FINAL REPORT

EXTENDING TEMPORARY STORAGE CAPACITY OFFSHORE WITH EMULSION BREAKERS

by

SL Ross Environmental Research Ltd.
Ottawa, ON

for

Minerals Management Service
Technology Assessment and Research Division
Herndon, VA
and
Canadian Coast Guard
Rescue, Safety and Environmental Response
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Summary

The objective this study was to develop a more complete understanding of the use of emulsion breakers injected into an oil spill recovery system at both lab-scale (in Ottawa at SL Ross) and mid-scale (in New Jersey at Ohmsett). The experiments were designed to assess the injection/mixing/settling regimes required for optimum water-removal performance from a meso-stable water-in-oil emulsion with an oil spill demulsifier. The ability of emulsion breaker addition to reduce pumping heads and the effects of demulsifier addition of the oil content of decanted water were also assessed. Various injection locations (skimmer head, cargo line, tank inlet, etc.) and mixing technologies (static in-line, mechanical, etc.) were investigated. The efficiency of emulsion breaking chemicals in resolving water-in-oil emulsions is highly parent oil/surfactant specific. The results are strictly valid only for the combination of demulsifier (Alcopol O 70% PG) and emulsion used (50% salt water in a blend of Hydrocal 300/Fuel Oil).

The use of a demulsifier injected into a recovery system, combined with decanting, substantially reduced the volume of water in temporary storage tanks and the water content of emulsions for disposal/recycling. The efficacy of the demulsifier was a strong function of free water content:
- If the free water content exceeded about 60%, the effect of the surfactant was substantially reduced.
- If no free water was present, the level of turbulence generated by the flow was insufficient to promote any significant emulsion breaking.
- A free water content of greater than about 33% was required to reduce the bulk viscosity of the fluid to the point where the flow regime was turbulent, and mixing energy was supplied to promote emulsion breaking.

The degree of emulsion breaking achieved increased with increasing mixing energy applied to the fluid. Increasing the flow rate (and hence turbulence level) and increasing the length of the flow path both resulted in increased emulsion breaking. The use of in-line mixers further increased the removal of emulsion water. The application of mechanical mixing energy, using a bladed impeller, after placing the recovered fluid in a tank, also increased demulsification.

The optimum location for injection of the demulsifier was at the skimmer pump for recovered fluids containing up to 50% free water to maximize the amount and time of the mixing. For recovered fluids containing more than 60% free water, decanting the free water followed by the application of mechanical energy would work best. If pure emulsion is recovered, injection at the skimmer pump and additional mixing in the temporary storage tank would be best.

Primary break occurred in only a few minutes (2 to 5 in the lab tests, less than 15 for the Ohmsett tests). The application of demulsifier did not appear to affect the time required. The Ohmsett results indicated that the use of a demulsifier increased TPH concentrations by approximately a factor of two in the decanted water. Although it is not known what portion of each TPH reading was associated with dissolved demulsifier in the water, the decanted water did contain a significant amount. As long as the recovered fluid contained at least 33% free water, the pressure

drops due to skin friction in the tubing and hoses approximated those expected for flowing water. The use of an in-line mixer significantly increased back pressures.

The implication of this research for oil spill response is that it may be possible to greatly reduce downtime for offshore skimming operations caused when the available onsite temporary storage systems are filled with fluids containing large amounts of water. The legislated requirements for onsite temporary storage systems could also ultimately be reduced by the use of these results, resulting in considerable savings in operating and disposal costs for OSRO's. Knowing that the separated water can be decanted quickly will optimize onsite recovery operations and greatly reduce the volume of fluids requiring disposal. In fact, the removal of most of the free and emulsified water from the recovered product would greatly enhance the likelihood that it could be recycled, as opposed to requiring disposal.

The results of this multi-project research is not ready to be transferred to the response community quite yet. There are several key question that remain to be answered. Most of these are regulatory questions (such as, can decanted free water containing more than 15 ppm oil be pumped overboard during a response operation?) that should be addressed in other forums. The key technical question that remains is: where do the constituents of the demulsifier (surfactants and solvents) end up? Do they remain with the oil phase after separation, where they would pose little problem, or do they partition into the water, which will be subsequently decanted overboard, releasing the surfactants into the water environment? Given that some demulsifiers are toxic to marine life, is their use to extend temporary storage capacity, and hence oil removal operations, a net environmental benefit?

Acknowledgements

Disclaimer

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1. Introduction

This research project involved conducting a series of six tasks to develop a clearer understanding of the use of chemical emulsion breakers in oil spill response. This joint project was funded by the Minerals Management Service and the Canadian Coast Guard. The project began in December 1999 and was completed in March 2002. Task 1 (Literature Review) was conducted between December 1999 and Marc 2000. Tasks 2 and 3 (Laboratory Tests) were conducted between February and May 2001). Tasks 4 and 5 (Ohmsett Tests) were conducted in July 2001, and Task 6 (Data Analysis and Report) were conducted between September 2001 and March 2002.

1.1 Background and Purpose

The preferred approach to cleaning up an oil spill is to contain and thicken the oil slick(s) with booms and then place skimmers in the oil or emulsion to recover it. The recovered fluids are placed in temporary storage containers for transfer to larger storage vessels or for direct input into the waste recycling and disposal system. The most common type of high-capacity skimmer in use today is the weir skimmer. A large amount of water, both in the form of water contained in emulsified oil and free water, is often recovered by these skimmers operating in waves. In some cases, the transfer pump built into the skimming system can impart enough energy to cause additional emulsification of the recovered fluids. The problem is that the recovered water (both emulsified and free) dramatically reduces the temporary storage space available at the site of skimming operations; this can result in having to stop skimming prematurely when the storage capacity is reached and having to wait until empty temporary storage containers arrive at the response site. **The treatment and separation of recovered water onsite is the largest area of neglected technology in mechanical response today (Schulze et al. 1995).**

Lab-scale and preliminary mid-scale tests were recently completed that give some quantitative insight into the oil/water separation processes occurring in temporary storage devices (SL Ross

1998 and 1999). The objective of those tests was to determine the optimum time to decant the water and maximize the available on-site storage space during a skimming operation. The results indicated that "primary break" (the initial separation of the recovered fluid into a layer containing most of the oil and a layer containing most of the free water) occurred within a few minutes to one hour, depending on the physical characteristics of the oil. Rapidly decanting this free water layer, in appropriate situations, may offer immediate increases of up to 200 to 300% in available temporary storage space.

One aspect of decanting not addressed in these initial research studies was that many skimmer operations are, sooner or later, faced with recovering a water-in-oil emulsion. These emulsions can easily contain 70 to 80% water that is tightly held and may not separate out, even after standing for days or months. This emulsion will quickly fill the available temporary storage space, even after decanting of the free water layer, with a product that contains mostly water.

In order to facilitate and optimize open ocean containment and recovery operations, the available temporary storage space could be further extended by using chemical emulsion breakers (also called demulsifiers) to cause the water-in-oil emulsion to break into oil and water phases, followed by decanting of the water separated from the emulsion. Although some skimmer systems (notably the Framo Transrec 350) incorporate chemical emulsion breaker delivery systems, the dynamics of the separation process are not well understood.

Preliminary research into the concept performed in the early-1990s (SL Ross 1991 and 1992, Lewis et al. 1995a and 1995b) gives some guidance on the concentrations of demulsifier required for rapid breaking and the importance of mixing energy to the process; however, these preliminary studies were not pursued further.

The research idea here was to conduct additional research on the use of emulsion breakers injected into a recovery system at both lab-scale (at SL Ross) and mid-scale (at Ohmsett). Experiments were developed based on the lessons learned from the previous research and the

early tasks of this project. They were designed to assess the effectiveness of an oil spill emulsion breaker on water-in-oil emulsions and the injection/mixing/settling regimes required for optimum water-removal performance. The ability of emulsion breaker addition to reduce pumping heads was also assessed. Various injection locations (skimmer head, cargo line, tank inlet, etc.) and mixing technologies (static in-line, mechanical, etc.) were investigated.

1.2 Report Contents

Section 2 of the report introduces the subject of water-in-oil emulsification using an updated version of a 1992 in-depth report on the subject of demulsifiers (SL Ross et al. 1992). Section 3 of this report details the results of the literature review. Section 4 covers the testing of the candidate oils. Section 5 presents the methods and results of the lab-scale tests. Section 6 contains the methods and results for the Ohmsett full-scale tests. Section 7 contains the conclusions and recommendations.

2. Basics of Water-in-oil Emulsification and Demulsification

2.1 Emulsion Formation and Stability

When most crude oils are spilled at sea, they tend to form water-in-oil emulsions. Emulsification occurs in the presence of mixing energy such as that provided by wave action. During emulsification, seawater is incorporated into the oil in the form of microscopic droplets. This water uptake results in several undesirable changes to the oil. First, there is a significant increase in the bulk volume of the oil (usually up to a 4- or 5-fold increase), greatly increasing the amount of oily material. Secondly, there is a very marked increase in fluid viscosity.

The mechanisms and rates of oil emulsification are poorly understood, especially in terms of oil spills at sea. Through some mechanism, the mixing energy associated with waves causes water droplets to become entrapped in the oil layer. Large droplets of seawater will rapidly drain from the body of the oil because of their greater density, but smaller water droplets will be retained for longer, especially if the viscosity of the oil phase is high. All water-in-oil emulsions are inherently unstable; they would eventually separate into the oil and water phases, unless there is a third component present to stabilise the arrangement of water droplets in the body of the oil phase.

Several theories have been advanced about the main chemical mechanisms involved in the process (Bobra 1990, 1991, Walker et al. 1993, Fingas and Fieldhouse 1994, Fingas et al. 1995a, Fingas et al. 1995b, Fingas et al. 1996). Most experts believe that precipitates of asphaltenes in the oil act as surface active agents to stabilize the water droplets in the forming emulsion. Asphaltenes are complex, high molecular weight components of crude oil. They consist principally of hydrocarbons, although there are frequently associated with small quantities of high molecular weight components containing oxygen, sulphur, vanadium or nickel (the metallo-porphyrins). Because of their large molecular size, asphaltenes are not in true solution within the oil, but are in a colloidal suspension that is stabilised by other oil components commonly known

as resins. Neither asphaltenes nor resins have a precise chemical structure; the name derives from analytical methods used to characterise the oil components into general classes, so that the properties of different oils could be compared. Resins have a lower molecular weight than asphaltenes, are principally hydrocarbons and contain less of the oxygen, sulphur or metal-containing compounds.

Precipitated asphaltenes act as water-in-oil emulsion stabilisers by migrating to the oil/water interface that exists around water droplets incorporated into the oil. Asphaltenes are slightly more polar than the purely hydrocarbon oil components by virtue of the oxygen, sulphur and metal containing compounds that are incorporated in their structure. The precipitated asphaltenes also act as bi-wetted solids. In addition, the precipitated asphaltenes are polymeric and elastic and can form a thin physical barrier around the water droplet. The asphaltene film that is formed will tend to thicken with time and the water-in-oil emulsion will become more and more resistant to the effects of emulsion breakers. Without such stabilizing agents the water droplets in the oil layer would tend to coalesce and settle from the oil phase.

Spills of some crude oils will start to form emulsion within a few minutes of release, and most will begin to form a highly viscous and stable emulsion within hours. This has been recorded many times during actual and experimental spills. On the other hand, a few crude oils and most refined petroleum products do not easily emulsify at all. Asphaltenes are precipitated in spilled oil on the sea because of the change in oil composition caused by evaporation of the more volatile components. This evaporation concentrates the aspahltenes in the remaining oil residue and this overwhelms the ability of the resins to stabilise them in colloidal suspension. The asphaltenes agglomerate into larger particles. These precipitate out of solution and then stabilise the water-in-oil emulsions that are formed by incorporation of seawater into the spilled oil. Excess asphaltenes can also be produced by photo-oxidation and polymerisation of lower molecular weight oil components when the spilled oil is exposed to the UV (ultra-violet) radiation in sunlight for prolonged periods.

Other factors which influence the stability of emulsions are the temperature, the viscosity and density of the oil phase, the particle size distribution of the water droplets, and the water content and age of the emulsion (Bobra 1991, Blair 1960, Mackay 1987, Nordi et al. 1991, Payne and Phillips 1985, Fingas et al. 1998, Fingas et al. 1999).

2.2 Emulsion Breaking with Surfactants

A surface active agent, or surfactant, is a chemical compound, or molecule, that contains both a water-compatible group and an oil-compatible group. These compounds are therefore unusual in that they are not completely water soluble or completely oil soluble. The water compatible group has polar constituents, which are readily hydrated and confer to some degree the property of aqueous solubility on the molecule; this portion of the molecule is called hydrophilic. The oil compatible group is composed of hydrocarbon, miscible with the oil phase and insoluble in water; this portion of the molecule is called lipophilic (lipos = oil). Thus a logical manner by which to classify surfactants is based on the ratio or balance of the water compatible portion (hydrophilic) to the oil compatible portion (lipophilic). Hence, surfactants can be designated by a scale referred to as the Hydrophilic-Lipophilic Balance (HLB). The scale was chosen as 1 to 20. As shown in Figure 2-1, the lower part of the scale 1-10 is lipophilic while the upper half, 10-20, is hydrophilic. Table 2-1 lists the actual HLB values for some common surfactants.

Bancroft's law states that the liquid phase in which the surfactant or emulsifying agent is more soluble will be the external, or continuous, phase of the emulsion. In the case of petroleum emulsions, it is high molecular weight components of the oil itself that act as the stabilizers, so oil is the external phase containing droplets of water as the internal phase, hence the term water-in-oil emulsions. It is evident then that the molecular structure of the emulsifying agent, which determines its relative solubility in water or oil, also determines the type of emulsion for which it can act as a stabilizer. Thus, an oil-compatible surfactant (HLB = 1-10) promotes oil as the
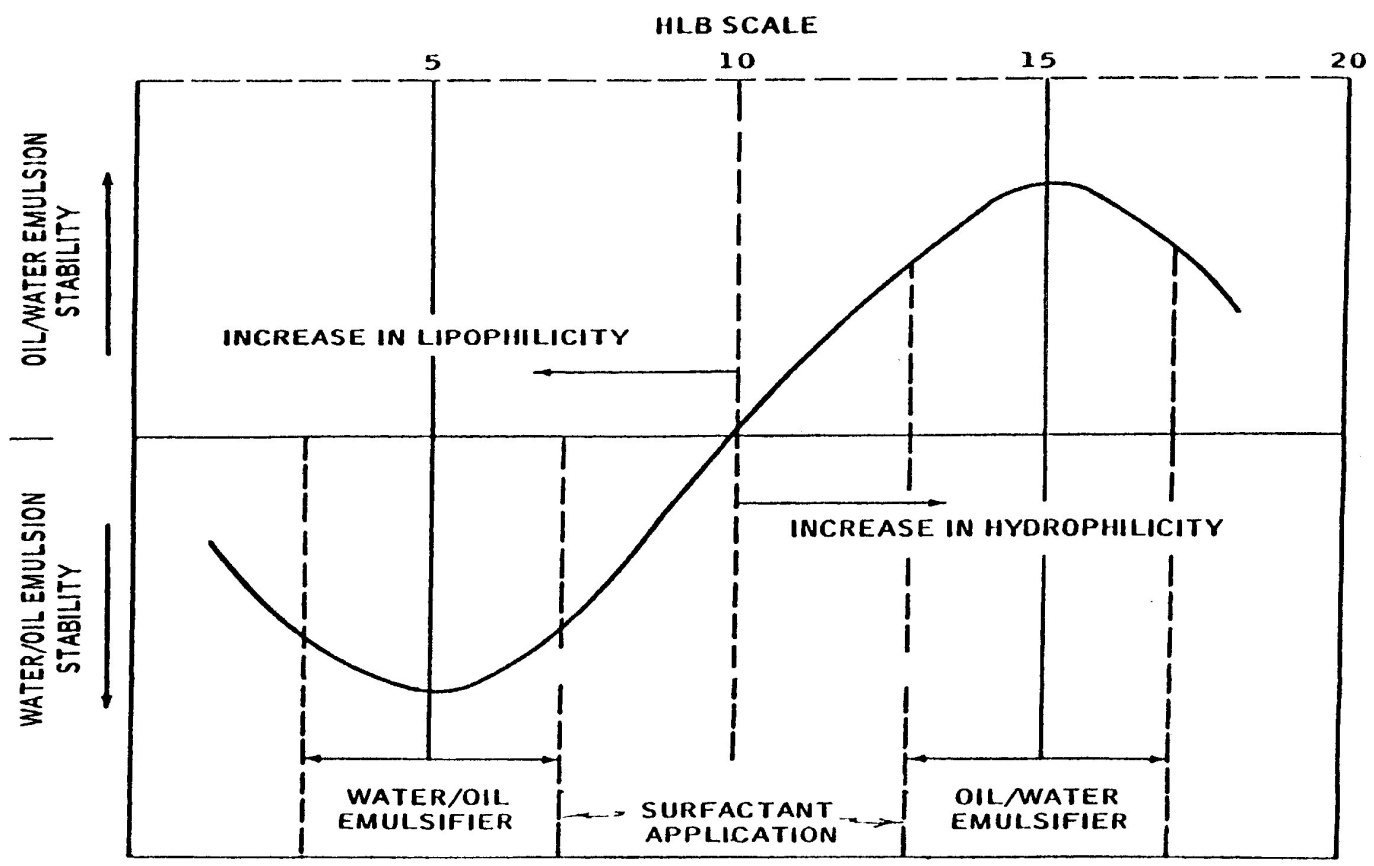
FIGURE 2-1   RELATIONSHIP BETWEEN HYDROPHILIC LIPOPHILIC BALANCE AND EMULSION TYPE

TABLE 2-1

EXPERIMENTALLY DETERMINED HYDROPHILIC LIPOPHILIC BALANCE
VALUES FOR SOME SURFACE ACTIVE AGENTS

SURFACE ACTIVE AGENT	HLB VALUE
SODIUM OLEATE	18
POTASSIUM OLEATE	20
TWEEN 80 (SORBITAN MONOLEATE + 20 MOLES ETHYLENE OXIDE)	15
TWEEN 81 (SORBITAN MONOLEATE + 6 MOLES ETHYLENE OXIDE)	10
SPAN 80 (SORBITAN MONOLEATE)	4.3
TWEEN 20 (SORBITAN MONOLAURATE + 20 MOLES ETHYLENE OXIDE)	16.7
ETHANOL	7.9
N-BUTANOL	7.0
CETYL ALCOHOL	1.0
OLEIC ACID	1.0

continuous phase (water-in-oil dispersion) and a water compatible surfactant (HLB = 10-20) promotes water as the continuous phase (oil-in-water emulsion). A more common classification of surfactants is based on the ionic character of the hydrophilic group of the surfactant. Thus surfactants are classified as either Ionic (cationic or anionic) or Nonionic.

Cationic surfactants are primarily aliphatic amines or quaternary ammonium salts. In this substance, the hydrophilic group is found in the cation. They are used for corrosion inhibitors, bacteriacides, water repellents, electroplating, emulsifiers for cosmetics due to their effectiveness at low pH, dye stripping agents and bleaches.

Anionic surfactants are perhaps the most common-soap being one of the oldest known surfactants. Replacement of the carboxyl group, COO by sulfates and sulfonates are modifications to enhance its usefulness as a detergent for specific application such as salt water, heavy duty, etc.

Nonionic surfactants are generally manufactured and are popular because of the ease with which the hydrophilic:lipophilic ratio can be adjusted. The most common consists of ethylene oxide adducts - polyethelene oxide chains attached to fatty acids, alcohols or other lipophilic molecules -the molecular weight of the ethylene oxide group being adjusted to control the hydrophilicity of the compound. Also, being nonionic, they are insensitive to pH or electrolyte concentration, are very stable and are also nonirritating (hence their use as shampoo, bubble bath, etc.).

An emulsion breaker functions by destabilising the asphaltene particles or layer that is stabilising the water droplets in suspension in the oil. This can be achieved in several ways. Since the presence of the asphaltene particles at the oil/water interface is due to the subtle difference in surface activity between the slightly polar asphaltenes and the purely hydrocarbon components of the oil, the most obvious way is to add a surfactant with much stronger surface active properties. This will compete with the asphaltenes for the surface area and displace the asphaltene particles back into the body of the oil. However, it is obviously important that the

surfactant should not stabilise the oil water interface; its role is to remove the asphaltenes and then promote coalescence of the water droplets.

The most effective surfactant for this purpose is sodium di-isooctyl sulfosuccinate. Sodium di-isooctyl sulfosuccinate is the most powerful 'wetting agent' that is commonly available; it drastically (but only temporarily) reduces the interfacial tension between oil and water surfaces. Sodium di-isooctyl sulfosuccinate is the main constituent in Alcopol O (or Drimax as sold by Allied Colloids) and Aerosol OT (as sold by Cyanamid). These trade name products are 60% or 70% solutions of sodium di-isooctyl sulfosuccinate (which is a waxy solid in its pure form) in mixed alcohol/water solvents.

The surfactant components of commercial emulsion breakers, both for oil production and for use in oil spill response, can be either a single anionic surfactant, such as sodium di-isooctyl sulfosuccinate, or sometimes a combination of an anionic surfactant in combination with one or more nonionic surfactants.

Sodium di-isooctyl sulfosuccinate is a very powerful wetting agent, but its high surface activity is not persistent; it will partition quite rapidly between the oil and water phases, and in the context of oil spills in the open sea will inevitably end up in the water phase. This has implications for its use as an emulsion breaker for oil spills and alternatives have been sought.

The active ingredient in Shell Demulsifier LA 1834 is thought to be an Ethylene Oxide/ Propylene Oxide (EO/PO) copolymer. This is also a powerful wetting agent, but being a nonionic surfactant, is not as powerful a wetting agent as sodium di-isooctyl sulfosuccinate. EO/PO copolymers form a vast range of nonionic surfactants. The hydrophilic EO component can be combined with the lipophilic PO component in a number of ways; as a block copolymer with discrete chains of EO and then PO or as a random copolymer with mixtures of EO and PO throughout the molecule.

The surfactants are generally considered to be the most active ingredients of the emulsion breaker, but the solvent also plays a role. Strongly aromatic solvents can function as additional 'active ingredients' in that their action is greater than just reducing the viscosity of the solid or high viscosity liquid surfactants. A very small quantity of highly aromatic solvent can exert a solubilising effect on the precipitated asphaltenes so that they are no longer capable of stabilising the emulsion. The aromatic solvent acts as an adjuvant to the resin components, enabling them to continue to stabilise the asphaltenes in suspension. Highly aromatic solvents are unlikely to be suitable for use in oil spill response because of their very high acute toxicity to most marine organisms.

The importance of the solvent in emulsion breakers for oil spill use has been recognised (Lewis et al., 1993). Shell Demulsifier LA 1834 is likely solution of the EO/PO copolymer in Surdyne X119 - a long-chain alkylbenzene solvent. If the same EO/PO copolymer was dissolved in odourless kerosene, the emulsion breaking capability was greatly reduced. Laboratory studies showed that the emulsion breaking capabilities were greatly enhanced when the EO/PO copolymer was used as a solution in toluene.

3. Literature Review

A computerized search of the published literature was conducted by the Canadian Institute for Scientific and Technical Information on the subject of oil-in water emulsions and demulsifiers. The following 7 databases were searched over the indicated time frames:

- National Technical Information Service (NTIS) from 1964 to January 2000
- Engineering Index (EI) Compendex from 1970 to January 2000
- Energyline from 1970 to December 1993
- Energy Scitech from 1974 to January 2000
- TULSA Petroleum Abstracts from 1965 to January 2000
- Pollution Abstracts from 1970 to January 2000
- Enviroline from 1975 to October 1999

After refining the search a total of 143 "hits" were obtained for which the abstracts were reviewed. Of these, 29 were ordered for detailed review. In addition, the libraries of the Emergency Sciences Division of Environment Canada and SL Ross Environmental Research were searched and several reports reviewed. All the documents retrieved have been archived in the SL Ross library.

3.1 Demulsification of Water-in-oil Emulsions in the Petroleum Industry

Commercial methods for breaking water-in-oil emulsions can be broadly classified as chemical, thermal, mechanical and electrical. In an industrial setting usually some combination of methods are used either simultaneously or sequentially. A typical chemical demulsification operation is comprised of several units. Treatment normally involves adding the demulsifier to the emulsion, agitating the mixture to provide intimate mixing, then applying heat or electricity, and allowing a settling period. Numerous variations and innovations have been applied to the chemical demulsification process. This is clearly evident by the voluminous technical and patent literature available (Becher 1985, Bransbach 1970, Colbert 1981, Gutzeit 1990, Menon and Wasan 1985,

Schwartz et al. 1958, Wilson 1989). Most of the literature pertains to the treatment of emulsions for the petroleum industry where demulsification can be considered to be a sub-industry that is provided by specialized service companies. It is estimated that between 2000 and 3000 patents directly refer to this subject with thousands more related to it, and about 20 new patents are granted each month (Lissant 1983, Reimer 1984). Several reviews provide excellent summaries of the literature on commercial demulsification (Becher 1985, Colbert 1981, Lissant 1983, University of Texas 1990).

3.2 Properties of Chemical Demulsifying Agents

To review in simple terms, demulsifiers break emulsions by destabilizing the interfacial film which will then rupture during droplet collisions and thus allow the droplets to coalescence. Like emulsifiers, demulsifiers are surface active. To be effective, demulsifier molecules must be able to migrate through the oil phase to the water-oil interface where they displace the natural surfactant emulsifiers from the interface. The effectiveness of a demulsifier is related to two general factors, its speed of migration to the interface and its performance at the interface site.

Factors which affect demulsifier performance include: the nature and properties of the interfacial film; the physio-chemical properties of the oil phase; the physio-chemical properties of the aqueous phase and temperature.

Unfortunately, due to the complexity and variability of petroleum emulsions, the selection of an effective demulsifier for a specific emulsion relies to a large degree upon empirical testing. Petroleum emulsions usually show a high degree of specificity in their response to chemical demulsifiers. A formulation that shows good effectiveness on a given emulsion can be completely ineffective on another emulsion formed from a crude oil of different composition. It is because of this specificity that most companies which distribute demulsifiers offer a series of formulations in the hope that one of the formulations can adequately resolve the emulsion. The

need for empirical field tests is still emphasized in literature. The tests generally use an actual sample of the emulsion and are conducted under conditions that simulate actual field conditions.

3.3 Demulsification of Oil Spill Emulsions

In this section, only literature directly related to oil spill demulsifier technology is summarized. Previous reviews of the demulsification of oil spill emulsions are presented by Payne and Phillips (1985) and SL Ross et al. (1992).

The concept of injecting demulsifiers into oil spill emulsions is not new. Various techniques for chemical demulsification are described by Van Oudenhoven et al. (1980). Figure 3-1 shows a typical heated demulsification system, suitable for use with a pumpable emulsion. If the mousse is not pumpable, the demulsifier should be directly stirred into the mousse container. Figure 3-2 shows an example method for adding demulsifier directly during collection. (The use of dracones - towable bladders - is not necessarily recommended for all spill situations; in this example the dracone is used to store the separated oil, and the water is transferred back to the vessel for further processing if necessary. Similarly, Figure 3-3 illustrates a system for adding demulsifier during the transfer to a vacuum truck. In-line injection and mixing of the demulsifier provides better control over dosage and more homogeneous mixing. Separation times of 10 to 20 minutes are cited but separation times will be lower or higher depending on the nature of the emulsion being treated. The Framo Transrec 350 offshore skimmer system is produced with an integral demulsifier injection skimmer used to inject the chemical into the skimmer head (Lode 1981). A portable stand-alone system to inject demulsifier into a skimmer of opportunity is also available (SL Ross and Glosten 1992)

Documentation of actual use of emulsion breakers during oil spill clean up operations is limited and the results were mixed (Bocard et al. 1979). During the clean up of the *Amoco Cadiz* spill, emulsion breakers were used in the intermediate storage tanks and then in the onshore mobile vacuum tanks. It was noted that the major benefit of using emulsion breakers was an immediate

reduction in viscosity which facilitated transfer operations and the separation of debris from mousse. Some effectiveness in breaking emulsions was found, provided that sufficient mixing was applied. It was suggested that the mixing energy provided during these transfer operations was insufficient to effectively distribute the demulsifier and promote separation of the emulsion. To make more effective use of emulsion breakers, it was recommended that demulsifiers be injected on-line upstream of the pump at a properly-metered dose. It was found that two to three weeks after the spill, the demulsifiers were ineffective on weathered mousse at ordinary temperatures, and that heat had to be applied for pumping.

Similar results were found by Bocard and Gatellier (1981) when demulsifiers were tested on mousse generated from a long-term experimental spill. It was concluded that thorough mixing of the demulsifier into the emulsion was required after the injection to obtain good breaking. It was hypothesized that products of photo-oxidation greatly enhanced emulsion stability and that the emulsions increased in stability over time. Other, more recent studies offer data in support of this hypothesis. Brandvik and Daling (1990) found that photolyzed oils have a greater tendency to form stable emulsions and that these emulsions were more resistant to chemical demulsification. This resistance to demulsifiers cannot be attributed to an increase in viscosity but is likely a result of the photo-oxidized compounds enhancing the stability and structure of the interfacial film. Thus, demulsifier molecules are effectively prevented from entering the interface and disturbing the interfacial film. Fingas et al. (1998) use the increase in viscosity and elastic modulus with time as an indicator of a truly stable emulsion.

Shell Demulsifier LA 1834 has been tested on a variety of emulsions and under different conditions. Again mixed results were reported. When beached mousse of topped Nigerian Light crude was treated with 2000 ppm during pumping operations, good separation of the oil-sand-water mass was observed and free water could be drained off from a vacuum truck after approximately 10 minutes (Van Eden 1983). Similar results are reported by Bridie et al. (1980), who also used a static in-line mixer to improve mixing of the demulsifier and emulsion. Beached mousse collected following a spill of Basra Light crude oil from the tanker *Irene's Serenade* was

FIGURE 3-1

HEATED DEMULSIFICATION SYSTEM
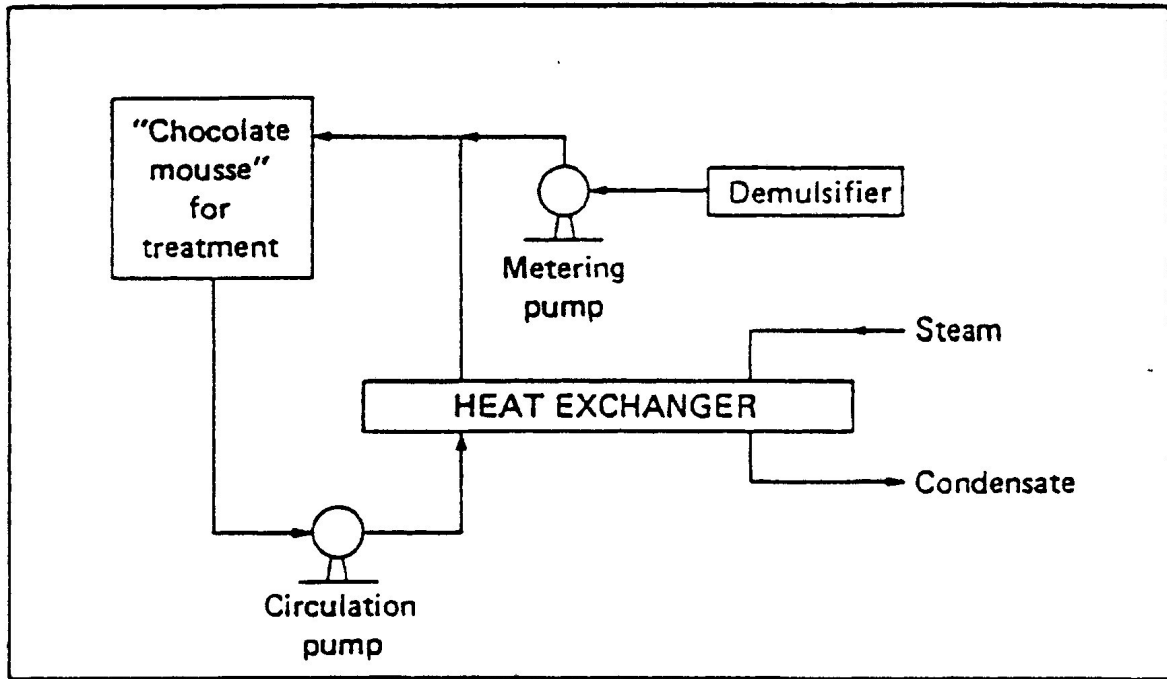
Reproduction taken from Concawe Report 9/80

FIGURE 3-2

MARINE DEMULSIFICATION SYSTEM
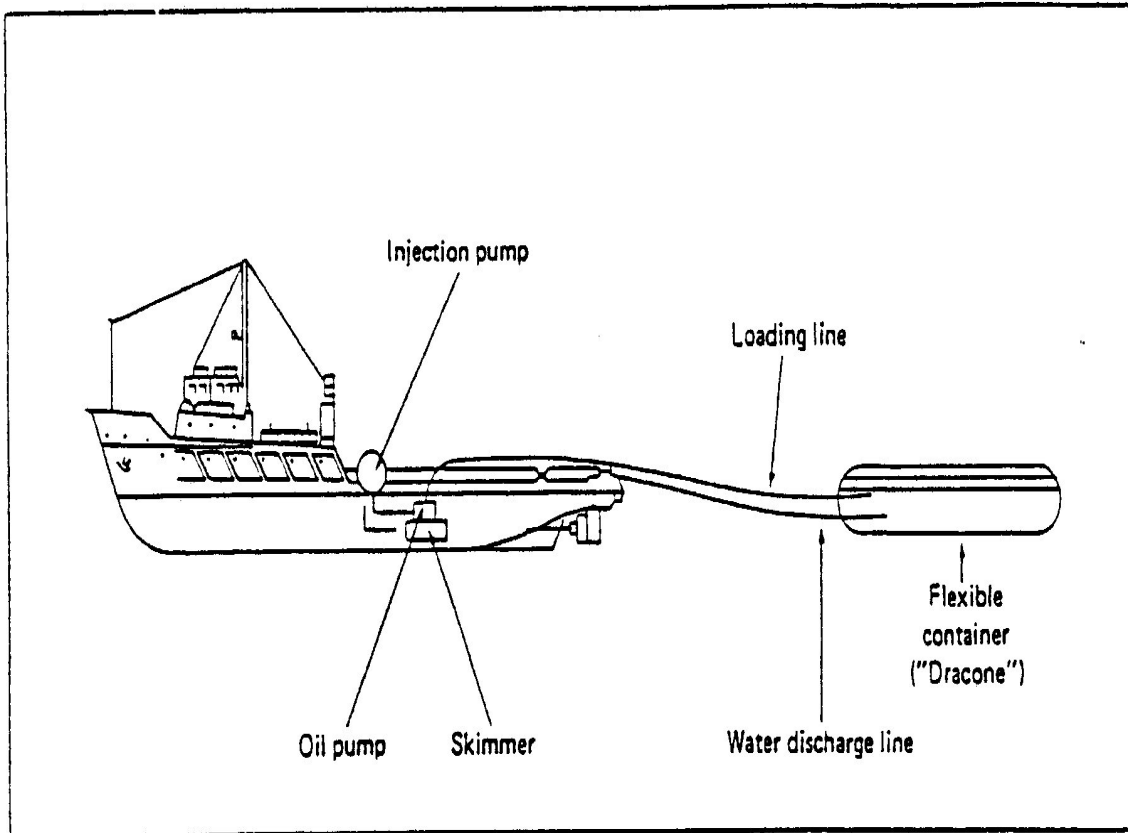
Reproduction taken from Concawe Report 9/80

FIGURE 3-3

MOBILE LAND DEMULSIFICATION SYSTEM
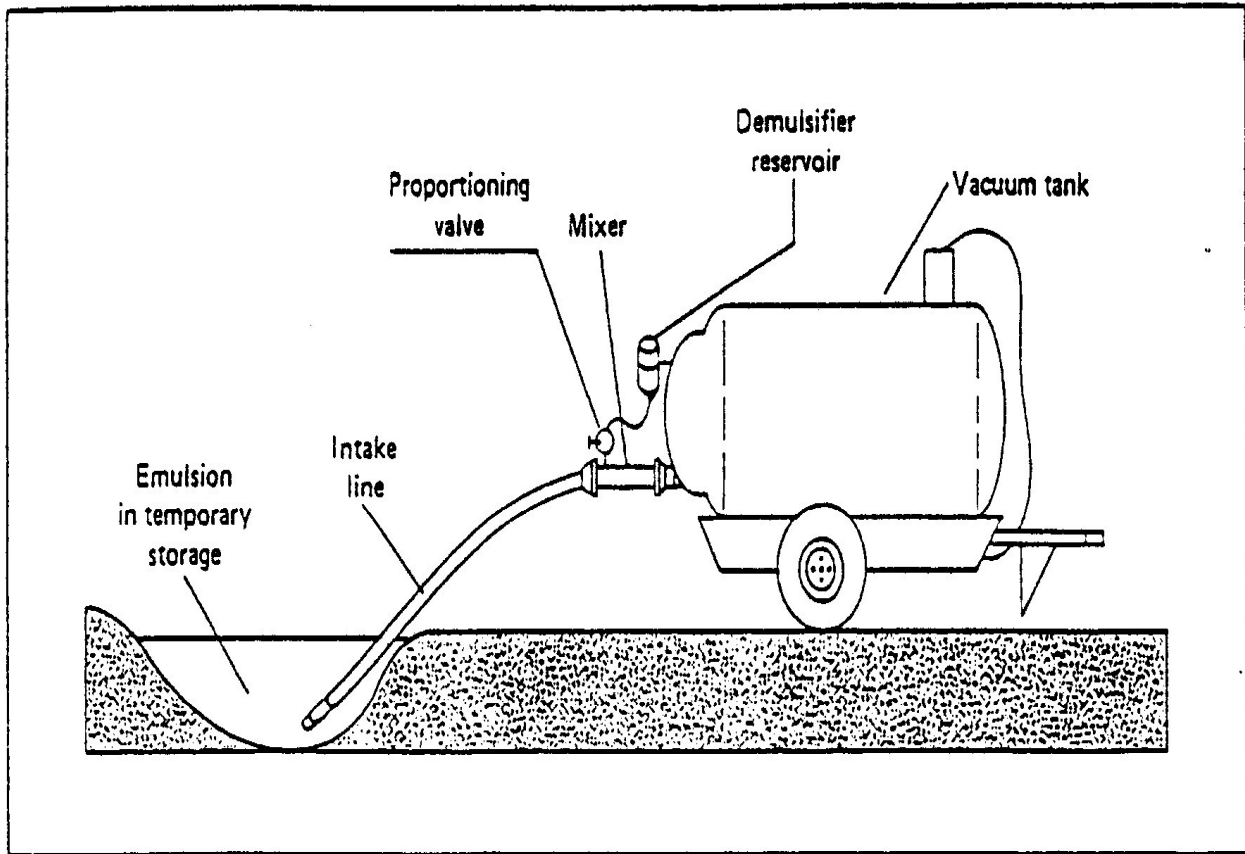
Reproduction taken from Concawe Report 9/80

treated with 200-400 grams of demulsifier for each 200 litre drum. After the demulsifier was stirred in, the previously non-transferable mousse could be readily pumped into disposal trucks. Van Oudenhoven (1983) reported that LA 1834 had no effect on beached mousse from the Hasbah 6 blow-out. Laboratory tests and large scale tank tests with LA 1834 showed that the demulsifier was effective in breaking emulsions and in reducing emulsion viscosity on a variety of different oils (Koops and Bridie 1979, Bridie et al. 1980, Hossain and Mackay 1980).

Aerosol OT (active ingredient: sodium di-isooctyl sulfosuccinate) was extensively tested on a variety of emulsions formed from fresh and weathered crudes, and fuel oils (Bolster and Little 1980, Little 1981). Effectiveness was found to be dependent on oil type, water content and temperature. Concentrations of 0.01% to 0.1% were useful for less viscous emulsions, while dosages of 0.1% to 1% were useful for highly viscous emulsions. It was noted that an excess of demulsifier could produce a more intractable emulsion. Therefore, small increments of demulsifier should be added to determine optimum dose. Low temperatures inhibited demulsifier effectiveness, while increased temperatures and mixing energy enhanced demulsification.

An extensive laboratory study conducted by Lee (1980) investigated the chemical demulsification of various natural mousse samples and laboratory- made emulsions. Twenty un-named but commercially available demulsifiers were tested under a variety of conditions on emulsions formed from nine different oils, as well as on mousse samples from three actual spills. The factors important to chemical demulsification were: the choice and amount of demulsifier, the temperature, and the time and degree of mixing during the addition of demulsifier. It was shown that a demulsifier that worked well on one particular emulsion, would not work well on another emulsion made from a different type of oil. However, some of the demulsifiers were effective to some degree under most of the test conditions. The results also indicated that there was an increased difficulty in breaking emulsions as the asphaltene content of the oil increased. It was also reported that there was an optimum degree of mixing for maximum demulsifier

effectiveness. Too little mixing resulted in poor breaking: too much mixing resulted in high concentrations of oil in the separated water.

Canevari (1982) describes the development program for a demulsifier formula named Breaxit OEB-9. The demulsifier has two primary components: a mixture of surfactants that displaces the interfacial emulsifying film and a mixture of wetting agents that displaces one liquid from the surface of bi-wetted solids. Laboratory tests showed the product could resolve water-in-oil emulsions within minutes when a low mixing energy was applied. The experimental demulsifier was claimed to be more effective than commercially available demulsifiers. Full-scale skimmer tests were conducted with a variety of transfer pump types using 50% seawater-in-oil emulsions formed from Kuwait crude oil. Injection of the product into various points of the skimmer recovery system was tested. The results showed that at a dose of 0.04% (400 ppm) complete emulsion separation occurred after 5-15 minutes. A concentration of 0.01% had no effect. A concentration of 0.2% over-treated the emulsion and produced an oily water phase, as did excessive mixing.

In the late 1908s, a new emulsion breaking product called Vytac DM was developed by Environment Canada. Vytac has undergone extensive testing in the laboratory, in tank tests, and during an open ocean experimental spill (Bobra et al. 1988a, Fingas and Tennyson 1991, Fingas et al. 1991, Seakem 1990). Most tests were performed to determine the product's effectiveness at preventing or inhibiting the formation of emulsions in oil slicks floating on water. Tests were also conducted to examine its ability to break fully-developed emulsions floating on open water. A 4000 ppm dose effectively broke mousse during the experimental spill. A large reduction in viscosity (105,000 to 22,600 cP) and a drop in water content (90% to 78%) occurred within 30 minutes of treatment. During the tank tests, recovery of the oil using a skimmer showed that Vytac-treated oil had a lower rate of recovery. A preliminary laboratory emulsion-breaker test established the minimum operative concentration to be less than 1000 ppm. This concentration is defined as the concentration that reduces the emulsion volume by 50%. At 5000 ppm, the same emulsion was reduced by 65%.

Successful sea trials of demulsifier addition to emulsion slicks at sea from aircraft have also been undertaken (Lewis et al 1993, Walker and Lunel 1995). Reductions in viscosity and water content have been measured in the test slicks.

The preliminary emulsion-breaker test developed by Environment Canada, referred to in the previous paragraph, was used to evaluate a total of seven products, including Environment Canada's Vytac DM (Fingas and Tennyson 1991, Fingas et al. 1991). The results showed that only Vytac and Dasic Slickgone Dispersant, were effective at breaking emulsions. The other products tested were dispersants (Enersperse 700, Corexit CRX-8 and Corexit 9527) or common household cleaners (Palmolive and Mr. Clean). Sodium di-isooctyl sulfosuccinate is commonly used as one surfactant ingredient in oil spill dispersants.

The emulsion breaking abilities of two products, Finasol OSR-5 Dispersant and Alcopol demulsifier, were determined on eight different types of oils (Brandvik and Daling 1990). Each oil was tested at four different states of weathering. Effectiveness depended on the stability of the emulsion, which in turn depended upon the characteristics of the oil. Emulsions formed from more weathered oils were more difficult to break than less weathered oils. Photolyzed oils were particularly resistant to chemical demulsification. Wax stabilized emulsions were easier to break than asphaltene/wax stabilized emulsions.

SL Ross and Glosten (1992) conducted a paper study of viscosity and drag reduction techniques for pumping and storing viscous oils and emulsions. They concluded that emulsion breaking chemicals showed good potential. SL Ross et al. (1992) also studied the state-of-the art in chemical demulsifiers in 1992 and concluded that further research was warranted. One of the working groups at the First International Oil Spill R&D Forum also came to the consensus that further R&D on demulsifiers was warranted (Technology and Management Services 1992).

Peigne et al. (1993) provide a summary of French efforts on demulsifiers up to 1993. Their work on demulsifiers began as a result of the *Amoco Cadiz* spill. They developed a standardized test

for determining demulsifier effectiveness, conducted toxicity testing of various demulsifiers, developed a static mixer for mixing demulsifiers and emulsions in hoses and conducted testing with various skimmers with demulsifier injection. They have concluded that: it is necessary to thoroughly mix the demulsifier into the emulsion; spraying demulsifier onto a slick prior to recovery is ineffective; when the skimmer is recovering pure emulsion, it is more effective to inject the demulsifier into the skimmer; when the skimmer is recovering free water, seaweed or sand it is better to inject the demulsifier when transferring from temporary storage; the presence of free water slows emulsion breaking (the more free water recovered, the less effective the demulsifier); and, with a static in-line mixer in the system, it makes no difference if the demulsifier is injected before or after the skimmer pump. Their tests showed that small-scale laboratory test results correlated well with full-scale skimmer trials.

Strom-Kristiansen et al.(1993a) report a series of test-tube experiments on the effects of demulsifier addition and heating on emulsion breaking with one oil. These tests were undertaken to support a full-scale test of the oil-water separators onboard MSRC's response vessels. They concluded that both heat and emulsion breaker addition accelerated emulsion separation. They noted that addition of the demulsifier prior to heating appeared to be most effective. The tests were expanded (Strom-Kristiansen et al.1993b) to include other oils. The same conclusions were reached.

Nordvik et al (1993) report on a series of trials with the oil-water separators on one of MSRC's response vessels. Although not directly applicable to emulsion breaking, they do report that when emulsion breaker was added to one of the separators, the oil content of the water phase increased dramatically. Heating of emulsion in the storage tanks on the vessel was generally inefficient (i.e., high thermal stratification developed in the tank containing an emulsion), unless the product was simultaneously circulated and mixed.

Lewis et al. (1995) carried out a theoretical analysis of the effects of oil slick properties on the efficiency of mechanical recovery devices, with a particular emphasis on the effects of

emulsification. As part of this, they assessed the potential benefits and drawbacks of demulsifier addition before, during and after recovery. They concluded that the use of demulsifiers to enhance mechanical recovery warranted further research. As such, they began an MSRC-funded study to test the effects of demulsifier addition on recovery efficiency. Unfortunately the study was severely cut back with the demise of the MSRC R&D program. Several tests with demulsifier addition to pump systems were completed using Alcopol O 60% demulsifier, fuel oil emulsions and three pump types. The conclusions were that: 300 to 400 ppm of demulsifier in various mixtures of free water/emulsion resulted in effective breaking; and, good mixing is required, not only to mix the demulsifier thoroughly into the emulsion, but also to cause the small water drops to collide and coalesce into larger droplets that can more easily separate out.

Nordvik et al (1996) summarize the work funded by MSRC on oil-water separation and emulsion breaking. They present a strong case for emulsion breaking and decanting from the perspectives of : increased skimming time on site before temporary storage tanks are full and require offloading; and, greatly reduced waste fluid disposal costs.

3.4 Summary of Findings in the Literature

- Many oils spilled at sea will eventually form meso-stable or stable emulsions that can contain up to 80 percent water and will not separate in temporary storage tanks in operationally-reasonable times.

- Oil spill emulsion slicks exposed at sea for long periods may be particularly difficult to break because the oil is highly evaporated, photolyzed, and contaminated with marine particulate matter.

- Unstable emulsions collected and stored in tanks can be treated on a large scale by gravity separation, perhaps assisted by heat treatment.

- Meso-stable and stable oil spill emulsions have been broken using commercially available demulsifiers at concentrations of 0.04% to 0.5%. No single formulation is fully effective on all types of oils/emulsions.

- Energy to mix the demulsifier into the emulsion and to cause small water drops to collide is crucial to the breaking process.

- Several previous studies have recommended that demulsifier be added to emulsion during pumping to maximize mixing. The use of in-line static mixers has also been studied. The most effective injection point appears to be a function of operating conditions and pump type.

- Products that have been tested and found to be successful on some oil spill emulsions include Shell's LA 1834, Exxon's Breaxit OEB-9, Environment Canada's Vytac DM, Allied Colloid's Alcopol 0, and Aerosol OT from Cyanamid. Other products have been found to be effective but these are un-named in the literature.

- There is considerable incentive to optimize on-site storage capacity, and reduce fluid disposal costs through the use of demulsifiers and subsequent decanting of free and separated water.

4. Screening of Candidate Oils for Laboratory and Ohmsett Tests

In this section, the results of a series of emulsion formation and demulsifier effectiveness tests are reported. The goal of these tests was to find an oil that could be used in both the laboratory and Ohmsett tests as a good analog of emulsified oil recovered during an offshore oil spill response with mechanical techniques. The necessary characteristics of this test oil were:

- good property stability and consistency (little variability in batches and little change in physical or chemical properties on exposure to the atmosphere) in order to minimize experimental variability;

- high tendency to form at least meso-stable emulsions (as defined by Fingas et al. 1998) that do not lose appreciable amounts of water over time periods of a day;

- relatively difficult to break with a resulting large range of dehydration, when treated with commercially-available oil spill demulsifier(s); and,

- easy to procure/prepare and mix with salt water using simple large-volume emulsion-forming techniques (i.e., gear pumps).

The candidate test oils chosen were the standard oils used at Ohmsett for boom and skimmer testing: Calsol, Hydrocal and Sundex. The nominal characteristics of each are given in Table 4-1.

Table 4-1: Nominal Properties of Ohmsett Test Oils.

Property[*]	Hydrocal 300	Calsol 8240	Sundex 8600T
Specific gravity	0.903	0.933	0.95
Viscosity (cP) @ 25˚C	150	1700	20000
Viscosity (cP) @ 10˚C	1100	11500	200000
Interfacial Tension (dyne/cm)	19	27	30
Surface Tension (dyne/cm)	34	36	37
Bottom Solids & Water (%)	0.2	0.2	2

[*] Properties may vary 10% between batches

Small amounts (2.5, 5 or 10 %) of a sample of Bunker C (also know as Fuel oil No. 6) available in the SL Ross Lab were added to these test oils to enhance their emulsion stability.

4.1 Emulsion Formation-Tendency and Stability

The tendency of the oils to form an emulsion and the stability of the resulting emulsion were determined using the rotating flask technique (Zagorski and Mackay 1982, Hokstad et al.1993). The test indicates whether or not the oil will form an emulsion (low, moderate or high formation-tendency)at the test temperature, as well as the stability of the emulsion (low, moderate or high). The data is presented in Appendix 1.

Calsol

Only the 100% Calsol showed any tendency to form an emulsion; however, the emulsion that formed was not stable and broke during the 24 hour settling period. The mixtures of Calsol and Bunker C (95/5 and 90/10) did not show any tendency to form an emulsion. None of the mixtures tested would be suitable for the laboratory testing.

Hydrocal

The 100% Hydrocal readily formed an emulsion; however, the emulsion was not stable. The mixtures of Hydrocal and Bunker C (95/5 and 90/10) both readily formed emulsions that were stable for 24 hours. The Hydrocal and Bunker C mixtures were the best candidates for the next phase of testing, and were subjected to the emulsion breaker effectiveness tests.

Sundex

Neither the 100% Sundex, nor the 95% Sundex, 5% Bunker C mixture showed a tendency to form an emulsion. The viscosities of these oils were too high for emulsions to form. None of the mixtures tested would be suitable for the laboratory testing.

4.2 Emulsion Breaker Effectiveness

The effectiveness of four commercially available emulsion-breaking chemicals (Alcopol O, Breaxit and either Wellaid 3316 or Vytac-DM) were tested on 50 % water emulsions made with the oil samples. The procedure described in Hokstad et al. (1993) was used. The emulsion samples for this test were made by recirculating 3.5 % salt water and oil through a small gear pump. The gear pump technique produces emulsions that are more stable than those that form naturally by wave action or in the rotating flask method because the intense mixing action in the gear pump creates smaller water droplets. The results of the emulsion breaker effectiveness test can therefore be considered as conservative. The test data is given in Appendix 1.

90% Hydrocal, 10% Bunker C

None of the emulsion breakers worked particularly well on this mixture. There are some anomalies with the results, particularly the high dehydration with the 0.03 mL (1:500) dose of Alcopol and the dehydration of the control funnel. These are both unusual results and indicate that the emulsion may not have been prepared properly.

97.5% Hydrocal, 2.5% Bunker C

Alcopol and Breaxit were the best demulsifiers with this mixture, with Alcopol slightly outperforming Breaxit. Some additional dehydration was achieved after the 24 hour settling period.

98.7% Hydrocal, 1.25% Bunker C

Alcopol O and Breaxit were the best demulsifiers with this mixture, with Alcopol O again slightly outperforming Breaxit. With Alcopol O at a dose of 1:500 (demulsifier to emulsion) within 2 minutes of stopping the mixing, 67% of the water had separated; one day after stopping the mixing, 96% of the emulsion water had separated. Only 4% of the emulsified water had separated from the untreated control emulsion after one day. This combination was initially suggested as the candidate test oil/emulsion breaker for the laboratory and Ohmsett tests, as it meet all the criteria.

Emulsion Formation and Breaking Tests with Ohmsett Bunker

Subsequent to these screening tests, a Bunker oil was ordered for an unrelated test series at Ohmsett. A sample of this was shipped to Ottawa to confirm it's suitability as the stabilizer for Hydrocal-in-water emulsions prior to beginning the laboratory tests. The intent was to use the "Ohmsett Bunker" to conduct both the laboratory and Ohmsett tests, and eliminate this as a source of discrepancy between the test series.

The results of the repeated formation and demulsifier effectiveness tests (Appendix 1) showed that the "Ohmsett Bunker" was less effective as an emulsion stabilizer than the "SL Ross Bunker" sample. Bunker fuel oils are produced from a variety of refinery residues and distillate fractions, that are added to produce the required viscosity. The chemical composition therefore varies over a wide range. The emulsion-stabilizing ability of these two bunker fuels oil varied, probably because the "Ohmsett Bunker" contained less asphaltenes and/or resins than the "SL Ross Bunker" sample. At least 2.5% "Ohmsett Bunker" in the Hydrocal was required to obtain reasonable emulsion stability. Alcopol O was the demulsifier that worked effectively on emulsions prepared with both 2.5% and 5% mixtures of "Ohmsett Bunker" in Hydrocal and was chosen as the demulsifier for the tests.

5. Laboratory Tests

This section describes the laboratory test apparatus and results. The tests were conducted at the SL Ross Laboratory in Ottawa, ON.

5.1 Laboratory Test Set-up Design Basis

Since the level of mixing in the system is important to the demulsification process, and much of an offshore recovery system involves flow in pumps and hoses, the use of the Reynolds number to scale the laboratory system seemed appropriate. A simple analysis of a typical offshore recovery system based on a circular weir skimmer (with fluid flow rates from 30 m^3/ hr of viscous - say 200,000 mPas - emulsion to up to100 m^3/ hr of mostly water pumped through a 6" hose) indicates that the Reynolds number could range from 0.4 to 230,000. For any fluid viscosity greater than about 100 mPas (which, in nearly all situations involving emulsions, would be the case) the flow would be laminar, with minimal mixing energy imparted to the fluid during its travel down the hose.

The Reynolds number (N_{Re}) is given by:

$$N_{Re} = Dv\rho/\mu \tag{1}$$

Where:

$D \equiv$ hose or pipe diameter (m)

$v \equiv$ fluid velocity (m/s)

$\rho \equiv$ fluid density (kg/m^3)

$\mu \equiv$ apparent fluid dynamic viscosity (Pas)

For the Reynolds number to be the same for different hose diameters, with the same fluid properties, it can be shown that:

$$D_1v_1 = D_2v_2 \qquad\qquad (2)$$

Which, combined with,

$$v = Q/A = 4Q/\pi D^2 \qquad\qquad (3)$$

Where:

$$Q \equiv \text{fluid flow rate (m}^3\text{/s)}$$

Yields:

$$Q_1/D_1 = Q_2/D_2$$

This simply states that the ratio of the flow rate and diameter of the model system are directly proportional to the ratio of the flow rate and diameter of the full-scale system.

Table 5-1 gives a series of required flow rates to achieve a full-scale Reynolds number in the scale model system as a function of different tubing diameters that are easily available.

Table 5-1:   Scale Model Flow Parameters

Full-scale Flow Rate (m³/hr)	Q_1/D_1 (m²/s)	Approximate Lab-scale Flow Rate (L/min)			
		¼" Tubing	⅜" Tubing	½" Tubing	¾" Tubing
30	0.055	20	30	40	60
50	0.092	33	50	66	100
100	0.184	66	100	130	200

In a recent test of decanting at Ohmsett (SL Ross 1999) skimmers were operated at a Fluid Recovery Rate on the order of 30 m³/ hr. Choosing this as the nominal "full-scale" recovery rate, and taking into account that many different types of viscous fluid service pumps in the 1 HP range deliver on the order of 10 US gpm (38 L/min), the selection of a scale model tubing

diameter of ⅜" or ½" seemed appropriate. Both of these diameters were used in the laboratory test apparatus.

5.2 Laboratory Test Methods

Laboratory Test Loop Layout

The lab-scale test system schematic is given in Figure 5-1. A photograph of the setup is shown in Figure 5-2. It was designed to mimic the pumping, mixing and flow processes that occur in an offshore oil recovery system. The system was based, in part, on lessons learned in the preliminary demulsifier tests carried out by SINTEF (Lewis et al. 1995). Pre-mixed 50% emulsion and nominally 50% free water were pumped separately, at measured, pre-determined rates, to the suction of the test pump being used (either a gear pump, a diaphragm pump or a progressing cavity pump). The flow rate, pressure and temperature were measured at the pump outlet and just before discharge into the receiving tanks. The fluid was directed either through, or to bypass, a static in-line mixer, down different lengths of plastic tubing (nominally with total lengths - copper + plastic - of 6', 9', 16' and 36' of ½" ID tubing and 36' of ½" / ⅜" tubing) and then to eight receiving tanks where samples were taken at different intervals to characterize the separation of the aqueous phase, the dehydration of the emulsion and the oil content of the decanted water. Demulsifier was injected, at a target dosage of approximately1:500 (demulsifier:fluid), into the system, using a chemical metering pump, either before the main pump, after the main pump or just before discharge into the recovery tanks. Full details of the various components in the laboratory test loop are contained in Appendix 2.

Test Procedeures

1. Mix enough salt water for emulsion formation and free water injection
2. Mix emulsion
   • Add Hydrocal and Bunker separately to emulsion tank
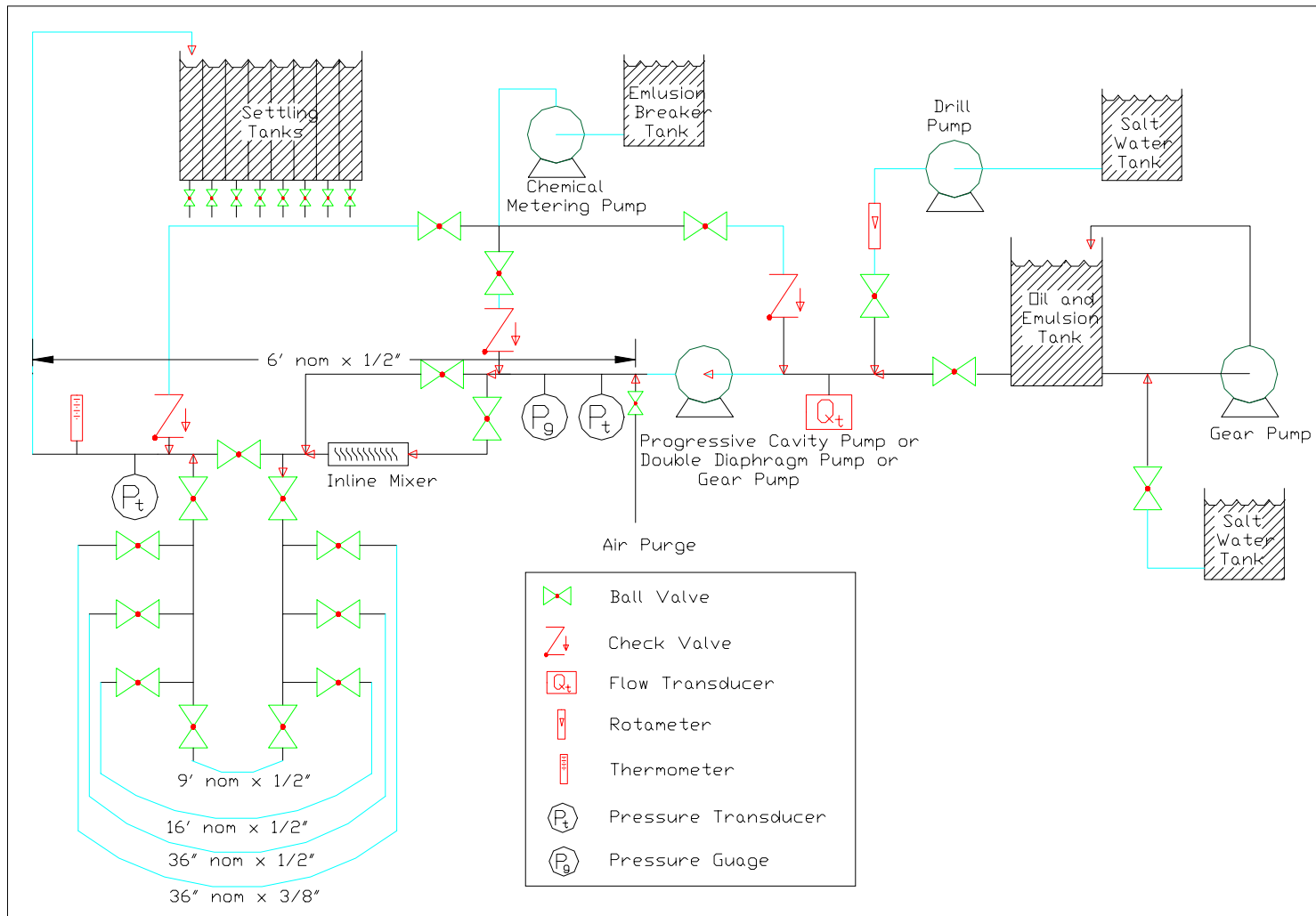
Figure 5-1. Schematic of laboratory test setup

Figure 5-2. Photograph of laboratory test setup

- Add salt water to blend tank
- Recirculate oil with gear pump
- Bleed in water slowly (approximately 2 L of salt water per minute)
- Measure gear pump output rate by timing fill of bucket and adjust to desired flow rate with valve

3. Randomly determine which sample time is to be repeated with tank 8
4. Start data logger
5. Open valves
6. Start chemical metering pump (if using)
7. Start water pump (if using)
8. Start main pump
9. Start emulsion pump
10. Discharge fluid into waste tank until fluid appears consistent
11. Discharge into sample tanks; start stopwatch; record time of day on data sheet

12. Fill tanks to 5 L or 2.5 L, depending on free water content; note time on stopwatch when each tank is filled

13. When 8th tank is filled, direct discharge to waste tank

14. Stop main pump, emulsion pump, water pump and chemical pump

15. Stop data logger

16. Decant water from sample tanks into graduated pitchers and record volume after appropriate settling times (2, 5, 10, 15, 30, 45 and 60 minutes); take 30 mL samples of water from tanks 1, 5 and 7 for oil content analysis

17. After decanting, mix oil remaining in sample tanks with spatula

18. Withdraw 20 mL with syringe and transfer to 30 mL glass bottle for water content analysis

19. Empty tanks in preparation for next test

Emulsion Sample Analysis

The emulsion samples in 30 mL glass vials withdrawn from each tank were treated with a few drops of Alcopol O emulsion breaker, shaken vigorously, then placed in a constant temperature bath at 70˚C for at least 24 hours to separate. The vials were then removed from the bath, wiped and the heights of water and oil in the vials measured with a steel rule. The water content of the emulsion remaining after decanting could then be estimated. Unfortunately, it turned out that, probably because the parent oil in the emulsion did not contain a significant amount of aromatics (Hydrocal is a de-aromatized lube stock oil) that the demulsifier could not completely resolve the emulsion, even with heating. This was presumed to be due to the need for an aromatic fraction in the parent oil to receive the asphaltenes displaced from the oil/water interface. Without an aromatic fraction, the asphaltenes could not be completely displaced and remained at the interface to stabilize some droplets. Subsequent to the laboratory and Ohmsett tests it was determined that addition of 25% diesel fuel (an oil high in aromatics) to the Hydrocal/Bunker mix produced an emulsion that was completely resolved by the Alcopol O.

Further evidence of the need for an aromatic fraction in the parent oil to solubilize the asphaltenes was found when the lab tests were first begun. A 55-gallon drum of Hydrocal was treated with 5% Bunker and thoroughly mixed to prepare a large batch of parent oil for the tests. Stable emulsion was formed from the first aliquot withdrawn from the drum, but subsequent aliquots could not be emulsified. It is believed that when the Bunker was mixed into the Hydrocal the asphaltenes were initially dispersed, but subsequently settled out over time, because there were insufficient aromatic compounds to act as resin components and maintain the asphaltenes in colloidal suspension. This left insufficient concentrations of asphaltenes in subsequent aliquots of the Hydrocal to stabilize the emulsions. Subsequent batches of parent oil for the tests were prepared by mixing the Hydrocal and Bunker just prior to creating the emulsion with salt water.

Oil-in-water Analysis

The water samples removed from Tanks 1, 5 and 7 were extracted with methylene chloride and the absorbance of the sample measured with a visible light spectrophotometer. Oil concentrations were determined by comparison with a calibration curve constructed with samples of known concentration of the oil. A calibration curve was constructed for both the Hydrocal with 2.5% Bunker and 5% Bunker, as the Bunker content of the oil strongly affected the absorbance readings. Due to a miscommunication, the test samples were extracted using the standard technique for the Labofina dispersant effectiveness test (ref - i.e. with 50 mL of solvent to extract a 30 mL water sample), instead of using solvent volumes less than the water sample volume in order to provide more concentrated extracts for spectrophotometric analysis. This resulted in some loss of accuracy, particularly for the samples taken from the water that was allowed to settle for 30 minutes and 1 hour (Tanks 5 and 7, respectively) as the measured absorbance for these was low, and near the limits of detection of the technique. The error in these samples is likely on the order of an absorbance reading of 0.005 (equivalent to 270 ppm for the 5% Bunker oil mix).

5.3 Laboratory Test Matrix

Table 5-2 gives the laboratory test matrix. The matrix varied:

- pump type (progressing cavity, gear or double diaphragm)
- demulsifier injection point (before pump, just after pump and just before discharge to the settling tanks)
- free water content (0% and nominally 50%)
- mixer in line
- length/diameter of test loop (6', 9', 16' or 36' of ½" ID or 36' of ½" / ⅜"ID)

Most of the test runs were done with the Hydrocal containing 5% Bunker by volume, but several were done with emulsions made with Hydrocal containing 2.5% Bunker to investigate the effect of this change. As well, there were several runs added to investigate the effect of different dosages of demulsifier. All tests were run at room temperature (approximately 20˚C).

5.4 Laboratory Test Results

5.4.1 Interpretation of Results

Table 5-3 gives the results for Test 2, one of the baseline runs (i.e., no demulsifier added) and Table 5-4 gives the results for one of the runs involving demulsifier added before the pump, with the flow directed through the in-line mixer, but not through an additional length of tubing.

The top row of Table 5-3 gives information on the test number, whether or not demulsifier was injected, the calculated free water content (based on the measured free water input rate divided by the total fluid flow rate determined by timing the filling of the eight tanks), whether or not flow was directed through the in-line mixer and the total length of the test loop used. The far right box on the top gives the calculated demulsifier dose rate (total fluid flow rate/demulsifier flow rate). The bottom row gives: the time measured to fill all eight tanks; the calculated total fluid flow rate (8 x volume put in tanks ÷ fill time); the free water flow read from the water

Table 5-2: Laboratory Test Matrix

Test Number	Demulsifier (Y/N)	Free Water (%)	Inline Mixer (Y/N)	Circuit Length (ft)	Test Description
1	No	0	No	6	Baseline with and without
2		50	No	6	water
3	Before Discharge	0	No	6	Demulsifier before tank, with
4		50	No	6	and without water
5	After Pump	50	No	6	Mixing from turbulence in
6		50	No	9	piping. Check line pressure
7		50	No	16	before increasing circuit
8		50	No	36	length
9		50	No	*36	
10	After Pump	50	Yes	6	Mixing from turbulence in
11		50	Yes	9	piping plus inline mixer.
12		50	Yes	16	Check line pressure before
13		50	Yes	36	increasing circuit length
14		50	Yes	*36	
20	Before Pump	50	Yes	6	Demulsifier before pump,
21		50	No	6	with and without mixer
22		50	No	36	
23		50	Yes	36	
23D		50	Yes	36	
23C		50	Yes	36	

* 3/8" tubing

Pump: Gear Pump

Test Number	Demulsifier (Y/N)	Free Water (%)	Inline Mixer (Y/N)	Circuit Length (ft)	Test Description
24	No	0	No	6	Baseline with and without
25		50	No	6	water
26	Before Discharge	0	No	6	Demulsifier before tank, with
27		50	No	6	and without water
15	After Pump	0	Yes	6	Mixing from turbulence in
16		0	Yes	9	piping plus inline mixer.
17		0	Yes	16	Check line pressure before
18		0	Yes	36	increasing circuit length
19		0	Yes	*36	
28	Before Pump	0	No	6	Demulsifier before pump,
29		50	No	6	with and without water
30		50	No	9	
31		50	No	16	
32		50	No	36	
33	Before Pump	50	Yes	6	Demulsifier before pump,
34		50	Yes	36	with water and inline mixer
41	Before Pump	0	Yes	6	Demulsifier before pump
42		0	Yes	36	with mixer but no free water

Pump: Double-Diaphragm Pump

Test Number	Demulsifier (Y/N)	Free Water (%)	Inline Mixer (Y/N)	Circuit Length (ft)	Test Description
35	No	0	No	6	Baseline with and without
36		50	No	6	water
37	Before Pump	0	No	6	Demulsifier before pump,
38		50	No	6	with and without water
39	Before Pump	50	Yes	6	Demulsifier before pump,
40		50	Yes	36	with water and inline mixer

Test Number	Demulsifier	Free Water	Inline Mixer	Circuit Length		Demulsifier Dose Rate Fluid:Demuls
2	No	44%	No	6 ft		
						0

Tank Number	Settling Time	Decanted Water (mL)	Corrected Water (mL)	Emulsion Remaining (mL)	Oil Height (mm)	Water Height (mm)	Emulsified Water Removed (%)	Free Water Removed (%)	Emulsion Dehydration (%)
1	2	1750	2100	2900	18	14	0	95	22
2	5	1700	2050	2950	19	14	0	92	26
3	10	1700	2050	2950	21	11	0	92	48
4	15	1750	2100	2900	17	13	0	95	24
5	30	1700	2050	2950	17	15	0	92	12
6	45	1700	2050	2950	18	16	0	92	11
7	60	1700	2050	2950	19	12	0	92	37
8	45	1750	2100	2900	16	15	0	95	6
						average:	0	93	23

Fill Time (s)	Fluid Flow (gpm)	Water Flow (gpm)	Emulsion Flow (gpm)	Oil Input (gpm)	Water Input (gpm)				
						repeat dif:	0	2	-5
						minimum:	0	92	6
						maximum:	0	95	48
76	8.3	3.7	4.6	2.3	6.0				

Table 5-3: Results for Test 2

Test Number	Demulsifier	Free Water	Inline Mixer	Circuit Length		Demulsifier Dose Rate Fluid:Demuls
20	B.P.	49%	Yes	6 ft		
						752

Tank Number	Settling Time	Decanted Water (mL)	Corrected Water (mL)	Emulsion Remaining (mL)	Oil Height (mm)	Water Height (mm)	Emulsified Water Removed (%)	Free Water Removed (%)	Emulsion Dehydration (%)
1	2	2600	2780	2220	22	11	27	114	50
2	5	2400	2750	2250	24	9	24	113	63
3	10	2500	2850	2150	28	5	32	117	82
4	15	2500	2850	2150	25	8	32	117	68
5	30	2500	2850	2150	23	10	32	117	57
6	45	2500	2850	2150	23	11	32	117	52
7	60	2650	3000	2000	25	8	44	123	68
8	10	2700	3050	1950	23	10	48	125	57
						average:	34	118	62

Fill Time (s)	Fluid Flow (gpm)	Water Flow (gpm)	Emulsion Flow (gpm)	Oil Input (gpm)	Water Input (gpm)				
						repeat dif:	16	8	-26
						minimum:	24	113	50
						maximum:	48	125	82
91	7.0	3.4	3.6	1.8	5.2				

Table 5-4: Results for Test 20

rotameter; the emulsion flow calculated from the difference between total flow rate and water flow rate and the total flow rate of water added (free water plus emulsion water). The first column in the main body of the spreadsheet is the designator for each of the eight tanks; the second column is the elapsed time between completing filling of the tank and commencing decanting that tank. The third column is the volume of water decanted from the tank into the graduated pitcher. The fourth column is the corrected volume of water removed from the tank (the drain fitting at the bottom of the tank extended above the floor of the tank a distance equivalent to a volume of 350 mL). It is clear that primary break was taking place very quickly - in 2 minutes or less. The fifth column is the volume of emulsion remaining in the tank (filled volume - corrected volume of water removed). The sixth and seventh columns are the heights of oil and water measured in the treated/heated samples of emulsion removed from the tanks after decanting - remember that this analytical technique was not effective in removing all the water from the parent oil. The results for this baseline test should give equal heights of oil and water, but don't, because of the problems with the analytical technique. The eighth column gives the percent of the water removed from the emulsion (based on a mass balance calculation, not the emulsion sample analysis - see below), and the ninth column shows the percentage of the free water in each tank that was decanted (again, based on a mass balance). The last column is the dehydration of the emulsion (as defined by Hokstad et al. 1994) based on the emulsion sample analysis. As noted previously, the analytical technique for water content was not accurate, and this dehydration was not used further in the analysis.

The four rows at the bottom right-hand corner of the spreadsheet give the average, maximum and minimum of the values in the last three columns. Also noted is the difference between the values determined for the eighth tank and the tank it was a duplicate of, as a measure of the repeatability of the test.

Table 5-4 gives the spreadsheet for Test 20, one in which demulsifier was injected before the progressing cavity pump at a dose rate of 1:752 into a flow containing 49% free water. The in-line mixer was used, but the flow was not sent through one of the longer flow paths of plastic

tubing. In comparison with Table 5-3 it is apparent that much more water was decanted, and that primary break takes longer(perhaps 10 minutes, in this case). This was confirmed by the second-last column which shows that more than 100% of the free water has been decanted - some emulsion water must be have been removed. The percentage of free water decanted was calculated by dividing the corrected volume of water decanted for each tank (fourth column) by the amount of free water that was calculated to have been added to each tank (the tank fill volume times the free water content determined from the measured water and total flow rates). A measure of the efficiency of the emulsion breaking is given in the third column from the left, for tanks in which the free water removal exceeded 100%. The percentage of the emulsified water removed was calculated as the corrected volume of water decanted from a tank less the calculated volume of free water added to that tank (see above) all divided by the volume of water in the emulsion in the tank (emulsion volume x 50%).

This method of calculating emulsion breaking efficiency gave more consistent and reasonable results than trying to use the flawed emulsion dehydration data; however, the accuracy of the mass balance technique is less than a better emulsion dehydration analysis would have been. The measurement error in decanted water volumes was 50 mL, using the graduated pitchers, and the error in accurately filling the tanks during a test was on the order of 5 mm, or about 100 mL. Thus the volumes of water decanted could be in error by as much as 150 mL. Emulsified water removal efficiencies could thus be in error by up to 12% (150/[2500 x 0.5]). Based on the results of the BS&W analysis for the Ohmsett tests (see Section 6), the error in directly analysing emulsion water content would be on the order of 5%.

The data in Table 5-4 indicate that injection of the demulsifier into the flow resulted in an average emulsion water removal efficiency of 34%. This is far from perfect resolution of the emulsion, but remember that the lack of an aromatic component in the parent oil significantly reduces the ability of the surfactant to displace the asphaltenes and allow the water droplets to coalesce and separate out of the oily phase. As well, the selected parent oil and the emulsion preparation (gear pump mixing) for these tests were intentionally chosen to not break too easily,

in order to allow trends in the effects of test variables on emulsion breaking efficiency to be discerned from the results. Little could be learned about the effects of the test variables if the emulsion breaker perfectly resolved every emulsion.

5.4.2 Summary of Lab Test Results

Table 5-5 summarizes the laboratory test results, grouped by the type of pump tested. The test matrix is reproduced at the left of the table for clarity. Full data on all the laboratory tests, including equipment calibrations, may be found in Appendix 3.

Emulsion Breaking

For the test series involving the progressing cavity pump, it was not possible to do the baseline tests (i.e., no demulsifier) with no free water: the pump could not move the emulsion at a reasonable flow rate down even the shortest flow path. The baseline run with free water (#2) resulted in no emulsion breaking. In comparison, the results of Test 4 (done with a parent oil containing 2.5% Bunker) show the effect of injecting demulsifier into the fluid stream just before it was discharged into the tanks for settling. There was no significant difference in emulsion breaking compared to the baseline, except for an increase in the concentration of oil in the decanted water. Injecting the demulsifier just after the pump (Test 5), and allowing it to work on the emulsion while it travelled through the 6-foot length of ½" copper tubing, resulted in some breaking of the emulsion. Increasing the hose length (Tests 7 and 8) further increased the degree of emulsion breaking. Note that Test 7 contained an abnormally low amount of free water (39%). Also, Test 8 involved a 2.5% Bunker parent oil and double the normal dosage of demulsifier, seemingly without affecting the overall emulsion breaking efficiency.

Table 5-5: Summary of Laboratory Test Results

Test Number	Demulsifier (Y/N)	Free Water (%)	Inline Mixer (Y/N)	Circuit Length (ft)	Test Description	Free Water Removed (%) Average	Minimum	Maximum	Emulsified Water Removed (%) Average	Minimum	Maximum	Concentration of Oil in Water (ppm) 2 min	30 min	60 min	Free Water %	Demulsifier Dose Rate	Fluid Flow (gpm)	Upstream Pressure (psi)	Downstream Pressure (psi)
1 No		0 No		6	Baseline with and without														
2		50 No		6	water	93	92	95	0	0	0	3743	835	1210	44%	0	8.3	11.6	6.1
3 Before Discharge		0 No		6	Demulsifier before tank, with														
4		50 No		6	and without water	90	86	93	0	0	0	4606	3839	1429	45%	406	8.5	10.5	5.0
5 After Pump		50 No		6	Mixing from turbulence in	110	106	115	16	10	24	2430	1867	741	44%	925	8.6	10.4	5.2
6		50 No		9	piping. Check line pressure														
7		50 No		16	before increasing circuit	77	133	145	48	42	59	2336	554	460	39%	964	8.9		
8		50 No		36	length	121	119	126	37	33	47	12604	2305	333	47%	346	7.2		
9		50 No		*36		108	104	114	25	12	42	2618	272	460	60%	617	5.7		
10 After Pump		50 Yes		6	Mixing from turbulence in	117	115	120	33	29	39	2711	85	366	50%	761	7.0	30.3	3.8
11		50 Yes		9	piping plus inline mixer.														
12		50 Yes		16	Check line pressure before	112	107	120	28	17	48	2336	85	178	55%	685	6.3		
13		50 Yes		36	increasing circuit length	120	114	139	35	32	40	na	na	na	54%	685	6.3		
14		50 Yes		*36		97	94	99	0	0	0	2149	741	460	80%	460	4.3		
20 Before Pump		50 Yes		6	Demulsifier before pump,	118	113	125	34	24	48	2618	1210	1492	49%	752	7.0		
21		50 No		6	with and without mixer	109	105	110	14	7	17	2711	929	647	45%	913	8.5	10.6	5.3
22		50 No		36		115	112	124	29	23	47	2336	741	835	49%	769	7.1		
23		50 Yes		36		112	99	119	24	0	38	7590	460	929	49%	699	6.5	40.8	3.1
23D		50 Yes		36		118	112	122	37	25	45	na	na	na	51%	678	6.3	45.8	3.6
23C		50 Yes		36		124	110	137	52	21	79	na	na	na	52%	296	6.2	45.1	3.6

* 3/8" tubing

Pump: Gear Pump

Test Number	Demulsifier (Y/N)	Free Water (%)	Inline Mixer (Y/N)	Circuit Length (ft)	Test Description	Free Water Removed (%) Average	Minimum	Maximum	Emulsified Water Removed (%) Average	Minimum	Maximum	Concentration of Oil in Water (ppm) 2 min	30 min	60 min	Free Water %	Demulsifier Dose Rate	Fluid Flow (gpm)		
24 No		0 No		6	Baseline with and without	NA			0	0	0	na	na	na	0%	0	3.9		
25		50 No		6	water	96	91	102	1	0	6	2805	1117	na	56%	0	6.1		
26 Before Discharge		0 No		6	Demulsifier before tank, with														
27		50 No		6	and without water														
15 After Pump		0 Yes		6	Mixing from turbulence in	NA			22	19	30	na	na	na	0%	151	3.1	80.0 na	
16		0 Yes		9	piping plus inline mixer.														
17		0 Yes		16	Check line pressure before														
18		0 Yes		36	increasing circuit length	NA			17	0	24	na	85	272	0%	181	3.7		
19		0 Yes		*36															
28 Before Pump		0 No		6	Demulsifier before pump,	NA			51	24	57	5807	741	929	0%	628	5.8		
29		50 No		6	with and without water	108	102	116	12	3	23	1492	1304	1586	42%	665	6.2		
30		50 No		9															
31		50 No		16		100	96	103	3	0	9	2242	1117	1304	61%	634	5.9		
32		50 No		36		119	107	128	33	11	48	1210	460	-103	46%	611	5.7	15.0 na	
33 Before Pump		50 Yes		6	Demulsifier before pump,	125	121	128	56	47	64	2618	85	366	53%	571	5.3	30.0 na	
34		50 Yes		36	with water and inline mixer	141	134	151	81	68	100	2618	741	272	50%	585	5.4		
41 Before Pump		0 Yes		6	Demulsifier before pump	NA			59	52	66	2055	741	na	0%	601	5.6		
42		0 Yes		36	with mixer but no free water	NA			63	46	72	5057	647	741	0%	552	5.1		

Pump: Double-Diaphragm Pump

Test Number	Demulsifier (Y/N)	Free Water (%)	Inline Mixer (Y/N)	Circuit Length (ft)	Test Description	Free Water Removed (%) Average	Minimum	Maximum	Emulsified Water Removed (%) Average	Minimum	Maximum	Concentration of Oil in Water (ppm) 2 min	30 min	60 min	Free Water %	Demulsifier Dose Rate	Fluid Flow (gpm)
35 No		0 No		6	Baseline with and without	NA			0	0	0	na	na	na	0%	0	2.0
36		50 No		6	water	98	86	113	4	0	16	4775	835	-9	37%	0	7.5
37 Before Pump		0 No		6	Demulsifier before pump,	NA			58	28	68	na	460	366	0%	543	5.0
38		50 No		6	with and without water	133	119	142	46	28	60	2242	835	272	41%	938	8.7
39 Before Pump		50 Yes		6	Demulsifier before pump,	113	104	119	38	12	56	4119	1210	929	60%	652	6.0
40		50 Yes		36	with water and inline mixer	105	98	107	21	0	31	1961	-103	-197	68%	571	5.3

For Test 9 the treated fluid was directed through the 36-foot length of ½" / ⅜" tubing. This resulted in a significant increase in the back pressure at the pump, and a corresponding decrease in emulsion flow rate with a commensurate increase in the free water content. The significant reduction in emulsion breaking efficiency for this test (when the increased mixing associated with the smaller-diameter hose would be expected to at least produce the same result), may be due to a critical amount of the demulsifier partitioning into the excess free water rather than mixing and reacting with the emulsion. The next few tests involved directing the flow through the in-line mixer. The emulsion breaking results of Test 10 are significantly better than Test 5; however the results of Test 12 are not as good as those of Test 7 - quite possibly because of the significantly higher free water content in Test 12 (a mixture with 55% free water contains almost twice the volume of water of a mixture that is 39% free water). The results of Test 13 are about the same as Test 8 and also show a slight improvement with increased hose length compared to Test 12.

No emulsion breaking apparently occurred in Test 14, presumably due to the very high free water content of 80%.

The final subset of tests involved injecting the demulsifier before the progressing cavity pump. Comparing the results of Test 20 to Test 10 shows no difference, as does comparing the results of Test 21 to Test 5. This is not surprising as progressing cavity pumps are specifically designed to impart little mixing energy to the fluid. Comparing the results of Test 20 to Test 21 shows that the energy imparted to the fluid by the in-line mixer improves emulsion breaking. The results of Test 22 indicate that increased hose length increases emulsion breaking too. Test 23D was included to determine the effect of reduced Bunker concentration in the parent oil (it involved 2.5% as opposed to the normal 5%); this seemed to allow the demulsifier to be more effective. Test 23C involved a 2.5% bunker parent oil with twice the normal dosage of demulsifier; this resulted in a further improvement in emulsion breaking.

The next set of tests used the gear pump, a type that adds much more mixing energy to the pumped fluid that a progressing cavity pump. Tests 24 and 25 were the baseline runs with and without free water - no emulsion breaking was observed. Tests 26 and 27 were skipped, since the type of pump used upstream would make no difference when injecting the demulsifier just before discharging it into the tanks.

The next subset of tests involved pure emulsion (no free water), injecting demulsifier into the flow stream just after the pump, with the fluid directed through the inline mixer. Note that the absence of free water decreased the overall flow rate (and thus turbulence in the inline mixer) by half and increased the relative dosage of demulsifier. In Test 15 (flow sent straight to discharge) some emulsion breaking was measured (22% of the emulsion water was removed, on average). There was no significant difference noted when the flow was directed down an additional 36' of ½" tubing. This may be due to the fact that, with no free water present, the flow is laminar, not turbulent.

The next subset involved injecting the demulsifier before the gear pump, without the inline mixer and with and without free water. The 51% emulsion water removal attained for Test 28 (no free water), compared to Test 15 indicates that the intense mixing energy supplied by the gear pump greatly assists the emulsion-breaking process. Note also that the more effective emulsion breaking reduced the viscosity of the fluid, allowing higher flow rates. Adding free water to the system seemed to reduce the effectiveness of the demulsifier. In Test 29, the free water content was 42% and the measured emulsion water removal averaged 12% (not significantly different from the results of the similar Test 21 with the progressing cavity pump which averaged 14%). For Test 31, despite the increased flow path length, the average emulsion water removal was only 3%; the free water content was 61%. In Test 32, with a path length of 36", an average emulsion water removal of 22% was achieved with a free water content of 49%.

The next two tests were conducted with the flow directed through the inline mixer. Test 33 (53% free water) gave an emulsion water removal average of 56%, a significant increase over that

achieved with Test 29. The best emulsion water removal for the entire laboratory program was obtained with Test 34 (81%) with the flow from the inline mixer sent through the 36' test loop. Test 41 and 42 repeated 33 and 34, with no free water. Increases in emulsion water removal (compared to Tests 28 , 15 and 18) were measured. A trend seems to exist of increasing emulsion water removal with increasing amount of mixing energy and length of time that the energy is applied (i.e., flow path length).

The final six tests involved pumping with a double-diaphragm pump, a common type used in the inshore spill response industry. Tests 35 and 36 were the baseline runs, with no demulsifier injected, and no emulsion water removal was detected. The positive values noted for Test 36 were a result of excess free water put into the last two tanks at the end of the test run, because the emulsion supply tank was nearing empty. Injection of demulsifier before the pump with no free water resulted in high emulsion water removal, as had been observed with the gear pump (Test 28). In the presence of free water, the emulsion water removal was reduced. It is not clear why, in Test 38, the addition of 41% free water caused a reduction in emulsion water removal from 58% to 46% while in Test 29 the addition of 42% free water with the gear pump caused a drop from 51% to 12%.

In the final two tests, the high free water contents (60% and 68%) caused significant decreases in emulsion water removal, when the addition of the inline mixer and an increased flow length would otherwise be expected to increase emulsion water removal.

To summarize the emulsified water removal results with the different pumps: there was no significant effect of pump type when the demulsifier was injected after the pump; however, when the demulsifier was injected before the pump, the gear pump, which imparted the most mixing energy to the system, gave the best results, the double diaphragm pump (with a moderate level of mixing) gave the second-best results, and the progressing cavity pump (with little mixing energy imparted to the fluid) resulted in the least amount of emulsified water removal.

Oil Concentrations in Decanted Water

Due to the inadvertent error made in extracting the water samples taken from the three settling tanks, little oil-in-water data of value was collected from the laboratory tests. The available numbers indicate that the initial concentrations of oil in water were on the order of several thousand ppm, and that these declined over a one-hour settling period to levels on the order of hundreds of ppm. Unfortunately, it was not possible to determine if demulsifier addition, mixing energy levels or mixing times had any discernable effect on the oil content of the decanted water.

Pressure Drop

Pressure readings were collected for selected runs, which allowed the calculation of pressure drops. These are given in Table 5-6.

Test Number	Demulsifier (Y/N)	Inline Mixer (Y/N)	Circuit Length (ft)	Emulsified Water Removed Average	Free Water %	Demulsifie Dose Rate	Fluid Flow (gpm)	Upstream Pressure (psi)	Downstream Pressure (psi)	Pressure Drop (psi/ft.)
2	No	No	6	0	44%	0	8.3	11.6	6.1	0.9
4	Before Discharge	No	6	0	45%	406	8.5	10.5	5.0	0.9
5	After Pump	No	6	16	44%	925	8.6	10.4	5.2	0.9
21	Before Pump	No	6	14	45%	913	8.5	10.6	5.3	0.9
32	Before Pump	No	36	33	46%	611	5.7	15.0	na	0.3
33	Before Pump	Yes	6	56	53%	571	5.3	30.0	na	
10	After Pump	Yes	6	33	50%	761	7.0	30.3	3.8	
23	Before Pump	Yes	36	24	49%	699	6.5	40.8	3.1	
23D	Before Pump	Yes	36	37	51%	678	6.3	45.8	3.6	
23C	Before Pump	Yes	36	52	52%	296	6.2	45.1	3.6	
15	After Pump	Yes	6	22	0%	151	3.1	80.0	na	

Table 5-6: Pressure Drops Calculated from Laboratory Test Runs.

The data are presented in two groups, test runs without the inline mixer, for which a pressure drop per unit length due to internal friction can be calculated, and test runs utilizing the inline mixer, for which pressure drop per unit length cannot be calculated. In the first group, all the

tests involved free water, which significantly reduced pressure drop per unit length by reducing the bulk viscosity of the fluid. For the 6' flow path (with two 90° ells and one fully-open ball valve) the calculated pressure drop for water flowing at 8.5 gpm would be 0.7 psi/ft, only slightly less than that measured. For the 36" path length the calculated pressure drop for water flowing at 5.5 gpm would be 0.3 psi/ft - very close to that measured.

The much higher pressures associated with the in-line mixer are apparent. Comparing the pressure data from Tests 33 and 10 to the first 4, the inline mixer adds about 20 psi of back pressure to the system; for water, the theoretical back pressure would be 17 psi at a flow of 6 gpm. The longer flow path (Tests 23, 23D and 23C) further increased the back pressure. The effect of the free water is best illustrated by the back pressure measure for Test 15 - 80 psi while flowing through the 6' path with pure emulsion, even with demulsifier addition.

6. Ohmsett Tests

This section describes the procedures and results for the meso-scale tests carried out at Ohmsett. The tests were completed during two weeks (the 9th through the 20th) in July 2001. The Ohmsett Test Plan may be found in Appendix 4.

6.1 Ohmsett Test Equipment and Methods

6.1.1   Preparations

The preparations for the tests included:
- installing the skimmer, hoses, Globe boom and instrumentation
- conducting required safety checks, calibrations and notifications.

Test Set-up and Instrumentation

All tests were to conducted in a stationary position (i.e., no towing down the tank). A schematic layout of the test equipment is given in Figure 6-1. Equipment specifications for non-standard Ohmsett equipment and calibrations may be found in Appendix 5.

The test area consisted of 50 feet of 24-inch Globe boom deployed in a square (12.5' per side) between the auxiliary bridge and the main bridge (Figure 6-2). The boomed area was approximately 156 ft^2 (14.3 m^2). The Desmi Terminator skimmer was placed in the test area and operated from the Auxiliary Bridge. The skimmer discharge was directed to the oil recovery tanks on the Auxiliary Bridge (Figure 6-3) via 3-inch flexible hose. Pressure transducers were located at either end of a 42.5-foot section of this hose. For some tests, the skimmer discharge was directed through a Lightnin Series 45 Model 4 Type 12H in-line mixer (Figure 6-4). The

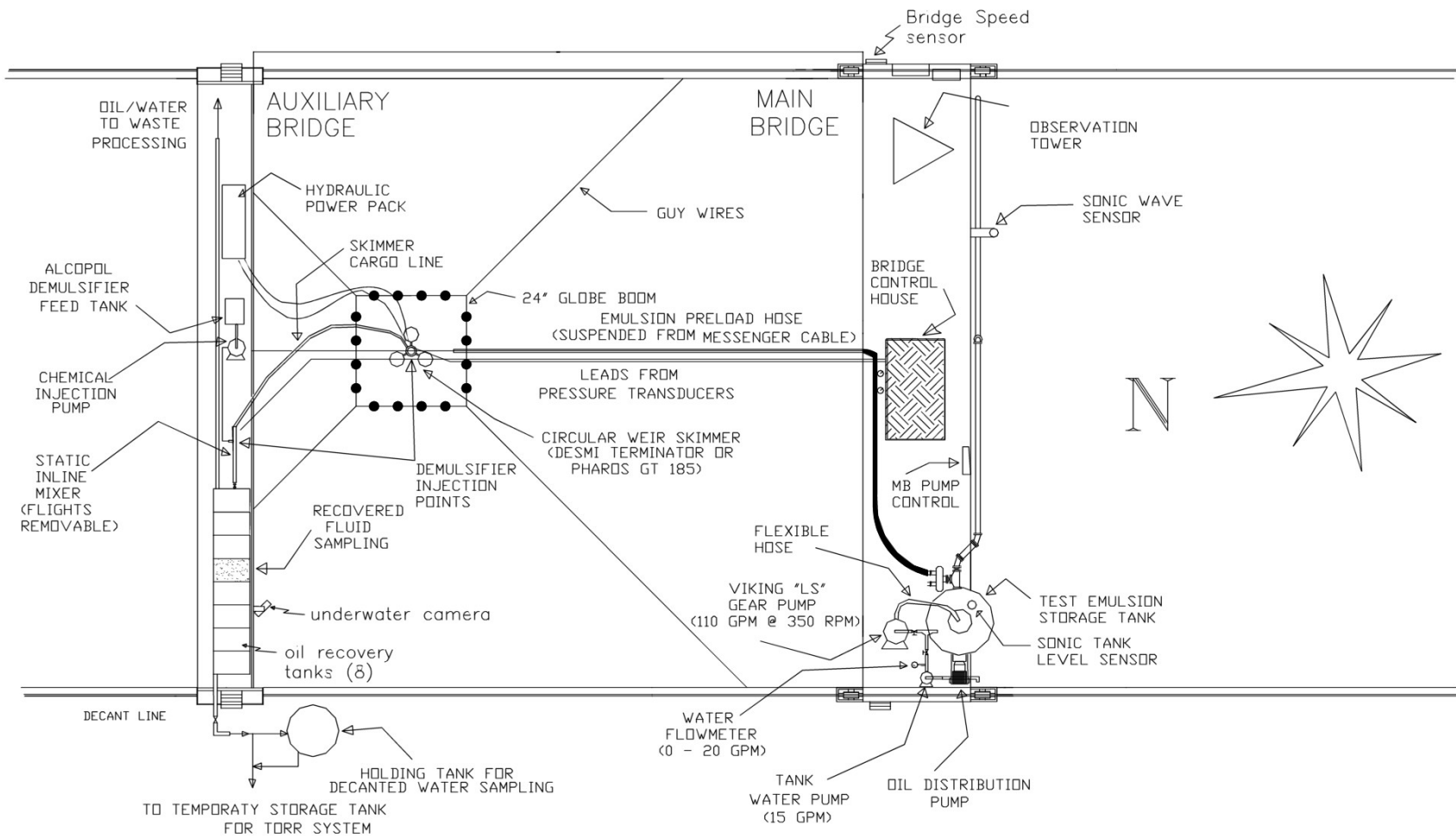**Figure 6-1**. Ohmsett test set-up.

Figure 6-2 . Boomed test area

Figure 6-3. Recovery tanks on Auxiliary Bridge

Figure 6-4. In-line mixer on Auxiliary bridge deck.

Figure 6-5. Steel temporary holding tank for decanted water.

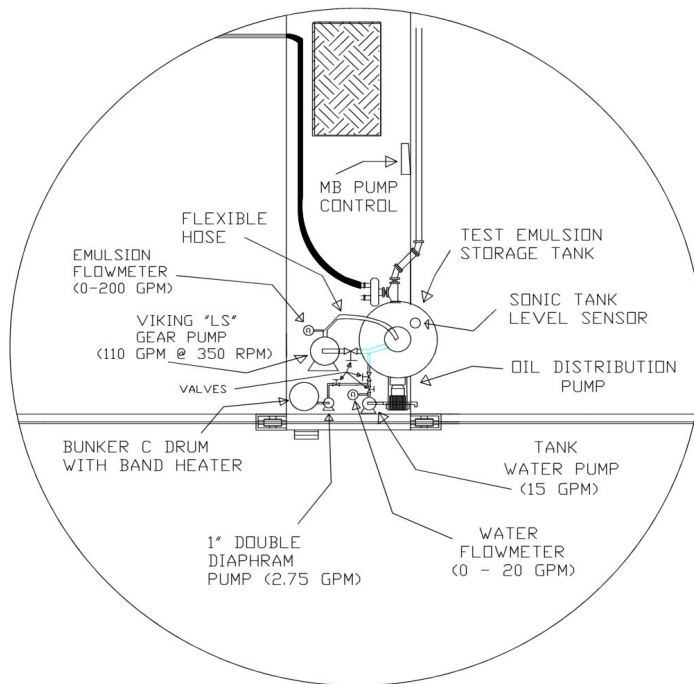**Figure 6-6.** Mixing tank for decanted water sampling

Figure 6-7. Plumbing for Main Bridge oil tank emulsion mixing and oil distribution.

separated water from the oil recovery tanks was directed to a temporary holding tank (Figure 6-5) for water sampling, then sent to a holding tank for eventual treatment and disposal to the sanitary sewer.

Demulsifier (Alcopol O 70% PG aka Drimax 1235B - a 70% solution of sodium diisooctyl sulfosuccinate in propylene glycol/water) was injected using a fixed-rate (0.25 gpm) peristaltic pump into the recovered fluid in one of two locations: directly into the skimmer weir or into the discharge hose just before the wye upstream of the inline mixer. For some tests the decanted water was sent to a sampling tank (Figure 6-6), where it was mixed thoroughly, and sampled for oil content analysis.   Oil or emulsion from the recovery tanks was pumped to the Ohmsett oily waster processing system then stored for disposal. The Hydrocal was not re-used for testing at Ohmsett because it contained some residual Alcopol that would reduce it's interfacial tension below the required standard.

 Portable video and still cameras were used to record the testing from various perspectives.

Waves were generated at the south end of the Test Basin and controlled by the Bridge Operator in the Control Tower at the north end. The wave profiles were recorded using a Datasonics ultrasonic distance meter. The signal from the wave meter was recorded and analyzed to confirm the wave characteristics.

Two wave conditions were generated during this test series. Their nominal characteristics are defined in Table 6-1.

Table 6-1. Nominal Wave Characteristics

Wave No.	Stroke (in.)	CPM	Type	Nominal $H^{1/3}$ (in.)	Wave Length (ft.)	Period (sec)
#1	3	22	Sinusoidal	16.5	37	2.8
#2	3	35	Sinusoidal	15	15	1.7

Emulsion Preparation

At the beginning of the tests, and subsequently as required, emulsions were prepared. A gear pump was used to prepare the emulsion, since large quantities of a consistent quality were required on a daily basis. The use of high-speed pumps, including gear pumps, to create emulsions for equipment testing is well known and widely utilized in North America and Europe (eg., Gåseidnes 1993). The capability of the Hydrocal 300 test oil doped with 2.5% Bunker C to form a meso-stable emulsion that is broken by the Alcopol O emulsion breaker had been confirmed by the lab tests. The use of 2.5% Bunker C for the Ohmsett parent oil, as opposed to 5% used in the laboratory tests was selected in order to ensure sufficient Bunker was available and to make the emulsions more amenable to breaking. A sample of the first batch of emulsion prepared was allowed to sit for 24 hours, and showed no signs of breaking. The target properties of the emulsion were: 50% (vol) water content with a viscosity of approximately 1000 cP at a shear rate of 1 s^{-1} at 70˚F. A 50% water content was chosen because it could be prepared reasonably quickly using the gear pump technique with little risk of inverting the emulsion, as can occur with higher water contents. The emulsion was prepared, using the Viking gear pump plumbed to the Main Bridge oil tank as shown schematically in Figure 6-7, as follows:

1. Add 700 gallons (2650 L) of Hydrocal 300 to the Main Bridge oil tank (Figure 6-8).
2. Warm Bunker in drum to 40 to 45˚C using electric band heater
3. Turn on Viking gear pump (at 350 rpm) and recirculate tank contents (nominally 110 gpm).
4. Turn on oil distribution pump (Moyno) and recirculate tank contents (nominally 350 gpm).
5. Slowly (2.75 gpm) add, using an air-powered double diaphragm pump, 66 L (17.5 gallons) of warm Bunker to the suction side of the Viking gear pump while circulating (Figure 6-9).
6. Continue recirculating for 10 minutes after last Bunker added.
7. Stop Viking gear and oil distribution pumps.
8. Record volume of oil in tank using ultrasonic probe.

Figure 6-8. Main Bridge oil tank and Moyno distribution pump manifold

Figure 6-9. Viking gear pump

9. Restart Viking gear pump at 350 rpm and recirculate tank contents.

10. Restart oil distribution pump (Moyno) and recirculate tank.

11. Open water valve and draw 15 gpm (57 L/min) of tank water into suction side of Viking pump.

12. Monitor tank level until a total of 717 gallons (2715 L) of tank water has been added (for a total volume in the tank of 1435 gallons (5430 L). Slow water addition to 10 gpm for last few minutes.

13. Continue recirculating for 30 minutes. Monitor water droplet size visually and collect sample for rheological analysis.

Each test required an estimated 530 gallons (2000 L) of emulsion, allowing approximately three runs per batch of emulsion.

6.1.2 Test Procedures

The following procedures were followed for each test:

Before each test the Emulsion Recovery Rate (ERR) for the skimmer was estimated and the volume of emulsion removed from the boomed area during the previous test calculated. The aim was to pump emulsion into the boomed area at the same rate that it was removed by the skimmer so that a constant thickness of emulsion was being presented to the skimmer. The following procedures were then used:

1. The required volume of test emulsion was added to the boomed area to make up the desired slick thickness (20 or 100 mm, see Test Matrix below).

2. The Main Bridge distribution pump speed was set to supply fresh test emulsion at the ERR estimated for the test.

3. The waves were turned on at the desired setting and allowed to come to apparent steady state (this required about two minutes). The data acquisition system was started.

4.   The emulsion distribution pump was started and the skimmer turned on, with its discharge directed to recovery tank #8. The chemical injection pump was started with flow to the desired location at the desired demulsifier flow rate (nominally $1/500^{th}$ of the Fluid Recovery Rate).

5.   When the cargo line was purged, the skimmer discharge was directed to the recovery tank cells sequentially (i.e., fill cell #7, then #6, etc.). The target volume of emulsion (exclusive of free water) in each cell was 200 L.

6.   The time when filling each tank cell was started and finished was recorded. The depth of fluid in each cell was measured and recorded.

7.   After the last tank cell was filled, the emulsion distribution pump, demulsifier injection pump, skimmer and waves were stopped.

8.   Simultaneously with the filling operation, two minutes after tank cell #7 was filled, the separated water was decanted until the discharge from the bottom was "black". The water was sent to a temporary storage tank and not poured back into the test basin. Note that cell #8 was also decanted to the temporary storage tank for processing.

9.   For selected cells in each test, the decanted water was directed to a Nalgene temporary holding tank on the deck beside the auxiliary bridge. When all water from the selected cell was transferred, the contents of the temporary holding tank were thoroughly mixed with an electric, bladed mixer and allowed to settle for five minutes to allow large droplets of emulsion to surface. The surface emulsion was removed with a sorbent pad, then the temporary holding tank was drained to the temporary storage tank. A small water sample, for oil content analysis, was taken when half the water had drained. The purpose of this was to estimate the average concentration of "permanently dispersed" oil in the decanted water - i.e., the droplets that would not rise out and re-coalesce with the slick if the decanted water was discharged back into a boomed area.

10.   The remaining emulsion recovery tank cells were decanted in sequence at 5, 10, 15, 30, 45, and 60 minutes after the time they were filled. The purpose of this was to determine the time required for "primary break" of the skimmer discharge product. "Primary break" is the point at which the bulk of the lower density phase has risen to the top and the

higher density phase has settled to the bottom; both phases typically contain small droplets of the other phase at this point.

11.   The depth of fluid remaining in each cell was measured (these depths, combined with the initial depths, were used to calculate the volumes of recovered product, decanted water and emulsion remaining).

12.   Each recovery tank cell was mixed and sampled to determine the water content of the fluid remaining.

13.   The contents of the recovery tank cells were transferred for waste processing.

6.1.3 Test Matrix

Originally, it had been planned to use two weir skimmers during the tests; however, due to circumstances beyond control, one skimmer was not tested (the Pharos GT-185). The test matrix variables were:

•   One circular weir skimmer (representative of OSRO stockpiles)
                - Desmi Terminator (USCG/Ohmsett) - nominal ORR in waves 20 m^3/hr (90 USgpm)

•   Two slick thicknesses (representing thicknesses typically expected for VOSS and large- scale boom/skimmer operations)
                - 20 mm (requires 300 L - 80 US gallons - preload in 12.5' square boomed area)
                - 100 mm (requires 1450 L - 335 US gallons - preload in 12.5' square boomed area)

•   Four demulsifier injection points
                - into the skimmer mouth
                - into the recovery tank inlet
                - into a static inline mixer at the recovery tank inlet
                - no demulsifier (control)

- Two Wave Conditions
  - wave #1, $H^{1/3}$= 16.5" with λ = 37'
  - wave #2, $H^{1/3}$= 15" with λ = 15'

A total of 36 tests were planned; however the inability to include one skimmer reduced the number of tests to 23, including several duplicates.

6.1.4   Sample Analyses

Each test involved collecting 3 oil-in-water samples and 7 water-in-oil samples, as well as selected duplicates. The oil-in-water samples were sealed in Nalgene jars and placed in a refrigerator for storage until such time as they could be analysed. The emulsion samples were analysed within 48 hours of collection. In addition, a sample of each batch of emulsion was subjected to a rheological analysis.

Bottom Solids and Water

The water content of the emulsion samples was determined using the procedures specified in ASTM D1796. The method involved splitting a well-shaken, 100-mL emulsion sample into two aliquots. Each aliquot was poured into a graduated, centrifuge tube containing 50 mL of toluene, filling the tube to the 100-mL mark. The tube was shaken vigorously, warmed and then placed in the centrifuge and spun for 10 minutes. The volume of water in the tubes was read directly from the graduations. For water volumes in the 10 to 25 mL range (20% to 50% water content emulsions) the reading error was on the order of 1 mL (2%); for higher water content emulsions the error ws likely in the 3 to 5 mL range (6% to 10%). For some samples, a small amount of demulsifier was added to aid in resolving the emulsion.

Total Petroleum Hydrocarbons

The decanted water samples were extracted with carbon tetrachloride (CCl_4) and then analysed with a scanning infra-red spectrometer. The techniques used generally followed those specified in EPA 413.2, except that the solvent used was not Freon. The error in this method was on the order of X ppm, with the limit of detection being Y ppm. The technique also detects the dissolved hydrocarbons in the tank water from previous testing. Generally, the "background" TPH level in the tank is 3 to 5 ppm. During the extraction process, the solvent could also remove some portion of the demulsifier that is dissolved in the water. It is not certain what this portion would be.

Emulsion Rheology

A sample from each batch of emulsion was sheared in a Haake VT550 rheometer; an SV-1 sensor was used. The shearing program involved ramping the shear rate up from 0.13 s^{-1} to 13 s^{-1} in ten equal time steps over a period of 60 seconds, maintaining the shear rate at 13 s^{-1} for a period of 600 seconds, then ramping the shear rate back down to 0.13 s^{-1} over a further 600 seconds. All samples were measured at room temperature: 25˚ to 27˚C.

6.2 Ohmsett Test Results

The results from the Ohmsett tests are summarized in Table 6-2. Full data and equipment calibrations may be found in Appendix 6.

Scaling Parameter

In terms of the scaling parameter used for the laboratory tests (Q/D [m^2/s] - see Table 5-1) the value for the Ohmsett tests ranged from 0.08 to 0.24, with the majority at a flow rate of 140 gpm having a value of 0.1 m^2/s. The degree of turbulence in the hose would thus be higher than that

achieved in the ½" or ⅜" tubing in the laboratory tests (Q/D = 0.04 m²/s). It had been intended to use 6-inch hose on the skimmer (giving a Q/D = 0.05 m²/s), but this was not possible.

Test Emulsion Rheology

A summary of the results of the rheological analyses of the various batches of emulsion mixed for the Ohmsett tests (50% seawater in 97.5% Hydrocal 300/2.5% Bunker) are given in Table 6-3. Full data plots may be found in Appendix 6. The emulsion exhibited a slight, but distinct pseudo-plastic (shear-thinning) behavior (the viscosity at 1 s⁻¹ was about 10% higher), with no evidence of thixotropy (time dependance). There was little difference between batches: the average viscosity was 990 mPas with a standard deviation (ignoring the slight temperature differences) of 107 mPas.

Table 6-2. Summary of Ohmsett results.

Test Number	Demulsifier Injection Point	Demulsifier Doseage (Fluid:Demulsifier)	Wave Type	Inline Mixer	Initial Slick Thickness (mm)	Final Slick Thickness (mm)	Fluid Recovery Rate (gpm)	Estimated Free Water (%)	Recovered Emulsion Water Content (avg %)	Extra Mix Water Content (%) Tank 4 Lab/Vol	Extra Mix Water Content (%) Tank 1 Lab/Vol	Oil Content of Decanted Water (ppm) 2 min	30 min	60 min	Back Pressure (psig)	Pressure Drop (psi/ft)
1	No	none	1	No	19	104	140	48	51	-	-	214	72	337	6.4	0.011
2	No	none	2	No	21	26	106	60	57	-	-	490	220	327	7.1	0.020
3	Skimmer	992	1	No	62	90	144	68	52	-	-	543	574	343	7.1	0.025
4	Skimmer	732	2	No	90	70	152	66	57	-	-	1086	514	404	7.1	0.020
5	Discharge	732	1	No	70	57	139	69	70	-	-	1079	629	479	7.0	0.019
6	Discharge	676	2	No	64	27	137	64	71	-	-	1376	606	543	7.0	0.022
7	Before Mixer	990	1	Yes	27	18	144	72	71	-	-	1113	433	432	10.2	0.031
8	Before Mixer	826	2	Yes	18	8	142	69	66	-	-	871	560	176	9.9	0.022
9 (DUP 8)	Before Mixer	787	2	Yes	20	5	135	66	67	-	-	1052	304	305	9.6	0.020
10	No	none	1	No	105	62	157	47	52	-	-	-	294	181	8.7	0.034
11	No	none	2	No	89	25	147	45	61	-	-	-	1110	301	8.1	0.028
12	Skimmer	1669	1	No	88	14	287	37	44	-	-	-	357	233	18.5	0.134
12A	Skimmer	624	1	No	100	28	135	8	54	-	-	-	-	-	10.4	0.050
13	Skimmer	646	2	No	53	18	134	44	55	-	-	2543	655	618	6.9	0.015
37	Skimmer	650	2	Yes	47	0	134	58	46	-	-	882	136	104	9.3	0.015
38 (DUP 37)	Skimmer	605	2	Yes	15	36	125	54	43	-	-	763	530	570	8.8	0.016
39	Skimmer	670	1	Yes	36	39	139	56	45	39/36	38/37	-	-	-	na	na
40	Skimmer	2397	1	Yes	87	130	323	54	33	36/23	42/32	-	-	-	37.6	0.142
41	Skimmer	2750	2	Yes	130	109	371	47	35	45/27	34/27	-	-	-	37.4	0.133
42	No	none	2	Yes	159	115	377	39	39	45/48	48/42	-	-	-	38.5	0.150
43	Skimmer	582	2	Yes	171	85	78	43	52	36/31	33/??	-	-	-	3.6	-0.035
44	Discharge	2854	2	No	86	73	385	75	43	57/27	39/42	-	-	-	20.8	0.159
45	Discharge	2800	1	No	172	68	377	32	50	45/41	40/37	-	-	-	23.2	0.192

Table 6-3. Emulsion Batch Viscosity

Emulsion Batch	Date Produced	Test Temperature [°C]	Viscosity at 10.7 s^{-1} [cP]
1	July 11, 2001	25.8	800
2	July 12, 2001	27	990
2 (duplicate)	July 12, 2001	27.8	990
3	July 13, 2001	25.7	1020
4	July 16, 2001	26.3	950
5	July 17, 2001	27.5	880
6	July 17, 2001	28	920
7	July 18, 2001	26.2	1040
8	July 19, 2001	25	1140
8 (duplicate)	July 19, 2001	25.7	1140

Decanting/Emulsion Breaking Results

The first five columns in Table 6-2 give the variables used for a specific test. Columns 6 and 7 give the estimated initial and final slick thicknesses in the boomed area before and after a given test. These are only rough indicators of the amount of oil in the boomed area at the beginning and end of a test because the errors in estimating slick thickness (based on emulsion added minus emulsion skimmer) accumulated in successive tests, until the boomed area was emptied at some point. The waves (both generated in the tank and reflected off the skimmer and boom) would also tend to push the oil to one side of the test area. As well, the flow of emulsion from the Main Bridge tank was spread out on a spill plate attached to the end of the distribution hose (Figure 6-10), and tended to flow directly towards the skimmer weir. Significant differences in the initial and final slick thicknesses are an indication that the system was not well balanced for a specific test (i.e., significantly more or less emulsion was being added than being removed) and that conditions were not likely at steady state during the test.

Figure 6-10. Spill plate and distribution of emulsion inside boomed area.
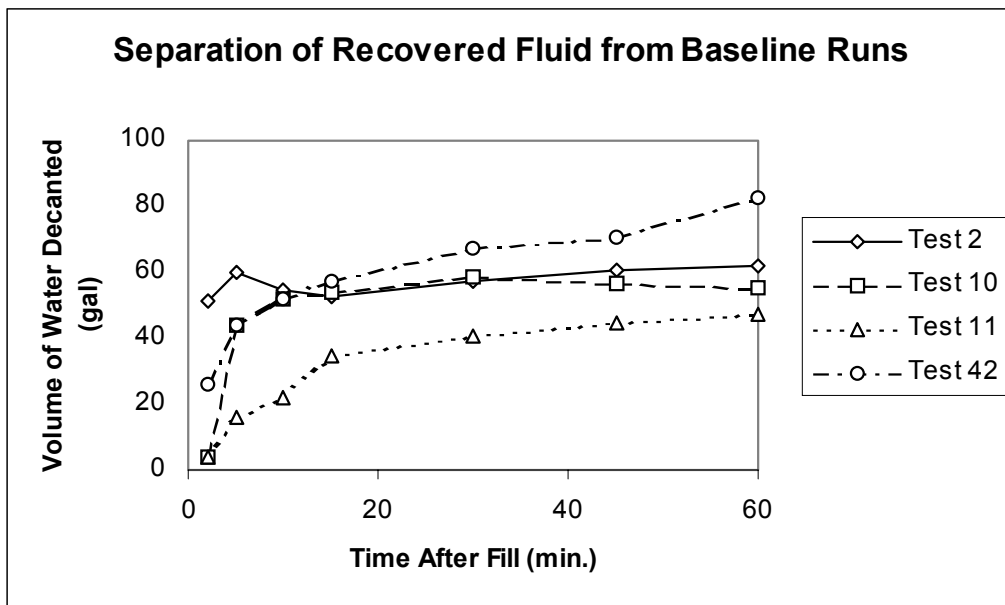

Figure 6-11. Separation of water from recovered fluid for baseline runs (no demulsifier)

Columns 8 and 9 give the measured fluid recovery rate (water + emulsion) and the percentage of the fluid made up of free water (based on comparing the total flow rate with the flow rate of 50% water content emulsion recovered - based on the doubling the volume of oil calculated to be contained in the recovery tanks after decanting from the water content analysis). The tenth column gives the average water content of the emulsion remaining in the seven tanks after decanting, based on the BS&W analysis of a well-mixed sample from each. In general, with exceptions noted in the discussions below, the water content in each individual tank did not vary significantly beyond the error estimate range (see Appendix 6), thus the average water content adequately represented the state of the emulsion in all the tanks after decanting. Note that, as discussed in the lab results, the parent oil composition (more specifically, the lack of a significant aromatic component) prevented the demulsifier (Alcopol O 70%) from completely resolving the emulsion. Based on the lab test results, demulsification down to a water content of about 30% represented the greatest achievable with the oil/demulsifier system used. The next two columns give the water content of emulsions exposed to additional mechanical mixing energy after decanting from tanks 1 and 4. The next three columns give the oil content (TPH) of the decanted water, and the final two give the pressures recorded in the skimmer hose.

Figure 6-11 shows the volume of water decanted from the recovery tanks as a function of time since they were filled for the baseline (i.e., no demulsifier) tests. In all cases the majority of the separation (called primary break) was over in 15 minutes for the tests conducted in Wave #2 (the steeper of the two). Primary break seemed to occur faster with fluid recovered from tests in Wave #1 - presumably because there is less uptake of large droplets of tank water (that slowly settle out once in the quiescent recovery tanks) into the test slick in the lower mixing conditions. These results are entirely consistent with results from previous decanting tests (SL Ross 1999) at Ohmsett with Hydrocal oil at 9°C, at which temperature it had a viscosity of 1000 mPas.

The recovered emulsion water content average for the first test (#1) showed no appreciable change, as would be expected since no demulsifier was added. The slight increase in average emulsion water content for Test 2 (again, no demulsifier) may have been due to increased mixing

energy from the increased wave steepness causing natural emulsification to add to the existing, 50% water content. Test 3 and 4 (demulsifier added to the skimmer hopper, but no inline mixer), showed no change in the water content of the emulsion in the recovery tanks, compared to Test 1 and 2 respectively. The free water content for these tests was 68 and 66% respectively, well above the free water contents in the lab-scale tests that significantly reduced the effectiveness of the demulsifier (ca. 60% free water).

The data from Tests 5 through 9 show an increase in the emulsion water content, despite demulsifier addition. The reason for this is not clear; however, several explanations are possible:

- The tests were completed sequentially (i.e., the emulsion remaining in the boomed area after Test 4 was used for Test 5, and so on) thus the wave action may have been continuously increasing the water content of the oil in the boomed area.
- Also the free water content of these tests was very high; meaning that the demulsifier would have been ineffective.
- The degree of turbulence in the hose was high, promoting emulsification. The Reynolds number in the hose, assuming that the high free water content fluid has a viscosity near that of water, would be about 150,000 at a flow rate of 140 gpm, well into the turbulent regime. The addition of the inline mixer to the flow path did not make a significant difference to the recovered emulsion water contents.

Tests 10 and 11 were baseline tests (i.e., no demulsifier addition), with the thicker slicks (ca. 100 mm). As with Tests 1 and 2, there was no emulsion breaking observed. In fact, in Test 11, as with Test 2, the steeper waves may have been further emulsifying the oil in the boomed area.

For Test 12, the skimmer was inadvertently run at full speed, recovering fluid at 287 gpm, about twice the intended rate. Test 12 was the first in which there was some evidence (albeit within the error range of the analytical technique used to determine water content) that emulsion breaking was occurring. The mean water content of the emulsion after decanting was 44%, with the samples from the first three tanks decanted (2, 5 and 10 minutes) averaging 53% and the last 4

(15, 30, 45 and 60 minutes) averaging 38% water. The free water in this run (37%) was significantly less than in the previous demulsification tests (64% to 72%). In the next test, 12A, intended to be a re-do of 12 at the correct recovery rate, almost no free water was recovered and no significant change in the emulsion water content was detected. In this situation, the recovered fluid would be much more viscous than in the case of significant amounts of free water, correspondingly reducing the turbulence level in the hose. For a viscosity of 1000 mPas, the Reynolds number would be 150, well below the 2100 cut-off point for laminar flow.

Test 13 was intended to determine the effect of steeper waves on demulsification with recovered fluid from the thicker slicks. The average water content of the recovered emulsion in the seven tanks was 55%, compared to 61% for the baseline case (Test 11) indicating no significant breaking, despite a free water content of 44%. It may be that the water content of the emulsion in the slick and recovery system had increased well above 50% (as was the case in Tests 4 and 6 and 11) and was subsequently reduced to 55% by the action of the demulsifier.

In Test 37, a slight demulsifying effect was noted, with the addition of the inline mixer to the recovery flow path; despite the relatively high free water content (58%). In the laboratory test results, there was a definite trend in increasing free water content above about 50% causing a decrease in emulsion breaking, with water contents in excess of about 60% almost completely negating the effect of the surfactant. The duplicate run of this test, Test 38, resulted in a slightly lower average emulsion water content in the recovery tanks, with a slightly lower free water content, albeit that the difference in water contents is less than the error for the water content analysis technique.

For the remaining tests, in order to see if more mixing energy could promote further emulsion breaking, an additional procedure was carried out on the recovered product in two of the tanks (#4 and #1, decanted after 15 and 60 minutes settling respectively). This involved dumping the entire contents of these two tanks into the Nalgene tank normally used to obtain a well-mixed water sample for TPH analysis. The volumes of water and emulsion added were measured by

height. Then, the emulsion and water were vigorously mixed with the Lightnin mixer for 10 minutes and allowed to separate for 20 minutes. After the separation period, the Nalgene container was decanted, with the volume of water and emulsion remaining measured again. A well-mixed sample of the emulsion was obtained for water content analysis in the lab.

Test 39 involved recovering fluid from relatively thin slicks, with the inline mixer in place in Wave #1. The free water content was estimated as 56%, and the average emulsion water content in the recovery tanks was 45%. The application of the extra mixing did result in further demulsification.

Test 40 involved a run with the skimmer operating at full speed. The free water content was about 54% and the recovered emulsion water content averaged 33%, indicating good breaking. Remember that, with the parent oil and surfactant system used, something on the order of 30% water content was the lowest achievable. Although the results from the additional mixing were scattered, the laboratory emulsion water content results after extra mixing also indicated good emulsion breaking. The high recovery rate (higher flow turbulence, inline mixer, and moderate free water) combined to make this the most effective test of the series. Test 41 repeated the conditions of Test 40, with the steeper waves. Good emulsion breaking was achieved again.

The results of Test 42, intended as a baseline run at the high recovery rate, are inexplicable. No demulsifier was injected, and yet the emulsion water content results from the recovery tanks indicate an average water content of only 39%. The same analyses of the samples from the tanks to which extra mixing was applied, indicate water contents in the range expected (near 50%) for both techniques (volume estimation and lab analysis). No trend in emulsion water content with time is apparent in the test data in Appendix 5.

Tests 43, 44 and 45 were conducted to investigate the effect of recovery rate on emulsion breaking. Test 43 was carried out at a low recovery rate (78 gpm), about half of the nominal rate (140 gpm) with the in-line mixer. No emulsion breaking was detected in the recovery system,

even with the inline mixer and an appropriate free water content. The extra mixing applied to the contents of tanks 4 and 1 did result in significant emulsion breaking. Test 44 was intended to be run with the nominal recovery rate, with no inline mixer to obtain a duplicate of Test 6, but due to a miscommunication, was actually run at the high recovery rate. Only moderate emulsion breaking was detected, probably because of the very high free water content (75%) in the recovered product. Although one volume measurement gave a water content of 27%, the rest of the extra-mix analyses indicated that the emulsion water content could not be reduced significantly with the addition of more turbulent energy, probably because much of the demulsifier was in the water, not in the emulsion. The results of Test 45 (high recovery rate, low free water, no inline mixer) compared to Test 40 (same conditions, but with the inline mixer) illustrate the importance of mixing energy to the emulsion breaking process. Note that in Test 45 almost no free water was collected in the first three tanks (7, 6 and 5); the free water in the recovered fluid was more likely in the 50% to 60% range. In conjunction with this increase in free water, and the commensurate increase in turbulence, the emulsion water content in the tanks decreased from 53% in the first three, to 45% in the last tanks filled. The addition of extra mixing energy to the contents of tanks 4 and 1 from Test 45 did result in significantly more emulsion dehydration.

In those tests in which significant emulsion breaking occurred (38, 39, 40, 41 and 42) primary break occurred within 15 minutes, no different than in the case of the baseline tests.

Oil Concentrations in Decanted Water

The TPH concentrations in the decanted water for the four baseline runs (i.e., no demulsifier addition) are shown on Figure 6-12 and in Table 6-2. The concentrations reported are oil-in-water, thus they should be doubled, at least for the baseline cases, to reflect emulsion-in-water concentrations. With this in mind, the results for the thinner slicks (Tests 1 and 2), at least for the 2- and 30-minute settling times, are entirely consistent with the results from the 1997 decanting tests (SL Ross 1998) with 1000-mPas Hydrocal in 20-mm thick slicks. It is not clear why the 60-

Figure 6-12: TPH concentrations.
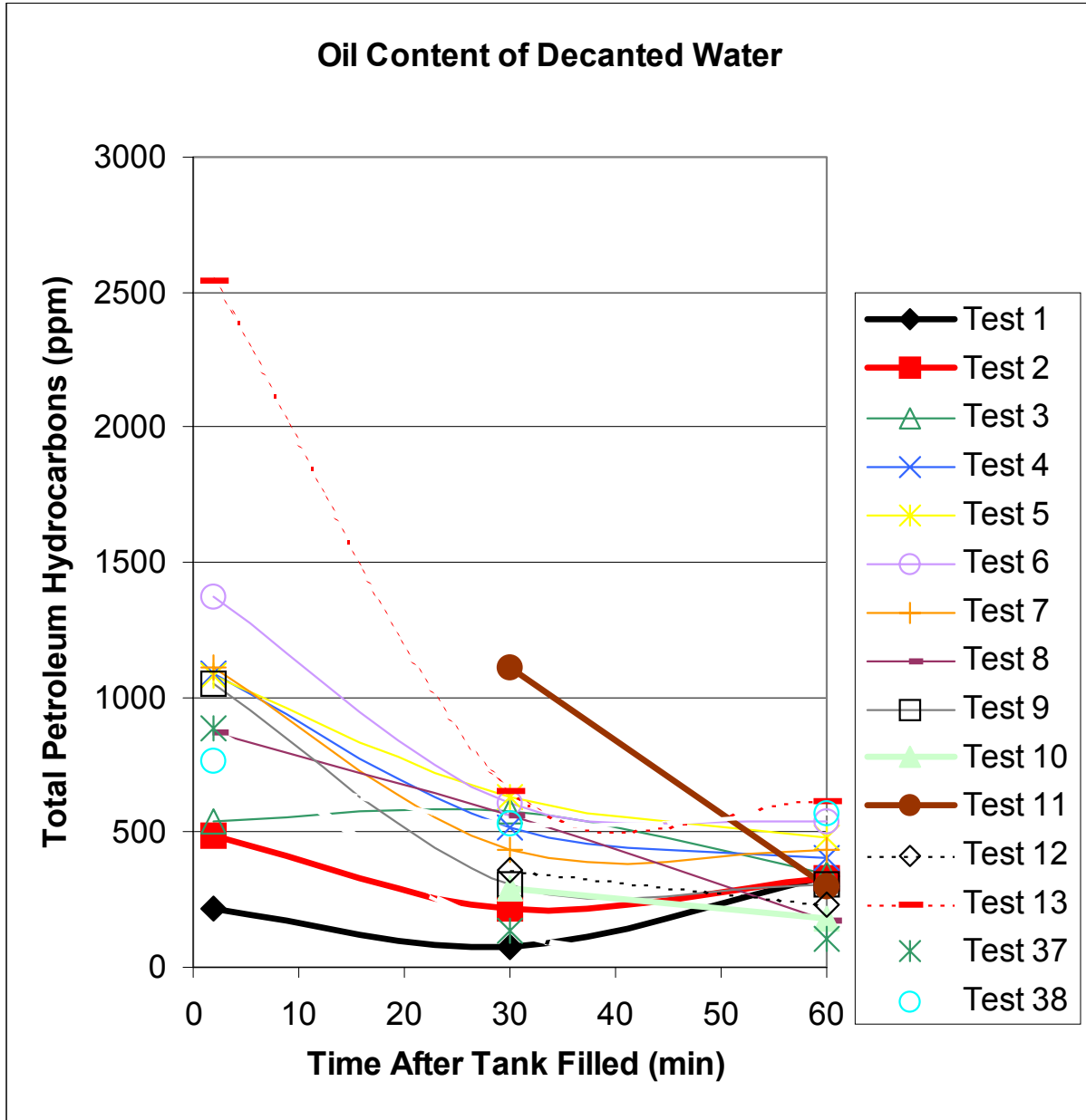
minute sample concentrations are higher than the 30-minute ones. The 30- and 60-minute oil-in-water concentrations for the thicker baseline slicks in Test 10 are also closely in agreement with the results from 1997 for 100-mm Hydrocal slicks. The results for Test 11 are higher, for no apparent reason. Almost no water was recovered from tank 7 (decanted after 2 minutes) for Tests 10 and 11, thus no water sample could be obtained for TPH analysis.

For tests involving demulsifier addition, the oil-in-water concentrations were generally higher than those of the baseline tests, by a factor of about 2. It is not clear what portion, if any, of the TPH is attributable to the Alcopol O (i.e., how much of the response from the IR was due to Alcopol O in the water sample that was extracted by the carbon tetrachloride). A simple test is planned at the next opportunity to evaluate this. The TPH readings (which would represent about one half the dispersed emulsion concentration for those tests in which the demulsifier was not very efficient) were on the order of 1000 ppm after 2 minutes, declining to 400 ppm after 60 minutes. Neither the demulsifier injection location, the presence of the inline mixer, fluid flow rate or wave height appeared to have an appreciable effect. There does not appear to be any obvious reason why the 2-minute and 60-minute samples for Test 13 gave such high results and the 30-minute and 60-minute samples from Test 37 had such low TPH's.

Pressure Drop

The average pressure recorded during steady-state recovery at the upstream pressure transducer, and the average pressure drop per unit length of hose (measured along a 42.5-foot length of 3-inch hose) are given in the last two columns of Table 6-2. If water were being pumped down the 3-inch hose at the nominal recovery rate of 140 gpm, the theoretical pressure drop would be 0.024 psi/ft (surface roughness of hose assumed to be 0.005 in.). The values in Table 6-2 are in this range, the differences probably being due to the error in subtracting low pressures measured with 0 to 200 psi range transducers with an accuracy of 0.25% of Full Scale, or 1 psi. This is probably best illustrated by the negative pressure drop recorded for Test 43, at a low flow rate.

The theoretical pressure drop for a 1000 mPas fluid (in laminar flow) would be 0.05 psi/ft, very close to the average value measured in Test 12A.

The tests involving higher flow rates gave higher pressure drops, as expected. Again, assuming water was the fluid being pumped, the expected pressure drops would be 0.096 and 0.15 psi/ft. at 280 and 350 gpm respectively, very close to the values measured. Even free water contents as low as 33% are sufficient to make the emulsion/water mixture almost as pumpable as pure water.

The average upstream pressures measured gave an indication of the extra effort required to pump fluids through the inline mixer. At 140 gpm with no inline mixer, the upstream pressure was on the order of 7 psi. Directing the flow through the inline mixer increased this to 10 psi. At flow rates on the order of 350 gpm the inline mixer caused an increase in pressure from 20 psi to 40 psi.

6.3 Comparison of Lab-scale and Ohmsett Results

Since the scaling parameter (Q/D) was different for the laboratory and Ohmsett tests, the results cannot be directly compared; however, there were several common features of the results of the two test series.

First was the importance of free water to the emulsion breaking process. At both scales, when the free water content exceeded about 60%, the efficacy of the demulsifier was noticeably reduced. This is presumed to be due to the surfactant ending up mostly in the free water, as opposed to the emulsion. This was particularly evident in the Ohmsett tests where often the decanted water drained into the steel temporary holding tank would foam. On the other hand, the presence of free water was necessary to allow efficient pumping of the emulsions and for the flow to reach turbulent levels. The free water resulted in a reduction in the apparent bulk viscosity of the fluid being pumped, which in turn increased flow rates and turbulence in the tubing and hoses. Only in the case of a system that utilized an energy-intensive transfer pump (i.e., a gear pump) with the

demulsifier injected before the pump, or one that utilized additional mechanical mixing, did the demulsifier work efficiently in the absence of free water. Reviewing the tests results at both scales shows that the demulsification was most effective when the free water content was between 33% and 55%. Once the free water content exceeded about 60%, demulsification was curtailed.

The second common feature of the two test series was the importance of mixing energy. Given that the free water content was in the correct range, emulsion breaking improved with increased mixing energy. There are two types of mixing required for effective demulsification. The first is that which distributes the small amount of demulsifier into the continuous phase of the emulsion and allows it to come in contact with the water droplet interfaces. Second, once the demulsifier has displaced the natural interface-stabilizing compounds mixing energy is required to cause the water droplets to collide and coalesce. Both series of tests showed conclusively that increased mixing energy, regardless of how it was added (increased flow turbulence/time, in-line mixer, or additional mechanical mixing with a bladed impeller) increased the emulsion breaking efficiency.

In the situation where the recovered fluid contains up to 50% free water, (such as would be expected in operations involving skimmers deployed in the thick oil in the apex of a long length of containment boom), the most effective location for the injection of the demulsifier appears to be at the skimmer, since this offers both the advantage of the longest possible time for the chemical to be mixed with the recovered fluid, and the possibility that, if little free water is being recovered, the surfactant will reduce the bulk viscosity of the recovered emulsion and assist in pumping. In the case where the recovered product contains more than 60% free water (as might be expected with weir skimmers deployed in small containment boom systems, such as a VOSS) demulsifier should be added to the oily phase after separation and decanting of the free water, with mechanical agitation (recirculating with a gear pump or using a bladed impeller) added to initiate the emulsion breaking process. If pure emulsion is recovered, injection at the skimmer pump and additional mixing in the temporary storage tank would be best. In any case, the

provision of some method of adding extra mixing energy to the oily phase after initial decanting would appear to be beneficial.

Once the mixing energy has been applied, it is necessary to allow the fluid to settle and the phases to separate. The results of both test series indicate that the emulsion breaking process is substantially finished in the same time frame as primary break occurs. For the small-scale lab tests this was on the order of 2 to 5 minutes, and for the Ohmsett tests this was 15 minutes, or less. The difference would likely be due to the different height scales of the settling tanks. The higher the column of fluid, the longer it takes for the two phases to separate. In the laboratory tests a volume of 5L was placed in a cylinder to a depth of approximately 200 mm, while at Ohmsett the recovered fluid volume in each tank was about 100 gallons (400 L) with a depth of 500 mm.. With all other things being equal, it should have taken about 2.5 times longer (500/200) for the Ohmsett test fluids to separate than the laboratory test fluids.

The pressure data indicate d that the bulk viscosity of the emulsion/water mixture was very near that of water, as long as there was some free water present, at least 33%. The in-line mixer caused significant increases in back pressure.

Although the analysis of the oil-in-water concentrations for the lab tests was flawed, the Ohmsett results indicated that the use of a demulsifier increased TPH concentrations by approximately a factor of two in the decanted water. Although it is not known what portion of each TPH reading was associated with dissolved demulsifier in the water, the water did contain a significant amount, as evidenced by its foaming in the steel temporary storage tank.

7. Conclusions and Recommendations

The efficiency of emulsion breaking chemicals in resolving water-in-oil emulsions is highly parent oil/surfactant specific and can be strongly affected by the dosage of the demulsifier and the weathering processes that an emulsified oil has undergone. The tests conducted for this study investigated the effects of mixing energy and other physical parameters on the efficacy of one emulsion breaker (Alcolpol O 70% PG aka Drimax 1235B, a solution of sodium diisooctyl sulfosuccinate in propylene glycol/water) on one, water-in-oil emulsion specifically "engineered" for the project by blending a Bunker C oil into Hydrocal 300 and adding 50% water via a gear pump. The conclusions drawn below are only strictly valid for the combination of demulsifier and emulsion used.

The implication of this research for oil spill response is that it may be possible to greatly reduce downtime for offshore skimming operations caused when the available onsite temporary storage systems are filled with fluids containing large amounts of water. The legislated requirements for onsite temporary storage systems could also ultimately be reduced by the use of these results, resulting in considerable savings in operating and disposal costs for OSRO's. Knowing that the separated water can be decanted quickly will optimize onsite recovery operations and greatly reduce the volume of fluids requiring disposal. In fact, the removal of most of the free and emulsified water from the recovered product would greatly enhance the likelihood that it could be recycled, as opposed to requiring disposal.

The results of this multi-project research is not ready to be transferred to the response community quite yet. There are several key question that remain to be answered. Most of these are regulatory questions (such as, can decanted free water containing more than 15 ppm oil be pumped overboard during a response operation?) that should be addressed in other forums. The key technical question that remains is: where do the constituents of the demulsifier (surfactants and solvents) end up? Do they remain with the oil phase after separation, where they would pose little problem, or do they partition into the water, which will be subsequently decanted overboard,

releasing the surfactants into the water environment? Given that some demulsifiers are toxic to marine life, is their use to extend temporary storage capacity, and hence oil removal operations, a net environmental benefit?

7.1 Conclusions

- The use of a demulsifier injected into a recovery system, combined with decanting, can substantially reduce the volume of water in temporary storage tanks and the water content of emulsions for disposal/recycling.

- The efficacy of the demulsifier was a strong function of free water content, between an upper and a lower limit. In these tests, if the free water content exceeded about 60%, the effect of the surfactant was substantially reduced. If no free water was present, the level of turbulence generated by the flow was insufficient to promote emulsion breaking. A free water content of greater than about 33% was required to reduce the bulk viscosity of the fluid to the point where the flow regime was turbulent, and mixing energy was supplied to promote emulsion breaking. It is possible that this phenomenon is demulsifier-specific and would not be observed with a different demulsifier. It is also possible that this phenomenon is related to the solvent used in the demulsifier, and use of a different solvent would yield different results.

- The degree of emulsion breaking achieved increased with increasing mixing energy applied to the fluid. Increasing the flow rate (and hence turbulence level) and increasing the length of the flow path both resulted in increased emulsion breaking. The use of in-line mixers further increased the removal of emulsion water. The application of mechanical mixing energy, using a bladed impeller, after placing the recovered fluid in a recovery tank, also increased demulsification.

- The best location for injection of the demulsifier was at the skimmer pump for recovered fluids containing up to 50% free water to maximize the amount and time of the mixing applied. For recovered fluids containing more than 60% free water, decanting the free water followed by the application of mechanical energy worked best.

- Primary break occurred in only a few minutes (2 to 5 in the lab tests, less than 15 for the Ohmsett tests). The application of demulsifier did not appear to affect the time required.

- The Ohmsett results indicated that the use of a demulsifier increased TPH concentrations by approximately a factor of two in the decanted water. Although it is not known what portion of each TPH reading was associated with dissolved demulsifier in the water, the decanted water did contain a significant amount.

- As long as the recovered fluid contained at least 33% free water, the pressure drops due to skin friction in the tubing and hoses approximated those expected for flowing water. The use of an in-line mixer significantly increased back pressures.

7.2 Recommendations

- A standard emulsion for use in testing at Ohmsett should be developed, incorporating an aromatic fraction (likely using a diesel oil) into the Hydrocal/Bunker mixture to allow better resolution of emulsions. This effort would also entail developing techniques to consistently "build" emulsions with water contents in the 70% to 80% range in order to achieve the high viscosities typical of oil spill emulsions at sea.

- A study of the partitioning of various oil spill demulsifiers between the resolved parent oil and the decanted water should be undertaken. The discharge of decanted water containing significant amounts of surfactants into the ocean environment may not be permitted if it contains toxic levels of surfactants, eliminating any advantage to offshore recovery operations that could be gained by the use of demulsifiers.

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Appendix 1 - Ohmsett Oils Emulsification and Demulsifier Test Results

Appendix 2 - Laboratory Test Equipment

Appendix 3 - Laboratory Test Results

Appendix 4 - Ohmsett Test Plan

Appendix 5 - Ohmsett Test Equipment

Appendix 6 - Ohmsett Test Results