

Selective Phase Transfer Technology Enhanced LNAPL and DNAPL Remediation Using Patented Non-Ionic Surface Active Agents

George A. Ivey, B.Sc., CES, CESA, Ivey International Inc.
PO Box 8396 Victoria, British Columbia, Canada V9W 3S1

&

David R. Craft, B.Sc., University of Alberta
10919, 71 Ave. Edmonton, Alberta, Canada T6G 0A2

ABSTRACT

Selective Phase Transfer Technology (SPTT) involves micro-petroleum encapsulation using four mixtures and two processes (in-situ & ex-situ) in the remediation of petroleum contaminated sites. The LNAPL petroleum molecules undergo a phase transfer, micelles encapsulate petroleum at the molecular level, such that it “dissolves” into water, (i.e., in smaller, more mobile units). The complexity of LNAPL compounds has resulted in the development of several SPTT mixtures selectively applicable to specific ranges of LNAPL compounds (i.e. light range gasoline, medium range diesels, and heavy range bunker-C in air, water, soil and LNAPL free phases). The SPTT molecules are highly biodegradable (97% in less than 27 days).

Underground (in-situ) contact between the SPTT mixtures and petroleum compounds are accomplished through injection wells and injection galleries. This results in the transfer of free phase petroleum that is extracted from soil and groundwater via a micelle-encapsulation. Extraction wells are used to recover the “dissolved” in water-petroleum fluid mixture. Further, SPTT reduces the petroleum mass that would otherwise be released through vapor air emissions. Case studies demonstrated that project goals were achieved at 95% of the sites within 18 months¹, and typically within 12 months.

The ex-situ application uses a modified roll-off (30-35 m³) de-watering unit for soil treatment. The contaminated soil is placed in the treatment units, and then partially submerged with the SPTT laden water. The SPTT/water phase is then circulated through the soil bed resulting in rapid treatment in approximately four hours. Case studies demonstrate this to be a portable, scaleable, economic soil treatment method². Two patents were granted in November 2001³ and May 2002⁴ for the mixtures and processes respectively.

1.0 INTRODUCTION

Current site remediation technologies and approaches include the use of sub-surface peroxide injections, bio-remediation, conventional pump and treatment, soil excavation, vapour extraction, air sparging, natural attenuation and risk management, to name but a few. Although these techniques are applied to contaminated sites, many site-specific

conditions (i.e., pH, salinity, hardness, temperature, geology, etc.) must exist for application, and many can only work for a limited type of contamination. Remediation is often lengthy and costly to implement. Selective Phase Transfer Technology is easily implemented for in-situ and ex-situ application, very rapid, works for a wide range of contaminants, and the costs are considerably lower than many alternatives.

The objectives of this paper are three fold. First introduce the reader to the field of non-ionic surface active agents (SAA), secondly illustrate their application for light and dense non-aqueous phase liquid (LNAPL & DNAPL) remediation of air, soil and groundwater contaminant systems. The third objective is to present a new patented remediation technology known by the trade names, Selective Phase Transfer Technology (SPTT™) and Ivey-sol™.

In brief, SPTT involves the micro-encapsulation of chemical petroleum products making them more soluble and mobile in water. The petroleum molecules undergo a phase transfer as encapsulated micelles at a molecular level such that they are dissolved into water as small very mobile units (Figure 1-1). Once dissolved, they are more easily removed from the contaminant system. The Patented Selective Phase Transfer Technology (SPTT™) will be discussed in detail. This will include laboratory and field application results, range of commercial applications, and case studies.

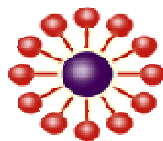


Figure 1-1 Micelle Encapsulated Oil Droplet.

2.0 BACKGROUND INFORMATION

Surface Active Agents (SAA), also known as Phase Transfer Molecules and Surfactant; can dissolve in both water and organic solvents. This ability is largely a function of their physical and chemical characteristics (Figure 2-1). Their molecular structure consists of a hydrophilic (water-loving/miscible) and hydrophobic (water-hating/immiscible) groupings. The hydrophilic groupings are also known as oleophobic (oil-fearing/immiscible), and hydrophobic groupings are also known as oleophilic (oil-liking/miscible). The chemical characteristics and behavior of SAA's are controlled by the functional groups on each molecule. Hence, a broad spectrum of chemical behavior and utility can be observed.

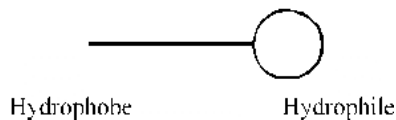


Figure 2-1 Surface Active Agent (SAA) Hydrophilic (water loving) and Hydrophobic (oil-liking) Groupings Shown.

A significant characteristic of SAA is their ability to greatly reduce the surface or interfacial tension between two liquids or a liquid and a solid. This ability extends to very low concentrations of the SAA. Surface tension is the force acting on the surface of a liquid, tending to bring the contained volume into a form having the least superficial area. Quantitatively, it is the force that appears to act across a line of a unit length on the surface (Figure 2-2). This is also known as interfacial force, interfacial tension and surface tension. In the case of water, the water molecules are strongly associated due to their polarity, the oxygen end of the molecule is more negative than the hydrogen end (Figure 2-3). This results in a special bonding attractive force called hydrogen bonding between the oxygen and hydrogen atoms of neighboring water molecules. Consequently, a significant amount of energy would be required to overcome surface tension and or break or loosen a water molecule into the gaseous state.

The surface tension of water is 72-dyne/cm⁵. SAAs can reduce this value to 30 dynes/cm or lower⁵. Under such conditions, SAA molecule overcome the liquid surface tension forces and demonstrate an ability to dissolve compounds that would otherwise not dissolved in a liquid such as water.

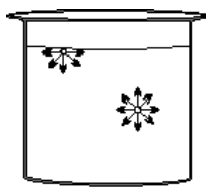


Figure 2-1 Surface Tension, Forces Shown Pulling Water Together.

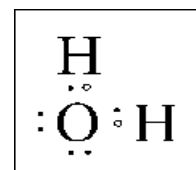


Figure 2-2 Polar Water Molecule

There are four main types or classes of SAA, which are primarily based on their hydrophilic groupings present. These include:

- Anionic:** They have one or more negatively charged groupings. They have very good detergent ability and hence are commonly used as laundry detergent.
- Cationic:** They have one or more positively charged groupings. They typically have poor detergency, but are well suited for use as germicides, fabric softeners, and emulsifiers.
- Non-ionic:** As their name implies, they have no ionic constituents or groupings. They are the largest single group of SAA and have a correspondingly wide range of chemical characteristics and application. SPTT mixtures, which have the unique ability to selectively dissolve LNAPL, DNAPL, polycyclic aromatic hydrocarbons (PAH's), trichloroethane (TCE), perchloroethylene PCE and other similar petroleum products.
- Amphoteric:** Which contains both anionic and cationic groupings have the characteristics of both anionic and cationic SAA. They work well at neutral pH and are found in products such as hair shampoo, skin cleaners, and carpet shampoo.

3.0 MECHANISM

When SAA are dissolved or dispersed in liquids, they are preferentially absorbed at an interface. This unique characteristic gives rise to a variety of physical-chemical properties of particular interest. As indicated above, the SAA molecules have a hydrophilic grouping with an attraction for the polar water surfaces. This grouping will ensure its solubility in water. Once a non-ionic SAA is dissolved, its hydrophilic grouping associates with the water at one or more of the oxygen atoms present in the said grouping (Figure 3-1). The hydrophobic groups aggregate within each other. When the concentration of the surfactant is raised micelles will form. This concentration is known as the critical micelle concentration (CMC). The SAA molecules align themselves with the water surface. The hydrophilic groups are outward toward the water and hydrophobic groups are squeezed inward away from the water (Figure 3-2). Because of this chemical behavior to reorient at a surface, the SAA aggregates as a function of the concentration, micelles will form once the CMC is met.

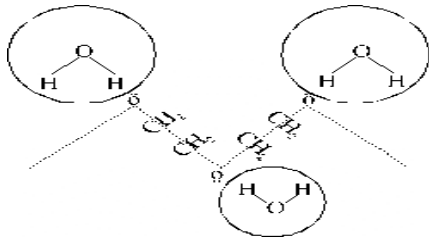


Figure 3-1 SAA Hydrophilic Interaction With Polar Water Molecule

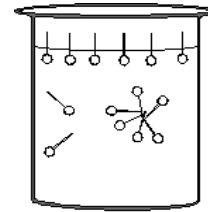


Figure 3-2 Alignment At Surface and Squeezed In Water Solution

The hydrophobic (water-attracted) groups on SAA may align themselves on non-polar molecular surfaces, such as those commonly found in petroleum products. The SAA will aggregate around the oil molecules, and form a micelle, which will dissolve the oil (non-polar) phase in the water (polar) phase. Through this mechanism, lift and remove oils from soil and or dissolve free petroleum product into the water phase (Figure 3-3).

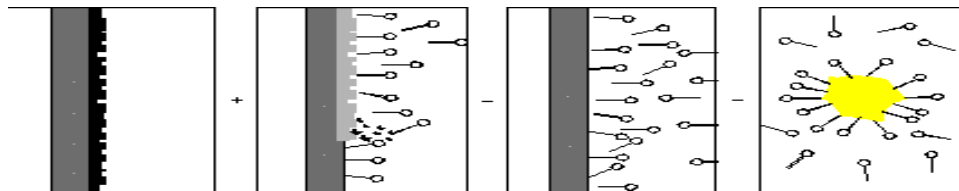


Figure 3-3 SAA Interaction With Oil On A Surface With Micelle Encapsulated Of Oil Droplet

This mechanism can be described as follows:

- a) Oil / petroleum product is absorbed on a soil grain. Water alone will not remove it from the soil. This is a function of the hydrophobic characteristics of the oil, which repels the water at its surface.

- b) With the addition of SAA molecules, the hydrophobic grouping is repelled by the water but attracted to the oil in the soil. At the same time, the hydrophilic grouping is attracted to the water molecules.
- c) These opposing forces loosen the oil from the surface of the soil grain and suspend it in the water phase. Once dissolved, the suspended oil is easily recovered and removed from water phase.

Emulsions can be described as either oil droplets suspended or dissolved in water, or water suspended or dissolved in oil or a mixture of both. It is the selection of the SAA and their order of addition that will dictate the type of emulsion that can be established, the concentration of SAA required and the range of utility. Solubilization is closely related to emulsification. As the size of the emulsified oil droplets become smaller, a condition is achieved where the droplet and the micelle are similar in size. Once this condition is achieved, the oil droplet can be described as being dissolved in solution as its chemical behavior and related properties will support this⁵.

To establish a micelle, the CMC of the SAA must be present⁶. For certain non-ionic SAA, such as those present in SPTT mixtures, the oil products are dissolved with SPTT mixture concentrations well below the CMC⁷. This procedure allows the SAA to aggregate around the petroleum molecule and substantially increase its solubility in water. This unique feature allows for the rapid and cost effective removal of oil products from the environment.

4.0 SELECTIVE PHASE TRANSFER TECHNOLOGY (SPTT™)

Selective Phase Transfer Technology, as outlined in Section 1.0, is a fully patented technology. The technology was developed between 1993 and 1998. This involved extensive collaboration with local University staff coupled with on-going field-testing. The result of the five-year effort gave rise to the development of two patented processes (in-situ and ex-situ) and four-patented mixtures^{3,4}. The SPTT mixtures are comprised of highly specific non-ionic surface-active agents. These specialized mixtures permitted the selective dissolving of LNAPL, DNAPL, PAH, TCE, PCE and other related organic compounds in water^{2,8}. The results achieved during laboratory research and field-testing proved to be an effective solution for air, soil and groundwater remediation. This section will discuss technology from an applied perspective, introducing supportive technical reference information where applicable.

4.1 TECHNOLOGY GENERAL FACTS

Some general facts are listed below regarding the technology. These are based on field performance results, laboratory testing and findings, client and regulatory feedback and work completed by others^{2,3,4,5,6,9,10,11,12}.

- Application of SPTT to petroleum contamination is 75% faster than pump and treat approaches;
- 90-95% of contaminated site are cleaned-up in less than 18 months;
- Average clean-up period for most small to medium sized sites is less than 12 months;
- Reviewed and approved for use in Canada (Provincial Departments of Environment) and USA (State Department of Environmental Protection);
- Mixtures are highly biodegradable (97% in less than 27 days). Hence no persistence in environment application;
- Generally regarded as non-toxic and safe for both land-based (in-situ & ex-situ) and off-shore spill applications;
- Reduces observed volatile organic vapour concentrations emanating from contaminated sites where technology is used;
- Application does not hinder performance of groundwater pump and treat systems.
- Can be used in conjunction with other remediation technologies;
- Not affected by salinity, hardness, pH, contaminant types and or concentrations.
- Does not cause matrix (masking) effect on hydrocarbon analysis (i.e., Solvent Extraction/GC-FID, Purge and Trap, GC-MS, or GC-FID)

4.2 IN-SITU APPLICATION

In-situ application of the technology is applicable air, soil and groundwater LNAPL and DNAPL contamination³. Once the site has been investigated and site conditions (hydrogeology, contaminant plume delineation, geology) are know, an application approach for SPTT can be developed (Figure 4-1). Typically, injection galleries (IG) and or injection wells (IW) are installed across the site to permit the introduction of the SPTT mixtures. These are typically constructed using PVC piping (diameter 100-mm / 4 inch) in a bed of porous/crushed rock. Once these mixtures are introduced they are flushed with a pre-set volume of water creating hydraulic-head to drive the mixture through the soil matrix making what is termed “effective contact” with the contamination. Once contacted, the contaminants are microencapsulated and liberated from the soil matrix (unsaturated zone) and dissolved into the groundwater table. Once dissolved, they are in a mobile form and rapidly recovered for treatment at an extraction well (recovery-well) on-site. If free-floating product is present on the surface of the groundwater, this will be dissolved and recovered at a near-by extraction well.

A special application for this technology has been to clean up contamination located under building foundations. Typically, most efforts to clean up contamination under a foundation are overshadowed by the potential structural failure and (Figure 4-1). SPTT has proven to be a useful alternative to soil excavation in this case. The drilling of IWs through the basement floor and injection of SPTT mixtures at these points has proven to be a successful alternative to excavation.

During SPTT treatment, any organic vapors emitting from the sub-surface typically diminish in concentration rapidly². The SPTT through their interaction and encapsulation of the potential vapour molecules, reduce their effective vapour pressure hindering their ability to become a gas.

SPTT mixtures are not negatively affected by metals, hardness, salinity, pH, contaminant concentration, and/or type of organic contamination. The range of soil types that have been successfully treated have included, silty sand to permeable till ($K = 1 \times 10^{-5}$ cm/sec) to sand and gravel ($K = 1 \times 10^{-3}$ cm/sec)².

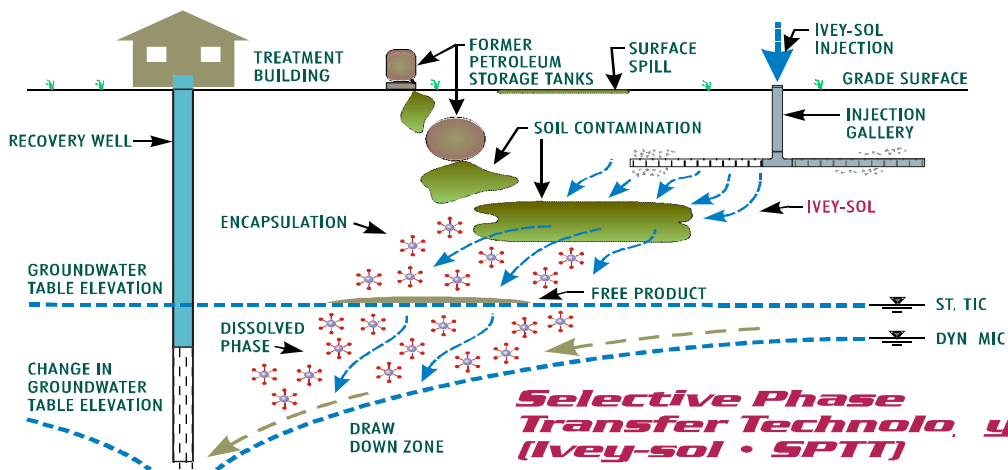


Figure 4-1 In-situ SPTT Injection, Contaminant Encapsulation, Solubilization and Removal At Recover Well On-site.

4.3 RESPONSE PROFILE

During in-situ treatment, the dissolved contaminant concentrations will increase in response to each SPTT injection. The term for this response, both in time and concentration over the life of the project, is referred to as the “Response Profile”. All sites exhibit this response profile phenomenon. The peaks and valleys in contaminant concentration are observed in direct response to a series of injections over time. The response profiles, although similar for every site, vary both in time and concentration. Following each injection a spike in contaminant concentration is observed. The intensity of each subsequent spike in concentration tends to decay as the original contaminate mass is being sequentially removed as site reclamation is realized (Figure 4-2). The observed variations from site to site are a function of numerous variables that include: site geology, hydrogeology, contaminant type and concentration, location and number of IGs and IWs, and pump and treat system specifications.

SPTT injections undertaken during the first three months use volumes and concentrations slightly lower than site conditions information would suggest. This approach, termed the “Initial Conservative Approach”, has proven an effective approach for interpretation of site conditions in response to SPTT applications. This interpretive period allows for

verification of adequate containment and control, and permit minor modification of the SPTT application approach. This in turn leads to expedited treatment in a managed and timely manner. This Initial Conservative Approach is well embraced by project stakeholders understanding the future benefits that this will generate to the project. SPTT injections are typically undertaken once per month until an appreciable portion of the original contaminant mass has been removed from the site, after which more frequent injections can be undertaken.

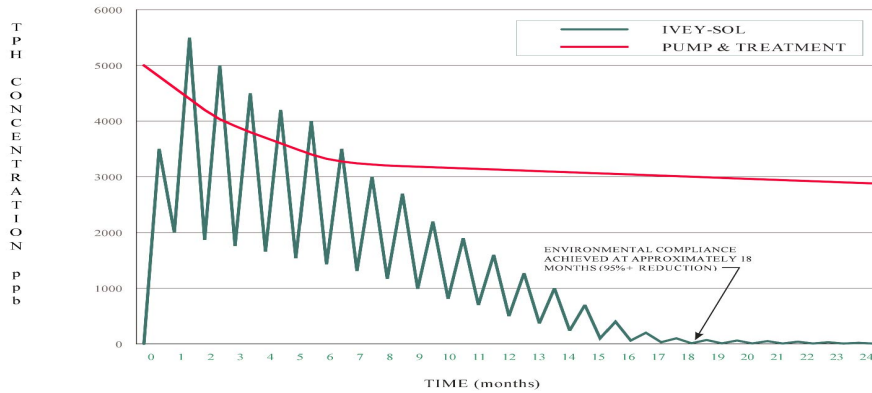


Figure 4-2 Concentration Response Profile At Recovery Wells Following SPTT Injections Over Time

4.4 ENCAPSULATION EFFECTS

Most SAAs must be present at a critical concentration in solution before they can form stable micelles, known as the critical micelle concentration (CMC). The molecules in the SPTT mixture are unique in that they can aggregate to organic molecules (i.e., partially encapsulate) and still render them soluble in water at concentrations well below the CMC (Figure 4-3). This is a function of the chemical characteristics of each SAA molecule in the SPTT mixtures. During site remediation, partial encapsulation of organic contaminants is dominant^{6,7}.

Encapsulation Effects

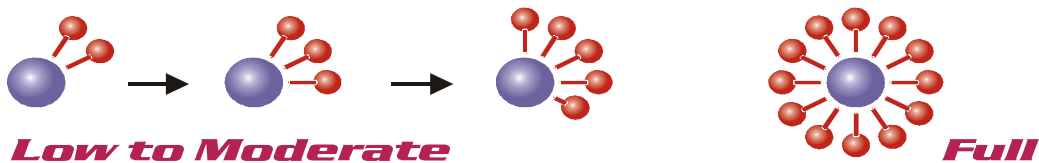


Figure 4-3 SPTT Aggregation On Oil Droplet Well Below The Critical Micelle Concentration Dissolving The Contaminant.

The SPTT concentrations used during site clean up result in a very low SPTT concentration in the influent water entering the groundwater treatment system on site.

Hence, this guards against negative effects on the performance and operation of the treatment systems, such as exceeding the treatment capacity, that could potentially be experienced with other SAA that require CMC to be effective. This has been verified during field applications.

4.5 SELECTIVITY AND RANGE OF APPLICATION

Selective micelle encapsulation is a unique quality of SPTT. This is a function of the hydrophobic (oil attracted) groupings on each SAA molecule that are attracted to organic molecules. As the functional hydrophobic groupings are changed, the type and/or class of organic molecules each SAA will have an affinity for aggregating and forming micelles will change. Hence, selectivity was achieved with SPTT through formulating mixtures of SAAs that had a desired affinity for the organic compounds of interest. With selectivity, formulations of SAAs were developed that had specific applications for specific type of organic contaminants such as gasoline, diesel, motor oil, bunker-C, PAHs, TCE, PCE, and CTET (Figure 4-4).

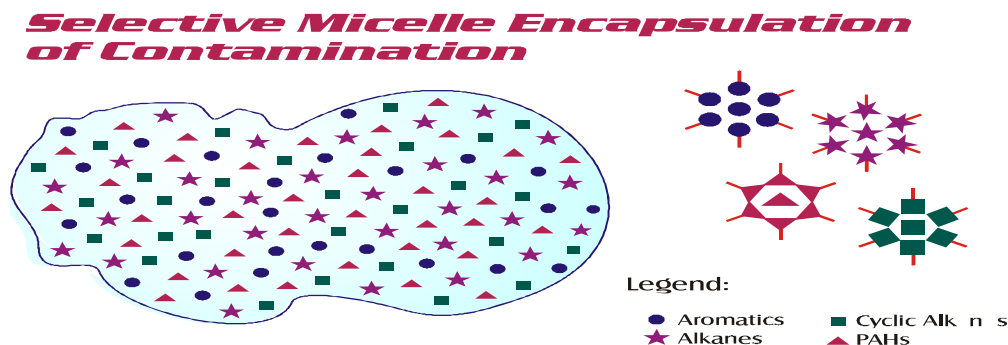


Figure 4-4 SPTT Selective Micelle Encapsulation A Function of Hydrophobic Groupings.

The four primary SPTT mixtures were formulated to remediate specific types and classes of LNAPL and DNAPL organic contamination. The original research focused on LNAPLs but was expanded to include PAHs and selected DNAPL compounds. A partial summary of the selectivity achieved for the primary SPTT mixtures are displayed in Table 4-1. In addition, this table also lists some of the dissolve concentrations achieved for selected organic contaminants in water^{6,7,13,14}.

Co-SAA effects were realized during the testing development of the SPTT. That is to say, in the presence of certain organic contaminants, the total contaminant-encapsulation capacity of the SPTT mixtures were greater than a sum of the contaminant-encapsulation capacities of the first, second, third and additional SAA components alone in the aqueous carrier. Co-SAA effects have lead to the development of selective SPTT mixture for the three main petroleum hydrocarbon ranges. Specifically; low range C₆-C₁₁ (i.e., gasoline), medium range C₁₁ -C₂₁ (i.e., fuel oil and diesel), and heavy range C₂₁₊ range (i.e., bunker-C).

SPTT mixtures have a wide range of commercial applications based on the laboratory and field results gathered to date^{2,6}. This would include, but not be limited to: LNAPL and DNAPL air, soil and groundwater remediation, degreaser, oil tank cleaning, enhanced oil recovery (oil-sand/oil-shale), off-shore oil spill dispersant, shoreline spill clean-up, medical applications, mineral floatation, industrial chemistry, odor removal/control, and stain removal.

Table 4-1 Application and Selectivity

Organic Contaminant	SPTT 101	SPTT 102	SPTT 103	SPTT 104	Concentration Dissolved In Water (ppb / ug/l)
C ₆ - C ₁₁	✓				> 700,000
C ₁₁ -C ₂₁)		✓			> 3,000,000
C ₂₁ -C ₃₅₊			✓		> 30,000,000
PAHs				✓	350,000
TCE				✓	25+Fold Increase
PCE				✓	25+Fold Increase
CTET				✓	25+Fold Increase
Aromatic: BTEX	✓				46,300-50,500
Aliphatic		✓	✓		9,100,000
Gasoline					760,000
Brake Fluid		✓			12,050,000
15w40 MotorOil		✓			3,020,000
Bunker C			✓		31,150,000

4.6 EX-SITU APPLICATION

An ex-situ STPP methodology was developed and patented for the treatment of excavated contaminated soils^{4,15}. The process uses a patented roll off de-watering unit (Figure 4-5). These are termed Ex-site Treatment Units (ETUs). Each unit can treat approximately 2 cycles of 30 cubic yards of contaminated soil per day. This translates to between 95 and 115 tons per day per unit. Advantages of this approach are that it is scalable to the quantity of contaminated soil to be treated, and soil can be treated on-site at the source, and is often cheaper than off-site transportation and disposal. This process is effective for a wide range of soil types with permeability between $K = 1 \times 10^{-3}$ and 1×10^{-5} cm/sec.

For a typical site application, two ETUs are placed side by side with approximately 3 meters of separation. Each unit is equipped with a high capacity transfer pump and related hosing and equipment. The contaminated soil, if stock piled, is referred to as the "Source Materials". It is transported and loaded into each ETU using heavy equipment operated by the environmental contractor. Once the ETU is loaded to capacity, it is flooded to approximately 65% to 80% saturation with a mixture of water and the required SPTTTM. The concentration of the STPP mixture is a function of the "Source Material" contamination levels and the cleanup objective for the project.

Soil treatment takes between 4 to 6 hours. The water/SPTT mixture is circulated through the soil bed allowing for the liberation of the petroleum hydrocarbons, which are encapsulated and dissolved into the water phase. Once completed, the water is drained off



easily and rapidly as the treatment units were designed for high rate de-watering¹⁵. The water can be treated directly or stored on-site for latter treatment.

Figure 4-5 Ex-situ Treatment Unit

The treatment units are dumped and the treated soil is placed in a treated soil stockpile. Once dumped, the treatment units are loaded for the next treatment cycle. This treated soil stockpile is referred to as the “Holding Pile”. Field sampling and petroleum analysis are conducted as per regulatory requirements to verify treatment objectives were achieved. Samples are subjected to off-site third part laboratory analysis. Once the soil has been verified “cleaned” to the Project Cleanup Objectives it is referred to as “Treated Material”. The “Treated Material” may be moved to a separate location on-site and/or transported to an off-site location in accordance with the Project re-use and/or post handling measures.

5.0 CONCLUSION

Selective Phase Transfer Technology has a very wide range of application for LNAPL and DNAPL organic contaminants. With in-situ to ex-situ remediation alternatives, this technology can often prove more suitable than alternative technologies for a given site and contamination. SPTT is advantageous in that it is not significantly affected by environmental factors that negatively affect other technologies (i.e., pH change, high salinity, water hardness, temperature variation, dissolves metals, reduction-oxidation potentials, geology, multiple contaminants and high contamination levels).

With favourable environmental and human health testing results and being highly biodegradable (97% in <27days), make this one of the most environmental friendly technologies available. This coupled performance data showing > 95 % of site being cleaned up in less than 18 months, with many small sites completed in < 12 months make this a versatile, rapid and cost saving alternative for remediation.

ACKNOWLEDGEMENTS

A special thanks and deepest of appreciation for the following individuals who supported the development of this technology over the years! Thanks to: Luc Bernard, M.Corey, David Craft, D.Gonyea, Julie Goulet, Richard Ivey, Mary MacLeod, David MaGee, See Hua Tan, Mario Theriault, Roger Snoden, Wolfgang Steffie, D.Smith, James Tong, and Paul Wierbicki.

REFERENCE LIST

1. Snoden, R, A Better way To Clean Up Soil, *Canadian Insurance*, Nov.1998.
2. Ivey,G.A., *Case Studies-Field Applications LNAPL and DNAPL Site Remediation*, 1993-2002)
3. Ivey,G.A., *Air, Soil and Groundwater Remedial Compositions*, 1998.
4. Ivey,G.A., *Air, Soil and Groundwater Remedial Methods*, 2001.
5. Kiwi Web, Chemistry and New Zealand, (www.chemistry.co.nz)
6. Craft,D., *Ivey-sol Phase Transfer Technology Final Report*, August 1998.
7. Kansa, A., *Surfactant Enhanced Solubilization and Mobilisation of Polycyclic Aromatic Hydrocarbons*, May 21, 1997.
8. Smith,J.A., Imbrigiotta, T.E., University of Virginia, US Geological Survey, *Effects of pH Change and Surfactant on Desorption Rate of Trichloroethylene (TCE) From Natural Soil to Water*, 1997.
9. Bunton, C.A., Foroudian, H.J., Gillitt, N.D.,and Whiddon, C.R., *Dephosphoryation and Aromatic Nucleophilic Substitution In Non-ionic Micelles. The Importance of Substrate Location*, p.946-954, 1998.
10. Ivey, G.A., MaGee, D., *Formation and Evaluation of Intermediates Products Through Microbial Degradation of Hydrocarbons*, June 1993.
11. Tan, S.H., *Evaluation of Matrix effect of SPTT Mixture to Hydrocarbon Analysis*, August 1999.
12. Buchanon, R.D., *LC50 Testing of SPTT Mixtures, Rainbow Trout and Daphnia Magna Bioassay Report*, July 1999.
13. Craft, D., *A Study of Hydrocarbon Emulsion In Surfactants and its Analytical Implications*, March 1998.
14. Laaksonen, L., Center for Scientific Computing Finland, *Molecular Dynamic Simulations of the Water/Octanoate Interface in the Presence of Micelles*, 1993.
15. Harris, R., *De-watering Separation Technology* (US Patents 5,670,039, and 5,830,353)