University of Alberta

Remediation of Bitumen-Contaminated Sand Grains: Development of a Protocol for Washing Performance Evaluation

by

Farnaz Mani

A thesis submitted to the Faculty of Graduate Studies and Research
in partial fulfilment of the requirements for the degree of

Master of Science

Department of Chemical & Material Engineering

Spring 2010
Edmonton, Alberta

Examining Committee

Dr. Tony Yeung (Supervisor), Chemical and Materials Engineering

Dr. Qi Liu, Chemical and Materials Engineering

Dr. Yang Liu, Civil and Environmental Engineering

Dedication

This thesis is dedicated to my beloved parents, who supported me all the way since the beginning of my studies and offered me unconditional love throughout my life. I am always in their debt for their invaluable advice and inspiration.

Abstract

In the development of a non-aqueous bitumen extraction process, a major obstacle is solvent loss due to hydrocarbon attachment to the reject sand grains. A proposed solution to this problem is to wash (i.e. remediate) the oil-contaminated sand grains with water and surfactants. This research is focused on developing a protocol to evaluate the performance of particular surfactant types and water chemistry; emphasis was placed on using minimal amounts of water to recover the residual oil. To start, a series of jar tests were conducted (using heptane and hexadecane as solvents) to study the phase behaviours of oil-water-surfactant ternary systems. This was followed by the development of a new washing protocol for the purpose of evaluating remediation performance. Finally, the correlation between overall remediation performance and the oil-water interfacial tension was discussed.

Acknowledgements

I would like to thank God for giving me the strength and hope to accomplish this research, for I strongly believe ” No matter how steep the mountain, the Lord is going to climb it with you,” Helen Steiner Rice (1900 − 1981).

From the formative stages of this thesis, to the final draft, I owe an immense debt of gratitude to my supervisor, Dr. Tony Yeung for his precious advice and careful guidance. Without his friendly supervision, generous encouragement and patient guidance, this thesis would have never been written.

I would also like to express my deep gratitude to dear Nima who supported me all the way throughout the course of this thesis, and helped me stand up and start again when I was frustrated. He has been a great source of motivation and inspiration.

For all her valuable assistance and training towards my research, a special thanks as well to Dr. Kavithaa Loganathan.

Finally, I would be remiss without mentioning my sister, Farnoosh, whose extreme inspiration and sacrifice will be always remembered.

Contents

List of Tables

List of Figures

Nomenclature

amu	Atomic Mass Unit
AOT	Aerosol-OT
ATF	Automatic Transmission Fluid
CMC	Critical Micelle Concentration
C_7	Heptane
C_{16}	Hexadecane
$d-b$	Diluted Bitumen
EOR	Enhanced Oil Recovery
HOC	Hydrophobic Organic Compounds
IFT	Interfacial Tension
$NAPL$	Non-Aqueous Phase Liquid
$PCBs$	Polychlorinated Biphenyls
RF	Remediation Factor
THF	Tetrahydrofuran
TCE	Trichloroethylene
WOR	Water-to-Oil Ratio

Chapter 1

Introduction

The oil sand deposits in Alberta is one of the largest hydrocarbon reserves in the world. Indeed, this province has far more oil than all $OPEC$ countries combined. The recoverable portion of Alberta's oil sands (i.e. using currently known technology) constitutes the world's second largest reserve (the first being that in Saudi Arabia). While the Alberta resource had long been known, the first production started only in 1967. Crude oil price and demand have increased during recent years, making the production of synthetic crude oil from oil sands very profitable. As a result, production of crude oil from Alberta's Athabasca oil sand deposits has become a huge industry in Canada. Internationally, the economic potential of the resource has also been recognized. According to the National Energy Board of Canada, oil sands processing is expected to more than double by 2015. Growth in global oil demand implies that oil sands output will increase. As the industry attempts to take advantage of this situation, significant challenges must be overcome, including sharply increasing natural gas prices, capital cost overruns and environmental issues.

At present, there are two major methods of extracting bitumen[1] from the oil sands.

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[1] Bitumen is an extra heavy oil that is abundant in the Athabasca oil sands

Three quarters of the total bitumen production is by open pit mining, which is more suitable for shallow formations. The remaining one quarter is produced by in situ operation, which is a technology that targets bitumen found in deeper formations.

Currently, open pit mining is the major method of bitumen extraction. Bitumen recovery from mined oil sands is achieved via a *water-based* extraction process. This technology proceeds as follows: Mined oil sand ore is first crushed and ”slurried” in warm water. Mechanical energy in the form of agitation and/or pipeline transport is then provided to promote detachment of bitumen from the sand grains. Following this step, the slurry is pumped to the extraction unit into large water-filled settling vessels where separation of bitumen from the sand is achieved by a flotation process. In addition to problems with high clay contents which may lead to poor recovery and oil losses to the tailings stream, water and energy consumption are main concerns of the water-based extraction process. Apart from economic issues related to high energy demand, huge water consumption in the current extraction process can result in the very serious environmental problems. To produce each barrel of bitumen, the water requirement for oil sands projects ranges between 2.5 to 4.0 barrels [1]. The following are the highest water demands in the current oil sands extraction process. An in situ facility requires fresh water:

- to generate steam and for various utility functions throughout the plant;
- to separate the bitumen from sand and hydrotransport the bitumen slurry;

The SAGD (Steam Assisted Gravity Drainage) process also requires large volumes of water to operate. A permanent loss of water to SAGD and in situ operation is estimated at one barrel of water for every barrel of oil produced. Although in SAGD the majority of water consumed - about $90\ \%$ - is from recycled water, it stills needs large amount of freshwater [2].

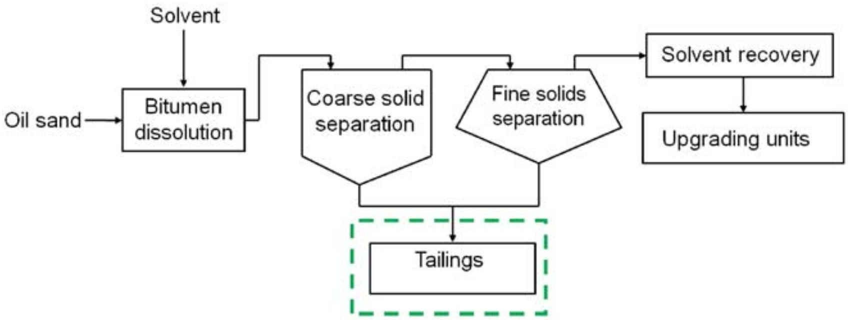


Figure 1.1: Schematic View of Non-Aqueous Extraction Operation

Due to the global oil demand, bitumen extraction operations using current water-based methods will continue to expand in scale. This will exacerbate the above-mentioned water consumption problems, and the resulting environmental issues will become increasingly severe. Therefore, it is predicted that oil sands industry will eventually shift to *non-aqueous* or *solvent-based* extraction methods to replace the present technique. The fundamental principles of the non-aqueous approach are simple. At the first step, to dissolve the bitumen component, mined oil sands is blended with an organic solvent. The mixture is fed into coarse and fine solids separation vessels in which the separation can be achieved via filtration, centrifugation or other means. This step is followed by a solvent recovery unit where solids free diluted bitumen goes under a distillation process or a multiple-effect evaporation or steam stripping to recover the solvent. The extracted bitumen is then sent downstream for further upgrading. The rest (the so-called tailings) consists of reject sand grains contaminated with solvent diluted bitumen (see Fig. 1.1).

In the past, different non-aqueous methods had been recommended for bitumen extraction. However, they were not successful enough to be developed into field-scale processes due to their costly technology and environmental problems.

One problem which any solvent-based extraction process must eventually encounter is the loss of solvent by way of hydrocarbon attachment to the reject sand grains.

The attached hydrocarbon contains bitumen and, more importantly, valuable solvent. For the following reasons, solvent losses will certainly be a key barrier to the non-aqueous process:

1. The solvent is a costly component of the operation.
2. The persistent release of volatile organic compounds to the environment will no doubt cause large scale pollution of the environment.

Accordingly, there will be strong motivations to recover residual oil attached to the waste sand grains. The surfaces of the reject sand grains are saturated with oil (in particular, solvent diluted bitumen) which is held at the sand grain surfaces by capillary forces. It is necessary to completely separate and recover this oil to prevent solvent losses. It is not feasible to force oil out of the porous sand piles by pressurization or gravity drainage since the interstitial spacing between the reject sand grains are much too small in comparison to the capillary constants which is on average several millimeters; the resulting Laplace pressure will generate strong resistance to oil flow. However, unlike the recovery of oil from porous rocks, in the reject sand grain pile we have the possibility of agitating the sand grains - for instance, by stirring in an aqueous suspension. Therefore, a washing process can be applied more efficiently instead of a flooding process to recover residual oil. The obvious method is to wash the reject sand grains with water and surfactants (similar to the washing of dirty dishes). On first impression, this is reminiscent of the current water-based extraction process. However, the following important points distinguish the washing process from the current aqueous operation:

1. Water consumption of the washing process must be negligible in comparison to water-based operations.

2. In contrast to significant loss of bitumen to the reject sand, which is a characteristic of the current bitumen extraction method, the recovery of oil in the non-aqueous process must be practically $100\ \%$.

In this process, we use water and surfactant as a ”pseudo solvent” to solubilize the residual oil. Although the main objective of the non-aqueous (i.e. solvent-based) technology is to eliminate water usage, the amount of water necessary for this purpose is very negligible and will not lead to any environmental impact. With the luxury of adding surfactants, it is now possible to manipulate the oil-water interfacial tension (IFT) in a washing operation. It is known from enhanced oil recovery (EOR) experiences that the most efficient way of recovering oil ganglia from porous rocks is to reduce the oil-water IFT to practically zero, at which point microemulsions will spontaneously form [3]. By certain types of microemulsions, it may be possible to fulfill the two above-mentioned characteristics that a washing operation must have. In addition, choosing a suitable surfactant, which is a very crucial parameter, helps to accomplish the above-mentioned recovery. The main goal of the present work is to focus on the first above-mentioned point, that is, minimizing water consumption. Accordingly, we have developed a protocol to recover residual oil (specifically solvent-diluted bitumen) from contaminated sand grains by means of minimal water use through a washing process. This will lead to a decrease in solvent loss to the environment. This research is organized into the following chapters:

Chapter 2 will provide background information on non-aqueous extraction methods and different remediation methods. Specifically, I will discuss soil washing, characterization of surfactants for enhance oil recovery, as well as the different microemulsion structures that will form in the presence of oil, water and surfactants.

Chapter 3 introduces an experimental approach to recover residual oil from contaminated sand grains; it comprises of three main sections. The first section relates to a guideline for washing experiments. Second section covers a detailed description of our novel washing protocol, which minimizes water usage in washing. In the third section, a series of macro-scale experiments are conducted to determine the correlation between washing efficiency and contaminant / washing solution interfacial tension. Chapter 4 provides the experimental results and discussion of the washing experiment. Finally, the contributions of this research and suggestions for future work will be covered in Chapter 5.

Chapter 2

Literature Review

2.1 Nonaqueous Extraction Technologies

The existing technology for bitumen extraction, the so-called water-based process, is using huge amount of water. At present, the oil sands industry collectively produces about one million barrels of synthetic crude oil per day [2], and this rate of production is certain to accelerate in the coming decades. If the industry were to remain with the current technology, there may not be enough fresh water to meet the industry's demands. The only way to solve this problem is to shift to an alternative extraction technology that requires very little or no water (i.e. nonaqueous extraction). This section covers the latest non-aqueous technologies for bitumen extraction. These technologies are:

- Solvent Extraction
- Solvent Vapor Extraction
- Thermal Solvent Process (ETS) - in situ processes
- Toe - to - Heel Air Injection Process (THAI) - in situ processes

- Microwave Assisted Extraction (MAE)
- Microbiological Processes

2.1.1 Solvent Extraction

In the first step of this process, oil sands are mixed with a hot hydrocarbon solvent to vaporize all the water present in oil sands. Bitumen should be soluble in the chosen hydrocarbon solvent; aromatic solvents seem to be a better option compared to paraffinic fractions. Apart from having good bitumen solubility, the chosen solvent should have a boiling range of $82 - 138°C$ to help water vaporization. Solvent in the diluted bitumen can be recovered by a distillation process and recycled to the first step. Centrifugation is used to separate bitumen from coarse sands and fine solids [2].

2.1.2 Solvent Vapour Extraction

In this technique, an organic solvent in its gaseous phase (e.g. propane or butane vapour) is injected into oil sands deposits to reduce the viscosity of the heavy oil. After it is pumped to the surface, solvent is going to be separated from the oil in a stripping column. In an ideal situation, the majority of the solvent can be recycled and the energy demand of such a process is much smaller than that of conventional extraction. It requires no water and reduces energy consumption by up to $90\ \%$. In spite of the environmentally-friendly characteristics of this technique, there are some challenges that one may encounter - such as high rates of solvent uptake and losses compared to the amount that is recovered. This is a serious hurdle as the solvent is an expensive component of the process [4].

2.1.3 Thermal Solvent Process (ETS)

This is a technique which involves injection of hydrocarbon solvents into a heated horizontal well in the oil sands site. The solvent diffuses into the bitumen and reduces its viscosity. This allows the bitumen to flow back into the well and be drained by an artificial lift. The organic solvent will be recycled (again, by a distillation process). This technology has the advantages of lowering the capital and operating costs as well as reducing the environmental impacts. It can also be used in thinner reservoirs [5].

2.1.4 Toe-to-Heal Air Injection Process (THAI)

This is a recovery technique that combines a vertical air injection well with a horizontal production well. The process ignites oil in the reservoir, thus creating a vertical wall of burning crudes which leads to its drainage into a producing horizontal well. As heat is created in-situ, there is no need to inject steam from the surface. Proponents of this method claim that this approach has a good control of the firefront due to usage of a horizontal production well. However, the technology has not been proven in the field yet [6].

2.1.5 Microwave Assisted Extraction (MAE)

This method involves heating mixture of solvent and sample by microwave power in order to separate compounds of interest from sample media into the solvent [7]. However, this method is not yet proven to be a reliable technology in the field.

2.1.6 Microbiological Processes

This technique exploits microbiological activities to extract hydrocarbon residues from the oil sands; the residues are usually asphaltic, bituminous and paraffinic substances of high viscosity. Recently, several attempts had been made to recover hydrocarbon from oil sands or oil deposits using specially chosen bacteria or byproducts of such micro-organisms (e.g. biosurfactant) [8].

In summary, the objective of all the above-mentioned non-aqueous extraction technologies is to reduce the environmental impact of the oil sands industry - specifically, to reduce water consumption in the bitumen extraction process. A problem common to all these methods is that the contaminated reject sand grains contain trapped organic solvent. This lost solvent is expensive and, more importantly, will lead to continual release of volatile organic compounds to the atmosphere, resulting in large scale environmental pollution. It is therefore essential to design different remediation techniques to assist in the cleaning of contaminated reject sand grains. These methods will be discussed in the next section.

2.2 Different Remediation Methods

In response to severe soil contamination problems, and due to rising interests in environmental remediation, numerous advanced technologies have been proposed for the remediation of contaminated sites. As discussed in what follows, the most common soil remediation methods are categorized into chemical, physical and biological techniques [9].

2.2.1 Excavation

Excavation, as the name implies, is the removal of contaminated soils by simple truck and shovel methods. This is a common and straightforward method of dealing with contaminated soil. There are advantages and disadvantages to this method. On the positive side, it is very fast and easy to perform, and can remove the contamination within hours (while other methods of remediation may take up to several months). It is often used when urgent and instant action is required. Despite such advantages, however, there are also drawbacks associated with excavation. Some of the problems are: uncontrolled release of contaminant vapours to the atmosphere, subsequent treatment/storage of the removed contaminated soil, etc [9].

2.2.2 Thermal Treatment

This is an innovative, non-incinerating technique of treating soils that are contaminated by organic compounds [10]. It is a proven method associated with non-hazardous wastes, and can be adapted for the treatment of petroleum-contaminated soils [11]. In this technique, the organic contaminants are separated from the soil matrix by heating the contaminated soil under an inert atmosphere, thus raising the vapour pressures of the organic compounds and eventually converting them into the gaseous phase. Removal of the organic vapours can then be easily achieved by convection.

2.2.3 Incineration

It is a high temperature thermal treatment and one of the most effective available. In reference [12], it was stated that more than $99.99\ \%$ of carbon tetracholoride, cholorinated benzenes, and polychlorinated biphenyls (PCBs) were destroyed through a trial burn with an EPA (Environmental Protection Agency) mobile incinerator. This technique is not suitable for the aqueous streams and is a relatively expensive process, and it may create incomplete combustion products and a residual ash that may have to be removed as hazardous waste. However, it is one of the best methods for destruction of organic compounds. On the other hand, due to the high cost of operation, it is not considered a suitable technique for remediation of petroleum -contaminated soils [13].

2.2.4 Bioremediation

This refers to the enhancement of biodegrading contaminants such as petroleum hydrocarbons and gasoline by microorganisms which can be found in subsurface soils. A suitable circumference is provided to degrade or convert the organic contaminants to low level and nonhazardous materials by stimulating naturally occurring microbes or adding modified microorganisms to contaminated soil [14]. Moreover, oxygen and nutrient are added to enhance the degradation and assist biological growth. However, this technique may not always work due to the nature of the microorganisms or contaminants. Moreover, although this is a cost-effective technique, the treatment process is often too slow to be of practical use.

2.2.5 Phytoremediation

This refers to the remediation of a contaminated site by natural plants. The plants can help accumulate contaminants or improve biodegradation [15]; they may also remove heavy metals and organic materials from contaminated soil. Phytoremediation is particularly effective in ”tight” soils (i.e. non permeable to water).

2.2.6 Soil Washing/Flushing

This is an extraction process in which organic and inorganic compounds are removed from the contaminated soils by injecting water or an aqueous solution into the contamination site. The contaminated elutriate is then pumped to the surface for removal, recirculation or reinjection [16]. During the washing process, the trapped contaminants are mobilized into the solution by means of solubility, emulsification or chemical reaction with the washing solution. The remediating solution (for flushing or washing a contaminant from the soil) can be collected through gravity (e.g. flooding, ponding) or forced systems (e.g. injection pipes) [16]; it can then be cleaned for reuse, and the chemical waste residue further treated or land filled. Flushing or mobilizing wastes can improve the recovery of contaminants from the subsurface for treatment on the surface or enhance the rate of biodegradation by solubilizing adsorbed compounds. Some solutions have great potential for use in soil flushing; some examples are: water, acidic aqueous solutions (e.g. sulfuric, hydrochloric, nitric, phosphoric), or basic solutions (e.g. sodium hydroxide), surfactants (e.g. alkylbenzene sulfonate) [17]). The type of surfactant, which is one of the key parameters in soil washing, will be discussed in section (2.3). Soil washing methods that involve the use of surfactants are generally the most practical and cost-effective remediation technique for organic compounds [16]. It is less time-consuming compared to other treatment methods such as bioremediation and phytoremediation; thus, this technique has been studied extensively in recent years. A series of experiments was conducted by Ang et al. to compare the washing efficiencies at different surfactant concentrations in the cleaning of automatic transmission fluid (ATF) from sandy soil; for these experiments, an alcohol ethoxylate surfactant was used. They observed that the washing efficiencies of the aqueous surfactant solutions were at least two times more than using just pure water and, not surprisingly, the efficiency of oil removal increased by increasing the surfactant concentration. According to their findings, three mechanisms were involved in the washing process; these are: displacement, dispersion and solubilization of oil. These different mechanisms led to non-uniform distribution of trapped oil along the column [18]. Many studies have been done to identify the most favorable conditions for the washing technique. Urum et al. conducted a soil-washing study to determine the optimal conditions for removing crude oil from contaminated soil using various biosurfactant solutions. They used the Taguchi experimental design; [19], to assess the robustness, stability and reproducibility of the experimental method for possible field-scale applications. In their studies, the temperature and concentration of surfactant solutions were identified as the most influential parameters. Applying the Taguchi protocol, and using rhamnolipid and saponin as surfactants, the removal of crude oil was about $80\ \%$ - with lower environmental toxicity and easier biodegradability compared to using sodium dodecylsulfate (SDS) as surfactant. The method of Urum et al. was stable for all the biosurfactant solutions tested except aescin and lecithin [19]. Urum et al. had conducted another study on soil washing to compare the abilities of a biosurfactant and a synthetic surfactant in remediating different type of contaminated soil, while varying the particle size distribution of the soil under different washing conditions. They studied SDS and rhamnolipid at various temperatures, volumes, surfactant concentrations, shaking speeds, and washing times. Two contamination cases were investigated, namely, weathered and non-weathered contamination. For the weathered contaminated soil, Urum et al. kept the soil under a heated environment to simulate the effect of naturally hot surroundings. The non-weathered contaminated soil was not subjected to such a thermal pre-treatment. According to their studies, due to the binding of crude oil to soil during weathering, the efficiency of washing the weathered contaminated soil was low compare to the non-weathered case. Surfactant concentration and washing temperature were the most prominent parameters on oil removal. The soil cation exchange capacity and pH played significant roles on the desorption of crude oil from soil. Large soil fractions in weathered samples have less initial oil content which in turn leads to higher crude oil removal. A reverse trend, however, was observed for the non-weathered soil samples. Generally, the efficiency by either SDS or rhamnolipid from both weathered and non-weathered soil samples was within the repeatability range of $6\ \%$ [20]. As mentioned before, the type of soil, solvent and surfactant played very important roles in soil washing and oil recovery. High permeability soil is favored for surfactant flushing since the surfactant solution can easily access the contaminated regions. A new approach was conducted by Chu et al. using a solvent/surfactant system instead of conventional surfactant-aided soil remediation to improve contaminant recovery. They investigated three types of surfactant (Brij 35, Tween 80 and SDS), along with three organic solvents (acetone or ACE, triethylamine or TEA, and squalane) and three different types of soil to examine f_{oc} - the fraction of organic carbon content of the soil - on the performance of washing. The contaminant that was chosen was 4, 4'-dichlorobiphenyl (DCB). Chu et al. had found that, regardless of the type of surfactant, the acetone/surfactant system always improved the overall recovery of DCB compared to using just surfactants. Moreover, a surfactant with a lower CMC led to a better recovery due to the higher concentration of surfactant micelles. Therefore, the recovery when using acetone as a solvent increased in the order of: ACE/SDS, ACE/Tween 80, and ACE/Brij 35. Squalane was not a proper solvent as it formed a stable emulsion (i.e. hard to separate surfactant, solvent, contaminant, water) and led consequently to poor recoveries. Thus, a non-polar solvent should not be used in these systems for soil washing. After investigating soil type, they found the lower the f_{oc} , the higher the recovery. TEA was found to be a better solvent for the types of soils that Chu and coworkers investigated. An average recovery of $88\ \%$ and $91\ \%$ were attained by using ACE and TEA respectively as solvent. It is noted that the amount of water used in such washing experiments was excessive - it was typically 500 times the mass of the contaminant. A declined-increment model was successfully used to predict the recovery in terms of f_{oc} [21].

In summary, the methods of excavation, landfill disposal and incineration - even under the most favorable conditions - are expensive and could lead to long term liabilities. Soil remediation by washing, on the other hand, is an interesting alternative; the current methods, however, does have some problems.

One of the problems in the present soil washing methods is use of too much water during soil remediation; indeed, excessive water consumption has become a major problem due to environmental issues. In this research, we propose to carry out washing of contaminated soil using very small amounts of water in comparison to the currents methods (which were briefly reviewed above).

As mentioned, surfactants are widely used in many aspects of the chemical industry; of particular interest to the present research is its usage in soil remediation. For the purpose of remediation, it is important to choose a suitable surfactant that will lead to high levels of contaminant recovery. The following sections will provide background information on the basics of surfactants, their physicochemical properties, toxicity and degradability. These are all properties that will significantly influence the selection of surfactants for soil remediation.

2.3 Surfactants

Surface-active agents, also known as surfactants, are amphiphilic molecules consisting of both hydrophilic and hydrophobic portions within the same molecular structure. The hydrophilic portion is often a polar head group, while the hydrophobic portion is usually in the form of single, double, or branched hydrocarbon chains (or ”tails”). The amphiphilic nature of these molecules causes them to be concentrated at interfaces (e.g. the oil-water interface), where they can be at their lowest energy states. Depending on their origin, such molecules can be categorized as synthetic surfactants or biosurfactants.

2.3.1 Synthetic Surfactant

These molecules are produced synthetically, with their building blocks derived from either natural or synthetic sources. The most common types of such surfactants are described below. Synthetic surfactants are normally categorized by the type of hydrophilic head group, which is an ionic or highly polar group that makes them soluble in aqueous environments.

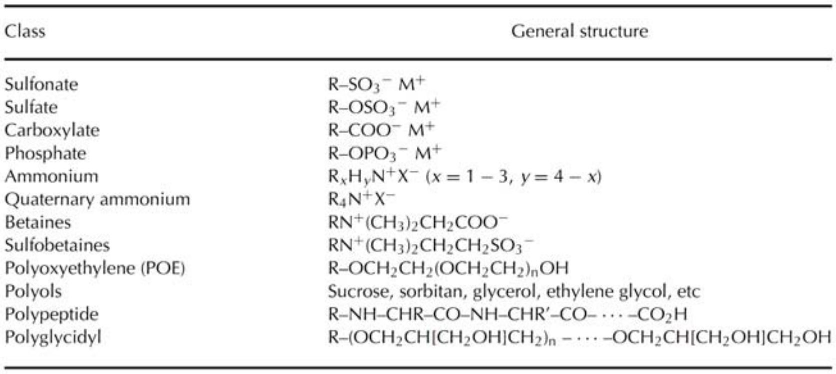
- **Anionic:** The most common type of surfactants - and one that is of particular interest to the present investigation - is the anionics in which the molecular head group bears a negative charge. Owing to the ease and low cost of synthesis, anionic surfactants are commonly used in applications such as detergency and emulsifisication [22].

- **Cationic:** The head groups in this type of surfactant have a positive charge. Cationic and anionic surfactants will dissociate in water into two oppositely charged parts. These molecules are applied, for example, as anticorrosion and antistatic agents, flotation collectors, hair conditioners, and fabric softeners [22].

- **Zwitterionic or Amphoterics:** For such molecules, both positive and negative charges may be present in the head group. Because of their high manufacture cost, they are among the least common of surfactants. This class of surfactants has strikingly extraordinary dermatological properties, and is commonly found in shampoos and cosmetics [22].

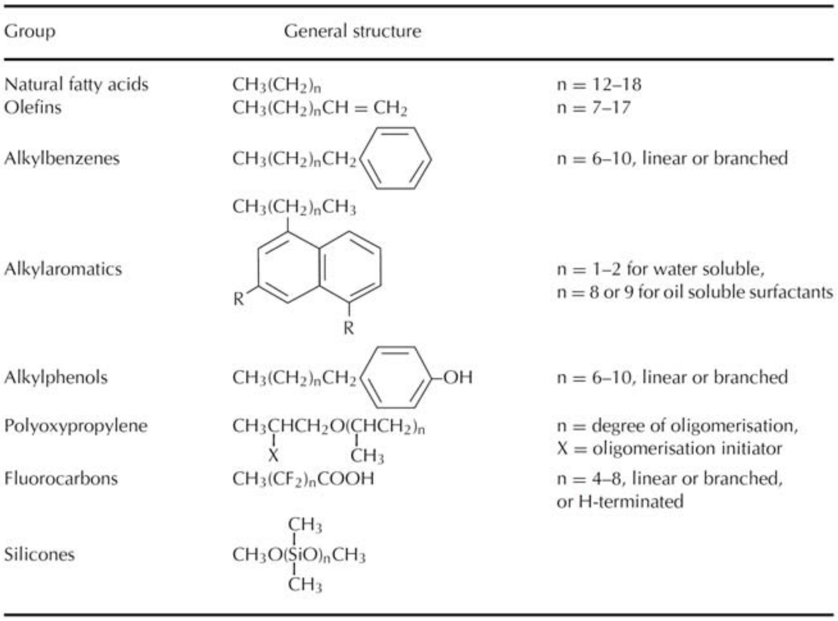
- **Non-anionic:** These surfactants have a surface-active portion that bears no charge but instead include a highly polar moiety. Due to strong dipole-dipole interactions from hydrogen bonding, they have a strong tendency to associate with water. The length of both hydrophobic and hydrophilic parts can be varied to achieve the maximum efficiency. Such surfactants are commonly used in low temperature detergents and emulsifiers [22].

Below are list of common hydrophilic and hydrophobic groups found in commercially available surfactants illustrated in Fig. 2.1 and Fig. 2.2.



Class	General structure
Sulfonate	$\mathrm{R{-}SO_3^-\ M^+}$
Sulfate	$\mathrm{R{-}OSO_3^-\ M^+}$
Carboxylate	$\mathrm{R{-}COO^-\ M^+}$
Phosphate	$\mathrm{R{-}OPO_3^-\ M^+}$
Ammonium	$\mathrm{R}_x\mathrm{H}_y\mathrm{N^+X^-}$ $(x = 1 - 3,\ y = 4 - x)$
Quaternary ammonium	$\mathrm{R_4N^+X^-}$
Betaines	$\mathrm{RN^+(CH_3)_2CH_2COO^-}$
Sulfobetaines	$\mathrm{RN^+(CH_3)_2CH_2CH_2SO_3^-}$
Polyoxyethylene (POE)	$\mathrm{R{-}OCH_2CH_2(OCH_2CH_2)_nOH}$
Polyols	Sucrose, sorbitan, glycerol, ethylene glycol, etc
Polypeptide	$\mathrm{R{-}NH{-}CHR{-}CO{-}NH{-}CHR'{-}CO{-}\cdots{-}CO_2H}$
Polyglycidyl	$\mathrm{R{-}(OCH_2CH[CH_2OH]CH_2)_n - \cdots -OCH_2CH[CH_2OH]CH_2OH}$

Figure 2.1: Commonly Hydrophilic Groups in Commercial Surfactants [22]



Group	General structure	
Natural fatty acids	$CH_3(CH_2)_n$	n = 12–18
Olefins	$CH_3(CH_2)_nCH=CH_2$	n = 7–17
Alkylbenzenes	$CH_3(CH_2)_nCH_2$	n = 6–10, linear or branched
Alkylaromatics	$CH_3(CH_2)_nCH_3$ R R	n = 1–2 for water soluble, n = 8 or 9 for oil soluble surfactants
Alkylphenols	$CH_3(CH_2)_nCH_2$ –OH	n = 6–10, linear or branched
Polyoxypropylene	$CH_3\underset{X}{C}HCH_2O(\underset{CH_3}{C}HCH_2)_n$	n = degree of oligomerisation, X = oligomerisation initiator
Fluorocarbons	$CH_3(CF_2)_nCOOH$	n = 4–8, linear or branched, or H-terminated
Silicones	$CH_3O(\overset{CH_3}{\underset{CH_3}{Si}}O)_nCH_3$	

Figure 2.2: Commonly Hydrophobic Groups in Commercial Surfactants [22]

2.3.2 Biosurfactant

These are biologically based compounds that are mainly produced by bacteria and a wide range of other microorganisms. Biologically produced surfactants occur naturally in soil; they are therefore more suitable for use in bioremediation processes. These surfactants are also available from plants, animals and humans, and can be categorized based on various molecular structures. Despite their bulky structures, biosurfactants often exhibit excellent surface activities. The hydrophilic part of a biosurfactant is a carbohydrate, amino acid, phosphate, carboxylic acid, alcohol or cyclic peptide. The hydrophobic moiety can be a long-chain fatty acid (hydroxyl fatty acid) [23]. The structure of biosurfactants depends on the availability of carbon source during microorganism growth [24]. The majority of the biosurfactantns belong to anionic or non-ionic types. A few, with constituent amine groups, are cationic. The CMCs of biosurfactants generally range from 1 to 200 (mg/L), and their molecular weights typically are between 500 and 1500 (amu) [25].

2.3.3 Physical And Chemical Properties Of Surfactants

In the presence of a non-aqueous phase liquid ($NAPL$), surfactant molecules will accumulate at the oil-water interface (i.e. liquid-liquid interface), leading to interfacial tension (IFT) reduction. A lowered IFT may lead to dispersion of $NAPL$ droplets and formation of a stabilized emulsion. Surfactant molecules will also concentrate at the solid-liquid interface and reduce the interfacial tension. This can result in spreading (i.e. wetting) of liquids on solid substrates [26]. Another important characteristic of surfactants is their tendency to spontaneously assemble into small (i.e. colloidal) aggregates. At low concentrations, surfactants exist as monomers. As the surfactant concentration increases, the monomers will aggregate. When the concentration of surfactants exceeds a certain critical value, monomers will cluster together and form aggregates consisting typically of 20 to 200 molecules. These self-assembled structures are called micelles, and the concentration at which micelles first begin to appear is known as the critical micelle concentration (CMC).
Micelle sizes can be as small as 3 to 4 (nm). They often occur as spherical structures with an oil loving core and a water loving shell. The apparent solubility of hydrophobic organic compounds (HOC) can be dramatically increased due to the presence of micelles (i.e. the HOC can be ”hidden” inside swollen micelles) [26].
Surfactant concentration has direct effect on the system’s physical properties such as surface tension, interfacial tension, solubility, adsorption, and detergency. As it is shown in Fig. 2.3, as surfactant concentration increases, surface tension and interfacial tension decreases up to a certain point where it remains constant. On the other hand, surfactant solubility capacities increase as concentration increases.
The CMC is strongly temperature dependent and is different for each surfactant type. It is normally between 0.1 to 10 (mM) at soil temperatures [26]. At higher

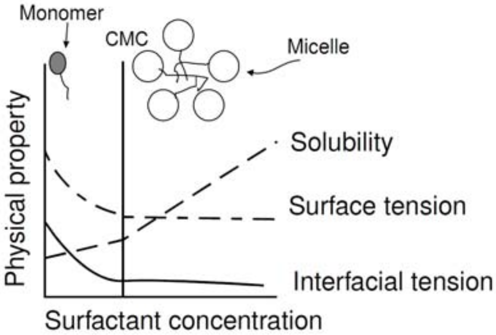


Figure 2.3: Variation of Surface Tension, Interfacial Tension, Contaminant Solubility with Surfactant Concentration [27]

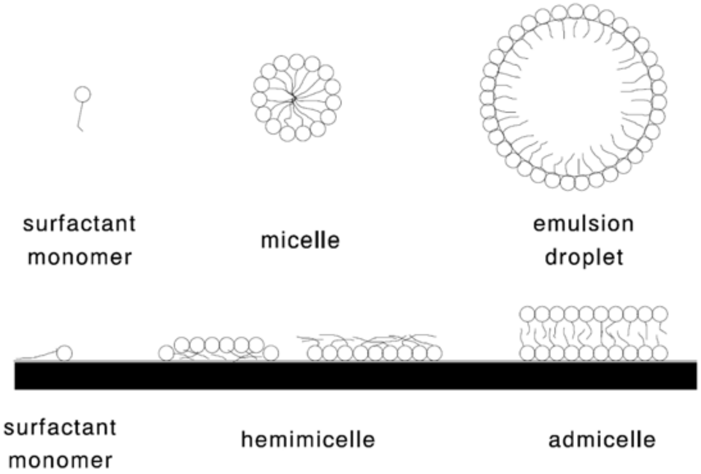


Figure 2.4: Schematic Representation of Different Surfactant Forms in Soil Adopted from [29]

concentrations, when surfactant molecules adsorb onto solid substrates (e.g. surfaces of soil), single or double layers of surfactant molecules (the so-called hemimicelles and admicelles, respectively) can form at the substrate. The concentration at which a two-layered surfactant is formed is called the admicellar concentration; it is typically lower than the CMC [28, 29]. A schematic representation of some important surfactant structures in relation to soil remediation is shown in Fig. 2.4.

2.3.4 Surfactant Toxicity

Due to increasing usage of surfactants in the chemical industry, specifically in soil remediation, global concerns have recently been intensifying in regard to the environmental impact of large scale surfactant application. The two over-riding factors in the selection of surfactants for soil cleaning are *toxicity* and *biodegradability*. The toxicity of a surfactant can change according to pH. For instance, anionic surfactants are more harmful at pH's lower than 7, while cationic surfactants exhibit their most toxic behaviours at pH 7 or higher. Most biosurfactants have lower toxicities in comparison to synthetic surfactants [26].

2.3.5 Surfactant Biodegradation

This is a very important consideration in the selection of surfactants for soil remediation. Since biosurfactants originate from microorganisms, they have the advantages of biodegradability, possible regeneration, and easy production using renewable resources. Biodegradation of surfactants can be both advantageous and disadvantageous. The disadvantages are caused by possible shortage of minerals and oxygen, and the possible toxicity of surfactant byproducts [30]. The most apparent advantage of biodegradation is the removal of surfactants from the polluted site. Surfactant degradation may also improve the uptake of hydrocarbons [26].

2.3.6 Surfactant Selection For Enhancing Oil Recovery

Biosurfactants have long been considered for enhanced oil recovery (EOR) applications [31]. In addition to reducing the oil-water interfacial tension, the surfactants may also lower the viscosity of the heavy hydrocarbon by breaking down the larger molecules [27]. Although most biosurfactants employed in EOR are aerobic, a few are anaerobic. For example, Bacillus *licheniformis JF-2* is well suited for enhanced oil recovery or soil remediation [32]. Harvey et al reported removal of three times more oil by rhamnolipids (a type of biosurfactant) than using just water from the beaches in Alaska after the Exxon Valdez tanker spill [33]. Scheibenbogen et al reported effective removal of a hydrocarbon mixture from a sandy loam soil by a rhamnolipid produced from *P. aerugunosa UG2* [34]. Jafvert had documented the successful removal of chlorinated solvents such as trichloroethylene (TCE) and polychlorinated biphenyls (PCBs) using a mixture of $NaCl$ and $CaCl_2$, cosolvent isopropyl alcohol, an anionic surfactant known as sodium dihexyl sulfosuccinate [35]. A mixture of surfactants and sodium hydroxide had been tested in enhanced oil recovery to reduce interfacial tensions [27]. Alkaline groups are capable of reacting with hydrocarbons to produce surfactants. Sodium hydroxide in combination with surfactants has been used in EOR to reduce interfacial tension, as alkaline agents are capable of reacting with hydrocarbons to produce surfactants [27]. A paper by Mulligan et al. has presented a summary of the laboratory research, field demonstration, background and application of surfactants for the remediation of contaminated soils. It discussed the advantages of using biosurfactants over synthetic surfactant from an environmental and economical perspective, and also in the improved removal of metals from contaminated soil [27].

In summary, the type of surfactant, its physicochemical properties and toxicity, as well as its degradability are among the most important factors in choosing a suitable surfactant for enhancing oil recovery applications.

As is known from enhanced oil recovery studies, the most effective way of removing oil is to lower the oil-water interfacial tension. As the concentration of surfactant increases, the interfacial tension (IFT) will in general be lowered. Depending on the surfactant concentration, different forms of emulsion (i.e. macroemulsion, microemulsion, and liquid crystals) can appear in presence of surfactant, oil and water. The structure and characterization of these emulsions will be discussed in the following section.

2.4 Macro and Microemulsion & Liquid Crystal

2.4.1 Macroemulsion and Microemulsion

Generally, oil and water will not mix unless a surfactant is added. In the presence of surfactants, the two immiscible liquids can mingle on different length scales. Mingling at the scale of micrometer or larger causes one phase to disperse as droplets in the other. Such a system is called macroemulsion; they are distinguished by their kinetic stability, thermodynamic instability, finite interfacial tension and spherically-shaped droplets.

On the other hand, microemulsions are transparent and thermodynamically stable dispersions that comprise at least there components: two immiscible liquids and a third component which is a surfactant. A cosurfactant (often an alcohol) may also be added to lower the oil-water interfacial tension. A transparent microemulsion is heterogeneous at the molecular level, while homogenous on the macroscopic scale. Such emulsions have a characteristic of high oil solubility, and therefore can be used to perform a more successful washing operation.

Properly-chosen surfactants can reduce the IFTs to ultra-low values. Under this condition, the interface is very flexible and thus will allow oil and water to mix on a submicron (i.e. colloidal) scale. This in turn can lead to formation of very complex and non-spherical structures that range from 1 to 100 (nm) in size (the so-called

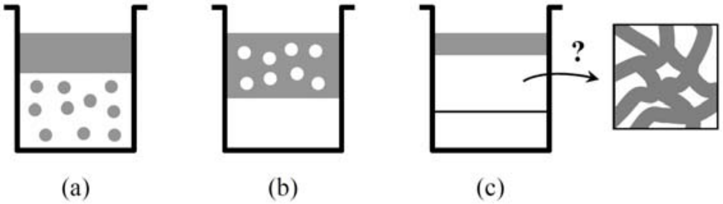


Figure 2.5: The Three Common Forms of Microemulsion: (a) Winsor I, (b) Winsor II, and (c) Winsor III. The Middle Phase of Winsor III is Likely Bicontinous.

microemulsions). Winsor was the first to classify microemulsions into three general types [36, 37]; they are:

- Winsor I System: oil-in-water (O/W) dispersion in equilibrium with excess oil, with nanometre-sized oil droplets existing as swollen micelles.
- Winsor II System: water in oil (W/O) dispersion in equilibrium with excess water, with nanometre-sized water droplets existing as swollen reverse micelles.
- Winsor III System: Microemulsion coexisting with both excess oil and excess water. The middle phase, with similar volumes of oil and water intermingle on the nanoscale, possibly exists as a bicontinous mixture.

In most cases, the phase that has the majority of the surfactant is the continuous phase. Therefore, in Winsor type I, water is the continuous phase and in Winsor II system, oil is the continuous phase; however, in Winsor III the surfactant is spread between the two phases; continuous and disperse phases are no longer distinguishable. Low viscosity and transparency are the two characteristics of all three types of microemulsions, at least when the oil phases are themselves transparent and non-viscous. Winsor I and II microemulsions can have small but still appreciable IFTs ($\sim 0.1\ mN/m$). Unlike the conditions with Winsor I and II, which have a large excess of either water or oil, the bicontinous phase can consist of roughly equal amount of the two liquids [38], and it is continuous in both water and oil. Therefore, when a bicontinous phase forms, the amount of water required to emulsify the residual oil may not be much more than the volume of the oil itself. Under this situation, the solubility of oil in water is at its highest. Indeed, it is a pseudo-solubilization in which the water-surfactant system acts as a pseudo solvent. As a result, this type of microemulsion may lead to minimum water usage in washing operations.

2.4.2 Liquid Crystals

Under certain changes in physicochemical properties of Winsor III systems (which is isotropic and low in viscosity), a high viscosity, anisotropic substance of complex rheological properties may form; such structures are called liquid crystals. The change in physicochemical properties may, for example, involve increasing the volume fraction of the surfactant in a micellar solution, normally above the value of about $40\ vol\%$ [22]. In such a case, a spontaneous arrangement of micellar structures into ordered arrays within the solution occurs. Interactions between surfaces of the micelles are repulsive. As the number of clusters increases, the micelles get nearer to one another; thus, change in size and shape of the micelles is the only way to maximize the separation. This point, along with molecular geometry, explain the reason behind formation of different structures and high viscosity in liquid crystals. The molecules have a random order as in a liquid on a short range ($< 5\mathring{A}$), while on the long-range ($> 15\mathring{A}$) they form crystalline structures and constitute molecular aggregates ordered in one, two or three dimensions which can be easily observed using X-ray diffraction. The main structures are spherical micelles, vesicles, bilayers or inverted micelles. Birefringent character (i.e. refraction of light in an anisotropic material) is a common characteristic among most of the liquid crystals when observed under cross polarizer.

A liquid crystal's physical properties are intermediate between crystalline and fluid structures. Depending on whether the system is comprised of surfactants or other types of material, there are two general classes of liquid crystals: *thermotropic* and *lyotropic* liquid crystals. In the former, the structure and properties are distinguished by temperature (such as those used in LCD cells), while in the latter, specific interactions between the solute and the solvent is responsible for the liquid crystal's structure. Surfactant liquid crystals are typical of the latter type. In regard to two-component surfactant-water systems, the common surfactant liquid crystalline phases are: hexagonal (normal or inverted), lamellar and several types of cubic phases [22].

- Lamellar phase is one of the most common structures of liquid crystals. It consists of surfactant molecules arranged in bilayers separated by layers of water. It exhibits a one dimensional periodicity when tested by X-ray diffraction, and shows a birefringent character when observed under cross polarizers. The hydrophobic chains have a significant range of randomness and mobility (see Fig. 2.6); [22].

- Hexagonal phase is made up of a close-packed array of long cylindrical micelles, ordered in a hexagonal pattern. Depending on the location of the hydrophilic head group (i.e. whether on the outer or inner surface of the cylinders), they are termed normal or inverted hexagonal structures, respectively. In the latter, all the gaps between neighbouring cylinders are filled with hydrophobic groups. As such, the cylindrical micelles are more closely-packed, and occupy smaller region. Such structures are however less common (see

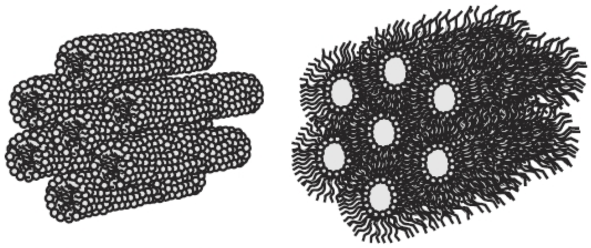
Fig. 2.6); [22].

- The cubic phase involves a vast variety of structural variations. They are optically isotropic and not birefringent (see Fig. 2.6); [22].

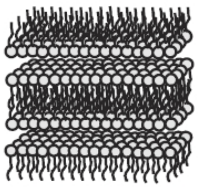
They have different viscosities in the following order:

$$Cubic > Hexagonal > Lamellar$$

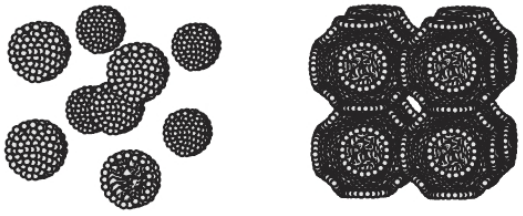
Cubic phases are the most viscous types because there is no clear shear plane and the surfactant aggregates cannot slide easily past one another. The second most viscous structures are the hexagonal phases, as the cylindrical micelles are free to slide only along the axial direction of the cylinders. Lamellar phases are the least viscous structures because each parallel layer can easily slide over one another during shear [22].



Hexagonal phase (H_1) Inverse hexagonal phase (H_2)



Lamellar phase (L_α)



Cubic phase (I_1) Bicontinuous cubic phase (V_1)

Figure 2.6: Common Surfactant Liquid Crystalline Phases [22]

Chapter 3

Materials and Methods

Preliminary jar tests were conducted as a guideline for washing contaminated sand, which is termed here as ”simulated tailings”. We did a preliminary study on the phase behavior of the ternary system (i.e. Surfactant, Oil, Water). Diluted bitumen was used as the oil contaminant; hexadecane and heptane were used respectively as diluents in order to compare the effect of carbon chain length in the washing experiments. These jar tests were followed by moisture content measurements and polarized light screening test; this was to determine self-assembled structure and the possibility of liquid crystal formation, respectively.

We had developed a protocol for washing contaminated sand grains. In addition, on the macroscopic (i.e. bench) scale, a series of spinning drop measurements were conducted in order to correlate the washing efficiency with the ”apparent” interfacial tension. This chapter discusses the details of such experimental procedures, where we correlated the efficiency of washing with the apparent oil-water interfacial tension.

3.1 Preliminary Jar Tests

3.1.1 Materials

Hydrocarbon Phase: In this study, ”vacuum topped” bitumen from Syncrude Canada Ltd was used as the heavy oil with no further purification. Two types of solvents were used separately to dilute the bitumen: n-hexadecane and n-heptane. They were selected as interesting phase behaviors were observed in previous studies using heptane [39] and high alkane chain-length hydrocarbons [40]. In both series, the solvent-to-bitumen ratio was $4{:}1$ by weight, i.e. $20\ wt\%$ bitumen and $80\ wt\%$ solvent; it considerably reduced bitumen viscosity. At lower ratios, mass loss would increase in soil washing experiments due to adhesion of viscous oil to glass jars.

Aqueous Phase: In this study, only deionised water, which was prepared by Millipore (Milli-Q Advantage A10 Ultrapure Water Purification System), was used.

Surfactant: Sodium bis (2-ethylhexyl) sulfosuccinate, abbreviated as ”Aerosol-OT” or ”AOT,” was used as received from Sigma-Aldrich (purity: $98\ \%$).

Salt: Sodium chloride was used as supplied from Fisher Scientific without any further purification. The salinity range was chosen based on the previous study on a system containing AOT/Brine/Oil [40].

3.1.2 Sample Preparation for Jar Tests

The aqueous and oil phases will not mix unless surfactant was added. Two series of jar tests were conducted: one with hexadecane-diluted bitumen, the other with heptane-diluted bitumen as the oil phase (see Figure 3.1). In both cases, a stock

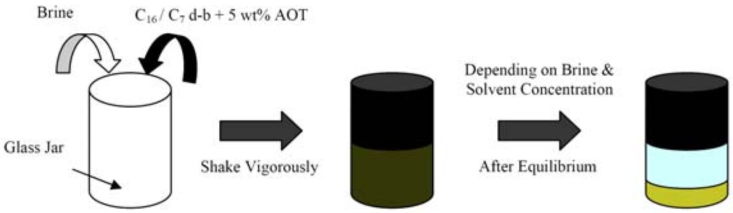


Figure 3.1: Sample Preparation Procedure

solution consisting of $5\ wt\%\ AOT$ in solvent diluted-bitumen (d-b) was prepared. Different weight percentages of sodium chloride were added to the aqueous phase to prepare a brine solution. Since our objective was to minimize water consumption, we chose to use equal amounts (by weight) of oil phase and brine solution in all our experiments. Having maintained water-to-oil ratio (WOR) at about 1, the overall concentration of AOT in the whole system was $2.5\ wt\%$. We chose this particular surfactant concentration because, based on previous studies, it was found to show interesting phase behaviors in the presence of brine and straight-chain hydrocarbons of various chain lengths [40]. Salt concentration as an important and effective parameter for an anionic surfactant such as AOT was chosen to be varied in jar tests. It was reported that by adding salt to water-surfactant mixtures in the absence of alcohol, the phase behavior is similar to systems that contained petroleum sulfonates with cosurfactants [40]; they have been widely used in enhance oil recovery. Therefore having a similar phase behavior as petroleum sulfonates might help to improve washing recovery.

It took one to two days for the samples to reach equilibrium. Figure 3.2 shows a series of photos of hexadecane-diluted bitumen from 1.0 to $2.5\ wt\%\ NaCl$ concentration.

3.1.3 Moisture Content Measurement

The objective here was to determine self-assembled structures via measurement of water contents in the series. Samples with volumes of $3\mu L$ were taken from different phases inside the container. The water content of each phase was then measured by Karl Fischer titration (Kam Control Incorporated). The apparatus was calibrated with standard solutions containing different concentration of water in methanol. Karl Fischer titration (see Figure 3.3) has been established as the primary analytical method of determining water content and humidity due to its speed, sensitivity and selectivity of the instrument. The basic principle of water content determination is the reaction of iodine and sulphur dioxide in the presence of an alcohol (ROH) and a base (B) as anode solution with water:

$$BI_2 + BSO_2 + B + H_2O \longrightarrow 2BH^+I^- + BSO_3 \tag{3.1}$$

$$BSO_3 + ROH \longrightarrow BH^+ROSO_3^- \tag{3.2}$$

Based on above formula, equal amounts of water and iodine are consumed to produce iodide. Following this step, the water content of the solution is determined by the electric charge that is required for the electrolysis of iodine in the Karl Fischer

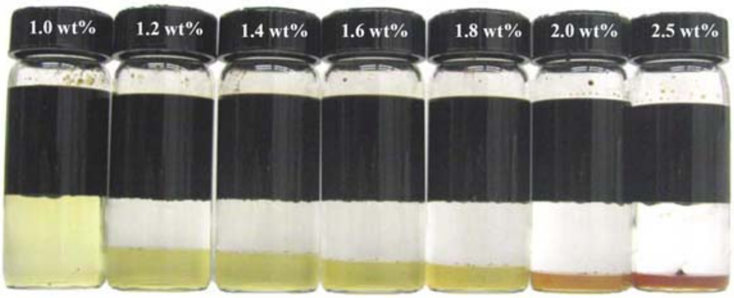


Figure 3.2: Hexadecane Diluted Bitumen series. NaCl Concentration is written on the jars

reagent.

3.1.4 Cross-Polarized Light Screening Test

The cross-polarized light screening technique was used to detect macroscopic phase behaviour of the samples. Diffused light source in an inverted microscope was made to pass through a ”polarizer” and an ”analyzer” (essentially two linear optical polarizers with their axes oriented at $90°$ with respect to one another). A small amount of sample was placed between the polarizer and analyzer, and the resulting image was observed. This technique provides information about the isotropy (directional independence) or anisotropy (directional dependence) of the emulsion phases that were formed. Liquid crystalline phases could easily be detected under cross-polarizers owing to their birefringent properties.

Figure 3.3: Photograph of the Karl Fischer Titration Apparatus

3.2 Development of a Protocol for Washing Bitumen-Contaminated Sand Grains

Following solvent extraction of bitumen, there will be a reject (i.e. tailings) stream which comprises of waste sand grains mixed with trapped residual oil. The trapped hydrocarbon contains bitumen and, more importantly, valuable solvent which is an expensive part of the operation. The continuous release of solvent, as an organic compound, to the environment can result in large scale pollution. Accordingly, there is strong motivation to recover residual oil associated with the waste sand grains. Currently, in the literature, large amounts of water are normally used for such washing operations. The common feature among most of the washing techniques in the literature is the use of centrifuge test tubes as a washing column, a settling time based on soil particle sizes distribution, and usage of large amounts of washing solutions (in comparison to the amount of oily contaminant). In addition, temperature was also varied during the experiments. As mentioned earlier (in the literature survey), Urum et al. had conducted a series of experiments to determine optimum conditions for washing Ekofisk crude oil-contaminated soils. They used 10 to 20 (mL) of washing solution for 5 (g) of contaminated soil - roughly 2 to 4 times more washing solution than contaminated soil to remove the contaminants. They reported temperatures of about $50°C$ as the optimal washing temperature [19]. In another series of soil-washing studies, a constant ratio of soil-to-surfactant solution ($3g/15mL$) had been used [41]. Ang et al. had conducted a set of continuous washing experiments, in which water or surfactant solution was continuously pumped through a column of contaminated soil for durations ranging from eight hours to several days [18]. Chu et al. reported usage of 5 (mL) of surfactant solution for about 0.5 (g) of contaminated soil - about ten times more washing solution compared to contaminated soil [21]. Having reviewed the existing methods, the objective of this study is to introduce a novel protocol to wash simulated tailings at room temperature using minimum amounts of water.

3.2.1 Materials

”Quack sand” (silica grinding sand with average diameter of $0.8\ (mm)$) was used as received from Quackenbush Company as the solid matrix for the washing experiments. In this study, ”vacuum topped” bitumen from Syncrude Canada Ltd was used as supplied. Toluene and two organic solvents (n-heptane and n-hexadecane) were obtained from Fisher Scientific and were used with no further purification. Sodium bis (2-ethylhexyl) sulfosuccinate (i.e. AOT) at $98\ \%$ purity was used as supplied from Sigma-Aldrich. Sodium chloride was used with no further purification. An Excella E2 platform shaker (New Brunswick Scientific) was used to agitate the sand and solvent-diluted bitumen mixtures. A Millipore filter apparatus with stainless-steel screen from Fisher Scientific and an ultrasonic vibration bath was used in these set of washing experiments. In this study, only deionised water, which was prepared by Millipore (Milli-Q Advantage A10 Ultrapure Water Purification System), was used.

3.2.2 Soil Washing Procedure

Preparing Solid Matrix: In this study, silica sand from Quackenbush Company Ltd was used as the solid matrix. It is noted that sand grains in an actual oil sand ore have been in contacted with bitumen for a very long time, resulting in modification of the silica surface properties. To simulate this, a two-step preparation procedure was employed to reproduce this surface modification effect.

As the first step, about 300 (g) of Quack sand was placed in a 300 (mL) glass jar and 200 (mL) of toluene was added. The jar was shaken vigorously by hand for about 30 seconds, then the mixture of toluene and sand was transferred to the funnel of a Millipore filter. The toluene was removed by filtration and the remaining sand inside the funnel was dried under vacuum. This step was repeated twice to have the sand surfaces cleaned; it will be referred to as pretreated sand.

In the second step, in order to change the wetting properties of the sand grains (i.e. increasing the degree of oil wettability), about 300 (g) of pretreated sand was mixed in a glass jar with a 200-gram mixture that consisted of 20 $wt\%$ bitumen and 80 $wt\%$ toluene. Following this, the mixture was shaken vigorously by hand, then mounted on the Excella E2 platform shaker and agitated at 200 (rpm) for 20 minutes. It should be noted that the amount of toluene-diluted bitumen should be enough to submerge all pretreated sand grains. The mixture of sand and toluene-diluted bitumen was left in the glass jar for 4 days to allow modification of the sand surfaces; it was then transferred to the Millipore filter apparatus and rinsed by toluene until the filtrated solution became clear. The remaining sand, which we will call ”treated sand,” was dried under vacuum. As a visual sign, treated sand grains appeared darker than their pretreated counterpart.

Preparing Hydrocarbon Phase: The hydrocarbon phase was a mixture of 80 $wt\%$ solvent and 20 $wt\%$ bitumen. Two types of solvent, *n-heptane* and *n-hexadecane*, were used in order to investigate the effect of alkane chain length in washing performance.

Washing Column: In these series of experiments, a Millipore filter apparatus was used as column for soil washing experiments. It comprised of a one-litre ground


Figure 3.4: A Millipore Filter Apparatus as Washing Column

joint flask, a 100 mesh stainless steel support screen, and a 300 (mL) ground glass funnel with outer bottom diameter of 47 (mm). A photograph of the setup is shown below in Figure 3.4.

Preparing Simulated Tailings: In this part of the experiment, we attempted to simulate real tailings by trapping oil (solvent-diluted bitumen) between sand grains inside a Millipore filter apparatus. This was accomplished in two steps:

In the first step, a known amount of pretreated sand and solvent-diluted bitumen was separately weighed. It should be mentioned that in the experiments, the amount of pretreated sand was matched to the diameter of funnel of Millipore filter apparatus in order to minimize solvent use (see Figure 3.4). Therefore, we were able to cover all of the pretreated sand grains with minimal amount of solvent-diluted bitumen (which was either heptane-based or hexadecane-based). In our case, about 60 (g) of pretreated sand and $16 - 17$ (g) of solvent diluted bitumen was enough to meet the above requirements. The mixture in the glass jar was shaken vigorously by hands then by Excella E2 platform shaker at 200 (rpm) for 20 minutes.

In the second step of simulated tailings preparation, the mixture was transferred to the column (i.e. the Millipore filter apparatus) and packed by a glass rod to accelarate drainage rate. The solvent-diluted bitumen was then drained under ”one-g” (i.e. by gravity alone) and collected in the flask of the Millipore filter apparatus, which was the bottom part of the column. Depending on the type of solvent (i.e. heptane or hexadecane), the filtration time was different; it was longer for hexadecane due to its higher viscosity. After the drainage step (i.e. until no more diluted bitumen dripped from the filter vessel under ($1 - g$), the contents of the filter vessel (m_2) was weighed. The contents of the filter vessel (i.e. sand grains + trapped diluted bitumen) were then transferred to a glass jar for the washing step. It should be noted that, to minimize evaporation of light hydrocarbons, the filter column was covered with an aluminum foil at all times. The amount of trapped oil was calculated from a simple mass balance;this amount will be denoted as (m_0). Details of this procedure will be discussed later in this section.

Preparing Washing Solution: The objective of this step is to remediate (i.e. clean) the simulated tailings, which was prepared as described in the previous section. The remediation was carried out by means of a washing solution that was a mixture of brine and surfactant used as a ”pseudo solvent” to solubilize the trapped oil between the sand grains. The washing solutions all consisted of $5\ wt\%\ AOT$ as surfactant and had different $NaCl$ concentrations. The brine concentration was varied from zero to $2\ wt\%\ NaCl$ in deionised water. An ultrasonic vibration bath was used to accelerate the solubilization and/or dispersion of AOT in the aqueous solution. Depending on the sodium chloride concentration, the viscosity of the washing solution was different. As mentioned earlier, for the methods of soil washing that have been proposed in the literature, enormous amounts of water is used in comparison to the amount of contaminated soil. In this research, however, the objective was to minimize water consumption; therefore, the amount of washing solution was chosen to be equal to the amount of trapped diluted bitumen (defined above as m_0). After adding the same amount of washing solution to the glass jar - which already contained sand grains plus trapped diluted bitumen - the mixture was again agitated on the Excella E2 platform shaker at 200 (rpm) for 20 minutes.

Soil Washing: After agitating the washing solution with the contaminated sand grains, it was time to transfer the mixture back to the column (the Millipore filter apparatus in Figure 3.4). The mixture was poured into the column, packed by a glass rod to achieve minimal (and repeatable) porosity, and covered by an aluminum foil to minimise evaporation of light hydrocarbons. The oil-water mixture, which was formed from the agitation process, was then allowed to drain into the collecting flask under one-g. Depending on the salinity of the washing solution, the washing time was different: it was much faster for salinities higher than 1.0 $wt\%$. Once there was no further dripping from the filter assembly into the collecting flask, the top and bottom parts of the column (i.e. the filter assembly and the flask below) were weighed separately. The drained mixture (denoted m_3) after washing was calculated through a mass balance. Details of this mass balance will be given later in this section.

Moisture Content Measurement: To determine the efficiency of soil washing, it was necessary to first measure the water content of the drained mixture (m_{wtr}). The difference between (m_{wtr}) and (m_3) will be the amount of oil (m_{oil}) that is recovered from the contaminated sand grains, i.e.

$$m_{oil} = m_3 - m_{wtr} \tag{3.3}$$

The water content (m_{wtr}) was measured by two analytical methods: Dean Stark distillation, which is a robust but time-consuming method, and a modified Karl Fischer titration technique, which we had developed specifically for this study.

- **Dean Stark Distillation:** Dean Stark distillation is one of the most common techniques in synthetic chemistry to measure water contents, especially in difficult-to-break emulsions and oil-water mixtures. This technique is perfectly suited for immiscible systems such as the collected drained mixture in our experiments. This apparatus comprises a condenser, a water trap, and a flask. In our set-up (see Figure 3.5), a 10 (mL) capacity water trap, a 185 (mm) simple condenser, and a 100 mL round bottom long neck flask were used. All parts had a $24/40$ joint, and were supplied from Chemglass. The set-up was placed on a 100 (mL) metal heating mantle with maximum power of 70 (W). Each heating mantle was connected to a 100 (W) variable transformer to control the temperature during boiling. High vacuum grease was applied between the joints to ensure perfect seals and to prevent leakage.

- **Modified Karl Fischer Titration:** As mentioned earlier, Karl Fischer titration is one of the most accurate analytical techniques in water content determination. The principle behind Karl Fischer was explained in Section 3.1.3. Two types of titration can be used to measure water contents of different samples: coulometric or volumetric titration. Coulometric titration is best suited for determination of water content in the range of 1 (ppm) to 5 $wt\%$ and volumetric titration is best suited for water content determination in the range of 100 (ppm) to 100 $wt\%$. Our samples had high water content (typically up to 50 $wt\%$). Due to limitations of coulometric titration (i.e. accurate only for 5 $wt\%$ moisture or lower), water contents of the drained mixtures could not be directly measured via this method. Volumetric titration was not applicable due to the inhomogeneity of our samples. As such, small samples($\sim 0.1\,mL$) taken from the mixture will likely not be representative of the overall water contents of the drained volumes. In order to properly apply Karl Fischer titration, it was necessary to first make two modifications: the drained mixture must be homogenized, and its water content must be lowered to the measurement range suitable for coulometric titration. These were accomplished as follows: Drained mixtures contained bitumen, solvent (*heptane* or *hexadecane*), salt, surfactant and water. Such a sample was first transferred to a $500\ (mL)$ flask with screw cap; a known amount of toluene was then added to dilute the sample. The amount of added toluene was calculated based on the weight of the drained mixture. We assumed that the whole mixture was water, and toluene was added to make the final moisture content $5\ wt\%$ (the maximum acceptable value for coulometric titration). The mixture was shaken several times to dissolve the oil into toluene and to disperse/homogenize the sample. At lower salinities, some gel-like material that seemed to contain high water content were formed at the bottom of the flask; this material was soluble in acetone. In order to minimize the use of acetone (used only when the gel-like material needed to be dissolved), it was gradually added. When there was no salt in the drained mixture, tetrahydrofuran (THF) and acetone were added in order to dissolve the gel-like materials. The flask was then put into an ultrasonic bath to homogenize the content. While the flask was still in the ultrasonic bath, a sample was taken by a syringe and its water content was measured by Karl Fischer titration. As all of the solvents, acetone, toluene and THF contained trace amounts of water; their water contents were measured and subtracted from the drained mixture. This modified Karl Fischer

Figure 3.5: Dean-Stark Distillation Apparatus

titration technique was shown to have the same reliability as Dean-Stark distillation, and has the advantage or requiring much less time (only $3\ min$ for every measurement, as opposed to 10 to $12\ hrs$ for Dean Stark titration).

Calculation of Remediation Factor: As mentioned earlier, the objective of this protocol is to minimize water consumption in washing contaminated reject sand grains. Thus, the amount of washing solution was as equal as initial trapped oil in order to remediate simulated contaminated soil. Subsequently, the washing efficiency known as remediation factor was calculated through a series of mass balance as follows:

$$m_0 = m_2 - m_1 - Initial\ Sand \tag{3.4}$$

$$m_{oil} = m_3 - m_{wtr} \tag{3.5}$$

$$\%Remediation\ Factor = \frac{m_{oil}}{m_0} \times 100 \tag{3.6}$$

Where m_0 denoted initial trapped oil before addition of washing solution, m_1 denoted empty filter assembly, m_2 denoted full filter assembly before addition of washing solution, m_{wtr} water content of the drained mixture, m_3 drained mixture.

3.3 Macro-Scale Experiment: Spinning Drop Interfacial Tension Measurement

The objective of this section is to measure the interfacial tension between the oil phase (i.e. hexadecane-diluted bitumen or heptane-diluted bitumen) and the aqueous phase in the presence of surfactants and salt; we will then see if any correlation exists between the interfacial tension and the amount of oil recovered from washing. A brief description of the spinning drop interfacial tension measurement technique is given below.

3.3.1 Sample Preparation

Hydrocarbon Phase (Light Phase): As mentioned earlier, two types of solvents were used to dilute the bitumen: *hexadecane* and *heptane*. In both cases, the solvent-to-bitumen ratio was $4 : 1$ by weight, i.e. $20\ wt\%$ bitumen and $80\ wt\%$ solvent. Both hydrocarbon phases contained $5\ wt\%\ AOT$ as the surfactant component. In a spinning drop experiment, the hydrocarbon is the ”light phase,” i.e. it constitutes the dispersed droplet that is surrounded by the ”heavy phase.”

Aqueous Phase (Heavy Phase): The aqueous solution constitutes the bulk or heavy phase in a spinning drop experiment. This is a brine solution containing different concentrations of sodium chloride dissolved in deionised water.

3.3.2 Density Measurements

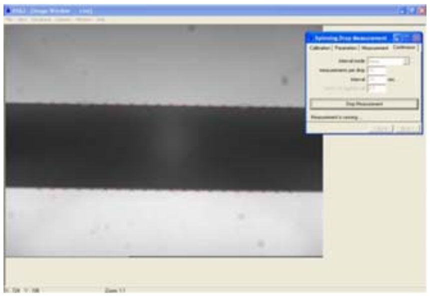
A portable digital density meter (Mettler Toledo Densito 30PX) was used for determining the density of the light and heavy phases. In order to fill the measuring cell, a built-in sample pump was used and the results were automatically calculated. The temperature's influence on the density was also corrected for more accurate measurements. Densities of both the light and heavy phases were measured individually at room temperature.

3.3.3 Spinning Drop Interfacial Tension Measurement

A spinning drop apparatus (Krüss SITE 100) was used to measure very low oil-water interfacial tensions (from 1 to 10^{-6} mN/m). It is a computer controlled tensiometer with the ability to control the temperature of the measuring cell within a range between $0°C$ to $100°C$. The apparatus consists of an adjustable platform, a high resolution camera equipped with an adjustable zoom lens, a glass capillary that is filled with the heavy (normally aqueous) phase, and a horizontal and vertical illumination control unit; a photograph of the apparatus is shown in Figure 3.6. Using a 10 (μL) syringe, the light phase (normally the hydrocarbon) is injected as a single droplet into the capillary. As such, the capillary is filled with the heavy phase, and contains a small droplet of the light phase.

By spinning the capillary about its axis, centripetal forces will be created which push the light phase droplet to the radial direction and also stretched it out into a cylindrical shape; the diameter of this cylindrical droplet is a direct function of the spinning speed and the interfacial tension (see equation 3.7 below). An image of a cylindrical drop rotating at a known frequency was captured by the camera in order to measure the drop diameter at pre-set time intervals. The image was sub-

Figure 3.6: The Krüss Site 100 Spinning Drop Tensiometer



Measurement is running ...

Figure 3.7: Drop Shape Analysis Software

sequently processed with a drop shape analysis software (Figure 3.7). Two sets of experiments was conducted - one with heptane-diluted bitumen, the other with hexadecane-diluted bitumen, as the oil (light) phase. In these two series of experiments, the hydrocarbon phase (the drop) was surrounded by an aqueous environment; the rotating capillary would reach angular velocities as high as $15000\ (rpm)$.

The principle behind the spinning drop tensiometer is based on the fact that drop radius normal to the axis of rotation is dependent on the interfacial tension between the two phases, the frequency of rotation, and the density difference between the two phases (the subscripts H and L denoted ”heavy” and ”light,” respectively). For a droplet that is stretched out into a cylindrical shape by centripetal forces, the interfacial tension can be calculated from the *Vonnegut* equation, which is a statement of force balance on the rotating drop:

$$\gamma = \frac{r^3\omega^2(\rho_H - \rho_L)}{4} \tag{3.7}$$

Knowing the capillary rotating speed and density difference between the two phases, the interfacial tension can be calculated from the measured drop radius r. The *Vonnegut* equation is derived for infinite liquid cylinders; in practice, it is valid when the drop length L is larger than four times the drop diameter (i.e. when $L > 8r$).

Chapter 4

Result and Discussion

The main contribution of this thesis is development of a protocol for characterizing the effectiveness of soil remediation - specifically, the washing of bitumen-contaminated sand grains using water and surfactants. In this chapter, the various aspects of this remediation protocol will be discussed, including the self-assembled structures that are formed in the ternary water-oil-surfactant systems, the effect of salt on water emulsification, and the possible mechanisms behind the washing process. To quantify the effectiveness of washing, careful mass balance will need to be performed; this will require accurate determination of water contents in ”messy” oil-water mixtures. The effectiveness of a particular surfactant in cleaning contaminated sand grains will be characterized by an index which we will term the ”remediation factor”; it will be introduced in section 4.6. To gain further insight into the washing process, we will also search for correlation between the oil-water interfacial tension (measured using the spinning drop technique) and the overall remediation factor.

4.1 Characterization of Jar Tests for Soil Washing

4.1.1 Distinguishing Self-Assembled Structure through Water Content Determination

As mentioned in the previous chapter, Aerosol-OT (AOT) will be used as surfactant in this study. There are two reasons for such a choice: Firstly, AOT is a sulfonated surfactant; such surfactants are known to be widely used in enhanced oil recovery operations. Secondly, as the hydrophilic and lipophilic properties of AOT are nearly balanced, i.e. $HLB = 10.5$ [42] (Figure 4.1), such a surfactant can lead to formation of microemulsions even in the absence of cosurfactants. As explained in section 2.4.1, microemulsions, in comparison to macroemulsions, are a better option in solubilizing residual oil and, as a result, can lead to better remediation performance. As mentioned in section 3.1.1, two types of oil (i.e. hexadecane-diluted bitumen and heptane-diluted bitumen) will be used as soil contaminants. Following the procedure described in this section, two separate series of phase behaviours were studied based on the two types of oil. As shown in Figure 3.2, the hexadecane-diluted bitumen series showed appearance of a third phase, suggesting the spontaneous formation of microemulsions at certain salinities. Likewise, the series involving heptane-diluted bitumen showed macroemulsion behaviours in roughly the same range of salinities. In this section, we will examine further the nature of the third phase that was formed in the hexadecane series.

In the presence of $2.5\ wt\%\ AOT$ (based on the total mass of the oil-water mixture), and as the salinity of the aqueous phase was increased, a third phase (yellowish in colour) began to appear at $1.0\ wt\%\ NaCl$. The yellow colour suggests dissolution of a trace amount of diluted bitumen in the third phase, most likely in the form of a

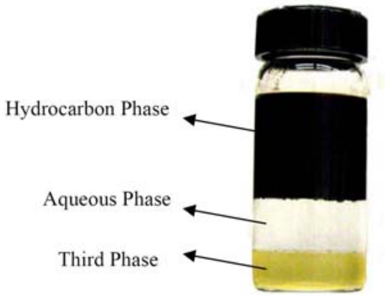


Figure 4.1: Phase Behaviour of AOT-Brine- N-Hexadecane Diluted Bitumen at $WOR\ = 1$, $[AOT]_{Overall} = 2.5\ wt\%$

microemulsion.

This third yellowish phase can have three possible nanostructures, depending on the type of dividing surface and water-to-oil ratio. Each structure has a different characteristic as follows:

- Lamellar phase
- Bicontinous microemulsion phase and L_3 phase
- L_α phase

Lamellar phase and L_α phase are characterized by stacks of parallel sheets. The sheets in a lamellar structure are comprised of surfactant monolayers separating alternating layers of oil and water, while the L_α phase consists of oil-swollen bilayers with water on both sides. Lamellar phases typically have water-to-oil (w/o) ratio of order unity, while L_α phases are characterized by having very high w/o ratios [43, 44, 45]. Both these two phases have ”liquid crystalline” structures, i.e. they exhibit a periodic, ordered pattern in the direction perpendicular to the surfactant layers. Unlike the lamellar and L_α phases, bicontinuous structures exhibit completely random conformations and are isotropic in behaviour. As indicated in Figure 4.2 (b), there are two types of bicontinous structures depending on the type

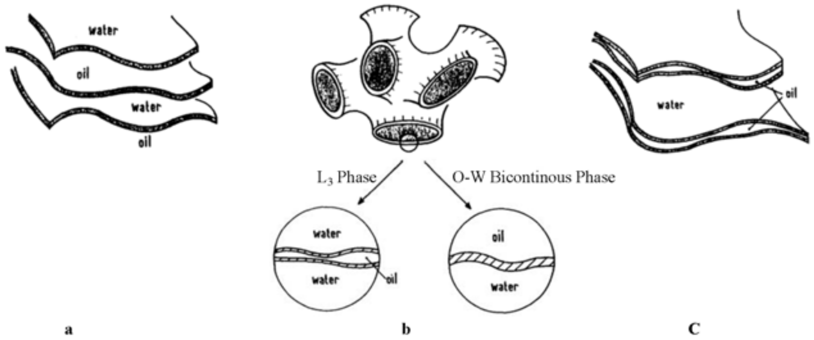


Figure 4.2: Third Phase Microstructure for the AOT+ Aqueous NaCl+ N-Alkane System [43] a) $N < 10$ Lamellar Phase b) $N = 12$, L_3 Phase or Bicontinous Microemulsion Phase c) $N = 10$, L_α Phase

of dividing surface. When the dividing surface is a surfactant monolayer, it is called bicontinous microemulsion; it is characterized by having w/o ratios of order unity. If it is made up of oil-swollen bilayers, the bicontinous structure is called the L_3 phase; such structures are characterized by very high w/o ratios. Experiments were conducted to create the above-mentioned microstructures for systems consisting of n-alkane, AOT and brine [43]. As shown in Figure 4.2, different types of microstructures could be formed by changing the alkane carbon number (N).

As the lamellar and L_α phases have partially crystalline structure, they possess characteristics of liquid crystals, in particular, flow-resistance and high viscosity. In contrast, the two types of bicontinous phases (i.e. L_3 phase and $O-W$ bicontinuous phase), due to their completely randomized microstructures, can flow easily and are characterized by low viscosities. These two characteristics make them more desirable for soil remediation purposes. Therefore, as a guideline for washing oil-contaminated sand grains, we wish to look for these structures through water content determination, bench-scale observation and imaging through crossed-polarizers.

A series of Karl Fischer measurements were conducted following the procedures

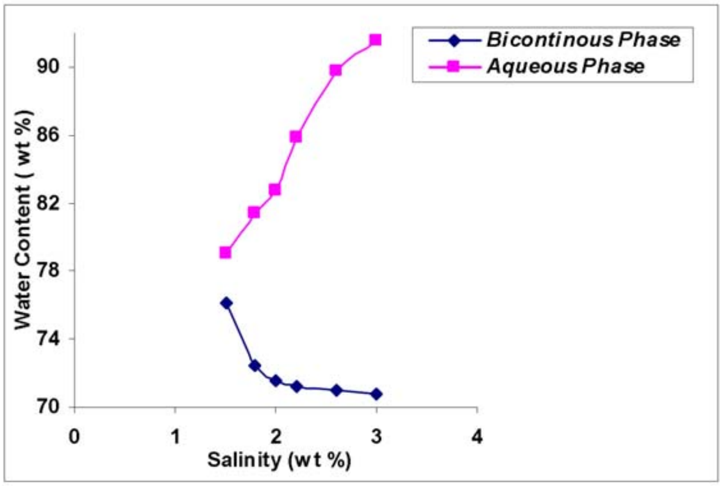


Figure 4.3: Bicontinous and Aqueous Phase Water Content

that were explained in section 3.1.3. The results showed high water contents in the third yellowish phase; the amount of water in the third phase was in fact almost equal to that of the aqueous phase (see Figure 4.3). From this, we conclude that the third phase must either be L_α phase or L_3 phase. Based on the observation that the third phase possessed low viscosity, it is more likely that it is an L_3 phase rather than an L_α phase.

Next, polarized light screening technique was used to provide information on the isotropy of the third phase. Following the procedure explained in section 3.1.4, the result showed an isotropic behaviour for all yellowish phases in the bottom of the jars. Specifically, after observing the bottom yellowish phase under cross-polarized light, it showed that this type of substance was independent of the direction of light that was a characteristic of L_3 phases. If the third phase was L_α in character, it would display birefringent behaviour.

Combining the Karl Fischer and cross-polarized light screening results, we were able to conclude that the third phase was indeed an L_3 phase.

After identifying the self-assembled structures in the bottle tests, it was time to examine closer the mechanism involved in soil washing. This will be the next topic of discussion.

4.2 Soil Washing Mechanism

Surfactant based technologies, such as soil remediation, is becoming more common in the treatment of organic contaminated soils. It is therefore important to have a better understanding of the underlying mechanisms behind such processes. Based on the surfactant concentration, the mechanism by which contaminants are removed by surfactants can be classified into two main categories:

- **Soil Roll-up Mechanism:** This mechanism occurs below the critical micelles concentration (CMC) at which surfactants exist only as monomers. Below the CMC, surfactants have minimal effects on the solubility of organic pollutants in water. Under such conditions, the removal of organics by surfactants occurs in two steps: In the first step, the wettability of the system is changed by accumulation of surfactants at the soil-contaminant and soil-water interface. In this step, the contaminants are removed from the soil particles due to a repulsion between the surfactant's head group and the soil particles. This repulsion is a result of adsorption of surfactant molecules on the contaminant surface. In the second step, the energy required to create additional surface area of the oil phase leads to separation of oil from the soil; it is provided by agitation that is a result of convective currents [41].

- **Solubilization and Dispersion:** These mechanisms are based on surfactant detergency and occur above the critical micelle concentration. The underlying mechanism is the partitioning of organic contaminants into the hydrophobic core of surfactant micelles. Polar or uncharged hydrophilic solutes prefer to be at the exterior of micellar core, while the hydrophobic core of the micelles acts as an organic pseudophase which accommodates hydrophobic contaminants (Figure 4.4). Micellar solubilization plays a significant role in decontaminating low solubility organic pollutants in water from the soil matrix. Solubilization acts to increase the apparent water solubility of the contaminant as they are hidden inside the surfactant micelles (Figure 4.5), while dispersion mechanism is due to decrease in interfacial tension between oil and water which results in oil dispersion. The dispersed oil will then be trapped within the hydrophobic interior of the micelles. Reduced interfacial tension leads to lowering the capillary force that holds trapped oil and soil [19]. Then the dispersed oil will trap within the hydrophobic interior of the surfactant micelles. This mechanism, dispersion, is more responsible for mobilizing oil below critical micelle concentration (CMC), since above CMC amount of adsorbed surfactant molecule on surface is constant [46].

For both mechanisms, decontamination involves transferring contaminants from the soil phase to the aqueous phase (i.e. the washing solution). Depending on the mechanism, the contaminants are either dispersed in the aqueous phase or solubilized inside the micelles. Decontamination of the soil is accomplished in either scenario [41, 18, 47].

In addition to the above two mechanisms, when the concentration of surfactants is near zero in the aqueous phase, washing predominantly occurs under a displacement mechanism where the short strands of trapped residual oil are displaced from the pores by the washing solution (Figure 4.5). As the primary short oil streams pass through the soil, they can form longer strands, which will be difficult to displace; therefore, they will be clogged in smaller pore spaces. There is also a possibil-

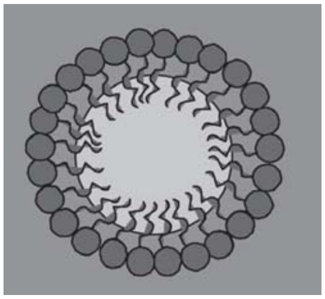


Figure 4.4: A Typical Surfactant Micelle with Hydrophobic Interior and Hydrophilic Exterior Characteristic [22]

ity that the displaced oil can be re-trapped in smaller pore sizes [22]. Abdul et al reported the dependency of oil ganglia displacement on the viscous pressure drop across the ganglion to the capillary pressure across the oil- water interface [48].

In summary, in the presence of surfactants, the first three mechanisms (i.e. soil roll up, solubilization and dispersion) are the most effective ones, while the last mechanism has minimal effect in washing contaminants. In the absence of surfactants, washing mostly is accomplished by the last mechanism.

4.3 Characterization of Washing Solutions

In selecting surfactants for enhance oil recovery operations (mentioned earlier in section 2.3.6), it should be noted that surfactant sorption onto soil also plays an important role. An effective surfactant is one that is not significantly adsorbed by the soil - otherwise there would not be much surfactant left for solubilizing the contaminants. In addition, hydrophobicity of the soil will increase by surfactant adsorption onto the soil, and will result in re-adsorbing of removed contaminants on soil surface which will eventually cause poor remediation. Most of the minerals carry negative surface charges in aqueous media. Therefore, between cationic

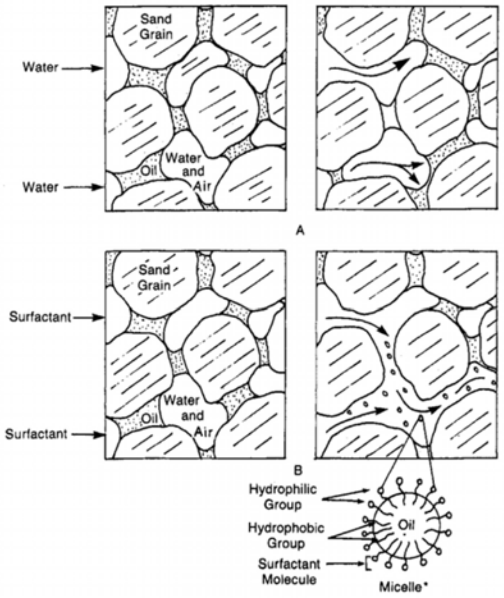
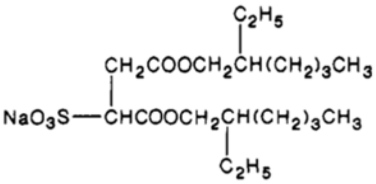


Figure 4.5: The Displacement and Solubilization of Oil (Adapted from [18])

and anionic surfactants, the latter is expected to have less adsorption on soil due to their surface charge. Non-ionic surfactants are also known to have the same effect as anionic ones. As a result, anionic or non-ionic surfactants are expected to act more effectively in remediating contaminated soils. Since solubilization plays a major role in soil washing, any factor that targets this mechanism is important. One of these important parameters is surfactant *hydrophobic tail length*. As this length increases, the micelle's diameter, and as a result the micelle size and aggregation number, is also increased. This augmentation is expected to enhance solubilization [47].

Based on the above two reasons and the wide application of sulfonated surfactants in enhaced oil recovery, we chose Aerosol-OT (AOT) as it is an anionic sulfonated based surfactant with moderately long hydrophobic chains for our washing experiments. (Nevertheless, it is reported in the literature that surfactants with straight hydrophobic tails have more solubilization power compared to those with branched



$$\begin{array}{l} C_2H_5 \\ CH_2COOCH_2CH(CH_2)_3CH_3 \\ NaO_3S-CHCOOCH_2CH(CH_2)_3CH_3 \\ C_2H_5 \end{array}$$

Figure 4.6: Aerosol-OT (AOT) Molecular Structure (Anionic Surfactant)

chains.) Regarding the behaviour of AOT in the presence of salt, it is stated that at low salinities, AOT remains more in the aqueous phase irrespective of the critical micelle concentration, while at higher salinities, AOT partitions more into the oil phase at a given temperature [49].

Currently, in all reported washing methods in the literature, large volumes of aqueous solution is required in comparison to the amount of organic contaminant. This, however, cannot be done in our case: According to the objective of our washing protocol, minimal amount of washing solution should be used (e.g. equal to the amount of trapped hydrocarbon between the sand grains).

Following the procedure explained in section 3.2.2, the washing solutions were prepared. It was seen that the solutions exhibited a fairly high viscosity at salinities ($NaCl$ concentrations) between 0 and 1 $wt\%$; the viscosity was significantly lower at 1 to 2 $wt\%$ salinity. To understand more about their microstructures, small samples of washing solutions were taken and examined under cross polarizers. The intention here was to investigate the possibility of liquid crystal formation, as liquid crystals are known to exhibit high viscosities. The results, as seen from Figure 4.7, show liquid crystalline behaviour between 0 to 1.5 $wt\%$ $NaCl$, and isotropic behaviour (suggesting absence of liquid crystallinity) at 2 $wt\%$ $NaCl$. It should be noted that as soon as the washing solutions are in contact with oil (i.e. diluted bitumen), their viscosity reduce. This was indeed confirmed by jar tests as there were no sign of liquid crystals in the jar under similar conditions.

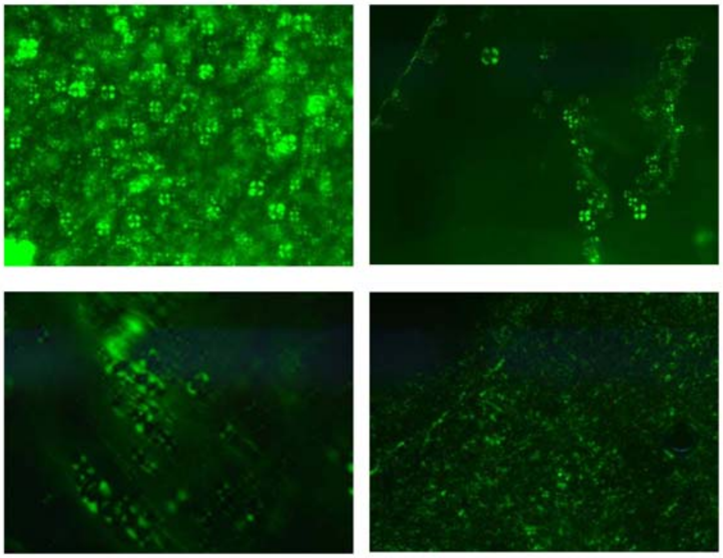


Figure 4.7: Formation of Liquid Crystals at Different Salinities. Zero NaCl (Top Left), $0.3\ wt\%\ NaCl$ (Top Right), $1.0\ wt\%\ NaCl$ (Bottom Left), $1.5\ wt\%\ NaCl$ (Bottom Right)

4.4 Effect of Salt on Appearance of Drained Mixture after Washing

Drained mixtures are liquids collected at the bottom flask (see Figure 3.4) in a washing procedure. Such mixtures contained aqueous phases with salinities ranging from 0 to $2\ wt\%$ NaCl; they showed different behaviours depending on the salt concentration. Different kinds of interface (Figure 4.8) were observed at different salinities - for instance, rigid and distorted interfaces in some, smooth and clear interfaces in others. It should also be noted that, even at the same salinity, depending on the type of solvent used to dilute the bitumen, the phase behaviour could be very different. For instance, at $0.1\ wt\%\ NaCl$, when heptane-diluted bitumen was used, the interface was distorted and an opaque brownish phase was formed at the bottom of drained mixture. In contrast, for hexadecane-diluted bitumen, no distinguishable interface was observed at the same salinity (Figure 4.9). The illustrated brownish

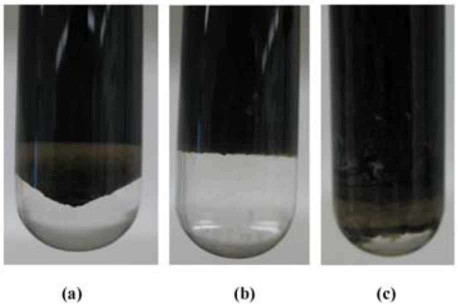


Figure 4.8: (a) Distorted Interface at $1.0\ wt\%$ Brine Solution, C_7-Diluted Bitumen ($4 : 1$ wt ratio), $[AOT]_{Overall} = 2.5\ wt\%$ - (b) Flat Smooth Interface at $0.7\ wt\%$ Brine Solution, C_7-diluted bitumen ($4 : 1$ wt ratio), $[AOT]_{Overall} = 2.5\ wt\%$ - (c) Distorted Interface at $0.7\ wt\%$ Brine Solution, C_{16}-Diluted Bitumen, $[AOT]_{Overall} = 2.5\ wt\%$

Figure 4.9: (a) Formation of Brownish Phase at $0.1\ wt\%$ Brine Solution, C_7-Diluted Bitumen ($4 : 1$ wt ratio), $[AOT]_{Overall} = 2.5\ wt\%$- (b) No Distinguishable Interface at the Same Salinity, C_{16}-Diluted Bitumen ($4 : 1$ wt ratio), $[AOT]_{Overall} = 2.5\ wt\%$

Figure 4.10: Formation of Yellowish Phase at the Same Salinities as in Guideline Jars, $1\ wt\%\ NaCl$ Concentration, C_{16}- Diluted Bitumen ($4:1$ wt ratio), $[AOT]_{Overall} = 2.5\,wt\%$

phase formed at lower salinities, contained lots of emulsified water drops. This occurred, even though there was no clear separate phase as aqueous phase. It will be discussed more in section 4.5.

Generally, rigid and distorted interfaces were seen mostly at lower salinities (less than $0.7\ wt\%\ NaCl$), and smoother and clearer interfaces were observed at higher salinities.

In addition to what was described, when hexadecane-diluted bitumen was used as the oil phase, a yellowish phase was seen to form at the same salinities, as it was formed in the jar tests (Figure 4.10).

4.5 Water Content Measurements

Drained mixtures that contained $NaCl$, water, surfactant (AOT), and oil (heptane-diluted bitumen or hexadecane-diluted bitumen) were prepared, following the procedure discussed in section 3.2.2. In order to calculate the washing efficiency, we needed to know the water content of the drained mixtures. As explained in that section, water content was measured by two analytical methods (i.e. Dean Stark and Modified Karl Fischer). The results are discussed in the next two sections, and

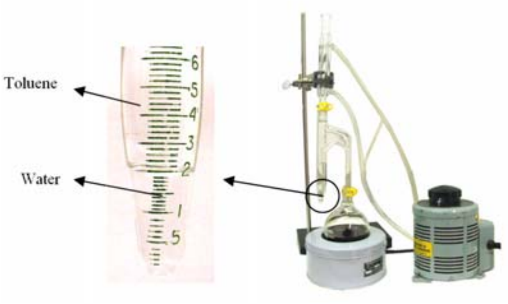


Figure 4.11: Dean Stark Water Trap

at the end the two methods are compared.

4.5.1 Dean Stark Method

As mentioned earlier in section 3.2.2, Dean Stark is the most robust and reliable analytical methods for quantifying water contents in a variety of mixtures. Following the procedure discussed earlier, water was collected inside the water trap underneath toluene after several hours of distillation (Figure 4.11).

On average, it took 8 to 10 hours to have all the water collected from a mixture. We ran the apparatus for some of the drained mixtures, and the results for both solvents are shown in Table (4.1) and (4.2). Water contents of the mixtures are expressed in terms of an absolute value (mass), and each reported value in the table represents an average of 4 measurements.

The first column of the above tables shows salinity ranges of the drained mixtures; the second column indicates the masses of water in the drained mixtures, and column three represents water-to-recovered oil ratios. It is seen from the third column that, as the salt concentration increased, the water-to-oil ratio decreased up to a certain salinity, then began to increase again.

4.5.2 Modified Karl Fischer Method

Water contents of the mixtures were also measured by a modified Karl Fischer method. Modification was required as the drained mixtures contained water contents that far exceeded the maximum level allowed in regular Karl Fischer procedures (typically a few percent, whereas our drained mixtures could have up to 80% water). Following the procedure in section 3.2.2, water content was quantified based on a modified technique. We encountered several challenges in this modified technique that are explained as follows:

1. Inhomogeneity of the drained mixtures due to immiscibility of mixture contents. As such, small samples could not be used as a representative of the

Table 4.1: Dean Stark Water Content Measurement Results for Mixtures Contained C_7-Diluted Bitumen ($4:1$ wt Ratio), NaCl, Water, $[AOT]_{Overall} = 2.5\ wt\%$

$NaCl\ Concentration\ (wt\ \%)$	$Water\ Content\ (g)$	$Water-to-Oil\ ratio$
0.0	2.55	0.948
0.3	1.95	0.631
1.0	2.35	0.764
2.0	2.05	0.807

Table 4.2: Dean Stark Water Content Measurement Results for Mixtures Contained C_{16}-Diluted Bitumen ($4:1$ wt Ratio), NaCl, Water, $[AOT]_{Overall} = 2.5\ wt\%$

$NaCl\ Concentration\ (wt\ \%)$	$Water\ Content\ (g)$	$Water-to-Oil\ ratio$
0.0	3.25	0.806
0.3	2.20	0.626
1.0	3.40	0.667
2.0	3.65	0.893

Figure 4.12: (a) Brownish Phase Caused Inhomogeneity and Formation of Gel-Like Materials in the Mixture While Quantifying Water Content at $0.1\ wt\%\ NaCl$ Concentration, C_7-Diluted Bitumen (4:1 wt ratio), $[AOT]_{Overall} = 2.5\ wt\%$ (b) the Same Mixture after Adding Acetone in Order to Homogenize the Mixture, as it is shown acetone dissolved the gel-like material and the brownish phase

whole mixture.

2. High water content of the drained mixtures that exceeded Karl Fischer measurement range.

In order to overcome these two issues, we used several appropriate solvents to both homogenize the mixture and decrease the water content to the allowed range for the Karl Fischer apparatus. At lower salinity, for instance 0.1 or $0.3\ wt\%\ NaCl$, we used acetone to dissolve the brownish phase that caused inhomogeneity (see Figure 4.12). For mixtures containing no salt, we used tetrahydrofuran (THF) as well as acetone to homogenize the mixture. At all salinities, in order to dilute the mixture, we used toluene as well as the above-mentioned solvents.

The results of water content measurements using the modified Karl Fischer method are listed in Table (4.3) and Table (4.4) for heptane and hexadecane respectively. All water content values are reported per recovered oil and are averages of 4 measurements.

According to Karl Fischer results for both solvents (i.e. heptane and hexadecane), as the salt concentration increased, the water-to-oil ratio decreased up to a point and began increasing. As mentioned in section 4.4, at lower salinities there was no clear aqueous phase. However, as seen in the above Tables, mixtures at these salinities

Table 4.3: Water Content Measurement Results for Mixtures Contained C_7-Diluted Bitumen ($4:1$ wt Ratio), Nacl, Water, $[AOT]_{Overall} = 2.5\ wt\%$ Using Modified Karl Fischer Method

$NaCl\ Concentration\ (wt\ \%)$	$Water\ Content\ (g)$	$Water - to - Oil\ ratio$
0.0	2.341	0.933
0.1	2.007	0.738
0.3	2.278	0.669
0.5	2.038	0.686
0.7	2.129	0.695
1.0	1.835	0.729
1.5	2.56	0.790
2.0	2.21	0.831

Table 4.4: Water Content Measurement Results for Mixtures Contained C_{16}-Diluted Bitumen ($4:1$ wt Ratio), Nacl, Water, $[AOT]_{Overall} = 2.5\ wt\%$ using Modified Karl Fischer Method

$NaCl\ Concentration\ (wt\ \%)$	$Water\ Content\ (g)$	$Water - to - Oil\ ratio$
0.0	2.925	0.755
0.1	2.994	0.753
0.3	2.783	0.657
0.5	0.736	0.271
0.7	1.891	0.445
1.0	2.7	0.623
1.5	3.155	0.733
2.0	3.12	0.944

contained high water contents. Accordingly, observation in combination with Karl Fischer results show that at low salinities, $NaCl$ as an electrolyte is significantly capable of emulsifying water drops.

4.5.3 Comparing Dean Stark and Modified Karl Fischer Method

Both methods are among the most accurate analytical techniques for quantifying water contents. Each technique, however, has advantages and disadvantages as follows:

Let us begin with the advantages of the Dean Stark method. This technique is very robust and reliable; it is applicable to the most complex and difficult-to-break emulsion systems, irrespective to the mixture content. The Dean-Stark method can be used to quantify both low and high water contents. However, there were also a few disadvantages that restricted the technique's applicability in our study. The biggest disadvantage in using Dean Stark to quantify water contents was the long operation time. Another disadvantage was foam stability problem, as we used a considerable amount of Aerosol-OT as surfactant. Aerosol-OT tends to form stable foams at high concentration in the presence of low $NaCl$ concentrations. Indeed, we encountered formation of stable foams that created a pressure inside the flask and prevented the vapours from reaching the condenser. In order to avoid this problem, we used about $3\ (mL)$ of non-water based anti foaming agent (100% active silicone polymer). The amount of anti-foaming agent used was substantial in comparison to the drained mixture weight; since such chemicals were expensive, its use was not economical.

On the other hand, our modified Karl Fischer technique was proved to be as accurate and reliable as the Dean Stark method. In addition, it is by far much faster than Dean Stark. Unlike Dean Stark method, it could be used for high surfactant concentration systems without encountering foaming problem; as a result, there was no need for expensive anti-foaming agents. Unlike the traditional Karl Fischer technique, our modified method could be used even for high water content systems (such as what was encountered in this study). Due to the above-mentioned problems with using Dean Stark distillation, and the advantages that our modified Karl Fischer method has over the Dean Stark technique, we decided to quantify water contents of all drained mixtures by the latter in order to eventually calculate washing efficiencies. Comparing the results from Dean Stark and modified Karl Fischer methods, as seen in Tables 4.1 to 4.4 for drained mixtures containing $C16$ and $C7$, it is clear that the two methods are in a close agreement (thus confirming once more the reliability of the two methods).

4.6 Remediation Factor

Having established a reliable and efficient method (i.e. the modified Karl Fischer technique) for quantifying water contents of drained mixtures, the washing efficiency, which we will here call the *remediation factor*, could now be calculated based on the mass balance approach discussed in section 3.2.2. As it is seen from equation 3.3, water content values are needed to determine the amount of trapped oil after soil washing. In the end, the ”remediation factor” was calculated using equation 4.1 as follows:

$$\%Remediation\ Factor = \frac{m_{oil}}{m_0} \times 100 \tag{4.1}$$

All the washing experiments were conducted for two types of solvents: heptane and hexadecane. In these series of experiments, we considered heptane-diluted bitumen

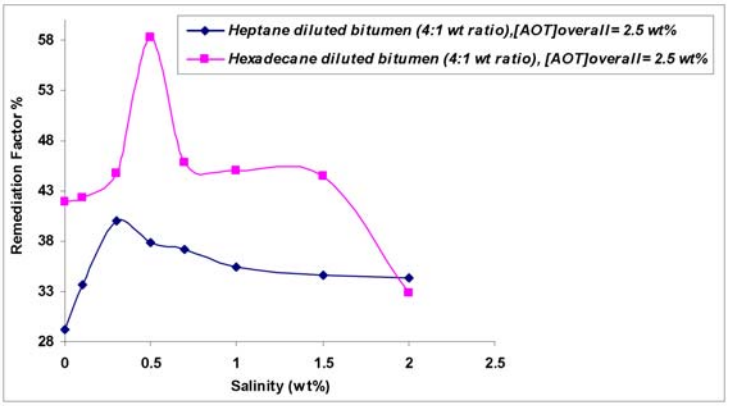


Figure 4.13: Remediation Factor for the Two Types of Soil Contaminants

and hexadecane-diluted bitumen as soil contaminants. The results are shown in Figure 4.13 in which each value represents an average of 4 measurements.

In the Introduction chapter, it was mentioned that due to environmental concerns associated with the current bitumen extraction technique, there is an urgent need to shift to solvent-based extraction methods. We also discussed possible problems that one may encounter with the proposed method, such as remediation of sand grains that are contaminated with residual oil (i.e. solvent diluted bitumen). Here, we intend to compare the performance of the two types of solvents in presence of $2.5\ wt\%$ overall concentration of AOT. Let us suppose that we use hexadecane as a solvent in the proposed solvent-based extraction. Based on the washing results of simulated tailings (see section 3.2.2), one finds the maximum remediation factor occurring at $0.5\ wt\%\ NaCl$ concentration. On the other hand, with heptane as solvent, the optimal salinity (for maximum remediation) is shifted to a lower salinity of $0.3\ wt\%\ NaCl$. It is concluded that using hexadecane as a solvent in the proposed solvent-based extraction, results in much higher remediation. According to Figure 4.13, the same trend is observed for the two types of oil (i.e. heptane-based and hexadecane-based diluted bitumen). It is seen that, by increasing salt concentration, the remediation factor also increased up to a certain salinity, at which point

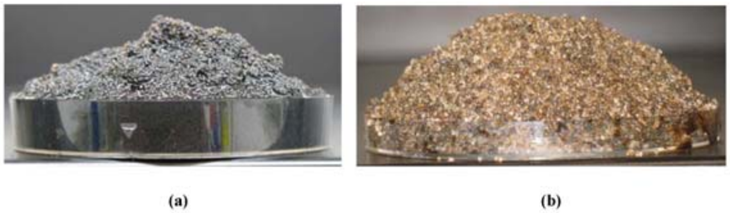


Figure 4.14: Color Change in Contaminated Soil (a) before Washing (b) after Washing

it began to decrease. This behaviour can be attributed to the effects of salt on the oil-water interfacial tension, which will be discussed in the next section.

We expect the underlying mechanism of the soil-washing process to be mostly due to solubilization, as the surfactant concentration was far above CMC. Another rationalization is that since we are using an anionic surfactant, contaminants are removed from the soil due to the repulsion between surfactant head groups and the soil surfaces (which are negatively charged). This repulsion results in soil remediation when the contaminants are solubilized into the surfactant micelles. Another possible mechanism of soil remediation stems from the fact that, since in the washing protocol, we agitate the oil-water mixture (see section 3.2.2), we are increasing the interaction of the oil phase with the washing solution, which leads to solubilization of more oil into surfactant micelles. After conducted washing experiments, we have noticed dramatic changes in colour between the contaminated sand (i.e. simulated tailings) before and after washing using both solvents; pictures of these sand grains are shown in Figure 4.14.

It should be emphasized that our new washing protocol was conducted under minimal water use, which gave significant superiority over all other reported washing procedures in the literature. In terms of water consumption, this protocol is far more environmental friendly in comparison to all other methods of soil remediation.

4.7 Interfacial Tension Measurement

In this section, we report a series of experiments conducted to determine interfacial tensions between the contaminant (diluted bitumen) and the washing solution (brine). Following the procedure discussed in section 3.3.1, the hydrocarbon phase and the aqueous phase were prepared. According to *Vonnegut*'s equation (equation 3.7), interfacial tension measurements required knowledge of the heavy and light phase densities. Therefore, a set of density measurements were carried out for both hydrocarbon and aqueous phases at room temperature and the results are as follows:

As explained in section 3.3, interfacial tensions between the oil phase (diluted bitumen containing AOT) and the aqueous phase (water of different salt concentrations) were determined by spinning drop tensiometry. Based on the *Vonnegut* equation for a known capillary rotating speed, and knowing the densities of the two phases, the

Table 4.5: Aqueous Phase (Heavy Phase) Densities at Room Temperature

$NaCl\ Concentration\ (wt\ \%)$	$Heavy\ Phase\ Density\ (g/cm^3)$
0.1	0.9988
0.3	1.0004
0.5	1.0018
0.7	1.0032
1.0	1.0045
1.5	1.0087
2.0	1.0126

Table 4.6: Hydrocarbon Phase (Light Phase) Densities at Room Temperature

$Contaminant\ (Hydrocarbon\ Phase) + Surfactant$	$Heavy\ Phase\ Density\ (g/cm^3)$
$C7\ Diluted\ Bitumen\ (4:1\ wt\ ratio) + 5\ wt\%AOT$	0.747
$C16\ Diluted\ Bitumen\ (4:1\ wt\ ratio) + 5\ wt\%AOT$	0.835

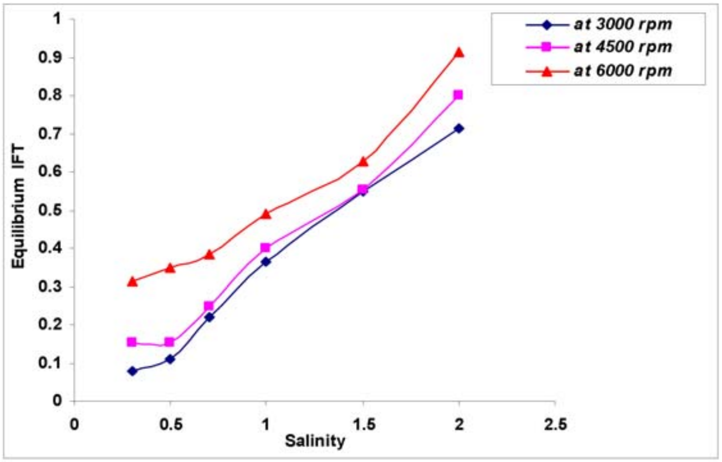


Figure 4.15: Equilibrium Interfacial Tension (IFT) between C_7 Diluted Bitumen and 5 $wt\%$ AOT and Different Brine Solutions

interfacial tension could be determined from the drop diameter. In principle, the interfacial tension should be independent of the rotating speed (i.e. as the rotating speed increases, the drop diameter should decrease accordingly). However, in our measurements, we observed interfacial tension dependence on capillary rotating speed: as we increased the rotating speed, the apparent interfacial tension also increased. These results, with heptane-diluted bitumen and hexadecane-diluted bitumen as the oil phases, are shown respectively in Figures 4.15 and 4.16. Each reported value in these figures represents an average of 2 equilibrium interfacial tension measurements (i.e. steady state tensions). We had noticed that the oil-water interfacial tensions equilibrated faster at higher salt concentrations (above 1.5 $wt\%$ $NaCl$) than at low salinities; equilibration times at low salinities may take up to two hours.

At zero and 0.1 $wt\%$ NaCl, equilibrium interfacial tension could not be achieved: the tensions exceeded the maximum level that was measurable by the spinning drop technique. For the remaining salinities, as seen in the above two figures, as salt concentration was raised, the equilibrium interfacial tension also increased. However

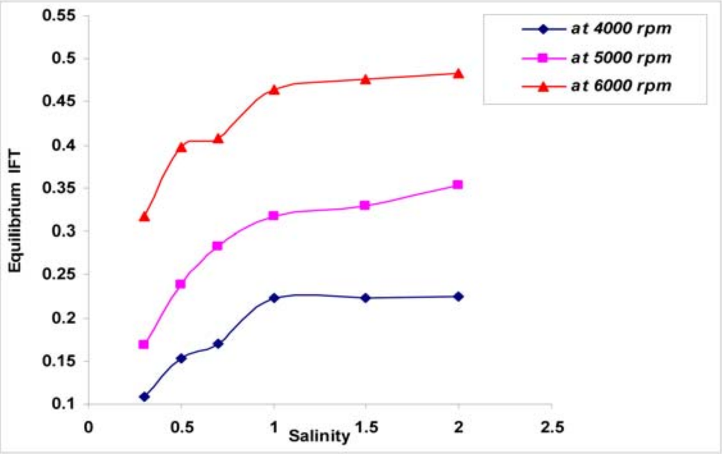


Figure 4.16: Equilibrium Interfacial Tension (IFT) between C_{16} Diluted Bitumen and $5\ wt\%$ AOT and Different Brine Solutions

the rates of change were different depending on the type of the hydrocarbon phase used. For heptane-diluted bitumen, the equilibrium interfacial tensions increased at roughly steady rates (see Figure 4.15). In contrast, with hexadecane-diluted bitumen as the oil phase, much higher rates of increase were observed at low salinities (see Figure 4.16).

The above spinning drop measurements show a clear dependence of the interfacial tension on the capillary rotating speed (ω). For both heptane- and hexadecane-diluted bitumen, as (ω) was raised, the interfacial tension also increased. It is interesting to note that, although the interfacial tensions depended on the rotating speed, the rates at which the tension increased with salinity (i.e. the slopes in Figs. 4.15 and 4.16) remained relatively insensitive to (ω).

As seen from the above plots, systems with heptane-diluted bitumen as the hydrocarbon phase exhibited higher interfacial tensions than systems with hexadecane-diluted bitumen, particularly at higher salt concentrations. The interfacial tensions from Figures 4.15 and 4.16 are replotted in Figure 4.17 for $6000\ (rpm)$. At higher salinities, we observed higher equilibrium interfacial tensions with heptane-diluted

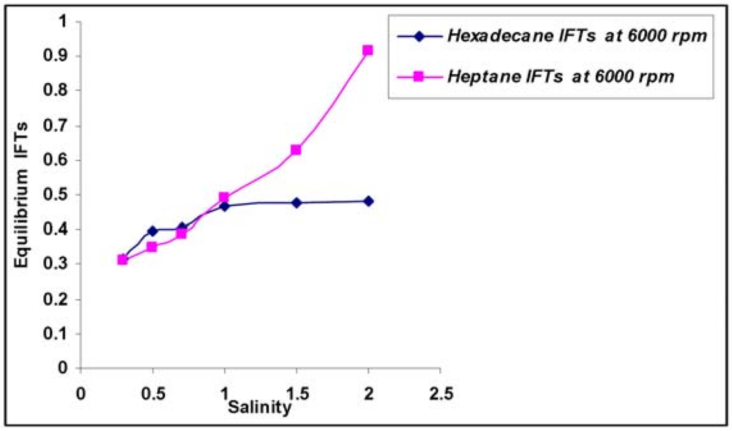


Figure 4.17: Comparing Equilibrium Interfacial Tension Using Hexadecane Diluted Bitumen and Heptane Diluted Bitumen at the Same Capillary Rotating Speed by Increasing Salt Concentration.

bitumen as the oil phase. Moreover, the difference in tension between the two systems is much more pronounced at high salinities.

4.8 Correlating Remediation Factor with Interfacial Tension Measurement

In this section, we will seek correlation between the overall washing performance (characterized by the so-called ”remediation factor”) and the corresponding oil-water interfacial tension (IFT). Figures 4.18 and 4.19 show the remediation factors plotted against the $IFTs$ for the two types of soil contaminants. In the case of heptane-diluted bitumen, it is seen from Figure 4.13 that maximum remediation occurred at a salinity of $0.3\ wt\%\ NaCl$; moreover, this corresponded to conditions at which minimum IFT was acquired. This observation was true independent of the capillary rotating speed (see Figure 4.18). In the case of hexadecane-diluted bitumen as soil contaminant, we do not see a clear correlation between maximum remediation factor and minimal equilibrium interfacial tension: optimal remedia-

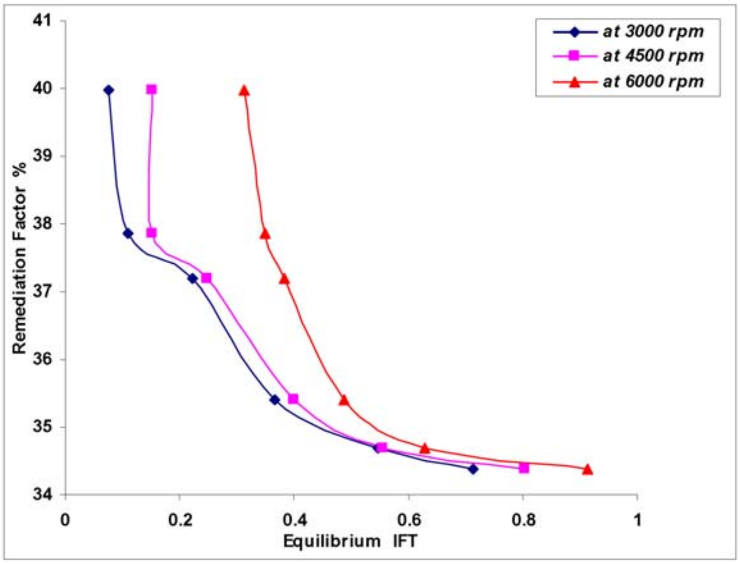


Figure 4.18: Correlating Remediation Factor with Equilibrium Interfacial Tension Using Heptane Diluted Bitumen as Soil Contaminant

tion, as seen from Figure 4.13, occurred at $0.5\ wt\%\ NaCl$, while the minimum oil-water IFT was detected at a salinity of $0.3\ wt\%\ NaCl$. This same correlation trend is seen irrespective of the capillary rotating speed when hexadecane-diluted bitumen was used as the oil phase (see Figure 4.19).

According to the above two figures, there is a strong correlation between the interfacial tension and remediation factor. That is, as the interfacial tension increased, a decrease in washing efficiency (i.e. remediation factor) is expected. In addition to such a declining trend, lower washing efficiencies, using heptane-diluted bitumen as soil contaminant, can be rationalize by the equilibrium interfacial tension values. As it is shown in Figures 4.18 and 4.19, we are observing higher interfacial tensions at high salinity ranges using heptane-diluted bitumen. This resulted in lower remediation performance for heptane-diluted bitumen in compare to hexadecane-diluted bitumen.

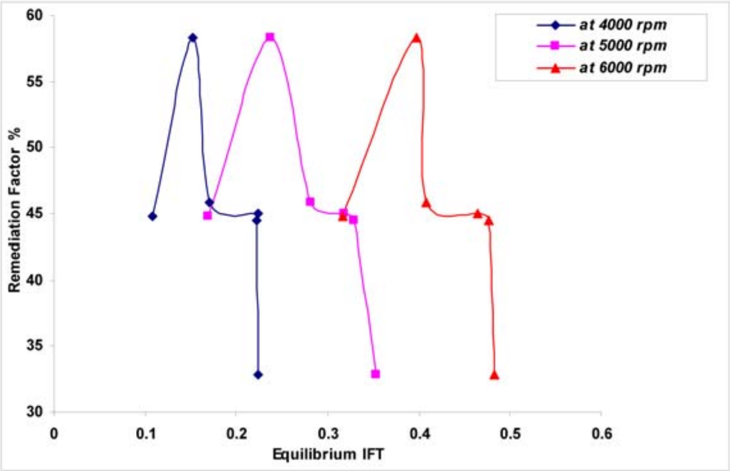


Figure 4.19: Correlating Remediation Factor with Equilibrium Interfacial Tension Using Hexadecane Diluted Bitumen as Soil Contaminant

Chapter 5

Summary and Future Work

This research is motivated by environmental concerns associated with the water-based bitumen extraction process that is currently used by the oil sands industry. An alternative solvent-based technology, which in principle uses very little or no water, must be developed. One of the major issues with this alternative process is the loss of solvent by way of hydrocarbon attachment to reject sand grains. The proposed solution to this problem is to use a combination of surfactant and water (as a pseudo solvent) to solubilize the residual oil. The key parameters in the proposed solution are:

1. To develop a method to minimize water consumption.
2. To recover as much residual oil (i.e. solvent-diluted bitumen) as possible, ideally $100\ \%$.

Recovery of residual oil involves interfacial science at oil-water interface and wetting of sand by the oil and water phases.

This study was mainly focused on developing a new protocol to minimize water consumption (the first key parameter above); the second key parameter is left for future work. We also conducted a series of interfacial tension measurements to gain further insight into the residual oil recovery process.

As a preliminary study, the phase behaviour of two different ternary oil-water-surfactant systems were studied. The oil was either heptane-diluted bitumen or hexadecane-diluted bitumen, and the surfactant was Aerosol-OT. To *minimize water* use, we had insisted on using only as much water as the amount of oil (the contaminant) in all systems (see section 3.1.2). In order to characterize the phase behaviour, a series of Karl Fischer titrations (section 3.1.3), followed by a set of cross-polarized light screening tests (section 3.1.4) were conducted. These jar tests constituted the preparatory step to the washing experiments; they gave us guidelines regarding the possible phases that may be formed during soil washing. In the heptane-diluted bitumen series, neither a third phase nor liquid crystal formation was seen. In the case of hexadecane-diluted bitumen, a third phase (i.e. L_3 phase) and no liquid crystal formation were observed (section 4.1). Following these jar tests, we developed a new protocol for determining washing performances. A series of washing experiments that used only as much water as the amount of residual oil were conducted. For determining the amount of recovered oil, a modified Karl Fischer technique was developed that was tailored for difficult-to-break emulsions with high water contents (section 3.2.2). Subsequently, the washing performance, measured by the so-called ”remediation factor,” was introduced (section 3.2.2). In our experiments, maximum soil remediation was observed at $0.5\ wt\%\ NaCl$ in the case of hexadecane-diluted bitumen as contaminant; this optimal salinity was shifted to $0.3\ wt\%\ NaCl$ when heptane-diluted bitumen was used as the oil phase (section 4.6). A likely scenario that could explain the higher remediation factor using hexadecane-diluted bitumen is related to formation of the third phase as demonstrated in the jar tests.

To gain insight into the mechanism behind the remediation process, we conducted a series of interfacial tension measurements (section 3.3) in order to study a probable dependency between the IFT and electrolyte (i.e. $NaCl$) concentration. Strong correlation between salt concentration and IFT was observed (section 4.7). While measuring IFTs using the spinning drop technique, we had observed an anomalous dependency of the IFT on the capillary rotating speed: the interfacial tension was seen to increase with increasing rotating speed in both types of solvent-diluted bitumen (section 4.7). In addition to that, depending on the type of solvent-diluted bitumen, different correlations between the remediation factor and the interfacial tension was observed (section 4.8).

In this study, we used a Millipore filter apparatus (see Figure 3.4) as a washing column. Mass loss due to multiple transferring of jar contents to the column before and after washing was observed; this mass loss was due to (a) evaporation of solvent, and (b) attachment of liquids to the container walls. For future work, we intend to look into a better design for the washing apparatus. One of the focuses should be on the quality of the material of which the apparatus is made in order to minimize mass loss (e.g. shift to Teflon instead of glass to minimize liquid attachment to walls). Another important point would be to design a cap for the column to reduce mass loss. A preliminary drawing of the new design is shown in Figure 5.1.

In choosing the types of surfactant for sand grain remediation, biosurfactants seem to be a better option in comparison to synthetic ones as they are environmentally friendly (i.e. biodegradable); such surfactants have indeed been tested in enhanced oil recovery field trials. Choosing a non-volatile, non-viscous solvent also helps to minimize the mass loss during the washing experiments. It is also important to study the underlying physics such as sand wetting affinity. In this regard, contact angle of sand at the hydrocarbon-water interface should be investigated. As part of

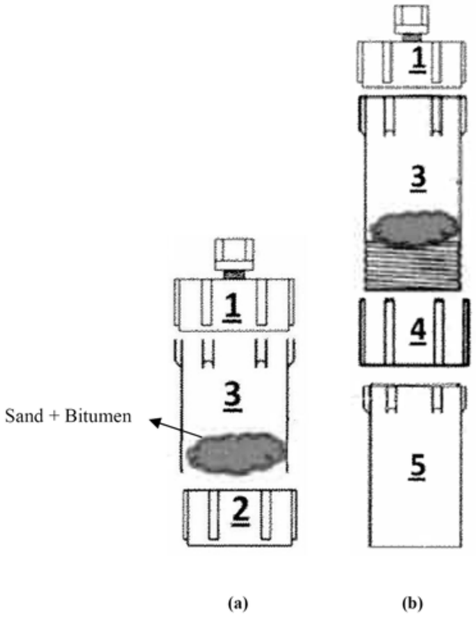


Figure 5.1: (a) Part 3 represents the washing column; part 2 is a solid end cap, while part 1 is an end cap with ventilation for atmospheric drainage. (b) Part 4 is the end cap with a screen and part 5 is the collector of the drainage mixture. All parts are made of Teflon.

the underlying washing mechanism, the surfactant sorption on soil, which plays an important role, should also be studied.

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