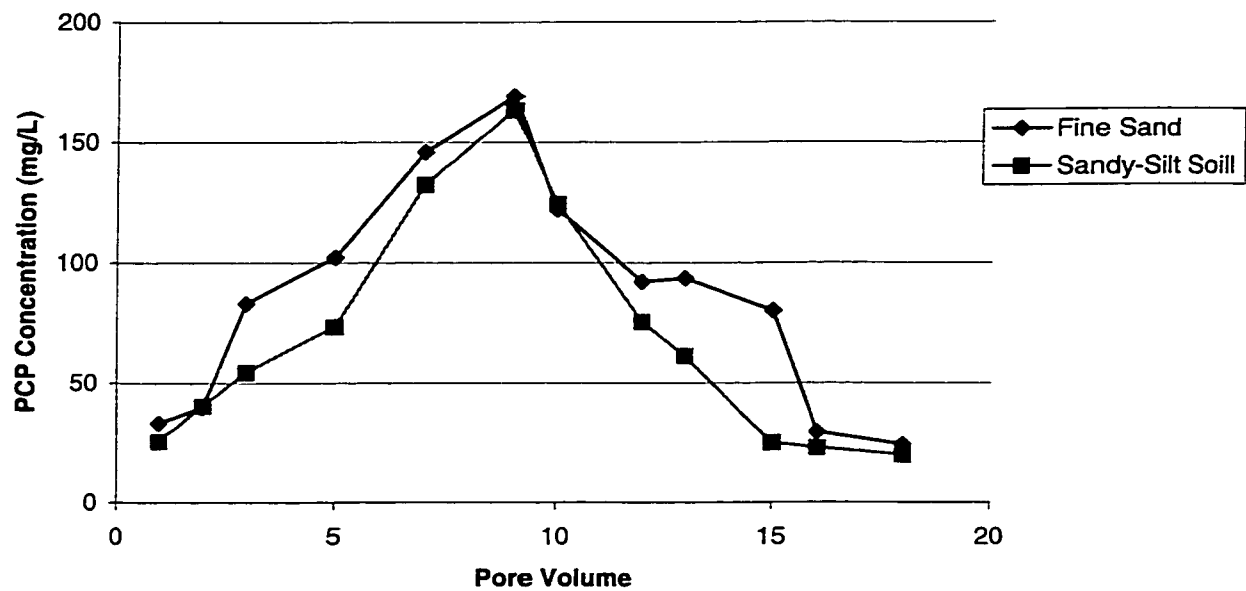


Figure 5.7 Effect of type of soil on PCP removal (0.5% TritonX100, 1000 mg/kg PCP)

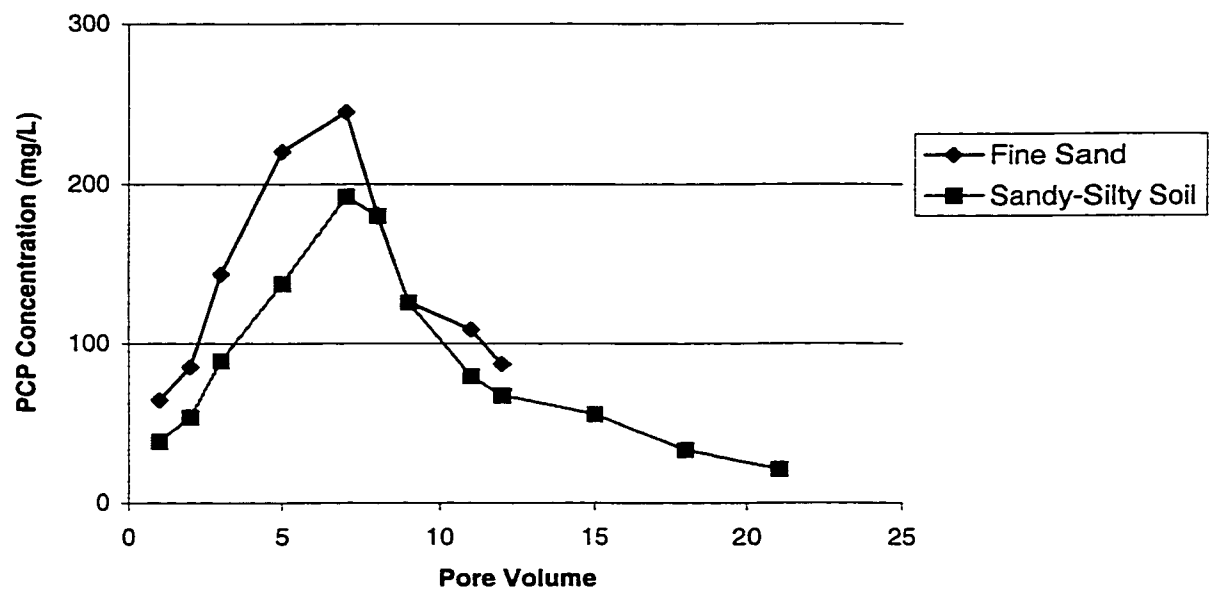


Figure 5.8 Effect of type of soil on PCP removal (1% TritonX100, 1000 mg/kg PCP)

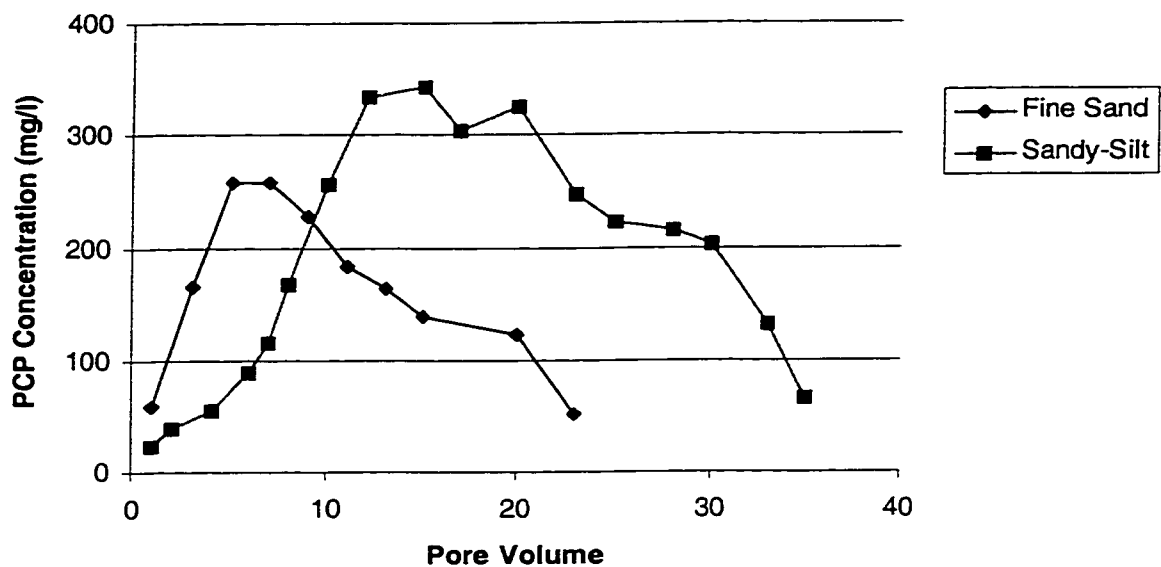


Figure 5.9 Effect of type of soil on PCP removal (0.5% TritonX100, 3000 mg/kg PCP)

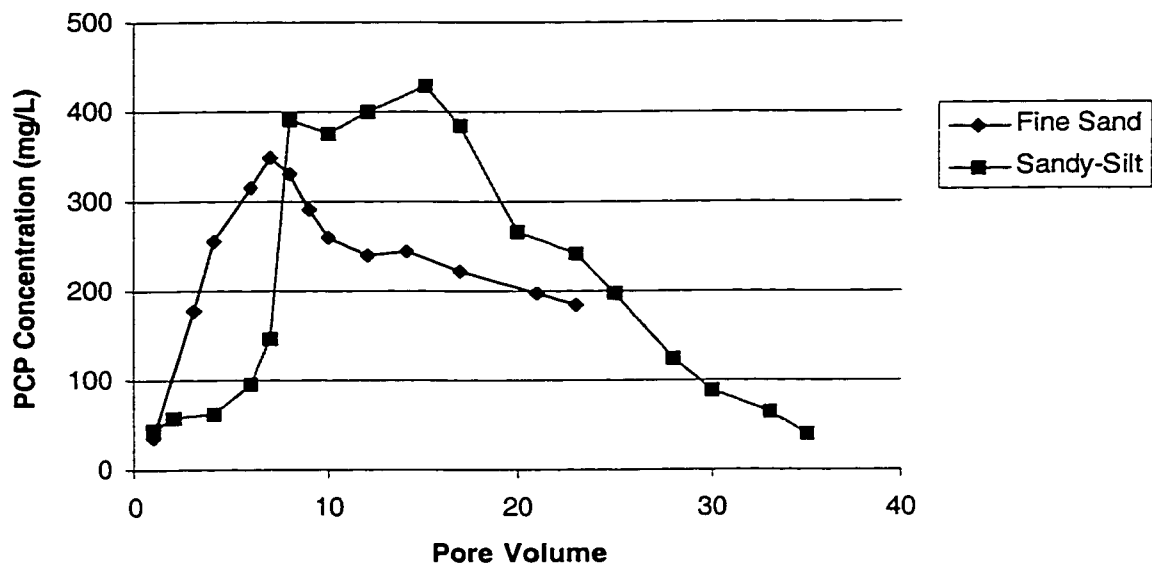


Figure 5.10 Effect of type of soil on PCP removal (1 % TritonX100, 3000 mg/kg PCP)

Flushing contaminated soil experiments were continued with the second type of surfactant (JBR425), which is anionic in nature. One percent solution was used and foam generated by this surfactant was injected into the contaminated soil. Results from these experiments are summarized in Figure 5.11.

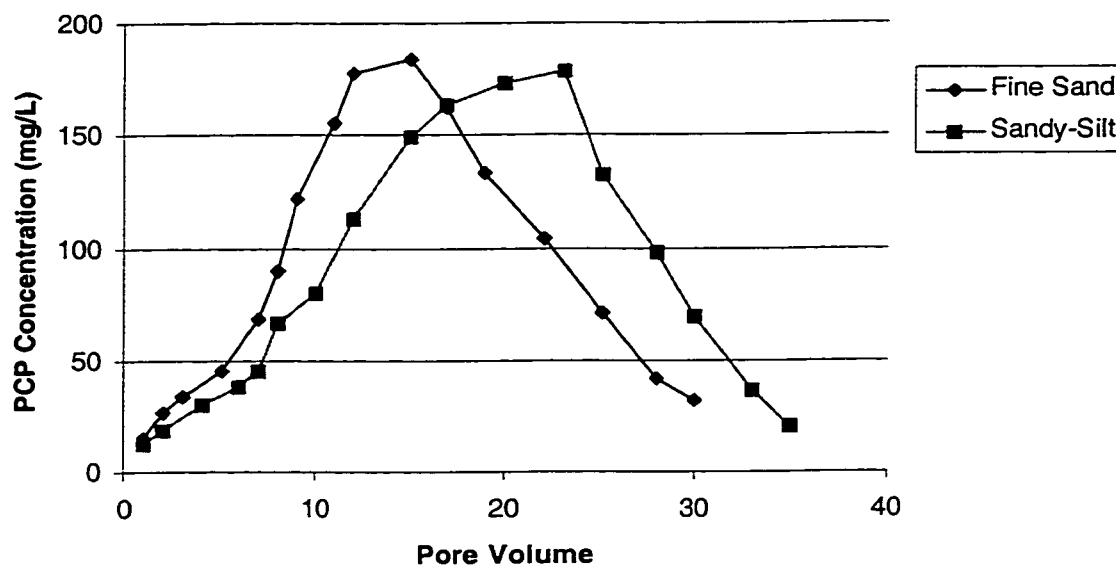


Figure 5.11 Effect of type of soil on PCP removal (1% JBR425, 1000 mg/kg PCP)

As this graph shows, the maximum concentration in the effluent was achieved after 14 and 25 pore volumes for 1% and 0.5% JBR425 solution concentration, respectively. This is similar to that obtained for TritonX100 in terms of increasing rate of PCP concentration in the effluent. Figures 5.12 and 5.13 compare the results from experiments with TritonX100 and JBR 425.

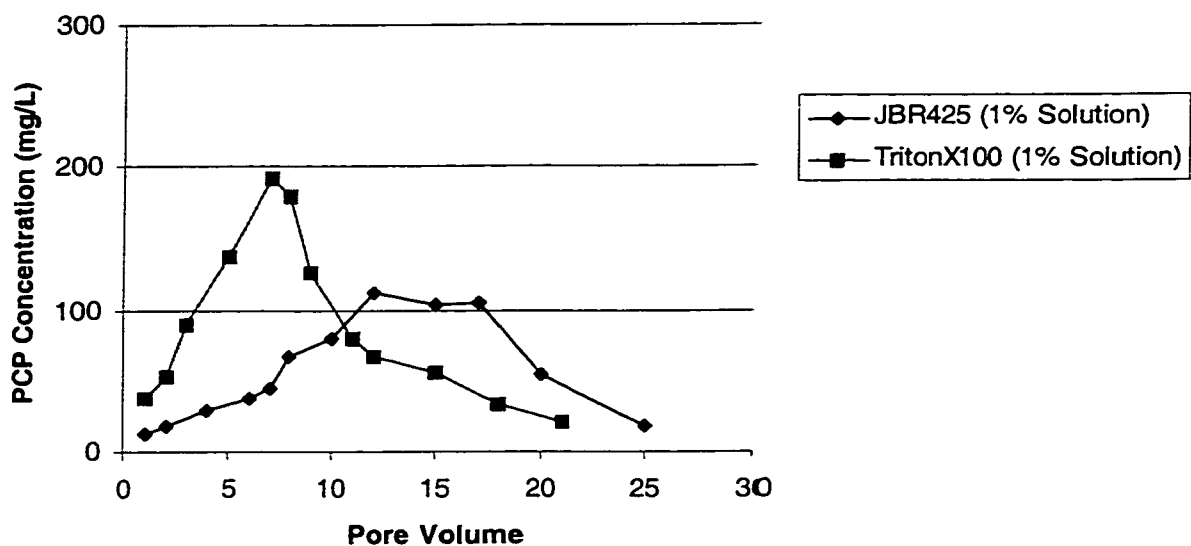


Figure 5.12 Effect of type of surfactant on PCP removal (fine sand soil, 1000 mg/kg of PCP)

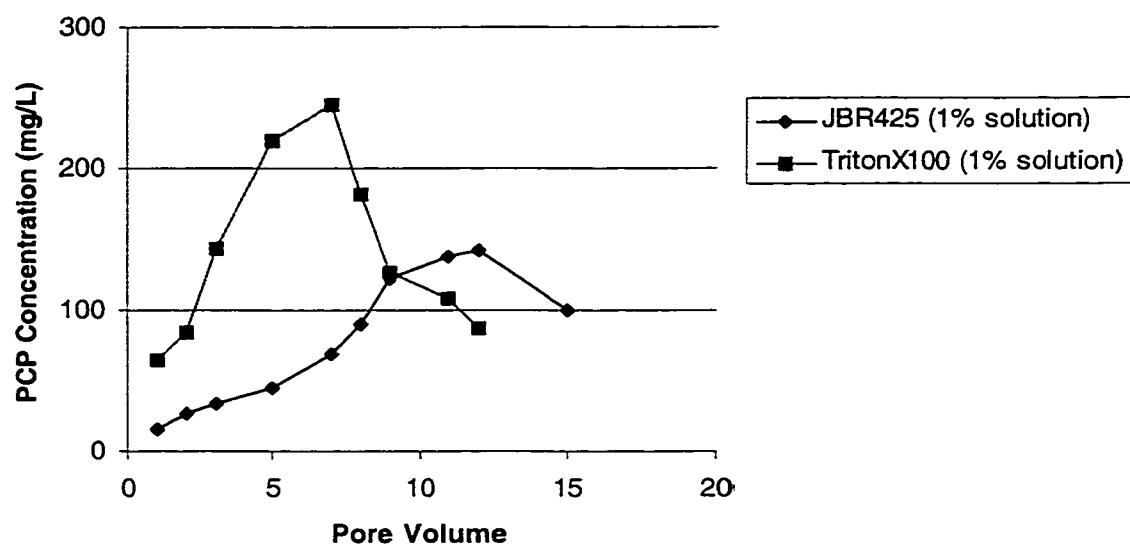


Figure 5.13 Effect of type of surfactant on PCP removal (sandy-silt soil, 1000 mg/kg of PCP)

These graphs (Figures 5.12 & 5.13) show that TritonX100 has a higher capability for the removal of PCP when it is used in the form of foam.

Washed soils from the test columns were analysed for PCP retained in the soil in each experiment. Results are summarized in Tables 5.2 and 5.3. Soil samples were taken from the top and bottom of the test column. The PCP was then extracted and measured.

Table 5.2 Removal Results for Different Experiments (Triton X100)

Type of Soil	Surfactant Conc. (%)	Level of PCP in the Soil (mg/kg) ⁽¹⁾	Initial PCP Conc. in the Soil (mg/kg) ⁽²⁾	Final PCP Conc. in the Soil (mg/kg) ⁽³⁾
Fine Sand	0.5%	1000	880	268
Fine Sand	1%	1000	880	132.4
Sandy-silt	0.5%	1000	895	283.6
Sandy-silt	1%	1000	895	215.7
Fine Sand	0.5%	3000	2630	448.2
Fine Sand	1%	3000	2630	363.2
Sandy-silt	0.5%	3000	2720	558.2
Sandy-silt	1%	3000	2720	436.2

Table 5.3 Removal Results for Different Experiments (JBR425)

Type of Soil	Surfactant Conc. (%)	Level of PCP in the Soil (mg/kg) ⁽¹⁾	Initial PCP Conc. in the Soil (mg/kg) ⁽²⁾	Final PCP Conc. in the Soil (mg/kg) ⁽³⁾
Fine Sand	1%	1000	880	316.9
Sandy-Silt	1%	1000	895	352.9

(1) Theoretical Concentration of PCP in the Soil

(2) Measured PCP Concentration in the Soil before the Experiments

(3) Measured PCP concentration in the Soil after the Experiments

As explained in chapter two, in foam-surfactant technology, two removal processes are involved in treating the contaminated soil. Mobilization occurs after contaminant compounds dissolved in the flushing agent (foam) are washed out along with foam flows in the contaminated soil. Transferring of contaminants adsorbed to the soil to the gas phase is called volatilization. Because 80 to 90% of foam volume is air, it increases the rate of volatilization when it flows through the soil contaminated with volatile and semi-volatile compounds.

Mass balance calculations have been done on the results obtained from the experiments to evaluate how each one of these removal processes participates in recovery of contaminated soil. Final PCP concentrations in the washed soil after each experiment were measured. In addition, the total amounts of PCP extracted by foam in the effluent were calculated. Because the initial PCP concentration in the soil was known, by using mass balance equations the total removal of PCP by volatilization can be calculated.

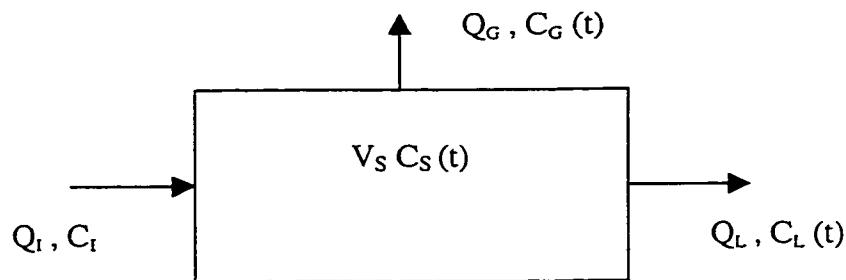


Figure 5.14 Mass Balance Diagram

Where:

Q_i = Influent foam flow rate (ml/min)

Q_G = Gas effluent flow rate (ml/min)

Q_L = Liquid effluent flow rate (ml/min)

C_0 = Initial Concentration of PCP in the soil (mg/l)

C_i = PCP Concentration in influent foam (mg/l) = 0

$C_G(t)$ = PCP Concentration in effluent gas at time t

$C_L(t)$ = PCP Concentration in effluent liquid at time t

$C_s(t)$ = PCP Concentration in the soil at time t

V_S = Total volume of soil in the column

As $C_i = 0$, Therefore we can write:

$$V_S \times (\partial C_s / \partial t) = Q_G \times C_G(t) + Q_L \times C_L(t) \quad (\text{Eq. 5.1})$$

Therefore:

$$V_S \times \int dC_s = Q_G \int C_G(t).dt + Q_L \int C_L(t).dt \quad (\text{Eq. 5.2})$$

$$\Rightarrow V_S \times (C_F - C_0) = Q_G \int C_G(t).dt + Q_L \int C_L(t).dt \quad (\text{Eq. 5.3})$$

Where:

C_F = Final PCP Concentration in the soil

$Q_G \int C_G(t).dt$ = Total Removal of PCP by Volatilization

$Q_L \int C_L(t).dt$ = Total Removal of PCP by Mobilization

Equation 5.3 can be written in another form as below:

Initial Mass of PCP in the Soil =

Total Amount of PCP in the Effluent + Amount of PCP Retained in the Soil (final Concentration) + Total Removal of PCP by Volatilization Process

Total removal of PCP by mobilization can be found by calculating the area under the PCP concentration vs. pore volume graph. This area which is an indication of total amount of PCP in the liquid part of exiting foam, must be calculated by substituting in equation 5.3.

An example and required steps for the mass balance calculations is explained below. The area under effluent the concentration vs. pore volume curve (Figure 5.3) is calculated using a bar chart (Figure 5.14), constructed according to the original graph.

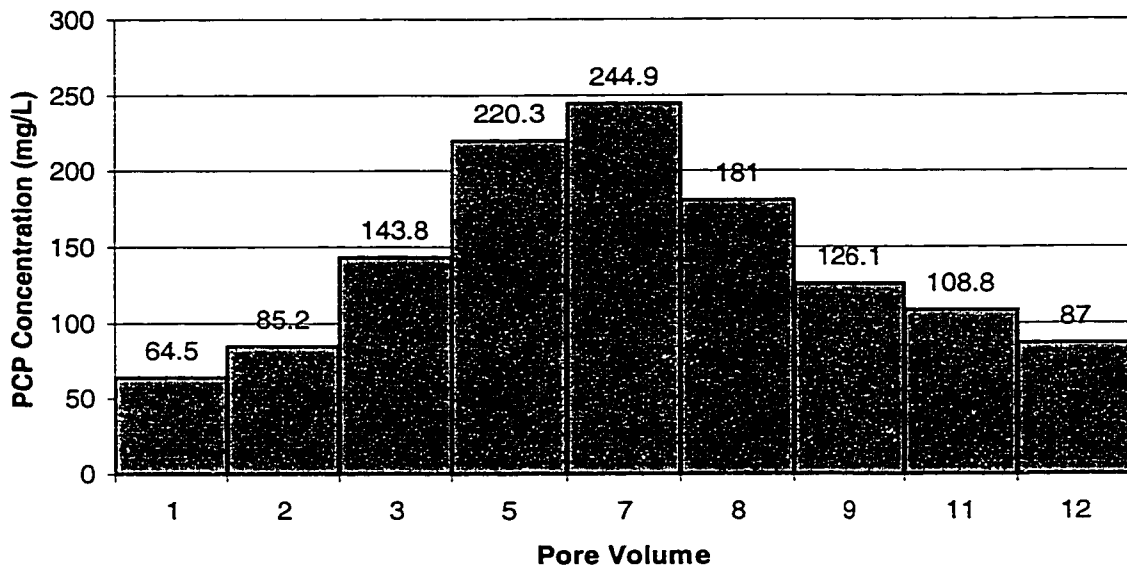


Figure 5.15 Concentration of PCP in the Effluent

Pore volumes were measured around 38 ml and 32 ml for fine sand soil and sandy-silt soil, respectively.

$$\begin{aligned} \text{Total Area} &= [(64.5)/2 + (64.5+85.2)/2 + (85.2+143.8)/2 + (143.8+220.3)/2 \times 2 + \\ &(220.3+244.9)/2 + (244.9+181)/2 + (181+126.1)/2 + (126.1+108.8)/2 \times 2 + (108+87)/2] \\ &\times (38) \text{ [mg/l]} \times [\text{ml}] \times [10^{-3} \text{ ml/l}] = \\ &[32.3 + 74.9 + 114.5 + 364.1 + 232.6 + 212.9 + 153.6 + 234.9 + 97.5 + 43.5] \times 38 \times 10^{-3} \\ &= 59.3 \text{ mg} \quad \text{Total amount of PCP in the effluent (12 pore volumes)} \end{aligned}$$

The initial concentration of PCP in the contaminated soil was measured before the column was packed (Table 5.2).

$$\text{Volume of the column} = (\pi D^2/4) \times h = \pi \times (3.5 \text{ cm})^2 \times 15/4 \text{ cm} = 144.3 \text{ cm}^3$$

$$\text{Total weight of soil in the soil column} = \rho \cdot V = 2.547 \text{ (g/cm}^3\text{)} \times 144.3 \text{ cm}^3 = 367.6 \text{ g}$$

$$\text{Initial PCP concentration in the soil} = 880 \text{ mg/kg}$$

$$\Rightarrow \text{Total PCP} = 880 \times 0.3676 = 323.49 \text{ mg}$$

As explained before, after all experiments, the final concentration of PCP retained in the soil was analysed and reported (Table 5.2).

For fine sand contaminated with level I concentration, after 12 pore volumes the value reported was 132.4 mg/kg (or $132.4 \times 0.3676 = 48.67$ mg for the column).

$$\Rightarrow \text{Total Removal} = 323.49 - 48.67 = 274.82 \text{ mg (85\%)}$$

$$\Rightarrow \text{Total volatilization} =$$

$$\text{Total removal} - \text{Total Mobilization (total concentration in the effluents)} =$$

$$274.82 - 59.3 = 215.5 \text{ mg (66\%)}$$

$$\text{Total mobilization} = 59.3 \text{ mg (19 \%)}$$

For all experiments these mass balance calculations were done to evaluate how mobilization and volatilization processes participate in soil decontamination using this technique. The results are summarized in Tables 5.4 and 5.5.

Table 5.4 Mass Balance Calculation Results (Triton X100 Experiments)

Type of Soil	Surfactant Conc.	Pore Volume	Level of Contamination (mg/kg)	Removal by Mobilization (%)	Removal by Volatilization (%)	Total Removal (%)
Fine Sand	1%	12	1000	19	66	85
Fine Sand	0.5%	18	1000	19	50	69
Fine Sand	1%	23	3000	25	61	86
Fine Sand	0.5%	23	3000	14	69	83
Sandy-Silt	1%	21	1000	19	57	76
Sandy-Silt	0.5%	18	1000	17	51	68
Sandy-Silt	1%	35	3000	22	62	84
Sandy-Silt	0.5%	35	3000	22	57	79

Table 5.5 Mass Balance Calculation Results (JBR 425 Experiments)

Type of Soil	Surfactant Conc.	Pore Volume	Level of Contamination (mg/kg)	Removal by Mobilization (%)	Removal by Volatilization (%)	Total Removal (%)
Fine Sand	1%	19	880	24	36	60
Sandy-Silt	1%	33	895	22	44	61

By comparing results obtained from mass balance calculation it can be seen that when higher concentrations of surfactant are used in the flushing solution, less pore volumes of flushing agent is needed to achieve final minimum concentrations in the effluent. For example, when TritonX100 with 0.5 and 1% concentration were used to flush fine sand contaminated with 1000 mg/kg of PCP, 18 and 12 pore volumes were injected respectively.

In all cases, higher concentrations of surfactant solutions resulted in higher percent removals with less pore volumes of washing agent. By using 1% TritonX100 solution, after 12 pore volume 85% removal was achieved (fine sand, 1000 mg/kg initial concentration of PCP), while only 69% removal achieved after flushing of 18 pore volume of 0.5% TritonX100.

TritonX100 showed a better result in terms of final removal efficiency. TritonX100 removed 85 and 84 percent of PCP from fine sand soil and sandy-silt contaminated with 880 and 895 mg/kg respectively, while these values were 60 and 61 percent for JBR425. The reason is higher ability of TritonX100 for dissolving PCP.

To calculate total PCP washed out by the surfactant solution, a series of control experiments were conducted. Surfactant solution in the absence of air was used for flushing into the contaminated soil.

The same experimental set up was used in this stage except that the air flow was closed in all experiments. Surfactant solutions of TritonX100 solution were injected into the contaminated soil with different levels of contamination (1000 and 3000 mg/kg of PCP). Results obtained from these experiments are shown in Figures 5.16 to 5.19.

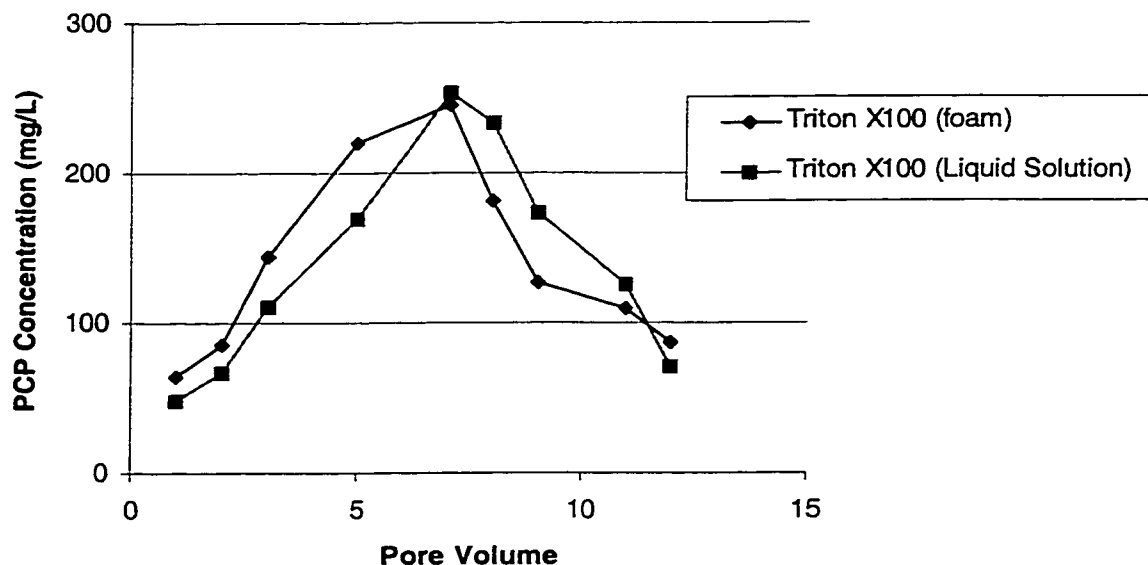


Figure 5.16 Control Experiment with 1 % Triton X100 Solution (fine sand, 1000mg/kg of PCP)

As can be seen from these graphs, concentrations measured for foam effluent and control experiments were slightly different. It can be concluded that the two removal processes explained before (volatilization & mobilization), effect each other and therefore change the overall removal efficiency of each process.

There is the possibility of channelling in the case of using conventional agents that cause lower removal at the beginning of the test. Conventional agents without foam need more

time to distribute throughout the contaminated soil column as compared to foam agent. This may result in lower removal in the beginning of the experiment.

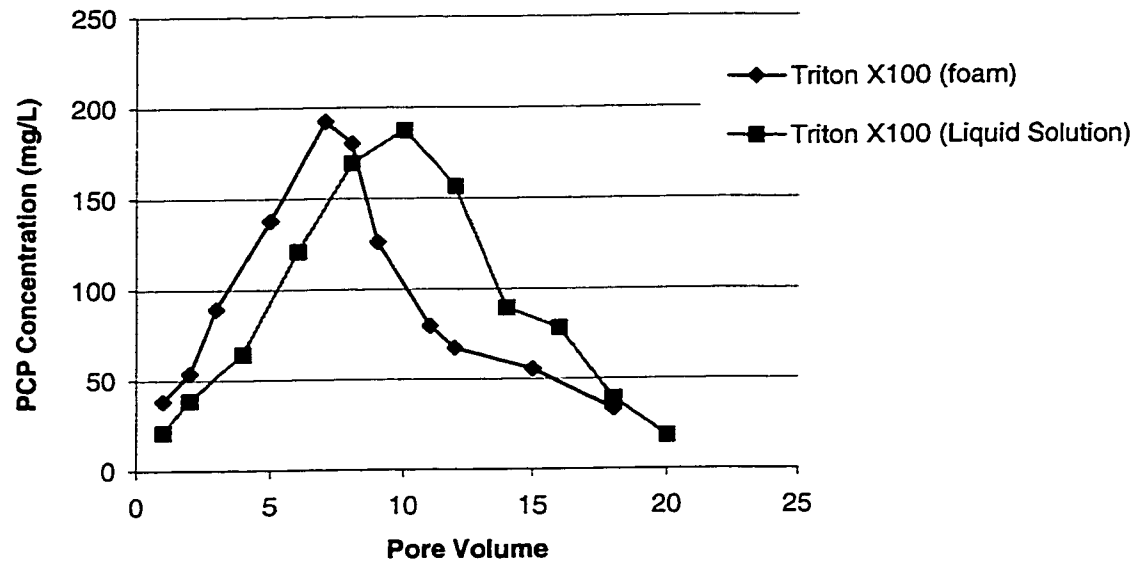


Figure 5.17 Control Experiment with 1% Triton X100 Solution (sandy-silt soil, 1000 mg/kg of PCP)

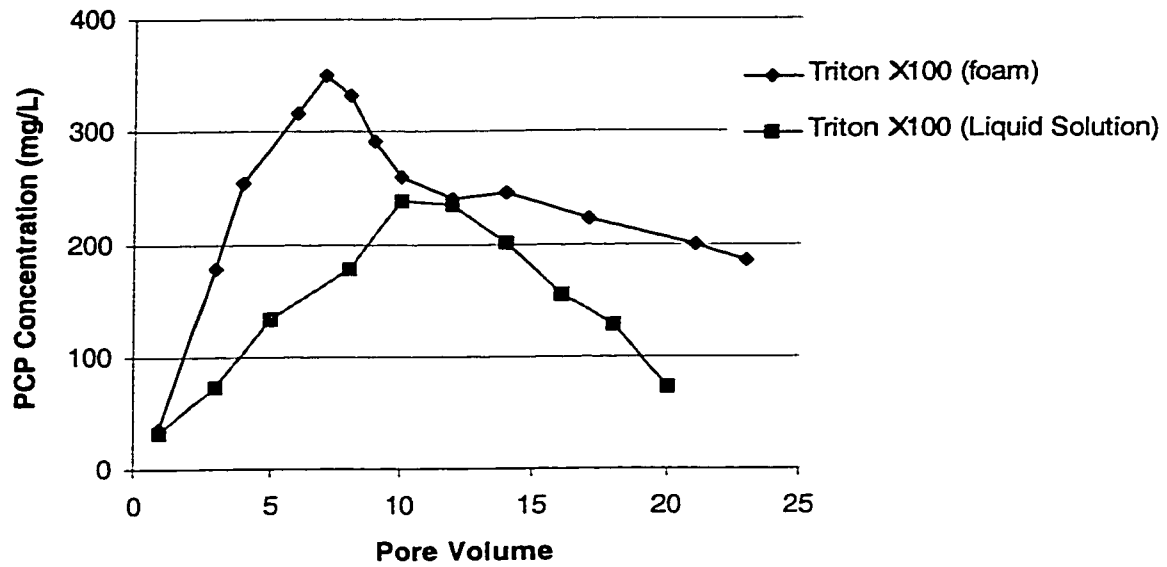


Figure 5.18 Control Experiment with 1% Triton X100 Solution (fine sand soil, 3000 mg/kg of PCP)

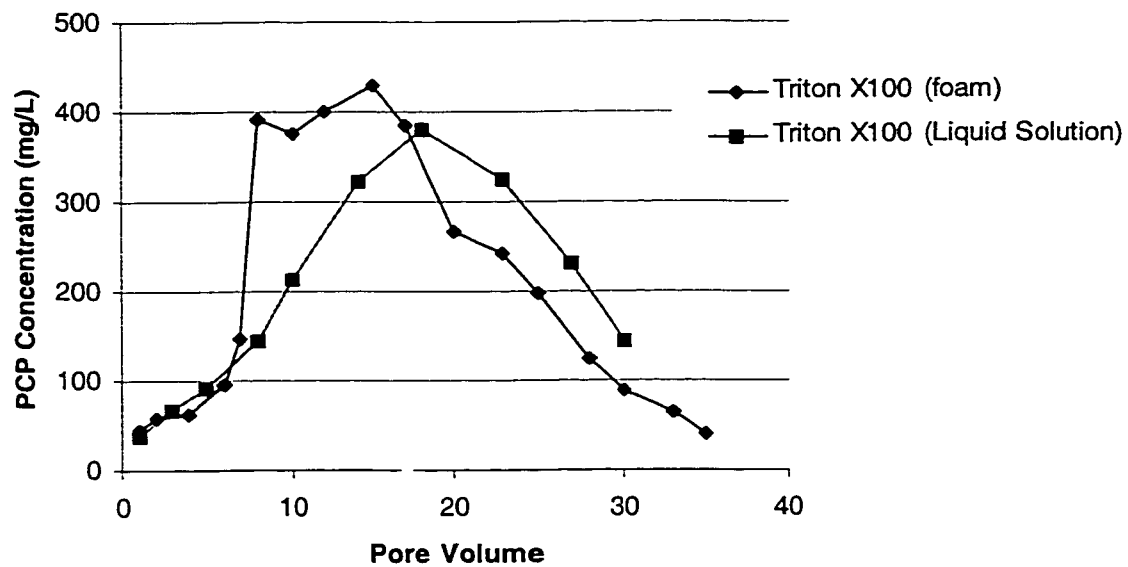


Figure 5.19 Control Experiment with 1% Triton X100 Solution (sandy-silt soil, 3000 mg/kg of PCP)

As we can see in most of these control experiments, in the beginning of all control test PCP concentration in the effluent was lower compared to the original experiments (using foam as injecting agent), however this concentration drops faster for foam experiments.

Since the solubility of PCP in water is very low (14 mg/l @ 20°C), the amount of PCP that will be removed by flushing with water is negligible. Some experiments had been run and the concentration of PCP in the effluent extracted by water was measured. It was observed that the mobilization process was less efficient when the solubility of PCP in flushing agent was lower.

CHAPTER SIX

Conclusions

Introduction

“There are thousands of contaminated sites in Canada. The contamination has arisen from private sector industrial activities and the public sector. Petroleum, petrochemicals, heavy metals, wood preservatives, farm or forestry chemicals and radioactive materials are common contaminating materials” (National Round Table on the Environment and Economy, 1997).

There are many sources that contribute to contamination of soil and groundwater. The most important and primary source of contamination is leaking of petroleum products. It occurs from refineries and other facilities that produce petroleum products or are operated by petroleum and it happens from the storage of these products at mine sites, manufacturing facilities, service stations, farms and residences.

A large number of remediation techniques, most of which focus on clean-up, are now available. Most of them are intensively applied in practice. Each case of soil pollution is different and the way to manage it requires, within the limit set by policy and the finances available, careful weight of all relevant factors (Rulkens, *et al.*, 1998).

Foam surfactant technology is a new technique that requires intensive investigation before it can be applied in the field. Few investigations have been done on this soil treatment technology that showed promising results.

In this chapter the most important conclusions obtained from this investigation have been summarized. The most important parameters and factors that affect the efficiency of this technology will be discussed.

6.1 Flow of Foam in the Soil

This study showed that the flow of foam in the soil and flow characteristics were not predictable without conducting extensive experiments in which both the soil and the foam are involved, this may be most likely due to the influence of numerous factors affecting the removal (highly complex problem).

Despite the unpredictable nature of foam flow, the results of this investigation point to some general considerations which are important to the use of foams for soil flushing during in situ soil remediation.

Some of these conclusions are:

- Foam quality (volume of gas in the foam) has a considerable influence on foam flow and pressure in the soil. Foam with higher qualities causes lower pressure in the soil, due to the fact that foam with a higher quality has a lower stability and it collapses easier when passing through the soil column, thereby resulting in less pressure build up.
- The foam flow rate directly effects the pressure in the soil in which higher flow rates causes higher pressure. It is important to take foam flow rate into consideration to prevent problems related to high pressure in the soil such as heaving and channelling.
- The pressure break point occurs when the quality of foam exceeds a certain quality. For qualities greater than this break point, pressure build up in the soil drops faster.

Information about these break points, that are different for different flow rates, is important in selecting design flow rates.

- At constant foam flow rates, maximum pressure gradient was observed at qualities around 94-96%, and for foam with qualities greater than 96%, pressure gradient drops sharply. In other words, there is a specific quality of foam by which the pressure in the soil drops dramatically for higher qualities.
- The type of surfactant affects the flow characteristics as well as pressure in the soil. The flow of foam in a porous medium involves breaking and regeneration of foam bubbles. Therefore, surfactants that generate foam with lower stability cause less pressure in the soil. In essence, fact the pressure created in the soil is the resistance of bubbles against this breakage.
- The pressure gradient was measured for the flow of foam with different flow rates through a medium (fine sand) with 7×10^{-2} cm/s varied from 40 to 100 kPa/m). This pressure was observed to be lower for JBR425 than TritonX100.

6.2 PCP Removal Efficiency

Some specific conclusions from this investigation in terms of pentachlorophenol removal from the contaminated soil are listed below.

- According to mass balance calculations, contaminant (PCP) removal mechanisms are mobilization and volatilization.
- Based on the investigations, high surfactant concentrations lead to better removal of contaminants from the soil. According to mass balance calculations, this is due to increased mobilization of contaminants.
- The maximum concentration of PCP in the effluent was achieved in less pore volumes of foam for fine sand than for sandy-silt soil. This means that for the decontamination of soils with low hydraulic conductivity, more washing agent is necessary compared to soil with relatively high hydraulic conductivity.
- Using TritonX100 resulted in a better removal efficiency compared to JBR425. In both fine sand soil and sandy-silt, solutions of TritonX100 were more effective for the treatment of soil contaminated with PCP.
- Most experiments and mass balance calculations showed that between 20 and 30% of the total removal is by mobilization of contaminant and 70 to 80% is by volatilization

process. Therefore, this technology might be an effective technique for treatment of soil contaminated with volatile organic compounds.

- Control experiments showed that there is considerable interaction between the two removal processes. Therefore, mobilization and volatilization do not act as separate processes and they affect each other along the soil column.
- This technology showed promising results for both soils contaminated with medium and high level of contamination. Final efficiency is slightly higher for highly contaminated soil.
- Although experiments showed better results for washing soil with higher hydraulic conductivity, this technology can be effectively used for soil with low porosity and it seems to be potentially useful for clays.

Based on the results of this study, foam-surfactant technology was found to have a good potential for enhanced remediation of contaminated soils. In the second stage of the investigation, the pressure gradient in the soil caused by the injection of foam was studied and results showed low pressure build up. This indicates this technology could be considered for field applications. In addition, it seems to be very effective for the treatment of soil contaminated with volatile and semi volatile compounds. Foam contains large amounts of air (oxygen) that causes a high rate of volatilization of VOCs.

With respect to channelling, conventional surfactants result in even removal of contaminants from the soil. Also low usage of chemicals and surfactants is another advantage of this technology that makes it more cost effective.

Further studies need to be done before this technique can be used in a large scale of operation. Efficiency of this method for removal of inorganic compounds from the contaminated soil, compatibility with other remediation techniques such as bioremediation, and also effectiveness of pulsed operation need to be investigated before field study.

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