Thesis for the Degree of Master of Science

Pilot Scale Experiment for the *in-situ* Flushing Coupled with High Pressure Air Jet Injection to Remediate the Bunker Fuel Oil Contaminated Site

by

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February, 2009

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고압 공기분사가 포함된 토양세정법을 이용한 실제 유류오염토양 및 지하수 정화

Advisor: Minhee Lee and Jungchan Choi

by

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Abstract

Pilot scale experiment for the in-situ flushing coupled with high pressure air jet injection was performed to remediate bunker A- and C- oil contaminated soil and groundwater. The contaminated site was located at Ulsan, Korea, which had been used as a roofing tile manufacturing facility area for 25 years. The average total petroleum hydrocarbon (TPH) concentration of soil in the site was 3449 mg/kg and it exceeded 6 times of the standard tolerance limit (500 mg/kg) regulated by Korean Soil Conservation Law.

A pilot scale test site (15 m × 19 m × 6 m) was selected in the contaminated area for the in-situ flushing with high pressure air jet injection and the selected test site was mostly composed of heterogeneous sandy and gravel-sandy soils, having the 2-3 m of contamination depth. Twelve injection wells and two extraction wells including the trench at the right boundary of the site were built in the test site. After two percent of surfactant solution was flushed into the injection well, the high pressure air jet was injected to accelerate the mobility of flushed solution in pore spaces underground and thus to increase the removal efficiency of the in-situ flushing. The effluent solution was treated by the chemical treatment process including oil separator for its recycling. Water samples taken from injection and extraction wells were analyzed on GC/FID (Agilent 6890, Hewlett Packard) and ICP/OES (Perkin elmer, Optima 3300 XL) for TPH and heavy metal concentration, calculating the removal efficiency of the in-situ flushing coupled with high pressure air injection at the test site.

Total 3.6 tons of TPH (about 86 % of the initial TPH) was removed from the contaminated site and TPH concentration of the residual soil was below the standard tolerance limit (500 mg/kg). The optimum surfactant solution injection rate and air jet injection rate was determined to be 11 L/min and 25 ㎏/㎠, respectively. Results from the pilot scale test suggested that the in-situ flushing coupled with high pressure air jet injection has a great possibility to remediate bunker fuel oil contaminated site.

Key word: In-situ flushing, Surfactant Enhanced Remediation (SER), High Pressure Air Injection (HPAI) and Total Petroleum Hydrocarbon (TPH)

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CHAPTER Ⅰ. INTRODUCTION

The organic pollutants are generated from various industrial processes such as manufacturing of fuels, halogenated compounds, pesticide derivatives or plastics, and their major sources are in underground (or on-ground) storage sites, coking sites and landfill sites. They have not only very low water solubilities but also very high toxicities to human being, becoming serious pollution sources to contaminate soil and groundwater in world scale. The maximum contaminant limits (MCL) of typical organic contaminants for drinking water and their health effects are given in Table 1 (Korea Ministry of Environment, 2001).

Organic pollutants mostly exist as the liquid phase at the earth surface and organic liquids that are lighter than water are referred to as light non-aqueous phase liquids (LNAPLs). Typical examples of LNAPLs are light fuels such as gasoline, kerosene and diesel and they tend to accumulate above and slightly below the water table (consistent with a fluctuating water table) when they spill into the ground. Organic liquids that are heavier than water are referred to as dense non-aqueous phase liquids (DNAPLs), which include chlorinated solvents such as PCE, TCE and PCBs. Because they are denser than water, DNAPLs have the potential to migrate to depths deep below the water table, and thus pose special cleanup challenges. The determination of NAPL distribution in a contaminated site is essential to attain the highest level of clean up, and the one of the most important factors controlling the NAPL distribution in the subsurface is the geological heterogeneity (Kueper *et al.*, 1993; Abdul and Ang, 1994; Fountain *et al.*, 1996; Pankow and Cherry, 1996; Fetter, 1998). It is now widely known that conventional pump-and-treat technologies are ineffective and costly methods to remove such NAPLs from the contaminated site (MacDonald and Kavanaugh, 1994).

As an alternative to clean up the soil and groundwater contaminated by NAPLs, the surfactant enhanced remediation (SER) process has been studied since 1990s (Jafvert, 1996; Jawitz *et al.*, and Nash, 1998; Lee *et al.*, 2005). Since most organic contaminants are naturally hydrophobic, the objective of using surfactants is to reduce the hydrophobicity of the oil phase to the point where it will be wetted by the water phase and detach itself from soil surfaces (Zhong *et al.*, 2003). Therefore, surfactants are used in a manner that will assist in enhancing the surface activities of the surfactant/oil/soil systems (Zhang *et al.*, 2001). At the fuel contaminated site, the in-situ SER (surfactant enhanced remediation) process may be the primary action to remove large amounts of fuels from the subsurface, by increasing the solubility and/or the mobility, creating emulsion (Kimball, 1992). However, SER process sometimes requires a great consumption of surfactant with low removal efficiency because of heterogeneous subsurface properties (Mackay, 1985). Various supplementary processes have been developed to overcome this disadvantage (Cheng *et al.*, 2007). This research provided a pilot scale in-situ SER process including a high-pressure air injection system to increase the removal efficiency of NAPLs from the subsurface. Lab scale solubility and column tests were performed to investigate the removal efficiency for SER process with the high pressure air injection. Finally, a field scale pilot test was conducted at a bunker fuel contaminated site, Korea.

Table 1. The maximum contaminant limits (MCL) of typical organic contaminants for drinking water and their health effects

Contaminant	MCL (mg/L)	Health effect	Source
Phenol	0.005	Skin burns, liver damage, dark urine, irregular heart beat, and some died	Production of phenolic resins and in the manufacture of nylon and other synthetic fibers
Diazinon	0.02	Anemia; decrease in blood platelets; increased risk of cancer	Discharge from factories; leaching from gas
Parathion	0.06	Death, loss of consciousness, dizziness, confusion, headaches, difficult breathing	Spraying on farm crops
Fenitrothion	0.04	Abdominal cramps, vomiting, diarrhea, pinpoint pupils and blurred vision, excessive sweating	Reaction of phosphorus pentasulfide with methanol in toluene
Carbary	0.07	Cancer and perhaps Parkinson?s disease	From carbamate chemical
1.1.1-Tri chloroethane	0.1	Liver, nervous system, or circulatory problems	Discharge from metal degreasing sites and other factories
Tetra chloroethylene	0.01	Liver problems	Discharge from industrial chemical factories
Tri chloroethylene	0.03	Liver problems	Discharge from industrial chemical factories
Di chloromethane	0.02	Liver problems; increased risk of cancer	Discharge from drug and chemical factories
Benzene	0.01	Anemia; decrease in blood platelets; increased risk of cancer	Discharge from factories; leaching from gas storage tanks and landfills
Toluene	0.7	Nervous system, kidney, or liver problems	Discharge from petroleum factories
Ethylbenzene	0.3	Liver or kidneys problems	Discharge from petroleum refineries
Xylene	0.5	Nervous system damage	Discharge from petroleum factories; discharge from chemical factories
1.1-Di chloroethylene	0.03	Liver problems	Discharge from industrial chemical factories
Carbontetra chloroide	0.002	Liver problems; increased risk of cancer	Discharge from chemical plants and other industrial activities
1.2-Dibromo -3-chloro propane	0.003	Reproductive difficulties; increased risk of cancer	Runoff/leaching from soil fumigant used on soybeans, cotton, pineapples, and orchards

CHAPTER Ⅱ. OBJECTIVE

Objective of this research is to investigate the removal efficiency of the in-situ SER flushing coupled with high pressure air injection as a remedial process for a genuinely contaminated site and to determine the optimum operation conditions such as surfactant concentration, solution injection rate and air injection pressure.

This study was divided into three main sections as followed.

1) Determination of optimum experimental conditions and parameters such as surfactant type, surfactant concentration, injection rate, air pressure and flushing time for SER flushing

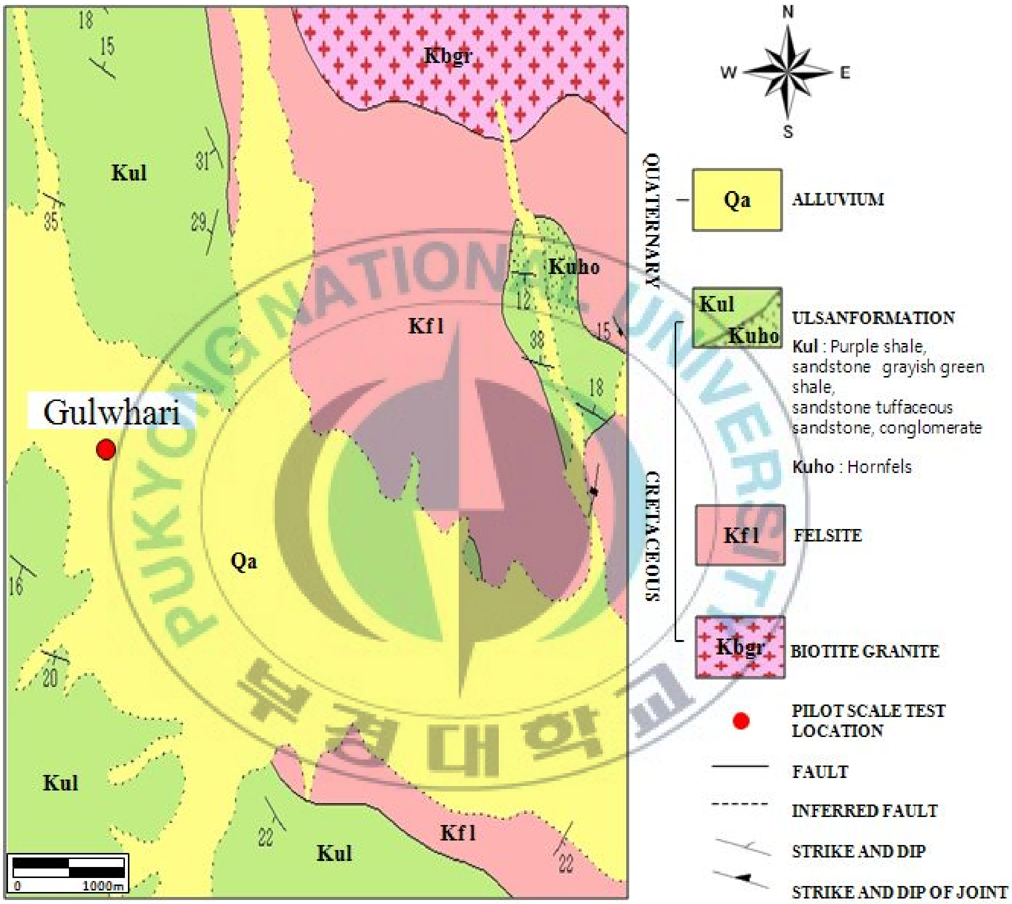
2) Application of the in-situ flushing coupled with high pressure air injection to remove the bunker A and C-oil from contaminated soil in lab scale

3) Evaluation of removal efficiencies and remediation technologies for the applied in-situ SER flushing coupled with high pressure air injection in the pilot scale test

CHAPTER Ⅲ. BACKGROUND

3.1 Outline of research area

3.1.1 Geological characteristics



Gulwhari (at Ulsan)

Fig. 1. Geological map in the research area (from Korea Institute of Geoscience and Mineral resources).

3.1.2 Research area

The geological constitution of the research area is mostly composed of quaternary alluvium and Ulsanformation, which are divided into four major groups such as purple shale, sandstone grayish green shale, sandstone tuffaceous sandstone and conglomerate. The site for the research was located at Ulsan metropolis, Gyeongsangbuk-do, Korea, which had been used as a roofing tile manufacturing facility area for 25 years. From previous investigation, the site was seriously contaminated by bunker A and C-oil due to the leakage from the UST (Underground Storage Tank), which was used to heat the facility and the buildings for 20 years (QEn Solution Inc., 2007). The pilot scale test site (15 m × 19 m × 6 m) was selected at the inside of the research site for SER process coupled with high pressure air injection. A church building was recently established near the left boundary of the test site (Fig. 2).

The test site was mostly composed of heterogeneous sandy and gravel-sandy soils and the average hydraulic conductivity (K) was 1×10^{-3} cm/sec. To identify precisely the distribution and the amounts of the contaminants at the test site, continuous soil cores (7 m in depth) were collected by means of a autometic geo-probe at fourteen locations in the pilot scale test site (Fig. 3). Total petroleum hydrocarbon (TPH) concentrations of the soil cores were analyzed by using sohxlet extraction method and Gas Chromatography (GC/FID). The average TPH concentration of the soil in the test site was 3450 mg/kg and bunker A and C-oil was mainly distributed around 2-3 m in depth at the site.

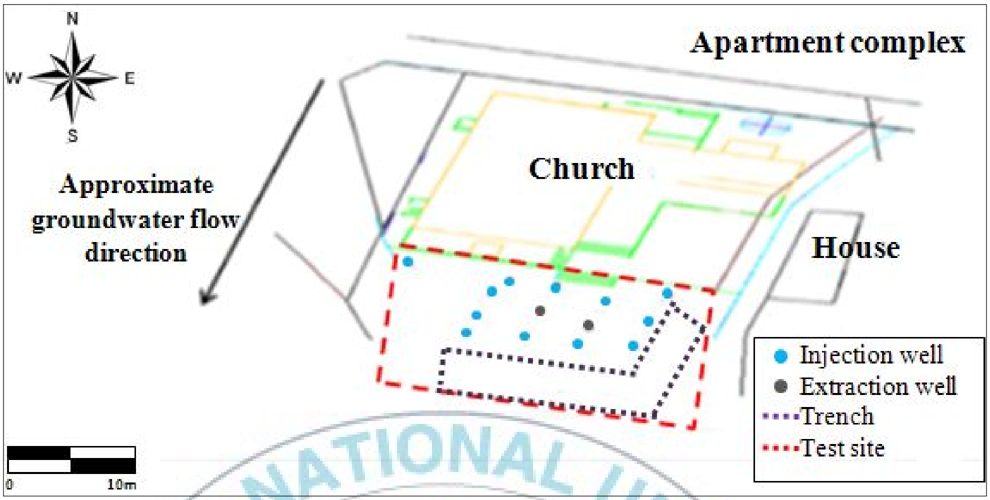


Fig. 2. Schematic illustration of the pilot scale test site with injection wells, extraction wells and trench established.

Fig. 3. Photography for the pilot scale test site taking soil cores and installing wells.

3.2. Properties of NAPLs as pollution sources

3.2.1 TPH and LNAPLs

Total petroleum hydrocarbons (TPH) is a term used to describe a large family of several hundred chemical compounds that originally come from crude oil. TPH is classified as four major groups: paraffine, iso-paraffine, naphthene and aromatic (Hajšślová *et al.*, 1998). Crude oil is used to make petroleum products, which can contaminate the environment. Because there are so many different chemicals in crude oil and in other petroleum products, it is not practical to measure each one separately. However, it is useful to measure the total amount of TPH at a site (Senn and Johnson, 1987). Table 2 is shows that contaminants in soils by Korea Soil Conservation Law. TPH is a mixture of chemicals, but they are all made mainly from hydrogen and carbon, called hydrocarbons.

Scientists divide TPH into groups of petroleum hydrocarbons that act alike in soil or water. These groups are called petroleum hydrocarbon fractions. Each fraction contains many individual chemicals. Some chemicals that may be found in TPH are hexane, jet fuels, mineral oils, benzene, toluene, xylenes, naphthalene, and fluorene, as well as other petroleum products and gasoline components. However, it is likely that samples of TPH will contain only some, or a mixture, of these chemicals (Zhou and Crawford, 1995; Liebeg and Cutright, 1999; Ting *et al.*, 1999; Vasudevan and Rajaram, 2001).

'Fuel oil' includes any liquid petroleum product that is burned in a furnace or boiler for the generation of heat or used in an engine for the generation of power. It is produced from petroleum distillation process and mostly contains long hydrocarbon chains, particularly alkanes, cycloalkanes and aromatics. Fuel oil could be classified into six classes, numbered 1 through 6 (No.1 ~ No.6), according to its boiling point, composition and purpose. Its boiling points, range from 175 to 600 °C (carbon chain length 20 to 70).

Carbon chain length and viscosity increase with the increase of class number. Among the six classes of fuel oil, Bunker A-oil means No. 2 fuel oil, bunker B is No. 4 or No. 5 and bunker C is No. 6. Since No. 6 is the most common, "bunker oil" is often used as a synonym for No. 6. (or Bunker C-oil). Bunker A and C-oil were the main pollutants in the test site and they were LNAPLs (Jezequel *et al.*, and Lee, 2003; Schwartz, 2004).

Contamination of the subsurface by LNAPL$_S$ has been a serious problem threatening groundwater and soil in Korea and the most prevalent form of LNAPLs contamination is that caused by hydrocarbon fuels, especially at site being used for fuel storage, transport or production (Seo *et al.*, 2001; Lee *et al.*, 2002; Moon *et al.*, 2002; Han *et al.*, 2005). Groundwater is very susceptible to contamination, unless protected by a low permeability layer such as clay. NAPLs like bunker oils are bonded strongly inside the soil matrix and present for a long time at the contaminated site. Most of NAPLs are sparingly soluble in water, so they can mix with water during the flow of water through the soil matrix. When the spillage of liquid organic hydrocarbon is sufficient, the spill liquid can reach the groundwater table. If the liquid is LNAPL that will float on the water surface and slowly solubilize in water. Since there is also a flow in the subsurface, the contaminated groundwater moves away from the contaminated site of the spill (Harwell *et al.*, 1999; Miles *et al.*, 2008).

Table 2. Soil contamination level (Korea Ministry of Environment, 2008)

Contaminant	Classification (mg/kg)			
	Apprehension standard		Counterplan standard	
	A area	B area	A area	B area
Cadmium	1.5	12	4	30
Copper	50	200	125	500
Arsenic	6	20	15	50
Mercury	4	16	10	40
Lead	100	400	300	1000
Chromium	4	12	10	30
Zinc	300	800	700	2000
Nickel	40	160	100	400
Fluorine	400	800	800	2000
Organic compound	10	30	-	-
PCB	-	12	-	30
Cyanogen	2	120	5	300
Phenol	4	20	10	50
BTEX	-	80	-	200
TPH	500	2000	1200	5000
TCE	8	40	20	100
PCE	4	24	10	60

* BTEX: benzene, toluene, ethylbenzene and xylene, TPH: total petroleum hydrocarbon, PCB: poly chlorinated biphenyl, TCE: tri chloro ethylene, and PCE: poly chloro ethylene

3.2.2 Interaction between LNAPLs and soil matrix

The NAPLs-soil interaction is mainly occurred by (i) sorption, (ii) complexation, and (iii) precipitation (Tan, 2000) and different physical forms possible for NAPLs in soil matrix are illustrated in Fig. 4. The general term of 'sorption' is used to indicate the process in which the solutes (ions, molecules, and compounds) are partitioned between the liquid phase and the soil particle interface (Mihelcic *et al.*, 1993). Physical adsorption occurs when NAPLs are attracted to the soil surfaces (from the aqueous solution present inside pore spaces) because of the unsatisfied charges (attractive forces) of the soil particles. In specific adsorption (chemical adsorption occur by chemical bonding), the ions penetrate the coordination shell of the structural atom and are bonded by covalent bonds via O- and OH- groups to the structural cations (Volkering, 1995). The interaction by complexation and precipitation is mainly occurred by heavy metals. Organic contaminants like petroleum hydrocarbons are often adsorbed physically due to hydrophobic forces on the soil surface.

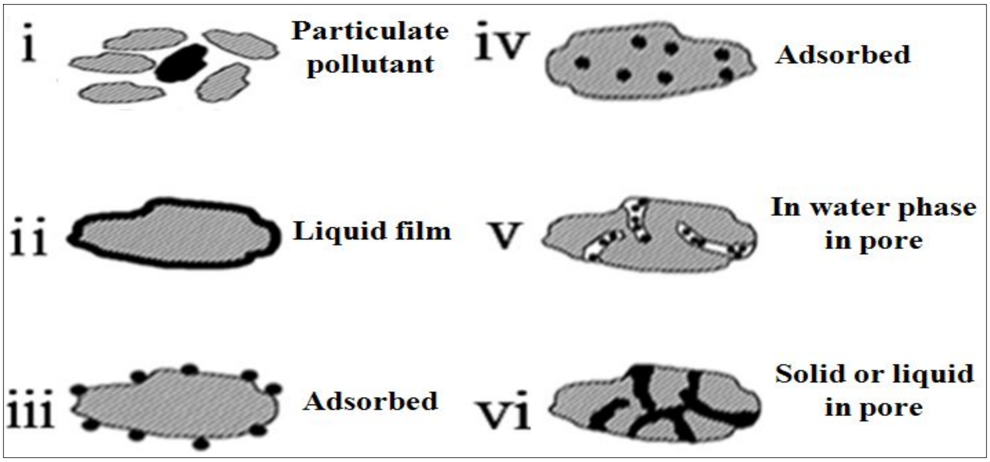


Fig. 4. Different physical forms of NAPLs in soil matrix: (ⅰ) solid particles; (ⅱ) liquid film; (ⅲ) adsorbed onto soil; (ⅳ) adsorbed into soil; (ⅴ) in soil macro pores; (ⅵ) in soil micro pores (Volkering *et al.*, 1998).

3.3 Principle of In-situ surfactant flushing with high pressure air injection

3.3.1. Surfactant

The term surface-active agent or "surfactant" represents a heterogeneous and long-chain molecule containing both hydrophilic (head: water like) and hydrophobic (tail: oil like) moieties (Rosen *et al.*, 2004). Depending on the nature of the hydrophilic group, surfactants can be classified as anionic, cationic, zwitterionic, and non-ionic (Westall *et al.*, 1992). Surfactants are used as potential agents for enhanced solubilization and accelerated mobilization of contaminants from soil and sediments (Sabatini *et al.*, 1992; Rouse *et al.*, 1996; Lee, 1998; Lee *et al.*, 2001; Zhu *et al.*, 2003; Paria, 2008).

Solubilization rates depend on the chemistry of the surfactant solution and vary over orders of magnitude among surfactant types (Chen *et al.*, 1997). Mixed surfactants are practical and fundamental interest in industrial applications and most commercial and industrial application surfactants generally consist of mixtures of surfactants.

Surfactant mixtures generally exhibit a number of synergistic advantages in their practical applications over the use of individual surfactant type because of the formation of mixed micelles (Holland and Rubingh, 1992; Rosen, 2004b; Cowell *et al.*, 2000; Zhao and Yang, 2006; Zhao *et al.*, 2006).

The surfactant also increases the mobility of NAPLs in the pore spaces of soil medium when the interfacial tension between

NAPL and water phase dramatically decreases, creating the microemulsion phase. Microemulsion is defined as a thermodynamically stable phase consists of ternary mixtures of oil-surfactant-water (Childs *et al.*, 2006). Microemulsion can be classified by three basic types: (i) microemulsion corresponds to oil solubilized in aqueous micelle (Winsor type I), (ii) microemulsion corresponds to water solubilized in reverse micelle present in the oil phase (Winsor type II), and (iii) microemulsion corresponds to oil and water bicontinuous phase that is stabilized by a surfactant membrane (Winsor type III) (Acosta *et al.*, 2002).

The typical transition is possible from Winsor type I to type III and to Type II microemulsions shown in this Fig. 5 (Tongcumpou *et al.*, 2003, 2005). The transitions are well correlated with the interfacial tension (IFT) of the system. The Winsor type I microemulsion can transfer to a Winsor type III microemulsion by decreasing the system hydrophile/lipophilie balance (HLB) (e.g., increasing salinity for ionic surfactants systems). When the HLB value decreases further, the system transforms Winsor type III to Winsor type II microemulsion. Microemulsions have not only high solubilization ability of NAPLs but also their high mobility in the pore spaces, with the similar micellar solubilization concept called 'super solubilization'. In microemulsion, reduction in the micelle curvature allow increased oil solubilization in the core of these “swollen” micelles (Ascota *et al.*, 2003). Solubilization capacity of these swollen micelles can be higher up to 1 or 2 orders magnitude than the regular micelle solubilization (Nagarajan *et al.*, and Wu *et al.*, 2000).

Super solubilization or microemulstion is becoming more attractive in many applications like hard surface cleaners, detergency, surfactant enhanced remediation of oil contaminated sites etc. due to its increased solubilization capacity (Marquez *et al.*, 1995; Doana *et al.,* 2003; Szekeres *et al.*, 2004).

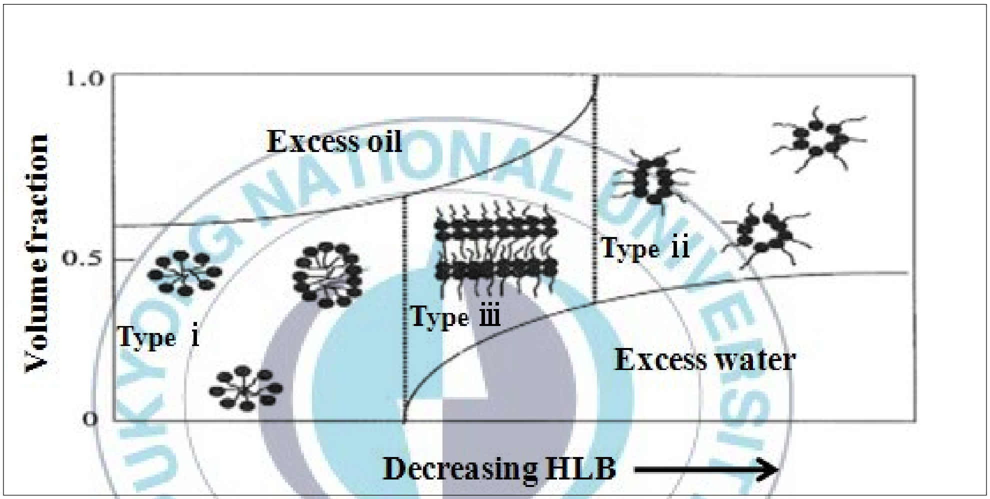


Fig. 5. Typical phase behavior of microemulsion showing the transition from oil in water (Winsor type I) to bicontinuous structure (Winsor type III) and water in oil (Winsor type II) (Tongcumpou *et al.*, 2003, 2005).

The use of surfactant to clean-up NAPL contaminated site has been limited because of its toxicity and long time residual property. The researches for the surfactants, which are non-toxic and easily degradable, have been actively performed and the pre-environmental surfactants called "biosurfactants' are considered as potential agents for SER process. Biosurfactants are biologically available compounds those exhibit surface-active properties, which are mainly produced by bacteria or yeast, and also available from plants, animals, including human (Christofi *et al.*, 2002). Recently biosurfactants have gained more attention over synthetic surfactants due to environmental compatibility nature of those compounds. Those can be classified according to different molecular structures. The hydrophobic part of the molecule is based on long-chain fatty acids, hydroxy fatty acids or ∝-alkyl-β-hydroxy fatty acids. The hydrophilic portion can be a carbohydrate, amino acid, cyclic peptide, phosphate, carboxylic acid or alcohol (Mulligan, 2005). Major types of biosurfactants and their origin are listed in Table 3. Most of the biosurfactants are anionic or nonionic. Only a few are cationic such as those containing amine groups. The potential environmental applications biosurfactants have been reviewed by some researchers (Volkering *et al.*, and Bai *et al.*, 1998; Maier *et al.*, 2000; Christofi *et al.*, 2002). Biosurfactants have recently received attention for use in NAPL remediation and have considerable potential for SEAR application because of the following reasons (Falatko and Novak, 1992; Zhang and Miller, 1992; Bai *et al.*, 1997; Park *et al.*, 1998).

1. biosurfactants are a naturally occurring, biodegradable product and, thus, may be acceptable for application at many waste sites; 2. biosurfactants are generally nontoxic to microorganisms, especially hydrocarbon-degrading microorganisms; 3. industrial production is likely to be cost effective relative to synthetic

surfactants; and 4. it may be possible to induce in situ production of a biosurfactant at a hazardous waste site.

Table 3. Classification and microbial origin of typical biosurfactants (Milligan and Gibbs, 1993; Banat, 1995).

Surfactant class	Microorganism
Rhamnolipids	*Pseudomonas aeruginosa, Pseudomonas sp., Serratia rubidea*
Lipopeptides	*Arthrobacter sp., Bacillus pumilis, Bacillus subtilis, Bacillus licheniformis Pseudomonas fluorescens*
Lipopolysaccharides	*Acinetobacter calcoaceticus, Pseudomonas sp., Candida lipolytica*
Phospholipids and Sulfonylipids	*Thiobacillus thiooxidans, Corynebacterium alkanolyticum*
Fatty acids (corynomycolic acids, spiculisporic acids, etc.)	*Penicillium spiculisporum, Corynebacterium lepus, Arthrobacter parafineus, Talaramyces trachyspermus*
Sophorose lipids	*Candida apicola, Candida lipolytica*
Trchalose lipids	*Arthobacter paraffineus, Corynebacterium sPP. Mycobacterium sPP. Rhodococus erythropolis Corynebacterium sPP.*
Glycolipids	*Arthrobacter sp., Corynebacterium sp.*
Sophorose lipids	*Candida bombicola, Candida lipolytica*
Polyol lipids	*Rhodotorula glutinus, Rhodotorula graminus*
Arthrofactin	*Arthrobacter sp.*
Surfactin	*Bacillus subtilis, Bacillus pumilus*
Alasan	*Acinetobacter radioresistens*

3.3.2 In situ surfactant flushing coupled with high pressure air injection

In situ soil flushing is an innovative treatment technology that floods contaminated soils with a solution that moves the contaminants to an area where they are removed (Dekker *et al.*, 2000; Conrad *et al.*, 2002). “"In situ”"—-meaning “"in place”"—- refers to treating the contaminated soil without digging up or disturbing it. The specific contaminants in the soil at any particular site determine the type of flushing solution needed in the treatment process (EPA, 1996).

Surfactant systems often exhibits complex behavior in removing NAPLs whereas, mobilization by lowering interfacial tension and micellar solubilization by surfactants are accepted as main mechanisms of NAPLs removal (Abriola *et al.*, 1993; Brown *et al.*, 1994; Goudar et al., 1999). Soil flushing using surfactants was originally developed in petroleum recovery operations and afterwards the surfactants are used for remediation of NAPLs contaminated sites (Mulligan *et al.*, 2001). The schematic presentation of SER (surfactant enhanced remediation) process is shown in Fig. 6. For this remediation scheme, the surfactant solution is injected by wells below the ground to enhance the extraction of the contaminant (NAPLs). Once the surfactant-contaminant effluent solution drains out above ground, separation processes are necessary for either re-injection of the surfactant solution or disposal of the waste stream. The main factors should be considered for the surfactant selection in this process are cost, biodegradability, low toxicity, low adsorption to soil, effective at concentrations lower than 3 %, low soil dispersion, and low surface tension (Mulligan *et al.*, 2001).

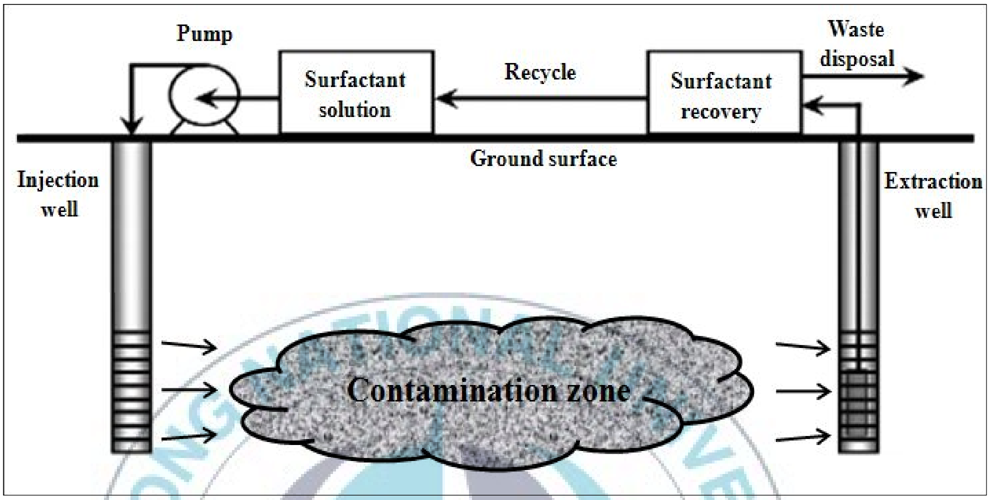


Fig. 6. Schematic illustration of SER (surfactant enhanced remediation) process (Cheng *et al.*, 2007).

It has been mentioned earlier that SER (surfactant enhanced remediation) process is based primarily on two recovery mechanisms (a) increased aqueous solubility of the organic compound due to micellar solubilization and (b) mobilization or displacement of NAPLs due to IFT (interfacial tension) reduction. Mobilization by using microemulsion has been shown to be an extremely efficient means for recovering NAPLs from sand and aquifer materials than solubilization (Ramsburg *et al.*, 2002). HOCs (Hydrophobic organic compounds) generally have low aqueous solubilities, and because of less availability of those compounds biodegradation is very difficult.

In presence of surfactants the solubilities of HOCs increased and micellized HOCs have increased bioavailability to microorganisms, as a result, improved the biodegradation rate. The surfactants affect the rate of hydrocarbon biodegradation in two ways: (i) by increasing dissolution of the molecules in aqueous phase and (ii) changing the affinity between the microbial cells and hydrocarbons by increasing cell surface hydrophobicity (Miller *et al.*, 1989; Zhang *et al.*, 1992, 1994, 1995; Volkering *et al.*, 1995). The biosurfactant enhanced removal efficiency for NAPLs could be accelerated by air flotation (Clifford, 1993; Underwood, 1995; EPA, 1995; Somasundaran *et al.*, 1997;). The process of air flotation relies on the differences in the wettability at solid particle (soil) surfaces (Kho and Sohn, 1989; Schramm, 1996). Soil surfaces are often naturally wettable by surfactant hydrophilic moiety while surface that is non-wettable will repel surfactant hydrophobic moiety (Urum *et al.*, 2004). If a surface is hydrophobic, it is also typically air attracting, and is strongly attracted to an air interface, which readily displaces water at the solid surface (Burns and Zhang, 2001). Thus, in air flotation process, the separation of NAPLs phase from soil may also be accomplished by the selective attachment of hydrophobic NAPLs to air bubbles (foams) (Reddy *et al.*, 2001; Adams and Reddy, 2003). These massive air bubbles carring NAPLs can move much more fast than water phase in the pore spaces and drag out NAPLs adsorbed on soil surfaces on the ground, resulting in the increase of NAPL recovery rate in SER process (Rutherford and Johnson, 2000; Zhang *et al.*, and Tse *et al.*, 2001; Urum *et al.*, 2003; Tsai, 2004, 2007, 2008).

However, the study for the application of air flotation to SER process has been stayed at very fundamental level (EPA, 1992, 1998; Chou *et al.*, 1998; Kim *et al.*, 2004a; Urum *et al.*, 2005; Kim *et al.*, 2006a; Kim *et al.*, 2006 ; Kim *et al.*, 2007). In this research, lab scale batch and column tests were performed to investigate the removal efficiency for SER with the air injection and determine the optimal operation conditions for the field test. Finally, the high pressure air injection was performed with SER process in the pilot scale test site to accelerate the mobility of flushed solution in pore spaces underground and thus to increase the removal efficiency of in-situ SER flushing. The schematic of SER process coupled with hige pressure air injection system applied in the test site was shown in Fig. 7.

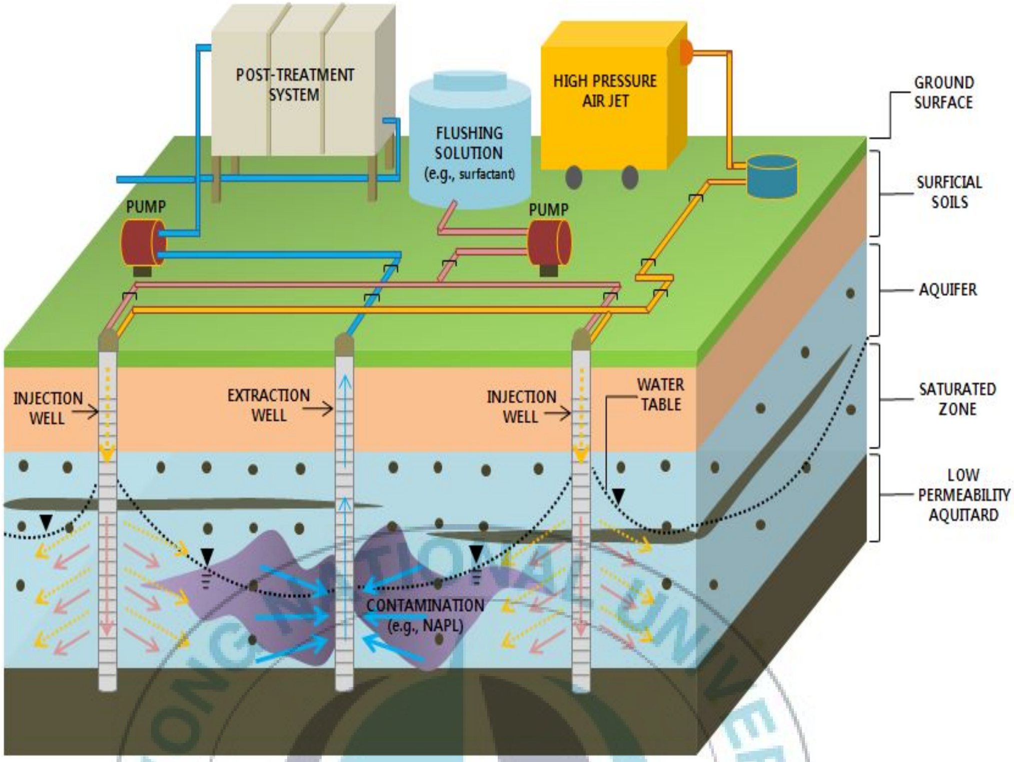


Fig. 7. Schematic of the in situ SER flushing coupled with high pressure air injection applied in the pilot test.

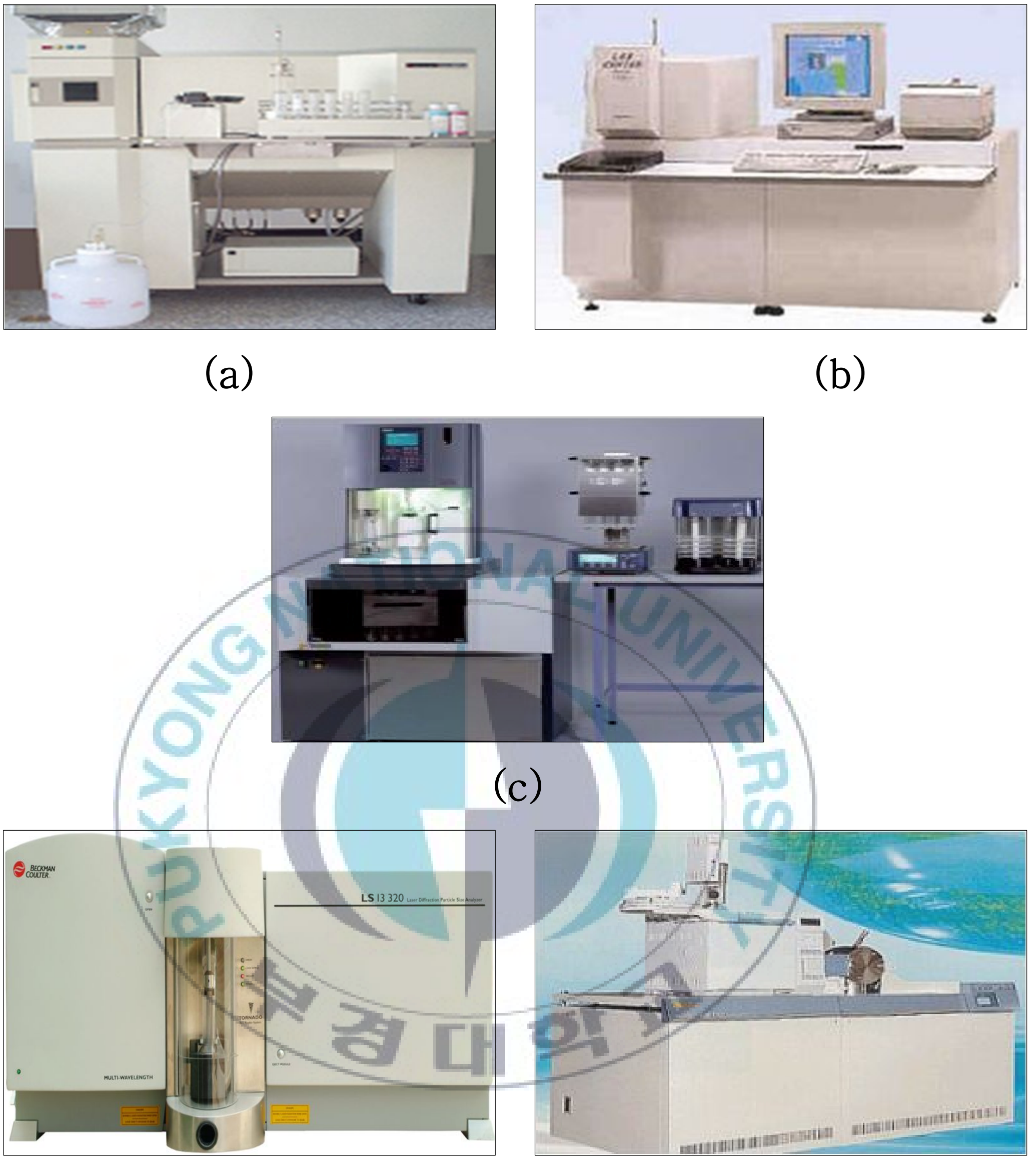
CHAPTER Ⅳ. EXPERIMENTAL METHODS

4.1 Experiment to measure soil properties

4.1.1. Soil characteristics

Several analyses were conducted to identify soil properties for the experiments. Soil cores were taken from the pilot test site and their particle distribution analyses were performed through the dry-sieving and pipetting method. Physical properties such as water content, bulk density and porosity were also measured by the processes referred from Fetter (1994).

For the chemical property, heavy metal concentrations of soils were measured on ICP/OES (Perkin elmer, Optima 3300XL) by Korean standard analytical process (Korea Ministry of Environment , 2001) and their principle component analyses were done by X-ray fluorescence (XRF) spectrometer (Shimadzu, XRF-1700). Cation exchange capacity (CEC) and total organic carbon (TOC) of soils were also measured by Kjeltec^{TM} 2400/2600 and HRMS, respectively. Fig. 8 shows instruments used for the soil analyses.



(a) (b) (c) (d) (e)

Fig. 8. (a) ICP/OES, (b) XRF, (c) Kjeltec™ 2400/2460 CEC analyser, (d) LS 13 320 LASER PARTICLE SIZE ANALYZER, and (e) HRGC/HRMS.

4.1.2. TPH contamination at the site

To investigate TPH contamination of the pilot test site, forty soil samples from fourteen locations (in different depth) in the site were collected by using the percussion boring instrument (Table 4). Collected soils were dried in the oven at 20 ℃ for one day and twenty grams of soils were ground into small particles and placed in a porous cellulose thimble. The thimble filter is placed in an extraction chamber, which is suspended above a flask containing the dichloromethane and below a condenser. The flask is heated on a hot plate at 250 ℃ for 8 h and the solvent evaporates and moves up into the condenser where it is converted into a liquid that trickles into the extraction chamber containing the sample. The extraction chamber is designed so that when the solvent surrounding the sample exceeds a certain level it overflows and trickles back down into the boiling flask (Fig. 9).

At the end of the extraction process, the flask containing the solvent and lipid is removed. The solvent in the flask is then evaporated into 2 mL and the mass of the remaining lipid in 2 mL is measured by gas chromatography (Agilent 6890 Plus) with a flame ionization detector (FID) (Fig. 11). A capillary DB-TPH column (30 m in length, 0.32 mm in diameter, and 0.25 mm in film thickness; purchased from Agilent Co., USA) was used to measure TPH concentration in the extraction solution. An auto-sampler was used to inject 2 μL (split ratio of 3:1) of the sample and the temperature of the inlet was 290 ℃. The initial oven temperature was 50 ℃ (2 min hold) and was increased to 300 ℃ at a rate of 8 ℃/min (10 min hold). The carrier gas was nitrogen (99.99 % purity) and its velocity in a column was 1.5 mL/min. The method detection limit (MDL) of this method was 10 mg/kg for bunker fuel oil.

Table 4. Soil sample location in the pilot test site

Location (well)	Depth (m)						
	0-1	1-2	2-3	3-4	4-5	5-6	6-7
A1		O	O	O			
A2		O	O	O			
A3		O	O				
B1		O	O	O	O	O	
B2			O	O			
B3			O	O	O		
C1			O	O	O		
C2				O	O	O	O
C3			O	O	O	O	
D1			O	O	O		
D2			O	O	O		
D3			O	O	O		
E1							
E2				O		O	

(O: soil sample taken from the core)

(a) (b)

Fig. 9. (a) Sohxlet extraction experiment for TPH concentration analysis of soils and (b) extracted bunker fuel from the soil in the test site.

Fig. 10. GC/FID (Agilent 6890 Plus with flame ionization detector) with a auto injector (Agilent 7683 series) for TPH analysis.

4.2 Batch experiments for surfactant solubility for bunker fuel oil

The surfactants exist as monomers below the surfactant's CMC (critical micelle concentration) in solution and have only minimal effects on the aqueous solubility of organics (Mukerjee *et al.,* 1979; Butler *et al.*, 1998). Micellar solubilization of organics occurs when the surfactant concentration exceeds CMC, where their aqueous solubilities are enhanced by the incorporation of hydrophobic molecules into surfactant micelles (Mukerjee *et al.*, 1979; Kile *et al.*, 1989). The extent of micellar solubilization depends on many factors, including surfactant structure, aggregation number, micelle geometry, hydrophile/liophile balance (HLB) value, ionic strength, temperature, and the size and chemistry of the solubilizate (Attwood *et al.*, 1983; Rosen, 2004).

Batch experiments to measure the solubility of bunker fuel oil for two kinds of biosurfactant (P.W. CLEANER and OIL MALKUMI: purchased from Valucan Korea Inc.) were performed. Leaked bunker A and C oil from the test site were used in experiments. Physical and chemical properties of two surfactants used in the experiments solutions were shown in Table 5 and conditions of surfactant solution with different concentration for solubility experiments were in Table 6. Boiled distilled water was mixed with P.W. CLEANER surfactant (called as "P.W. surfactant" hereafter) or OIL MALKUMI surfactant (called as "O.M. surfactant" hereafter) to create surfactant solution.

Ten mL of surfactant solution was mixed with bunker fuel oil of 10 mL (1:1 : v/v) by using a magnetic stirrer in 20 mL glass vial for 10 min at 20 ℃. The mixed solution was separated to two distinct liquid phases (aqueous phase and bunker fuel oil phase) after mixing for 10 min (Fig. 11). Surfactant solutions of 2 mL from only aqueous phase were taken and mixed with dichloromethane of 10 mL (1:5 : v/v) to 20 mL glass vials in order to extract fuel oil in the aqueous phase (Fig. 12). Extracted dichloromethane of 2 mL was analyzed on GC/FID to determine the solubility of bunker fuel oil in each surfactant solution.

Table 5. Physical and chemical properties of surfactant solutions

Properties	Surfactants	
	P.W. CLEANER (P.W.)	OIL MALKUMI (O.M.)
Specific gravity (g/mL)	1.01	0.99
Vapor density (Air=1)	>1	0.613
pH	9.0 – 10.0	9.0 – 10.0
Solubility in water (%)	100	100
VOC content (volatile/volume)	< 10 g/L	< 50 g/L
Freezing point (°C)	0	-16
Toxicity	None known for blend	None known for blend
component	*Bacillus Licheniformus*, *Bacillus subtilis* and *Arthrobactor*	*Bacillus subtilis*

Table 6. Conditions of surfactant solutions for solubility experiments

Mixing ratio	Surfactant solution type	
	Type of P.W. surfactant (concentration %)	Type of O.M. surfactant (concentration %)
(1:1 wt)	0	0
	2	0
	20	0
	100	0
	0	2
	2	2
	20	2
	100	2
	0	20
	2	20
	20	20
	100	20
	0	100
	2	100
	20	100
	100	100

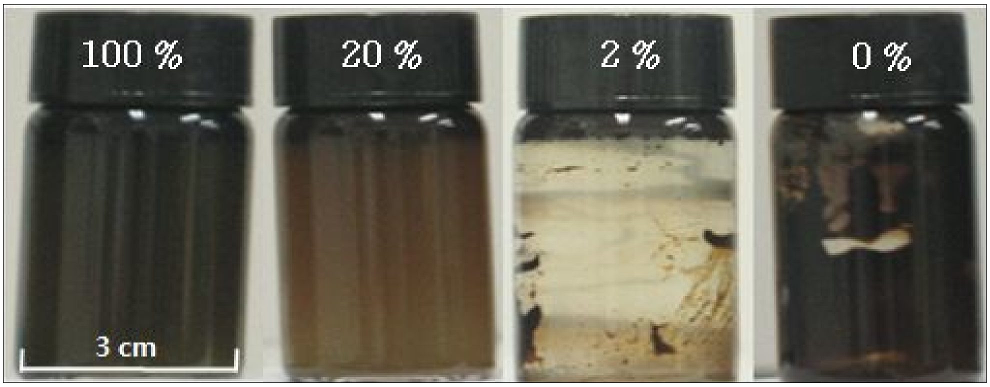


Fig. 11. Mixed solutions of the P.W. surfactant solution with bunker fuel oil (1 : 1 v/v).

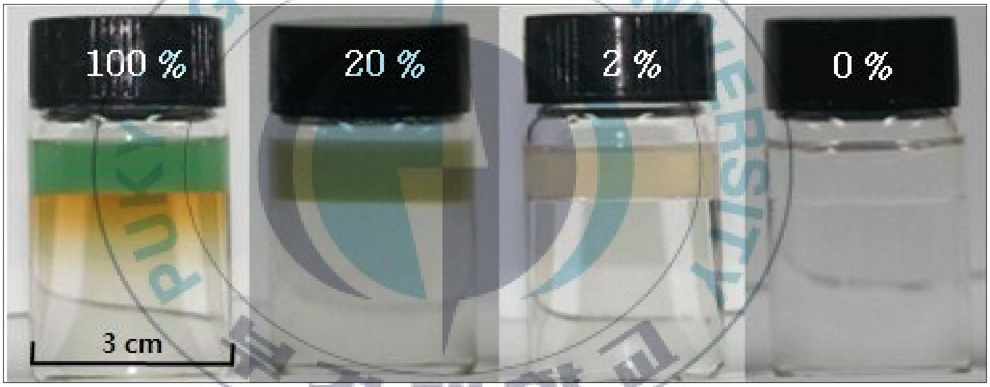
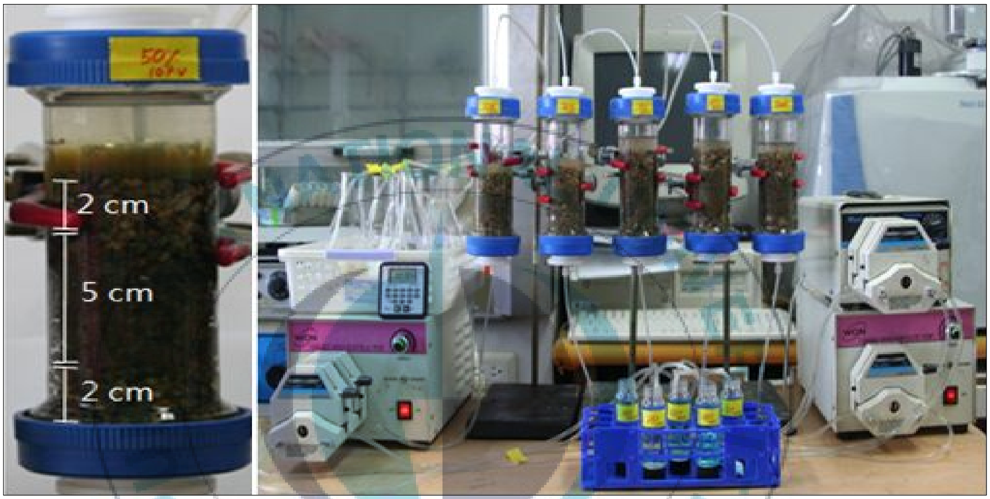


Fig. 12. Mixed solutions of the P.W. surfactant solution with dichloromethane (1 : 5 v/v) (bottom phase is dichloromethane solution).

4.3 Column experiments for SER (Surfactant Enhanced Remediation) flushing

Continuous column experiments were performed to investigate the removal efficiency of TPH for SER flushing and to determine its optimum operation conditions. Genuinely contaminated soil (an average TPH concentration: 8,718 mg/kg) taken from the test site was dried at 20 ℃ for a day. A glass column including capping plates, valves, and tube (purchased from Kontes Glass Company, USA) was used (15 cm in length and 4.8 cm in diameter). Before the contaminated soil was packed in the middle of the column (5 cm in thickness), the fine pebbles (I.D. 3-6 mm) were packed at 2 cm in thickness at the bottom and the top of the packed soil in the column (Fig. 13a). For all experiments, P.W. surfactant solution were used because O.M. surfactant solutions not yield correct TPH concentration values due to overlap the same time of TPH peaks and surfactant peaks during the analysis. First one pore volume (1 PV: about 40 mL) of distilled water was injected from the bottom of the column as up-flow system and then surfactant solutions were injected the column at a constant velocity (2 mL/min), respectively (Fig. 13b). The first column was flushed with the boiled distilled water for 5 pore volumes and the second column was with surfactant solution of 10 % for 15 pore volumes. The third column was flushed with surfactant solution of 20 % for 15 pore volumes. The fourth and fifth column were flushed with surfactant solution of 50 % for 15 and

20 pore volumes, respectively. The drained solution from the top of the column was taken to measure TPH concentration of the flushed solution during SER flushing and TPH concentration of the remained soils was also measured after the flushing to calculate the removal efficiency of TPH from the soils.



(a) (b)

Fig. 13. Photography of column experiments for SER flushing ((a): column packed with contaminated soil and (b): set of SER flushing column).

4.4 Column experiment of SER flushing coupled with HPAI (high pressure air injection)

Column experiments for SER flushing coupled with HPAI were performed to evaluate the effect of HAPI on the TPH removal from the column and their results were compared with those of water flushing and surfactant solution only flushing. Schematic of SER flushing with high pressure air injection in column experiment is shown in Fig. 15. In order to mimic real contamination condition, fifteen grams of kerosene (purchased from a 00gas station) were dyed with a Sudan Ⅳ and injected in the middle of a glass column (15 cm in length and 5 cm in diameter) fully packed with Ottawa sand (size: 0.42 - 0.85 mm and weight: 435.69 g) (Fig. 15). For the first one pore volume (1 PV: about 120 mL), distilled water was injected from the bottom of the column as up-flow system at a constant velocity (2 mL/min). The first column was flushed with only distilled water for 15 pore volumes and the second column was flushed with 10 % of P.W. surfactant solution for 15 pore volumes.

Air highly pressured (1 ㎏/㎠ or 2 ㎏/㎠) was injected to the third or the fourth column for 2 min after each one pore volume flushing with surfactant solution. To investigate TPH mass removed from the column during the flushing, TPH concentration of total effluent solutions and residual soil in column were analyzed on GC/FID (Fig. 15).

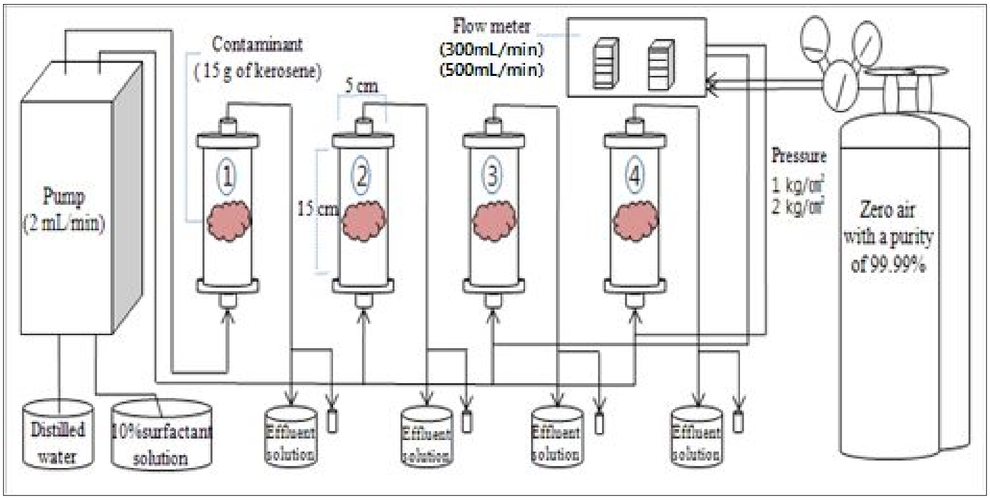


Fig. 14. Schematic illustration for SER flushing with HPAI in column experiments.

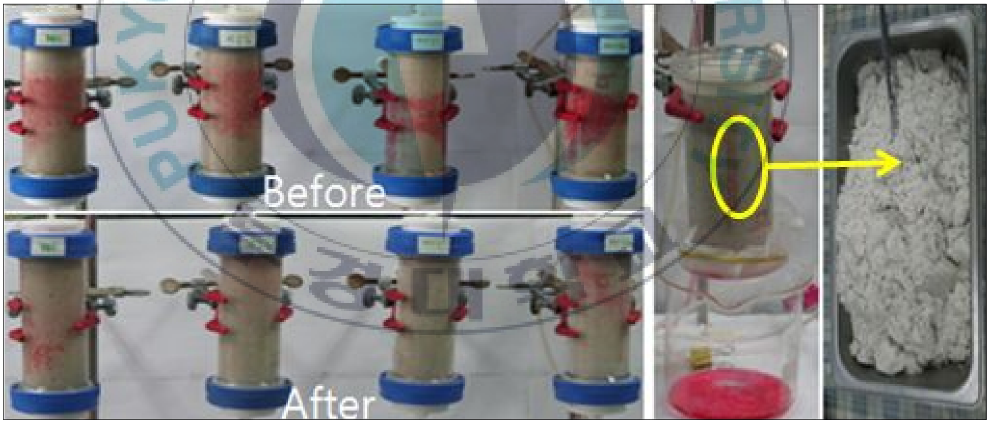


Fig. 15. Photography of column experiments for SER with high pressure air injection (kerosene dyed with Sudan IV in column).

4.5 Pilot scale field test for SER flushing coupled with HPAI (high pressure air injection)

A site contaminated bunker A- and C- oil (15 m x 19 m x 6 m) was selected for SER flushing coupled with HPAI and the estimated volume of the contaminated soil was about 570 m^3. Twelve injection wells and two extraction wells including the trench (1 m × 5 m × 19 m) at the right boundary of the test site were installed for the in situ SER flushing with HPAI. Photography of HPAI instrument and conditions of high pressure air injection system applied to the test site were shown in Fig. 16 and Table 7. Prior to surfactant solution flushing, about 63 tons of uncontaminated groundwater was circulated through twelve injection wells and two extraction wells in the test site. A 2 % surfactant solution was created in an injection tank (10 m^3 in capacity). The injection procedure of surfactant solution in the test site was based primarily on two main injection steps: (i) 2 % of "O.M." surfactant solution were injected for 4 L/min for 25 min with 4 kg/cm^2 of high pressure air jet for 25 min and then (ii) 2 % of "P.W." surfactant solution was injected for 11 L/min for 25 min with 25 kg/cm^2 of high pressure air jet for 25 min into twelve injection wells. These two steps were repeated during the daytime (8 h per day) for a month (from November 1, 2007 to November 30, 2007). The effluent solution from two extraction wells and trench was accumulated in a storage tank (37.68 m^2 in capacity) and analyzed TPH concentration on GC/FID to calculate TPH mass removal by SER with HAPI.

During the remediation process, total 190 tons per day of flushed solution were produced and treated by the chemical treatment process including oil separator. The treatment system was included several treatment tank: a storage tank, a settling tank, a separation tank, a reaction tank and a oil floating. The flow-chart of post treatment system was shown in Fig. 17 and 18. Treated solution, which was satisfied to the standard discharge tolerance limit of Korea Water Conservation Law, was re-used as flushing solution for the remediation.

Table 7. Condition of high pressure air injection

Compressed air	
Model	XHP 900 CAT
Air outturn (CFM)	900 / 425
Proper operation pressure (psig/kg)	350 / 23.8
Pressure range (psig)	150 - 350
Number of air outlet	1
Air outlet size	3 inch
Facility size (mm)	4,851 × 2,261 × 2,591

Fig. 16. Injection of high pressure air in the site.

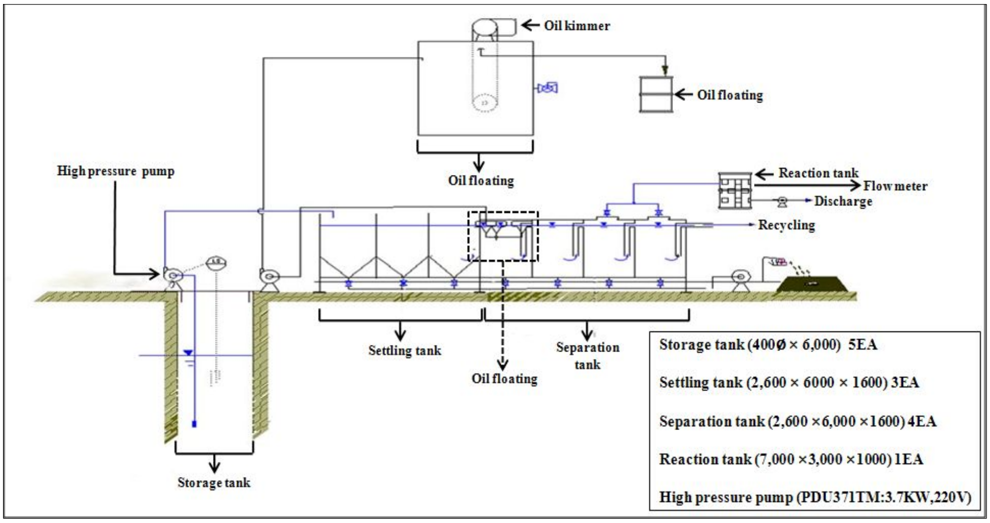


Fig. 17. Schematic of post-treatment system for flushed solution in Pilot test.

Fig. 18. Photography of oil separator and post-treatment devices for flushed solutions.

CHAPTER Ⅴ. RESULTS AND DISCUSSION

5.1 Results of experiment to measure soil properties

5.1.1. Results of soil characteristics

Physical and chemical properties of soils were measured and their results were shown in Table 8 and Table 9. Soil was composed of 14.7 % silt, 40.2 % sand and 45 % gravel. More then 45 % of soil particle was belong to under >2 mm size and the soil average porosity was 27 %, suggesting that the in-situ SER flushing is potential to apply for the test site.

The results of average CEC (cation exchange capacity) and TOC (total organic carbon contents) of soil were 13.50 cmol/kg and 0.1 %, respectively (Table 9). The major soil components were SiO_2 (silicon oxide), Al_2O_3 (aluminum oxide), Fe_2O_3 (ferric oxide), CaO (quicklime oxide) and K_2O (potassium oxide) in order of abundance (Table 10). Heavy metal concentration of soils was also shown in Table 11. From results of heavy metal analysis, the test site was not contaminated by reason that the concentration range was below the standard tolerance limit.

Table 8. Result of the analysis of soil properties

	Size distribution (%)			pH	Water content (%)	Bulk density (g/cm^3)	Porosity (%)
	Silt	Sand	Gravel				
Average value	14.7	40.2	45.0	8.5	14.9	1.5	27

Table 9. Result of cation exchange capacity and total organic carbon analysis of soils

Soil sample location (depth)	CEC (cmol/kg)	TOC (%)
A2 well (3 m)	13.51	0.57
C3 well (3 m)	13.48	0.46

Table 10. Result of principle component analysis by XRF for the soil

Main components	Soil sample location (depth) and mass distribution ratio (wt %)		
	A2 well (2 m)	B1 well (1 m)	C2 well (2 m)
SiO_2	67.39	68.87	68.59
Al_2O_3	15.98	13.67	16.11
Fe_2O_3	5.05	4.62	5.23
CaO	4.22	5.33	2.61
K_2O	2.77	2.38	2.66
MgO	1.99	2.24	2.40
Na_2O	1.18	1.39	0.95
TiO_2	0.84	0.82	0.91
SO_3	0.21	0.20	0.11
P_2O_5	0.16	0.16	0.20
MnO	0.12	0.15	0.14
ZrO_2	0.03	0.03	0.02
Cr_2O_3	-	0.04	-
SrO	0.02	0.02	0.02
Total	99.96	99.92	99.95

Table 11. Result of heavy metals analysis of soils

Soil sample location (depth)	Heavy metal concentration (mg/kg)					
	Cd	As	Cu	Pb	Zn	Ni
A2 well (2 m)	0.15	0.39	7.58	33.32	6.73	2.99
B1 well (1 m)	0.19	0.34	1.89	0.92	6.32	2.59
C2 well(2 m)	0.17	0.29	7.00	16.27	6.77	3.35

5.1.2. Results of TPH contamination at the site

Total forty soil samples were taken from the site and their TPH concentrations were analyzed on GC/FID. From the results of soil analysis, the main pollutants in the test site were determined to bunker A- and C-oil (diesel or kerosine) and the typical GC peak of contaminant of soils in the site was shown in Fig. 19. Fig. 20 shows TPH concentrations of soil at each well location in the test site and the average TPH concentrations of the site was determined as 3,450 mg/kg. TPH concentrations of soils at D2, E1, and E2 well location were below less than 500 mg/kg (Korea soil warning limit and the treatment tolerance limit at the site). However, most of soils at other 11 well locations were seriously contaminated by fuel oil (exceed Korean soil counterplan limit: 1200 mg/kg). Soil of A2 well location in 2-3m depth has the maximum TPH concentration of 70,162 mg/kg.

The 3-dimensional interpolation of TPH concentration in the site was performed to visualize the pollutant distribution map of the site by using 'Sufer 8' code (purchased from Golden Software Inc.) and their results were shown in Fig. 21. The southern east area of the site (around A and B well locations) was seriously contaminated by fuel oil (mostly 2 - 3 m in depth).

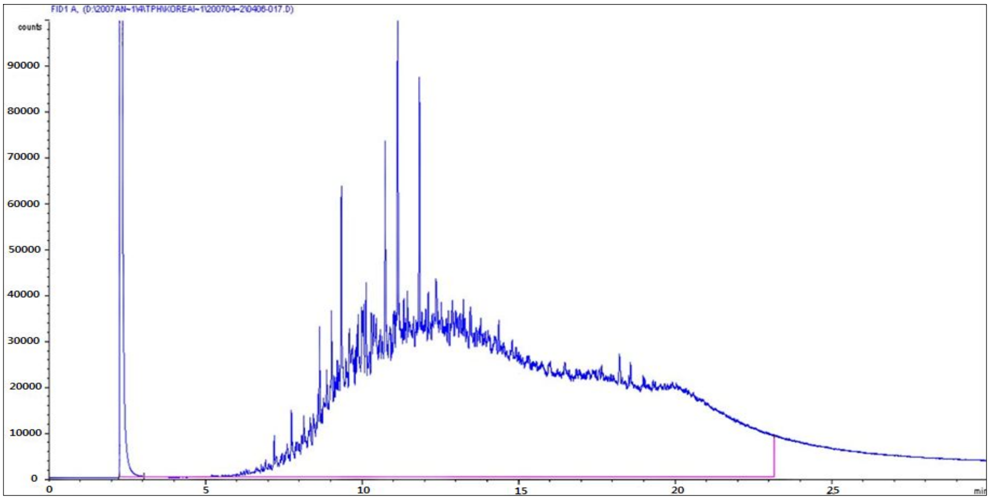
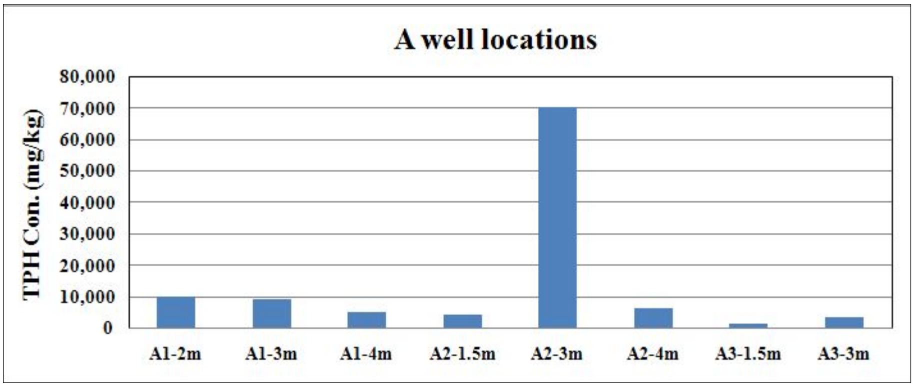
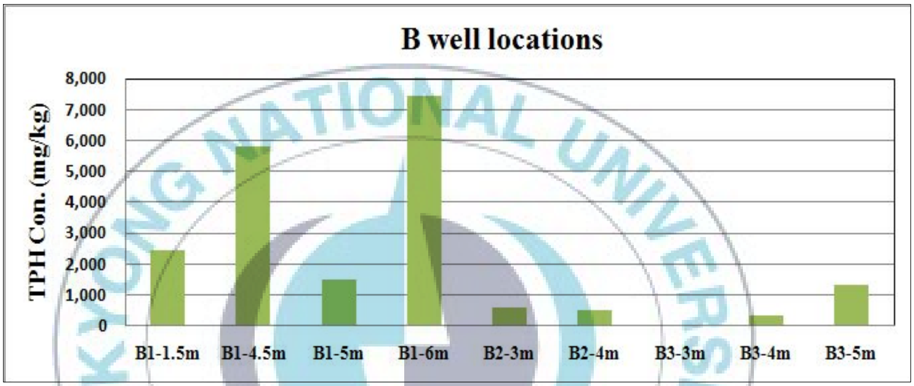


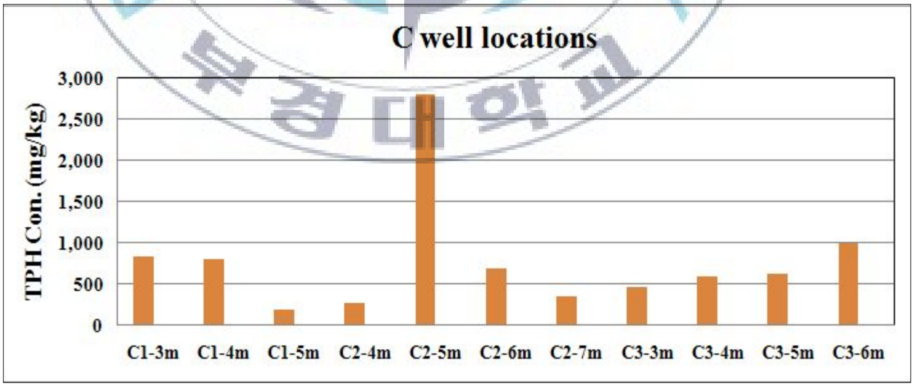
Fig. 19. Typical GC peak of bunker fuel oil in the test site.


A well locations
TPH Con. (mg/kg)
80,000
70,000
60,000
50,000
40,000
30,000
20,000
10,000
0
A1-2m
A1-3m
A1-4m
A2-1.5m
A2-3m
A2-4m
A3-1.5m
A3-3m

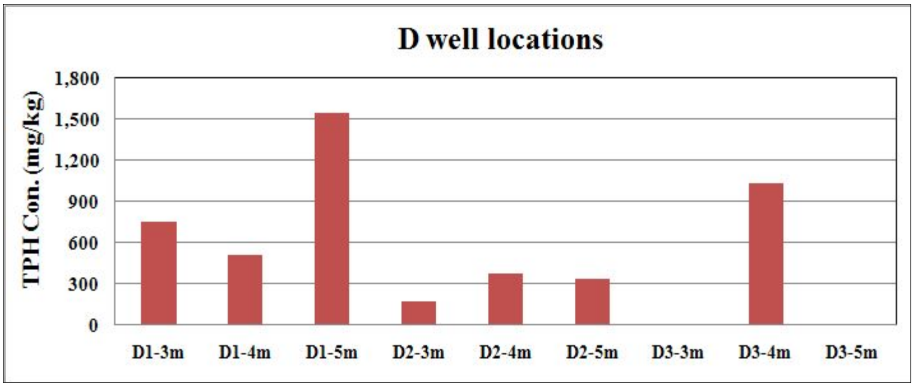
(a)


B well locations
TPH Con. (mg/kg)
8,000
7,000
6,000
5,000
4,000
3,000
2,000
1,000
0
B1-1.5m
B1-4.5m
B1-5m
B1-6m
B2-3m
B2-4m
B3-3m
B3-4m
B3-5m

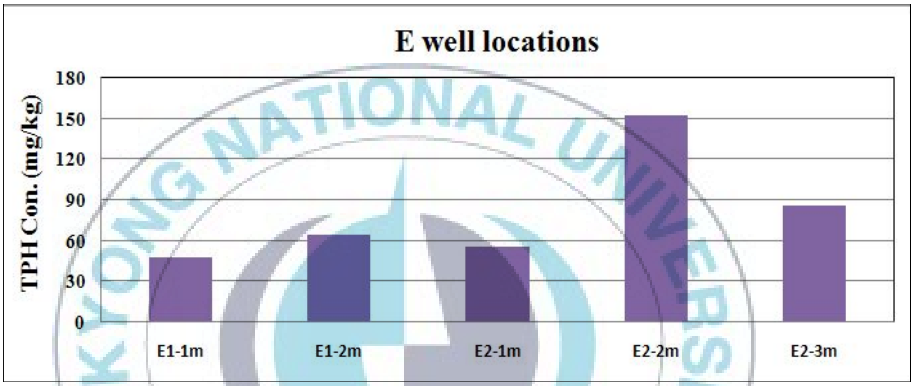
(b)


C well locations
TPH Con. (mg/kg)
3,000
2,500
2,000
1,500
1,000
500
0
C1-3m
C1-4m
C1-5m
C2-4m
C2-5m
C2-6m
C2-7m
C3-3m
C3-4m
C3-5m
C3-6m

(c)

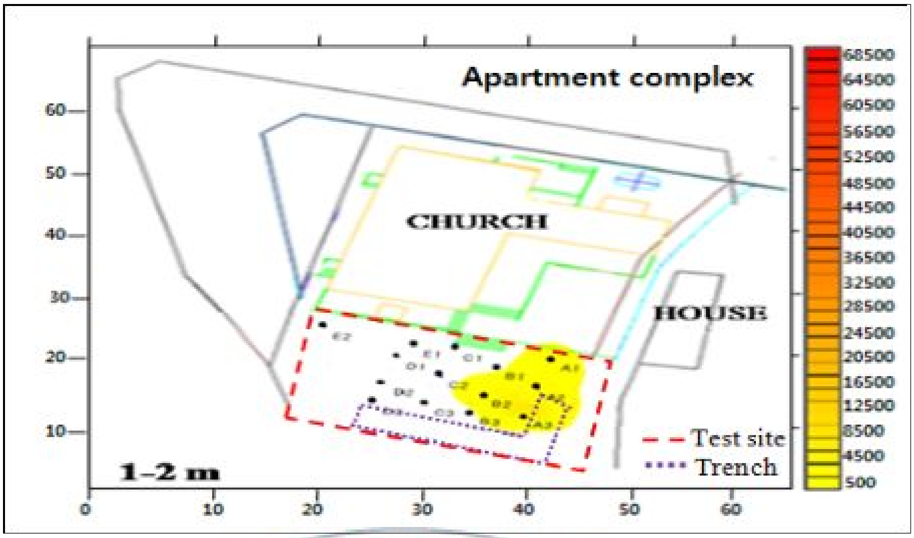


(d)

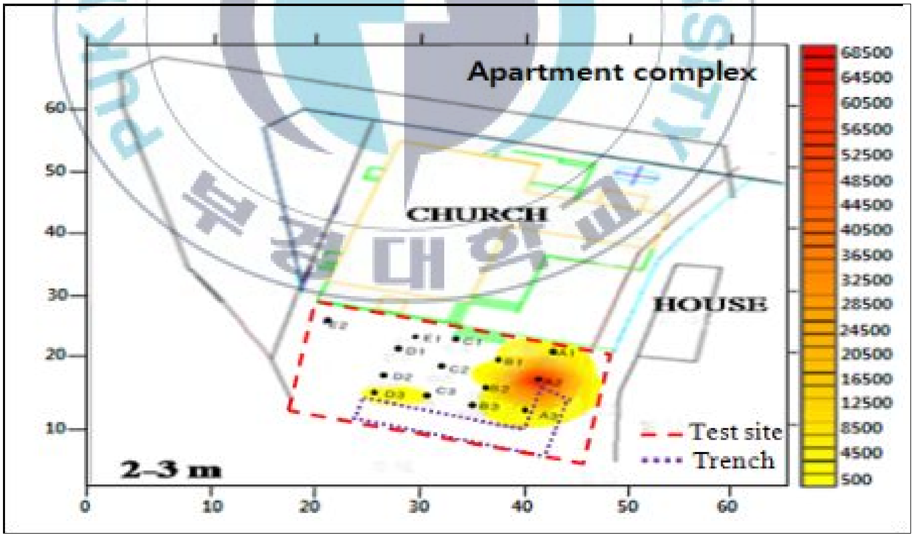


(e)

Fig. 20. Results of TPH concentration analysis of soils taken at different well locations (A, B, C, D and E well) in the site.


Apartment complex
CHURCH
HOUSE
1-2 m
Test site
Trench
E2
E1
D1
C1
B1
A1
D2
C2
B2
A2
D3
C3
B3
A3
0
10
20
30
40
50
60
68500
64500
60500
56500
52500
48500
44500
40500
36500
32500
28500
24500
20500
16500
12500
8500
4500
500

(a)


Apartment complex
CHURCH
HOUSE
2-3 m
Test site
Trench
E2
E1
D1
C1
B1
A1
D2
C2
B2
A2
D3
C3
B3
A3
0
10
20
30
40
50
60
68500
64500
60500
56500
52500
48500
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40500
36500
32500
28500
24500
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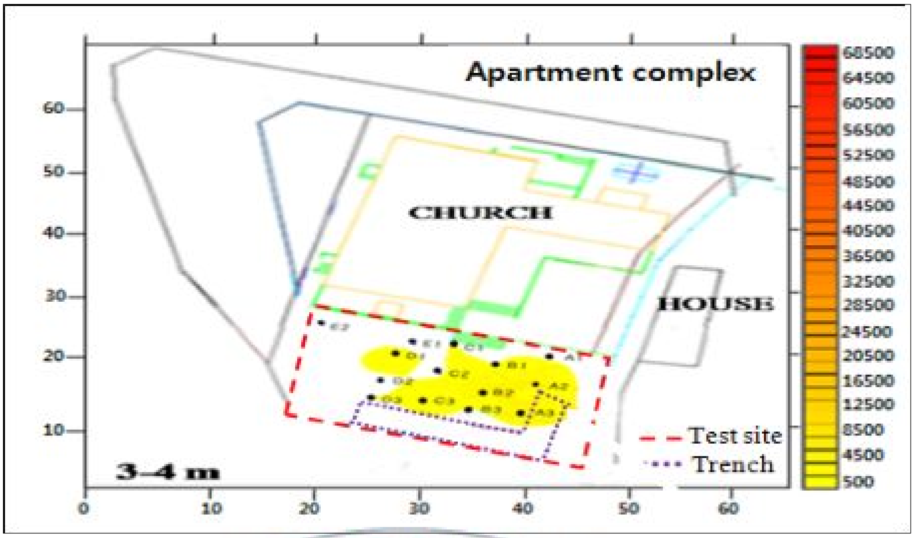
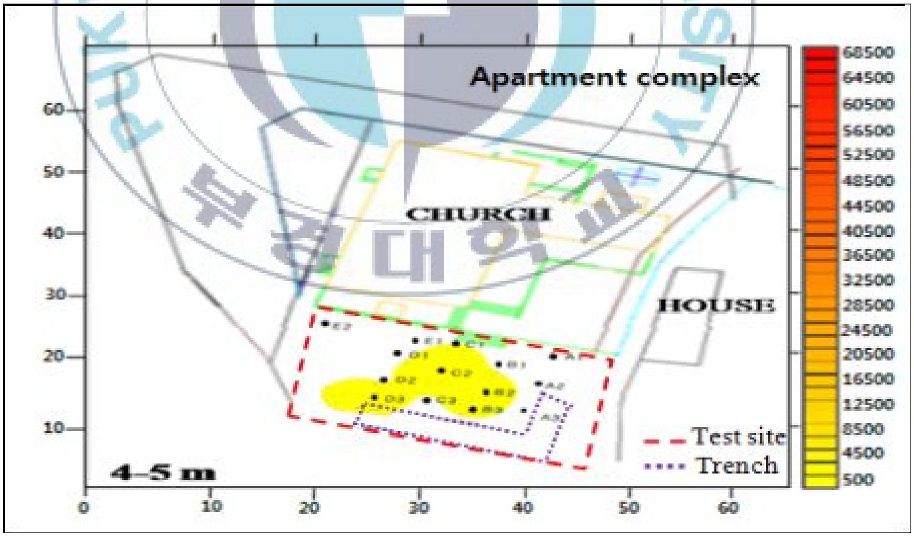
16500
12500
8500
4500
500

(b)


Apartment complex
CHURCH
HOUSE
E2
E1
C1
D1
A1
B1
C2
D2
A2
B2
C3
D3
B3
A3
Test site
Trench
3-4 m
0
10
20
30
40
50
60
68500
64500
60500
56500
52500
48500
44500
40500
36500
32500
28500
24500
20500
16500
12500
8500
4500
500

(c)


Apartment complex
CHURCH
HOUSE
E2
E1
C1
D1
A1
B1
C2
D2
A2
B2
C3
D3
B3
A3
Test site
Trench
4-5 m
0
10
20
30
40
50
60
68500
64500
60500
56500
52500
48500
44500
40500
36500
32500
28500
24500
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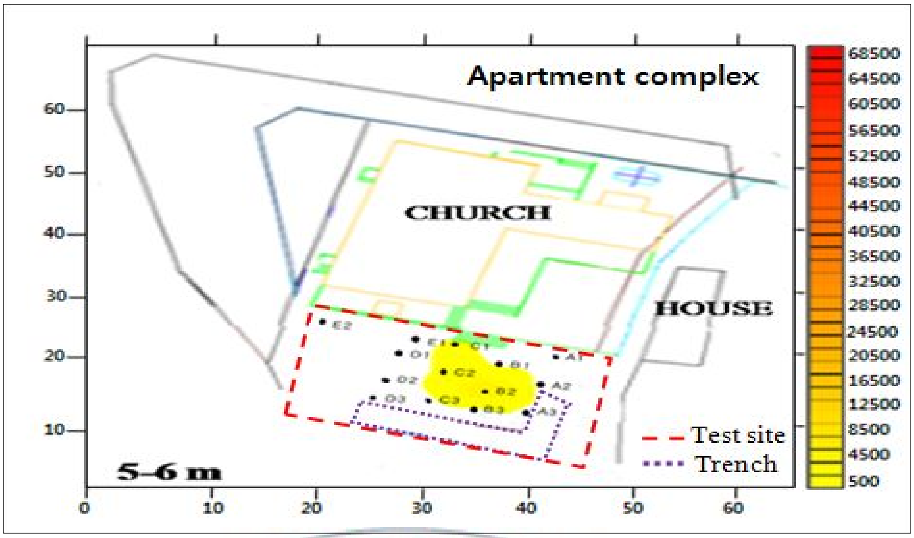
12500
8500
4500
500

(d)



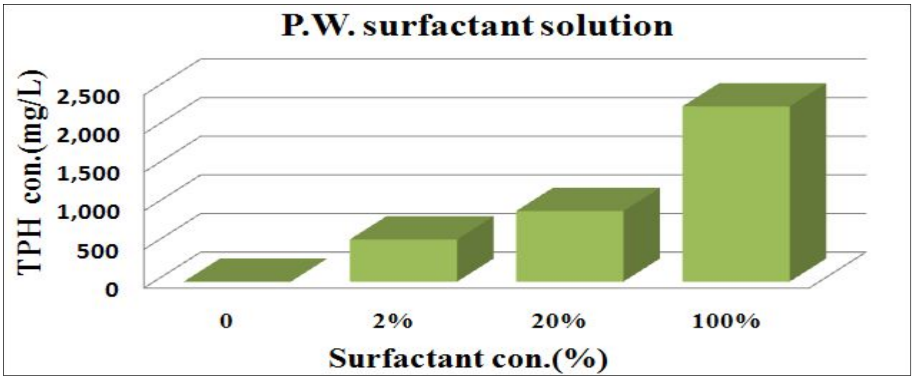
(e)

Fig. 21. TPH contamination distribution map at different depths (a: 1-2 m, b: 2-3 m, c: 3-4 m, d: 4-5 m and e: 5-6 m) in the test site.

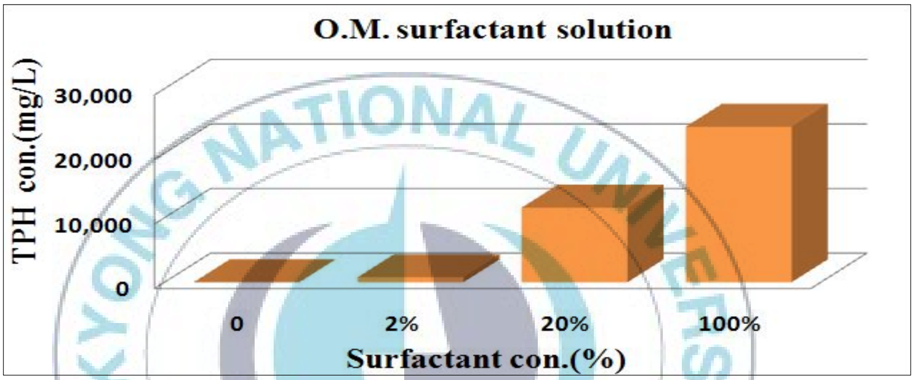
5.2 Results of batch experiments for surfactant solubility to bunker fuel oil

Batch experiments to determine TPH solubility of surfactant solution were performed. Results of solubility experiments for two kinds of surfactant in different concentration were shown in Fig. 22.

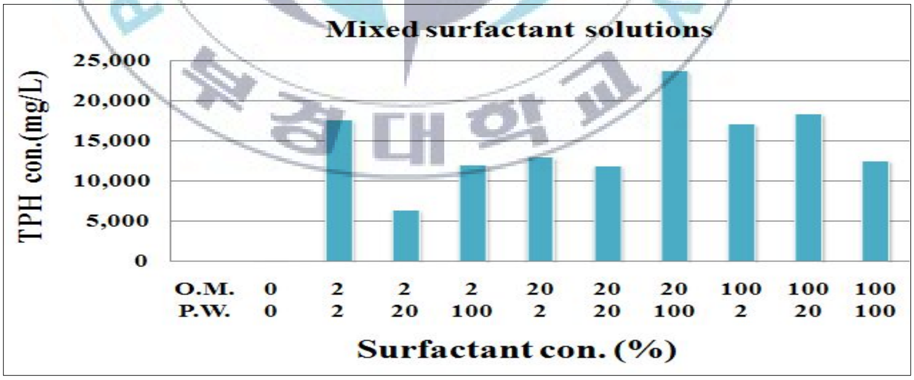
From the results, 100 % of O.M. surfactant solutions had the highest solubility of bunker A and C oil (24,112 mg/L) and 2 % of P.W. surfactant solution had the lowest solubility (547 mg/L). As the surfactant concentration increased in solution, the solubility of bunker A and C oil proportionally increased. In mixed surfactant solutions, their solubilities of the bunker A and C oil were higher than those of single surfactant solution at low surfactant concentration. The solution with O.M. 20 % + P.W. 100 % had very high solubility (23,685 mg/L). From the results, only 2-20 % of mixed surfactant solution could increase the solubility of bunker A and C oil more than 100 times, compared with only water.



(a)



(b)



(c)

Fig. 22. Result of solubility experiment for bunker A and C oil (a: P.W., b: O.M. and c: P.W. + O.M. surfactant solution).

5.3 Results of column experiments for SER (Surfactant Enhanced Remediation) flushing

In column experiments, a genuinely contaminated soil (an average TPH concentration: 8,718 mg/kg) from the site and 0, 10, 20 and 50 % of surfactant solutions were used and their removal efficiencies of TPH for SER flushing were calculated at certain pore volumes of flushing. Fig. 23 shows the results of the residual TPH concentration of soils packed in column after P.W. surfactant flushing. From SER flushing by 10 % of P.W. surfactant solution for 20 pore volumes, TPH removal efficiency was about 50 %. When 50 % of surfactant solution was used for 20 pore volumes, the removal efficiency dramatically increased to 88%, suggesting that SER flushing has a great possibility to remove bunker fuel oils from the contaminated sites.

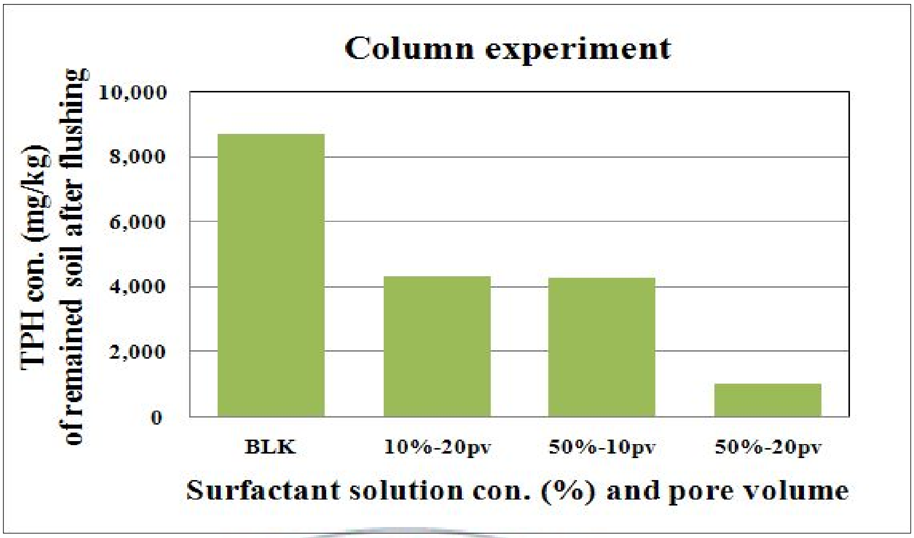
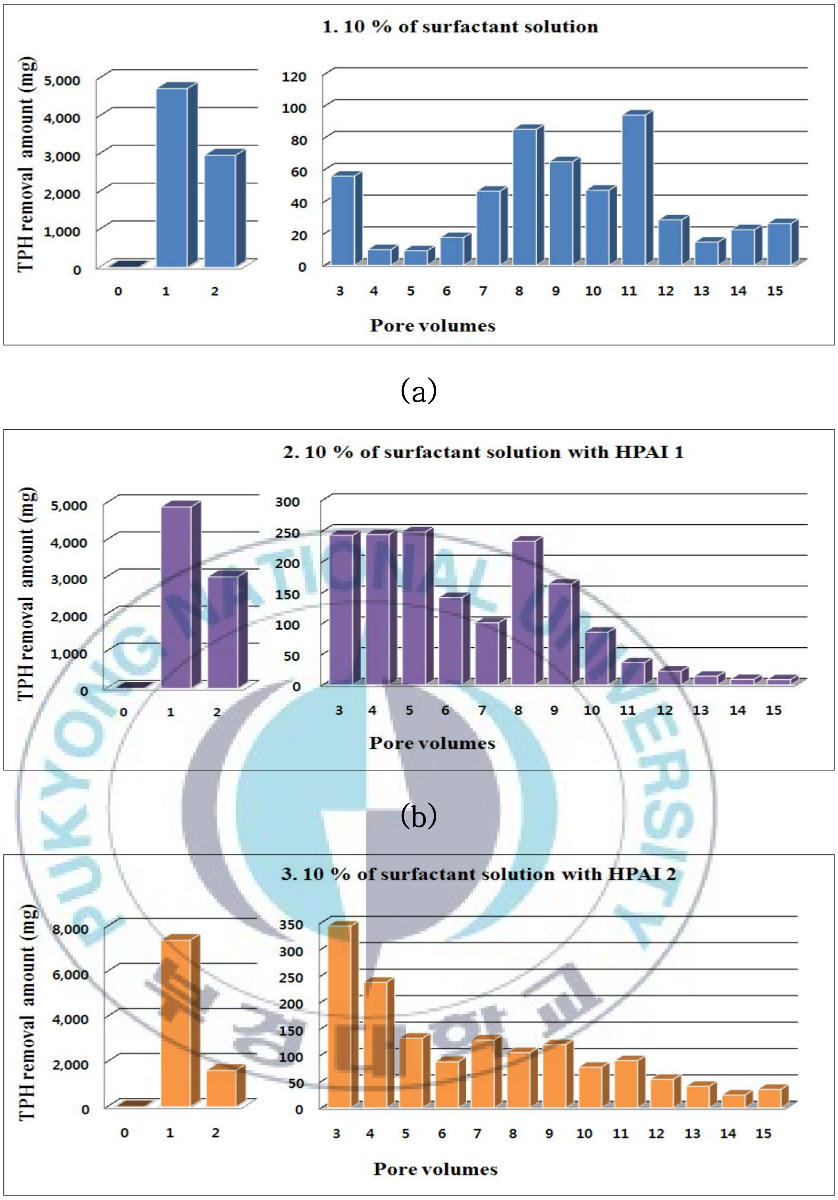


Fig. 23. Result of SER flushing column experiment with various surfactant solutions.

5.4 Results of column experiment of SER flushing coupled with HPAI (high pressure air injection)

To confirm the effect of HPAI on SER flushing, column tests using artificially kerosine contaminated Otawa sand packed column and 10 % of P.W. surfactant solution were performed. For each column test, TPH removal amount extracted from the column at every pore volume flushing were measured to quantify TPH removal efficiency. Results of column experiments were shown in Fig. 24, Fig. 25 and Fig. 26.

For only SER flushing and SER flushing with HPAI-1 (1 kg/cm^2 in air pressure), most of kerosine were removed from the column within 2 pore volumes of SER flushing (Fig. 24). However, for SER flushing with HPAI-2 (2 kg/cm^2 in air pressure), most of TPH were removed with only one pore volume of flushing. SER flushing with HAPI-2 showed the highest TPH removal efficiency of 92 % and the removal efficiency of only SER flushing was about 81 % (Fig. 25). The highest TPH concentration of effluent solution for SER flushing was about 55,790 mg/L, but for SER flushing with HPAI, it were over 167,280 mg/L, suggesting that micro-emulsions, accelerating kerosine mobility in pore spaces of the column, were created during SER flushing with HPAI (Fig. 26). From the results, the air injection pressure of HPAI to maximize TPH removal efficiency of SER flushing should be greater than 2 kg/cm^2.



(a)

(b)

(c)

Fig. 24. Results of SER flushing column experiment with HPAI (a: only SER flushing with 10 % of P.W., b: SER flushing with HPAI-1(1 kg/cm^2), and c: SER flushing with HPAI-2 (2 kg/cm^2)).

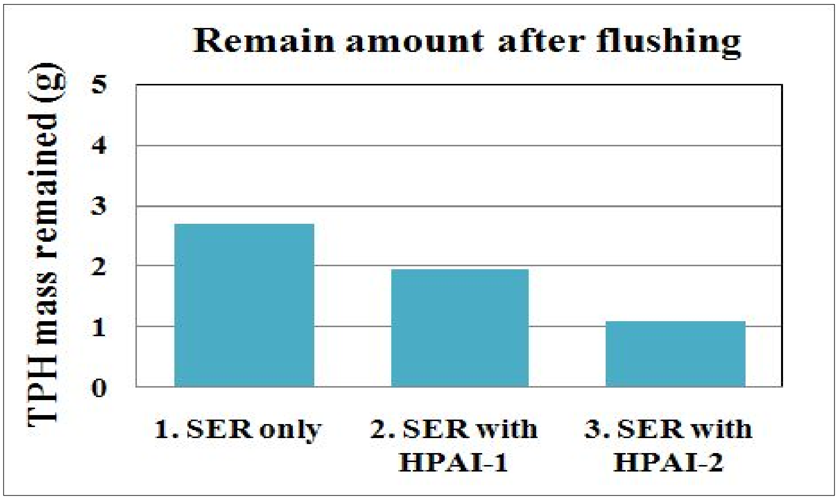
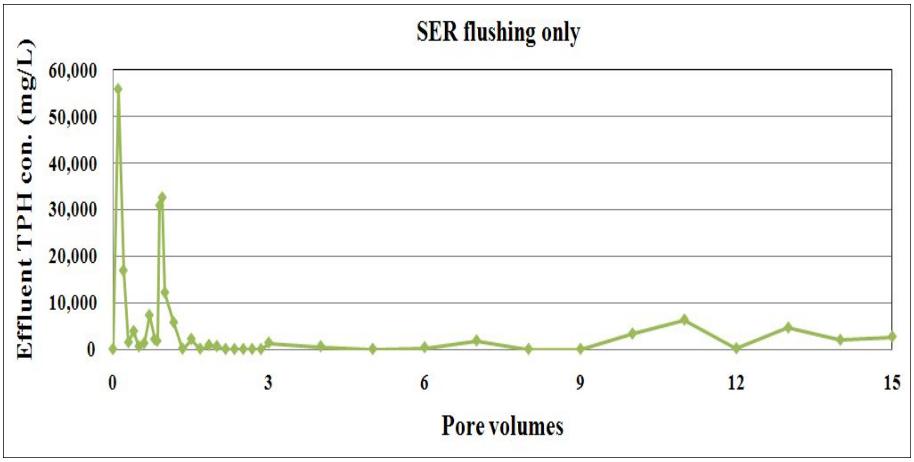
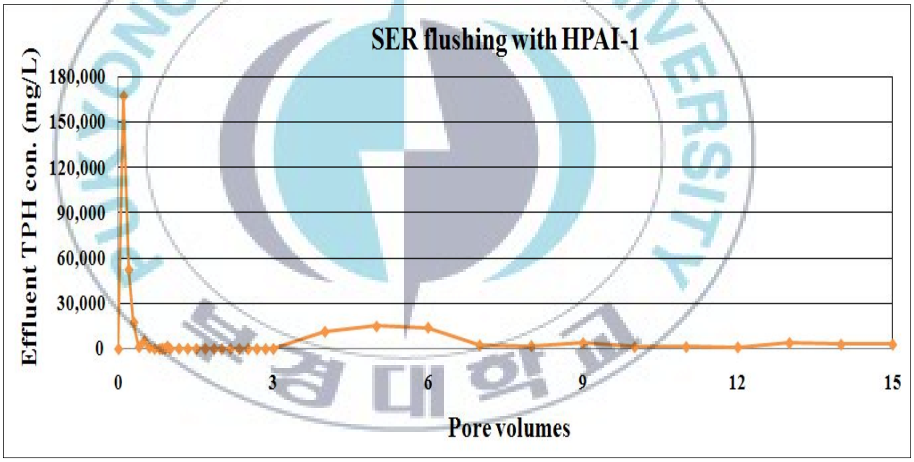


Fig. 25. Total TPH mass remained in column after SER flushing with/without HPAI (SER only, SER with HPAI-1 (1 kg/cm^2), and SER flushing with HPAI-2 (2 kg/cm^2)).



(a)



(b)

Fig. 26. Results of effluent TPH concentration for SER flushing without/with HPAI-1 (1 kg/cm^2) in the column experiments (a: SER flushing only and b: SER flushing with HPAI-1).

5.5 Results of pilot scale field test for SER flushing coupled with HPAI (high pressure air injection)

To remediate the real contaminated site using in-situ SER flushing coupled with HPAI, the pilot scale test was performed. To verify the remediation efficiency of in-situ SER flushing with HPAI, two locations were randomly determined after the flushing (30 days of operation) and soil samples were taken in different depths (1-6 m), which were analyzed on GC to measure TPH remained in the soil. TPH concentrations of soils remained after flushing as location 1 and location 2 were 454 mg/kg and 453 mg/kg, respectively, showing that they were below Korea soil warning limit (500 mg/kg : the treatment tolerance limit at this site) (Fig. 27). From the calculation based on the analysis of TPH concentration in flushed solution at the site was about 3.6 tons and the final TPH removal efficiency of SER flushing with HPAI at the site was about 86%. Results investigated that SER flushing with HPAI successfully remediated the test site for 30 days with 11 L/min of solution injection rate and 25 kg/cm^2 of air injection pressure.

All flushed solution produced from the test site by the in-situ SER flushing with HPAI were treated by the post-treatment system including chemical processes with oil separator. Results of analysis of flushed solution in the storage tank before/after the post-treatment were shown in Table 12. By the post-treatment process, pH of flushed solution became neutral and the concentrations of SS (suspended solid), dissolved organic contents extracted by n-hexane, and fluorine decreased to below Korean discharged water tolerance limit. Heavy metal concentrations (Cd, Cu, As and Pb) and COD (chemical oxygen demand) value of treated soil in the site were similar to those before the treatment. From the results of pilot scale test site remediation, it was investigated that in-situ SER coupled with HPAI is available process to remove bunker fuel oil from the contaminated sites.

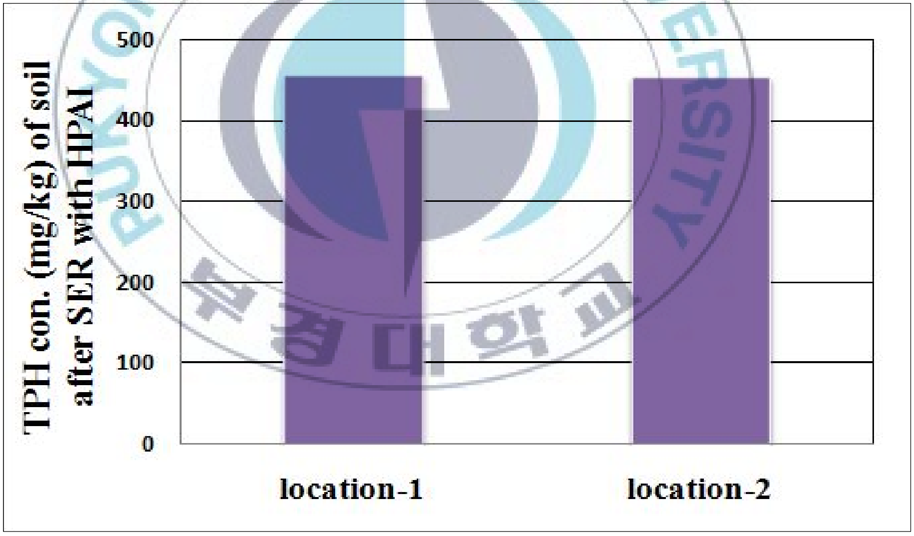


Fig. 27. Result of analysis for TPH concentration of soil in the site after the in-situ SER flushing coupled with HPAI.

Table 12. Result of analysis for flushed solution before/after treatment of solution

Pollutant	Concentration (mg/L)		Korea drained water tolerance limit (mg/L)
	(Before)	(After)	
pH	5.4	6-8	5.8-8.6
COD	9.6	9.6	130
SS	115	50	120
n-H	0.134	0.067	5
Cd	0.031	0.031	0.1
Cu	0.037	0.037	3
As	0.030	0.030	0.5
Pb	0.046	0.046	1
F	301	10	15

CHAPTER VI. CONCLUSIONS

Batch experiments such as the solubility test and SER column test with/without high pressure air injection carried out to yield the parameter for the field scale test. Finally, pilot scale test for SER coupled with the high pressure air injection performed to remediate the real contaminated test site.

The following conclusions of this study were presented:

1. The result of site investigations for the contamination distribution showed that the test site was seriously contaminated (an average TPH concentration: 3,450 mg/kg). From the analysis of 40 soil samples, it was exceeded 6 times of the standard tolerance limit (500 mg/kg). The site has 2-3 m of contamination depths, including 70,162 mg/kg of maximum concentration in 3 m depths of the location-A2.

2. Results of solubility experiment, O.M. surfactant solutions of 100 % has the highest solubility rates (24,112 mg/L) and solubility rate of mixed surfactant solutions (O.M. surfactant solutions of 2 % + P.W surfactant solutions of 2 %) for TPH was 17,532 mg/L. Only 2 - 20 % of surfactant solution could increase TPH solubility more

than 100 times in comparison with only water. As a result, mixed surfactant solutions could be useful for the application of SER over a seriously contaminated conditions than the individual surfactant solution.

3. Results of the continuous column experiments, TPH removal efficiencies using P.W. surfactant solution (concentration : 50 % and 20 pore volumes) were higher than 89 %. In case of 10 % of surfactant solution, showed more than 50 % of TPH removal efficiencies.

4. For SER column experiment coupled with HPAI (high pressure air injection), results indicated that SER with HPAI-2 (10 % of surfactant solution with 2 kg/cm^2 of pressure air jet) showed the highest TPH removal efficiencies of 92 %. All the SER flushing column experiment with 15 pore volumes of 10 % P.W. surfactant solution indicated the removal efficiency of TPH more than 81 %. This experiment result shown that the SER coupled with HPAI indicated the higher TPH removal efficiency than SER alone.

5. During the remediation process, total 190 tons of effluent solution were produced for a day. The result indicated that TPH concentration of both location-1 (454.37 mg/kg) and location-2

(452.69 mg/kg) showed below Korea soil standard tolerance limit of TPH (500 mg/kg). Total 3.6 tons of TPH (about 86 % of the initial TPH) were removed from the test site and two percent surfactant solutions with HPAI were shown to have potential applications for the remediation of bunker fuel contaminated sites.

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고압 공기분사가 포함된 토양세정법을 이용한 실제 유류오염토양 및 지하수 정화

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벙커C유로 오염된 지역(울산광역시 울주군 00번지)의 토양과 지하수 정화를 위해, 고압 공기분사를 적용한 현장원위치(In-Situ) 토양세정 실증시험을 실시하였다. 연구부지는 25년간 기와를 생산한 공장부지로, 공장 폐쇄 후 공장의 난방용 유류를 보관·저장하는 지하탱크(UST)로부터 누출된 벙커C유에 의해 토양 및 지하수 오염이 발생하였다.

오염토양의 평균 TPH 농도는 3449.95 mg/kg 으로 토양오염 우려기준('가' 지역 500 mg/kg)을 6 배 이상을 초과하였다. 실증시험을 위해 자갈과 모래로 이루어진 파일럿 규모의 실증시험 부지(15 m × 19 m × 6 m)를 선정하여 부지 내에 14개의 추출정 및 주입정을 설치하여 세정액을 주입 후 고압의 공기분사를 추가하는 형태로 토양세정을 실시하였다.

본 실증시험에서는 기존의 토양세정법을 적용하는데 가장 문제시 되어왔던 토양 입자 사이의 작은 공극 내를 세정액이 잘 통과할 수 있도록 세정액을 주입 후 일정 시간 동안 고압의 공기를 분사함으로써 공극 내 세정액의 흐름을 활발히 하여 오염물질의 제거 효율을 높이는 방법이 적용

되었다.

파일럿 규모의 현장 실증시험에 적용한 세정액은 국내에서 생산되는 OO생물계면활성제를 사용하였으며, 세정액 및 고압공기분사 주입율은 각각 11 L/min, 25 ㎏/㎠ 이었다. 추출정과 함께 지하수 흐름 방향으로 부지 경계부에 트랜치(2.5 m × 10 m × 6 m)를 설치하여 오염부지를 통과한 세정액을 추출한 후, 유수분리를 통해 배출수 수질 기준치 이하로 처리한 후 방류하였다.

일정한 시간간격으로 샘플링한 폐 세정액은 GC/FID(Hewlett Packard, Agilent 6890) 및 ICP/OES(Perkin elmer, Optima 3300XL)로 TPH 및 중금속 농도를 분석하여 배출 세정액당 오염물질의 제거량을 계산하였다. 실증시험 결과 오염된 부지로부터 약 3.6 ton의 TPH를 제거함으로써, 86 %의 제거 효율을 나타내었으며, 부지 내 잔류토양의 TPH 농도도 기준치 이하로 나타났다.

본 실증시험을 통하여 고압 공기분사를 적용한 현장원위치 토양세정법은 유류로 오염된 지역을 정화하는데 효과적인 처리 방법임을 입증할 수 있었다.

주제어: 현장원위치 토양세정, 계면활성제, 고압 공기분사, 석유계 총 탄화수소

감사의글

먼저 이 논문이 완성되기까지 많은 관심과 격려로 늘 변함없이 따뜻하게 지도해 주신 이민희 교수님께 진심으로 감사드립니다. 바쁘신 가운데 열과 성의로 논문 심사를 해주신 황덕홍 박사님, 최정찬 교수님께도 감사드립니다. 그리고 학과 박맹언 교수님, 정상용 교수님, 박계헌 교수님, 백인성 교수님, 송용선 교수님, 김영석 교수님께도 감사드립니다.

힘들 때 마다 위로와 질책해 주셨던 환경 지질과학과 선 후배님들 (강희철 박사님, 강동환 박사님, 병우선배, 태형선배, 규열선배, 필근선배, 남훈선배, 광민선배 학과사무실에 명진이누나, 정윤 그리고 진혁, 석준, 민주, 오영, 호일, 그리고 동기 상건, 성일, 태영, 문호, 숙주, 민주, 성수형) 께도 감사합니다. 모든 과정을 마치고 마지막을 글로 남기려 하니 대학원 생활하는 동안 베풀지 못하고 받기만 한 점을 반성하게 됩니다. 처음 실험실에 왔을 때 타 대학 출신인 아무것도 모르는 저를 선뜻 받아주신 교수님을 잊을 수 없습니다. 그때는 무작정 열심히 하면 된다고 생각했지만, 시간이 지남에 따라 시련과 역경으로 흔들렸습니다. 그 때 마다 나에게 힘을 준 우리 환토방 식구들 (방장인 현민이형, 끝까지 내 편인 인수누나, 언제나 고마운 애정, 지혜, 세은, 원우, 재정, 지영, 신지, 상종, 민혜, 진영 지금은 취업한 차원이 형, 재연 그리고 실험실에서 하루 12시간 이상을 함께한 민준) 다들 정말 고맙습니다.

그리고 논문에 도움을 주신 (주) 벌켄 사장님과 (주) 큐엔솔루션 사장님, 기기분석실험에 많은 도움을 주신 공실관 류영철 선생님, 정숙이누나, 소라, 수정이누나, 언제나 따뜻하게 격려해주신 정화누나, 우리 수도사 친구들, 정말 감사합니다. 끝으로 내 삶의 이유인 부모님과 믿음직스러운 큰형, 작은형, 형수님, 귀염둥이 수연이 모두 사랑합니다. 이제 졸업을 앞두고 사회를 나가는 문턱에 서니 설레임과 두려움이 앞섭니다. 후회 없는 삶을 살도록 노력하는 사람이 되겠습니다.

감사합니다.

APPENDIX

PUBLICATIONS
(In English & Korean)