DISPERSANT EFFECTIVENESS LITERATURE SYNTHESIS

FINAL REPORT

SwRI® Project No. 18.19404

Prepared for:

BSEE Oil Spill Response Division
381 Elden Street, HE3313A
Herndon, VA 20170
BSEE Contract No. E13PC00010

May 21, 2014

SOUTHWEST RESEARCH INSTITUTE®

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EXECUTIVE SUMMARY

Southwest Research Institute (SwRI) was contracted to conduct a study for the Bureau of Safety and Environmental Enforcement (BSEE) to synthesize the available research literature on dispersant effectiveness. The goals of this study were to:

- Provide technical background on previously-conducted dispersant effectiveness research studies in order to better equip regulatory and enforcement personnel to make policy and procedure decisions regarding the use of dispersants.
- Develop a practical database tool that can be used to organize and search the considerable amount of research conducted to date on dispersant effectiveness.
- Identify areas of potential knowledge gaps and suggest roadmaps to maximize the information available for future dispersant use.

A database application that can be used to organize, search, and sort the large amount of dispersant effectiveness literature available has been delivered to the BSEE. This database has been pre-populated with the literature reviewed during the course of this project and provides capabilities for future inclusion of additional literature as it is available.

The extensive amount of literature published on the topic of dispersant effectiveness in the past 35 years provides a general picture on effective, practical use of dispersants under more traditional circumstances (warm, open waters with average salinity). However, gaps in the fundamental understanding of dispersant effectiveness in these applications, as well as more recent extreme applications such as low salinity, arctic, or subsea environments, still exist.

Additionally, data and methods for data collection required for effective, practical use of dispersants in low salinity, arctic, and subsea environments currently present a knowledge gap. More data and more effective means for making the data available would improve the industry's ability to deal with these unconventional and unique operating environments.

1. INTRODUCTION

In the event of an offshore oil spill, several responses are available to mitigate the hazards and environmental impact of the released oil, including mechanical containment and recovery (booms and skimmers), surface/in-situ burning, and chemical dispersants. Chemical dispersants are applied to oil spilled in bodies of water in order to break down the oil into relatively small droplets that will more easily mix into the surrounding water. The use of dispersants potentially decreases the environmental impact of the spilled oil, although the ultimate fate and effects of dispersed oil remain a current topic of research and debate.

Prior to oil spill responses, a National Response Team and Regional Response Teams combine federal, state, tribal, and local government representatives to develop procedures and policies for oil spill responses in different areas within the U.S. These policies and contingency plans may address situations in which oil dispersants should or should not be used and may preauthorize the use of oil dispersants by the Federal On-Scene Coordinator. If not preauthorized, the Federal On-Scene Coordinator may authorize the use of dispersants with the concurrence of the Environmental Protection Agency (EPA) and appropriate state representatives and in consultation with the Department of Commerce and the Department of Interior. In order to effectively produce policies prior to oil spills and make response-time decisions for use of chemical oil dispersants (with or without preauthorization), all involved response personnel must have accurate knowledge of the effectiveness of dispersants.

Outside of environmental research, considerable amounts of research regarding oil dispersant effectiveness have been conducted with funding by government and industry sources, and dispersants were utilized in over 200 oil spills from 1968 to 2007. In a report authored by the U.S. Government Accountability Office (GAO) in May 2012, a number of uncertainties related to the effective use of oil dispersants were identified. The findings from the GAO included:

- Although a considerable body of research on dispersant effectiveness exists, additional studies on the emerging areas of subsea dispersant injection and use of dispersants in arctic applications should be conducted.
- The existence and outcomes of completed and ongoing research studies on dispersant effectiveness are not always well-communicated across federal agencies, academia, and industry. No comprehensive, regularly-updated mechanism exists to track previous and ongoing research efforts in this area.

1.1 Project Objectives

To address the need for a comprehensive review and record of completed and ongoing research in dispersant effectiveness, this study is designed to review, summarize, and report on the literature available regarding dispersant effectiveness research. This project aims to:

- Develop reference documents that can be used by federal agency personnel for the review of research in dispersant effectiveness.
- Develop and deliver a searchable database of historical research on dispersant effectiveness that can be queried, sorted, linked, or integrated into additional database systems.

- Analyze the gaps in the existing knowledge bank and suggest possible future topics for dispersant effectiveness research studies.

The deliverables for this project include:

1. This Final Report document which provides:
    a. A narrative summary of literature reviewed regarding factors affecting dispersant effectiveness and dispersant effectiveness testing methods.
    b. An analysis of gaps in the existing knowledge bank and recommendations for future research topic areas.
    c. An appendix containing single-page summaries of each article reviewed during the course of this project.
2. A database application that can be used to organize, search, and sort the large amount of dispersant effectiveness literature available. This database has been pre-populated with the literature reviewed during the course of this project and provides capabilities for future inclusion of additional literature as it becomes available. This database and accompanying user's manual was delivered to the BSEE separately.

1.2 Report Structure

Section 2 of this report provides technical background on the function and formulation of dispersants. The concept of dispersant effectiveness is generally discussed, with a summary of factors that affect dispersant effectiveness. The technical literature reviewed to date during this study is summarized in the subsequent sections of this document, organized by topical area.

Section 3 discusses the effect of dispersant composition on dispersant effectiveness. Section 4 presents a discussion on literature reviewed to investigate the effect of oil properties and composition on dispersant effectiveness. Section 5 discusses literature reviewed on the effect of application "environment" effects on dispersant effectiveness, including cold or salt/fresh waters. Additional "environment" effects are explored in Section 6 where the topics of subsea environment effects, and effects of mixing energy are discussed.

Section 7 provides a summary overview of the large array of dispersant effectiveness testing methods used in the literature reviewed. Section 8 provides an analysis of the knowledge and research gaps encountered during the literature synthesis. The collection of single-page summary documents compiled for each of the articles reviewed during this project is provided in Appendix A.

2. TECHNICAL BACKGROUND

Chemical dispersants can be used in response to oil spills to help mitigate the effect of the liquid hydrocarbons on the environment. The literature shows that dispersants have been used in over 200 oil spills from 1968 to 2007, and a significant amount of research has been conducted in this area. This section provides an introduction to the topic of chemical dispersants, their general functions and formulations, as well as a brief discussion on dispersant effectiveness.

2.1 General Function of Dispersants

Dispersants are chemicals that are formulated as a blend of one or more surfactants (surface-active agents) and one or more solvents. Surfactants have special chemical structures with an oleophilic ("oil-loving") end and an opposing hydrophilic ("water-loving") end. Solvents are used as carriers for the surfactants (which are often solids or highly-viscous liquids) and allow for the surfactants to penetrate the oil and migrate it to the oil-water interface. Additional additives may be present to improve mobility of the surfactant, increase the biodegradability of the dispersed oil/dispersant mixture, or increase long-term stability of the dispersion.[27]

Once present at the oil-water interface, the surfactants orient with hydrophilic end in water and oleophilic end in the oil phase, reducing the oil-water interfacial tension. Under wave action or other mixing energies, this reduced interfacial tension allows small oil droplets – 1 to 30 microns for a potent dispersant[27] – to be pulled off of a slick and dispersed into the water phase. When enveloped by surfactant molecules with hydrophilic ends facing out, a dispersed oil droplet in a water phase can be stabilized. This process is illustrated in Figure 2-1.

2.2 General Formulation of Dispersants

Surfactants of different types have varying affinities for oil and water. This affinity can be classified by the hydrophilic-lipophilic balance (HLB) number. This number ranges from zero to 20 for non-ionic surfactants and can extend up to 60 for ionic surfactants. In general, substances with HLB numbers greater than ten have an affinity for (and dissolve more readily in) water, whereas substances with an HLB number less than ten have a greater affinity for (and dissolve more readily in) oil. The dominant end of a surfactant molecule (i.e., lipophilic or hydrophilic) will tend to orient in the external phase of an oil-water mixture; thus, surfactants with low HLB numbers (3-6) will tend to form water-in-oil emulsions, while surfactants with higher HLB numbers (8-18) will tend to form oil-in-water emulsions (i.e., oil droplets dispersed in water). Most oil dispersants obtain an HLB number between eight and 12 through a mixture of two or more surfactants.

The first chemical dispersants were formulated from industrial degreasers, often developed to clean tanker compartments and engine rooms.[26] These first-generation dispersants were relatively toxic in the marine environment and are no longer in use as oil spill dispersants today. Second generation dispersants were the first dispersants designed specifically to treat oil spills. These dispersants, also known as "Type 1," "UK Type 1," "conventional," or "hydrocarbon-base" dispersants, typically contain 10% to 25% surfactant in a hydrocarbon solvent base. They are designed to be applied undiluted (neat) and require a relatively large dosing ratio of 1:1 to 1:3 (volumetric parts dispersant to spilled oil).

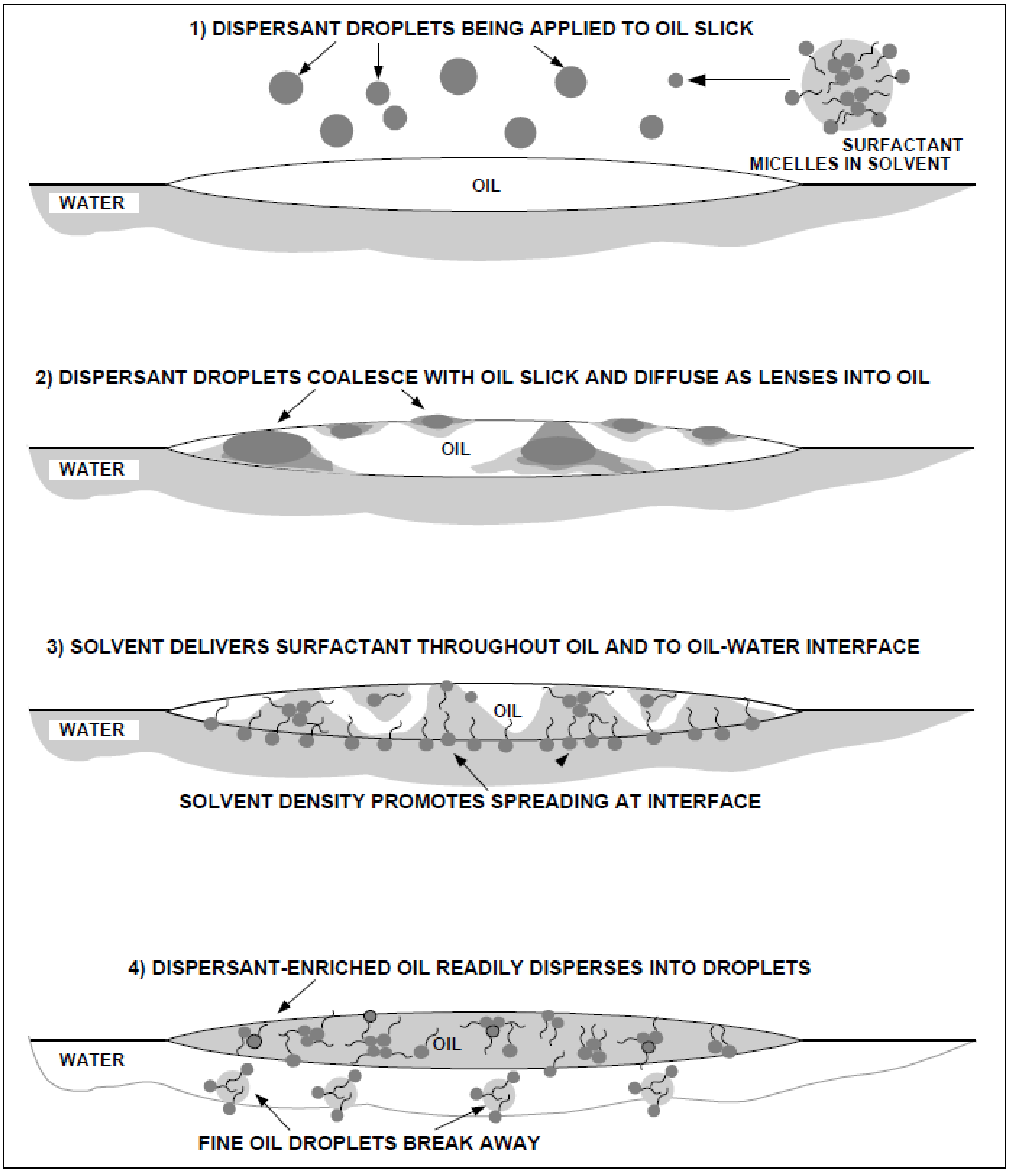

Figure 2-1. Mechanism of Chemical Dispersion. From ExxonMobil Research and Engineering Company.[31]

On surface slicks, the solvent carrier enhances the surfactant's ability to penetrate the oil and migrate it to the oil-water interface. The surfactant molecules orient at the oil-water interface to lower interfacial tension and promote droplet breakup under wave action or other mixing energy.

Third-generation dispersants can be classified into Type 2 and Type 3 dispersants. Type 2 dispersants, also known as "water-dilutable," are intended to be diluted with seawater before use; thus, their application is limited to surface vessel use. These dispersants are generally diluted at 90% seawater to 10% dispersant ratio and applied at one part of the water/dispersant mix to 2-3 parts spilled oil. This dose rate is comparable to that recommended for Type 1 dispersants, with the exception that the dispersant mixture is 90% water.

Type 3 dispersants, also known as "concentrate" oil spill dispersants, were designed primarily to be applied from aircraft, but can also be used from vessels. These dispersants are more concentrated solutions of surfactants, with minimal solvents, and are designed to be applied neat (undiluted). Recommended dosage rates range from 1:5 to 1:100 (neat dispersant to oil ratio).

2.3 Dispersant Effectiveness

Although the phrase can mean several different things across different contexts, in general, "dispersant effectiveness" is defined as the degree to which the dispersant "works" or disperses oil into the water column. For each laboratory test, for example, dispersant effectiveness is defined and measured in a different manner. Dispersant efficiency, in contrast, is associated with the amount of dispersant required to achieve a certain level of dispersant effectiveness.

Several factors can affect dispersant effectiveness. First, the formulation or composition of a dispersant itself affects the dispersant's effectiveness. Additionally, the properties of the spilled oil (such as viscosity, density, and chemistry) can significantly affect the dispersant effectiveness. The environment in which the dispersant is used (i.e., arctic water temperatures, the presence of ice or other variations in available mixing energy, or subsea dispersant injection) can significantly affect the dispersant effectiveness.

3. EFFECT OF DISPERSANT FORMULATION ON DISPERSANT EFFECTIVENESS

Perhaps the most obvious contributor to dispersant effectiveness is the composition of the dispersant formulation itself. Several of the literature studies encountered during the course of this literature review included effectiveness testing using more than one identifiable dispersant (either commercial or experimental). Examples of these studies are summarized in this section.

Aurand et al.[4] reported on effectiveness studies conducted on fresh Mississippi Canyon (MC) 252 crude oil conducted on nine dispersants (Corexit EC9500A, Corexit EC9527A, Finasol OSR 52, JD 2000, Dispersit SPC 1000, Nokomis 3AA, Nokomis 3F4, SAF-RON Gold, and Sea Brat #4) using both the Swirling Flask Test (SFT) and the S.L. Ross wave tank test. As shown below in Figure 3-1, results showed that Corexit 9500, Corexit 9527, and Finasol OSR 52 performed better in the laboratory tests at all conditions reported.

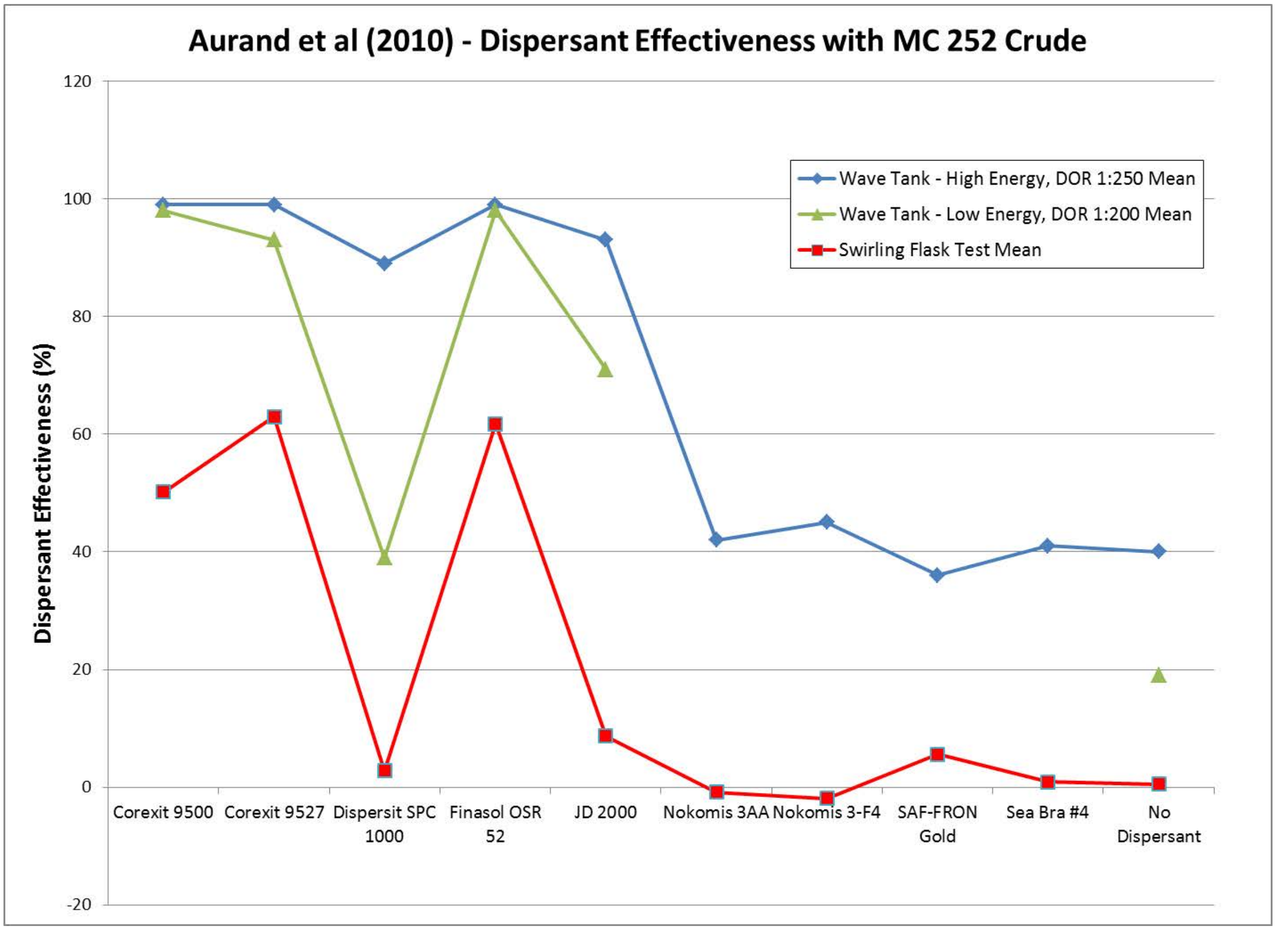

Figure 3-1. Dispersant Effectiveness on MC 252 Crude Oil by Wave Tank and Swirling Flask Test. *Aurand et al.[4] (2010) reported on dispersant effectiveness testing with nine commercial dispersants using fresh MC252 crude oil.*

Fingas et al.[35] reported on effectiveness testing completed for three commercial dispersant formulations using the Swirling Flask Test. The results, as shown in Figure 3-2, showed that the relevant effectiveness of each of the three formulations was dependent on the oil tested.

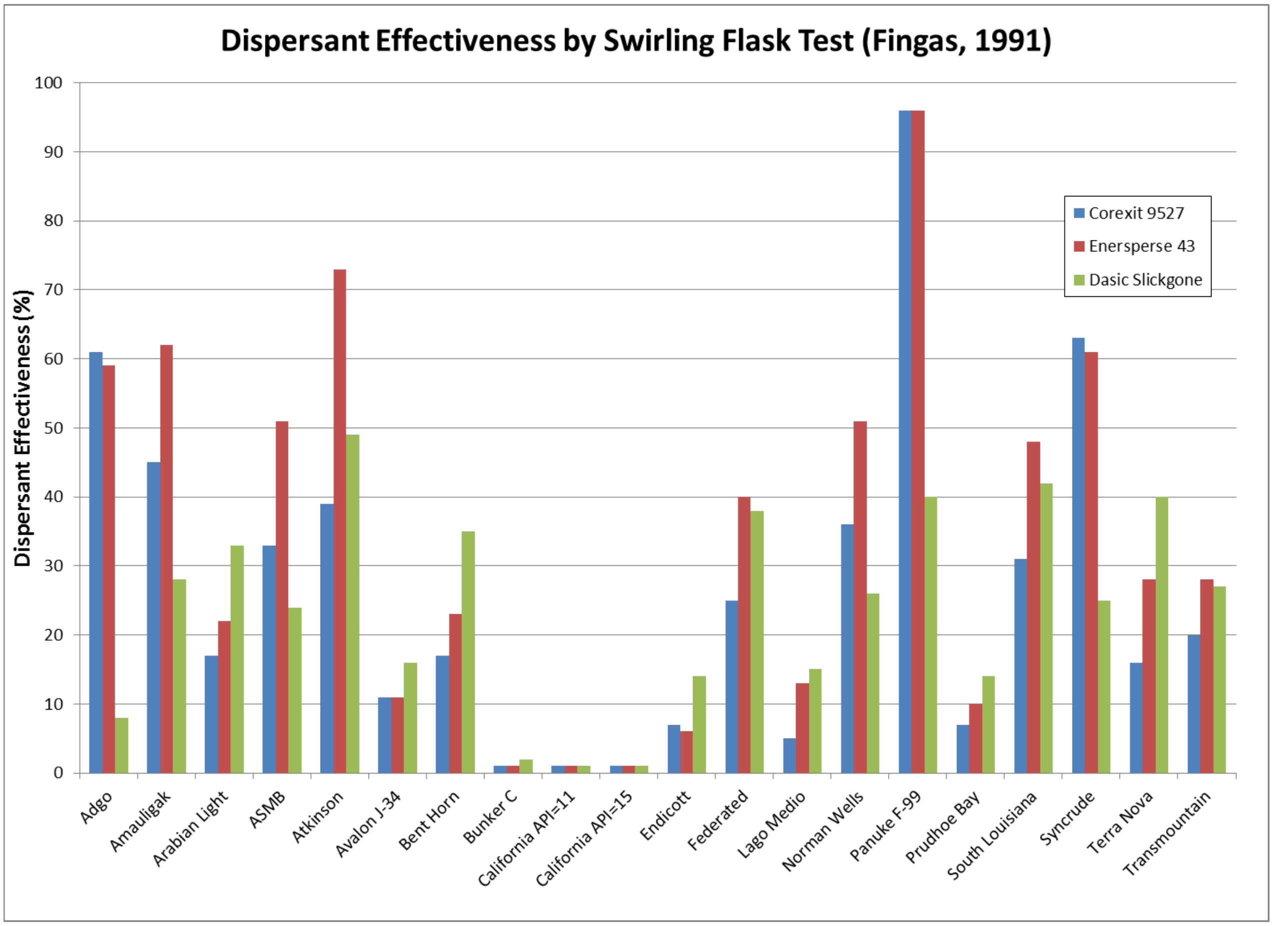

Figure 3-2. Effectiveness of Three Dispersants across Different Crude Oils.
Fingas et al.[36] *conducted Swirling Flask Tests with three commercial dispersants. The relative effectiveness of each of the three dispersant formulations varied depending on the oil tested.*

Resby et al.[77] conducted experiments to determine the effect of significant time durations passed between dispersant applications at low mixing energy and subsequent higher energy dispersion testing. Two commercial dispersants (Corexit 9500 and Finasol OSR 52) were first tested using the IFP laboratory test with the standard, one-minute contact time on four weathered crude oils. Additional tests were conducted with longer contact times between oil and dispersant and seawater. The results, shown graphically below in Figure 3-3, Figure 3-4, Figure 3-5, and Figure 3-6, show that, for the most part, trends in increasing and decreasing effectiveness versus contact time were consistent across the two commercial dispersants tested. Tests on Corexit 9500 exhibited higher laboratory effectiveness in the IFP test than did Finasol OSR 52, in all except one data point. The authors attributed increased effectiveness values measured after 24 hours for the three lightest oils (Figure 3-3, Figure 3-4, and Figure 3-5) to the possibility that some time after application of the dispersant is required for surfactants to completely penetrate and uniformly mix into the oil.

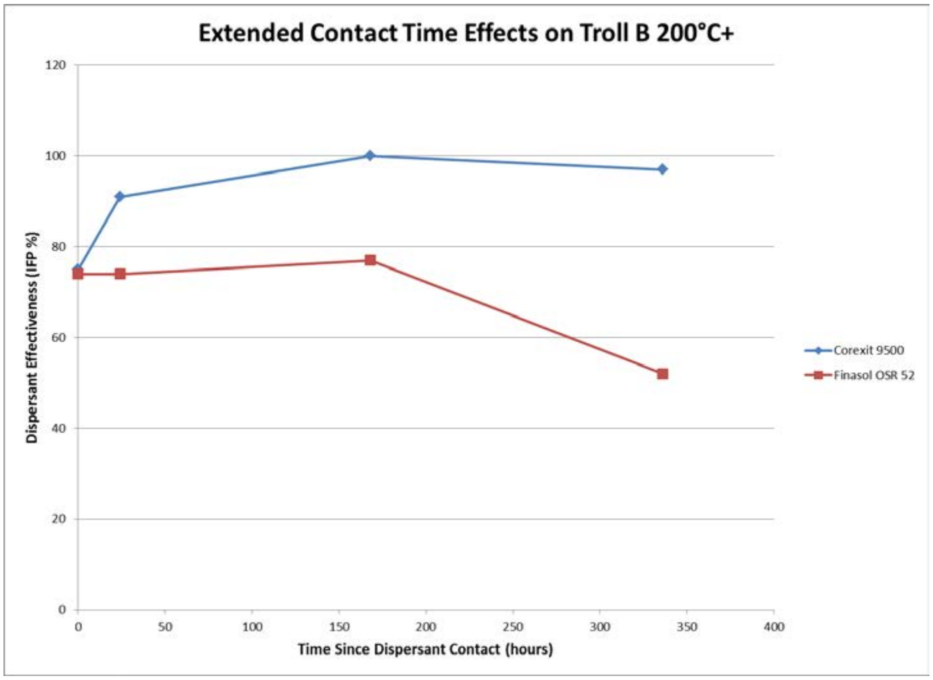

Figure 3-3. Commercial Dispersant Effectiveness with Extended Contact Times: Troll B 200°C+. *Effectiveness testing*[77] *was conducted using the IFP method for a weathered napthenic oil (Troll B) with extended contact times and two commercial dispersants. The general trend of effectiveness with respect to increased contact time was consistent among the dispersants tested, although absolute values of effectiveness were different.*

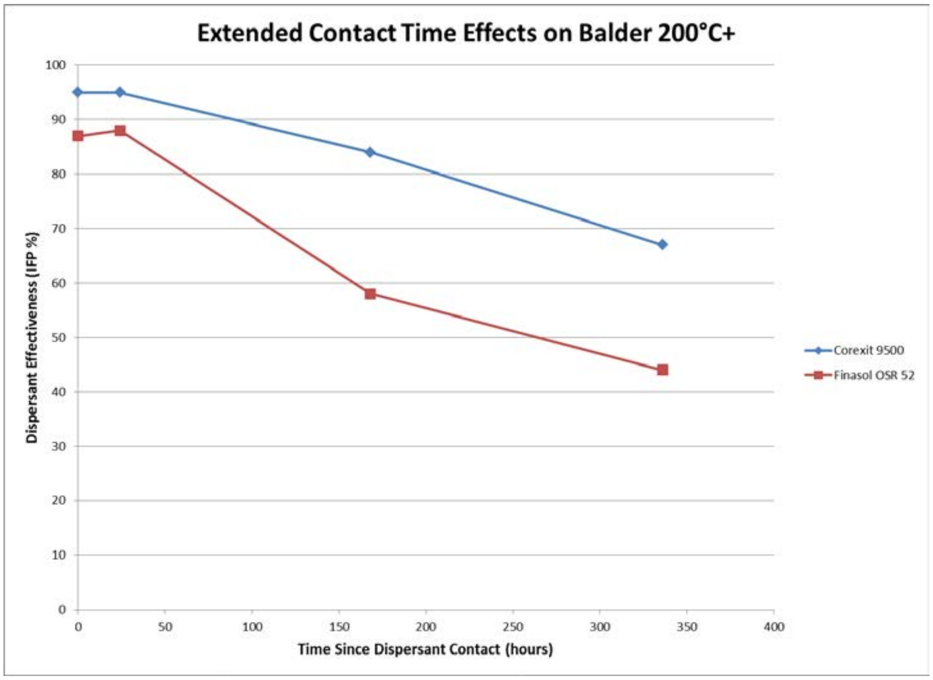

Figure 3-4. Commercial Dispersant Effectiveness with Extended Contact Times: Balder 200°C+. *Effectiveness testing*[77] *was conducted using the IFP method for a weathered asphaltenic oil (Balder) with extended contact times and two commercial dispersants. The general trend of effectiveness with respect to increased contact time was consistent among the dispersants tested, although absolute values of effectiveness were different.*

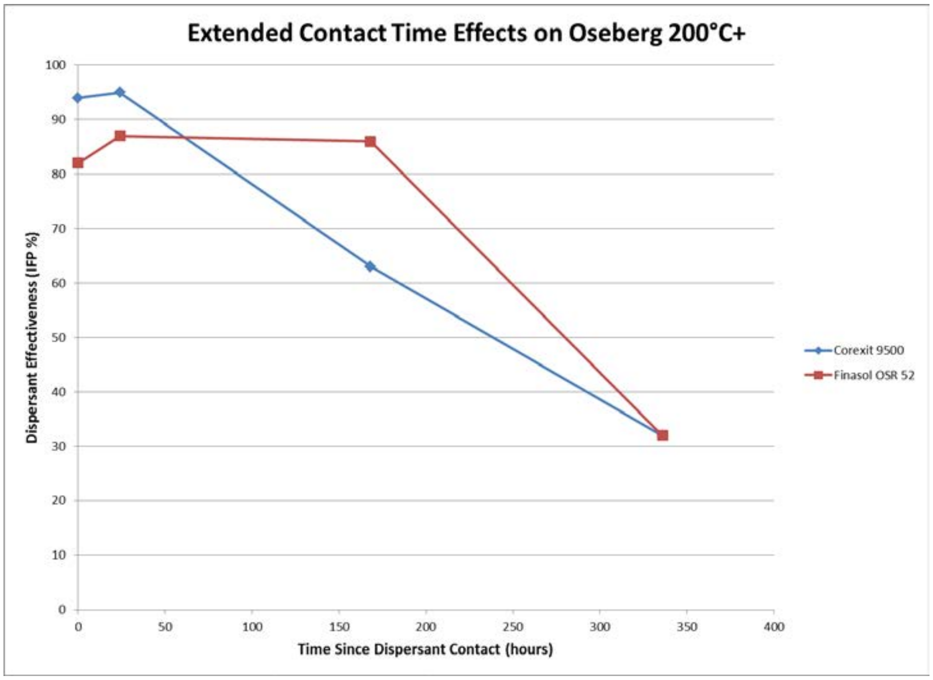

Figure 3-5. Commercial Dispersant Effectiveness with Extended Contact Times: Oseberg 200°C+.
Effectiveness testing[77] was conducted using the IFP method for a weathered paraffinic oil (Oseberg) with extended contact times and two commercial dispersants. Corexit 9500 achieved higher laboratory effectiveness in all cases, except at 168 hours.

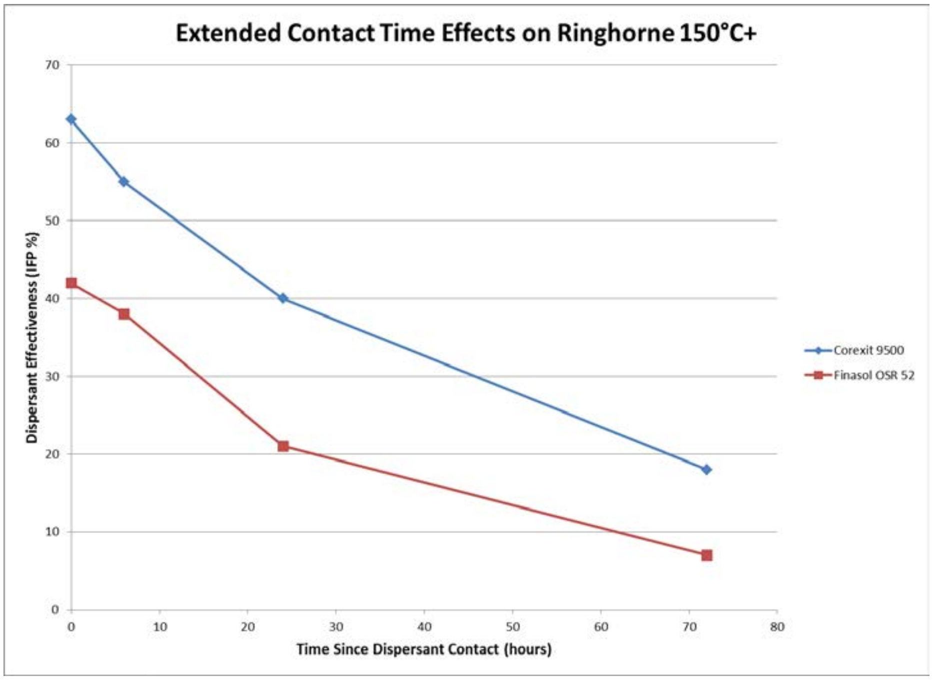

Figure 3-6. Commercial Dispersant Effectiveness with Extended Contact Times: Ringhorne 150°C+.
Effectiveness testing[77] was conducted using the IFP method for a weathered waxy oil (Ringhorne) with extended contact times and two commercial dispersants. The general trend of effectiveness with respect to increased contact time was consistent among the dispersants tested, although absolute values of effectiveness were different.

Venosa and Holder[95] conducted a comparison study with South Louisiana crude oil and 3.4% salinity synthetic seawater on eight commercial dispersant formulations at two temperatures. In general, trends across the temperatures and formulations were consistent, with decreased dispersant performance at lower temperatures. However, the trend was reversed with both ZI 400 and Sea Brat #4. Dispersit SPC 1000 performed the best at both temperatures, with Corexit 9500 and JD 2000 performing well. Total Dispersed Oil results are shown below in Figure 3-7.

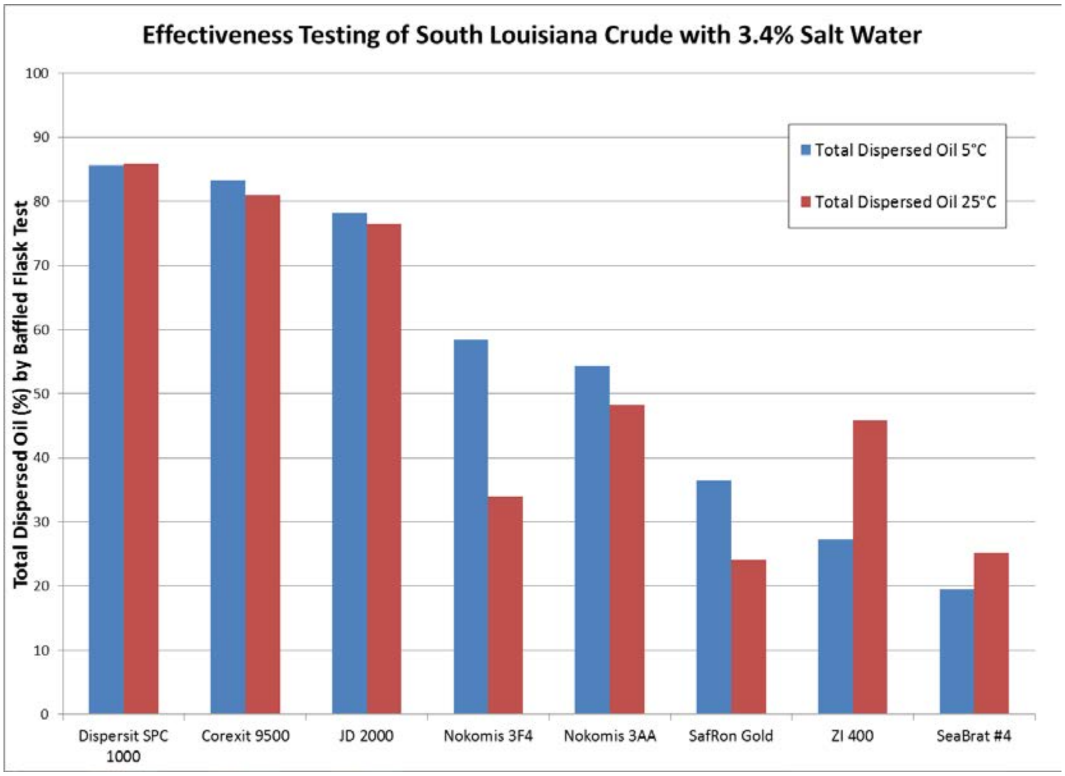

Figure 3-7. Commercial Dispersant Effectiveness by Baffled Flask Test: South Louisiana Crude.
Holder[94] used the Baffled Flask Test with South Louisiana crude oil and 3.4% salinity synthetic seawater.

Nedwed[72, 74, 75] compared a newly-developed gel dispersant to several commercial dispersants. The new dispersant is designed with the consistency of honey to persist in breaking wave conditions and adhere to an oil slick. The new design also allows for large droplets via spraying applications and is roughly 90% active ingredient. Using the S.L. Ross wave tank test, the gel dispersant outperformed Corexit 9500 across light, medium, and heavy crudes, as well as heavy fuel oil HFO-580 at water temperatures between 10°C and 15°C.[74] The dispersant also outperformed Finasol OSR 52, Slickgone Dasic, and Corexit 9500 (based on visual assessments of dispersion effectiveness) when tested using a non-standard, high-energy, short-duration flask test (designed to simulate conditions of a subsea injection) on a single light Gulf of Mexico crude oil.[74]

4. EFFECT OF OIL PROPERTIES ON DISPERSANT EFFECTIVENESS

The composition and properties of the oil phase itself heavily contribute to the effectiveness of a dispersant application. Various studies in the past 35 years have investigated the effects of oil density, viscosity, weathering state (loss of light ends and/or solidification), and chemical composition on dispersant effectiveness. Selected studies in this area are summarized in this section.

The effect of oil viscosity has received a large amount of attention in dispersant effectiveness research. In general, many researchers reported that increasing viscosity resulted in decreasing dispersant effectiveness. Others have gone even further, suggesting that an upper viscosity limit exists, over which a crude oil cannot be chemically dispersed. However, several studies have shown that this effect is more complicated and that, in fact, if the oil viscosity is increased in a lower range (up to 1,000 cP), other factors can offset the effect of the increasing viscosity, and dispersant effectiveness is not always decreased.

When examining viscosity, researchers typically argue for either a strong correlation between oil viscosity and dispersant effectiveness, indicating that viscosity is the most important parameter when determining whether to include dispersants in a spill response plan, or a more general correlation, suggesting that other parameters are equally or more important in dispersant effectiveness.

Stevens,[85] Colcomb,[28] and Holder[45] all argue for a strong correlation between oil viscosity and dispersant effectiveness. Stevens[85] tested seven crude oils and IFO-380 from nine sources with seven dispersants using the Warren Spring lab test. The authors noted that, especially in the fuel oil cases, increasing viscosity decreased dispersant effectiveness.

Colcomb[28] conducted small-scale field tests with IFO-180 and IFO-380 with three dispersants at varying dispersant-to-oil ratios. Effectiveness was judged visually by expert observers. IFO-380, the more viscous oil, was found to be non-dispersible.

Holder[45] performed baffled flask tests on 23 oils with Corexit 9500. An exponential relationship was found between effectiveness and viscosity, with an R^2 value of 0.84, indicating that, in the oils tested, viscosity is strongly tied to dispersant effectiveness.

Belore[8] and Trudel[87] both performed a series of tests at the Ohmsett National Oil Response Test Facility. In addition to supporting the argument for a strong correlation between viscosity and effectiveness, both reported a maximum viscosity above which dispersant application was ineffective. Belore[8] reported 10,000 cP as a limit, while Trudel 2010 reported a limit between 18,690 and 33,400 cP.

Several papers have argued that viscosity is more of a general indicator of dispersability. Two examples are Canevari[22] and Clark.[26] In Canevari,[22] No. 5 and No. 6 fuel oils were tested with Corexit 9500 using the EXDET testing method for dispersant effectiveness. Although a general relationship of increasing viscosity and decreasing effectiveness was observed, the authors note significant variability with oils near 5,000 cSt ranging in effectiveness from 14% to 44%.

In Clark,[26] a literature review was performed on the dispersion of heavy and viscous oils. The authors also note the significant variability of dispersant effectiveness at specific viscosity; one study found three oils near 20,000 cP whose effectiveness ranged from 5% to 55%.

Canevari[22] reported on a novel experiment in which the effectiveness of an experimental (unnamed) dispersant was tested against La Rosa crude oil (73 cSt) and Murban crude oil (6 cSt). As shown in Figure 4-1, the effectiveness of the dispersant was found to be 30% in the La Rosa crude oil versus 78% in the lower viscosity Murban crude oil. The La Rose crude was then mixed with pure isoparaffin oil of low viscosity to reduce its viscosity to match the Murban crude at 6 cSt. The effectiveness of the dispersant was found to be increased to 50%, but was still quite short from the 78% value in the Murban crude. This concluded that, while oil viscosity is certainly a factor in dispersant effectiveness, oil chemical composition can sometimes dominate the response.

Fingas[35] used the swirling flask test to evaluate three dispersants and 25 oils for dispersant effectiveness. Oil composition was defined by bulk compounds: asphaltenes, aromatics, polar compounds, saturates, and waxes. Increased saturate levels were found to increase dispersibility, while increased aromatic, asphaltene, and polar compound levels were found to decrease dispersibility. No correlation was found for wax content.

The EXDET test was used to evaluate dispersibility of 14 heavy fuel oils with Corexit 9500 by Canevari.[22] Oil composition was measured by saturate, aromatic, resin, polar compound, and paraffin content. Increased saturate content was found to decrease dispersant effectiveness. Increased paraffin content also decreased dispersibility.

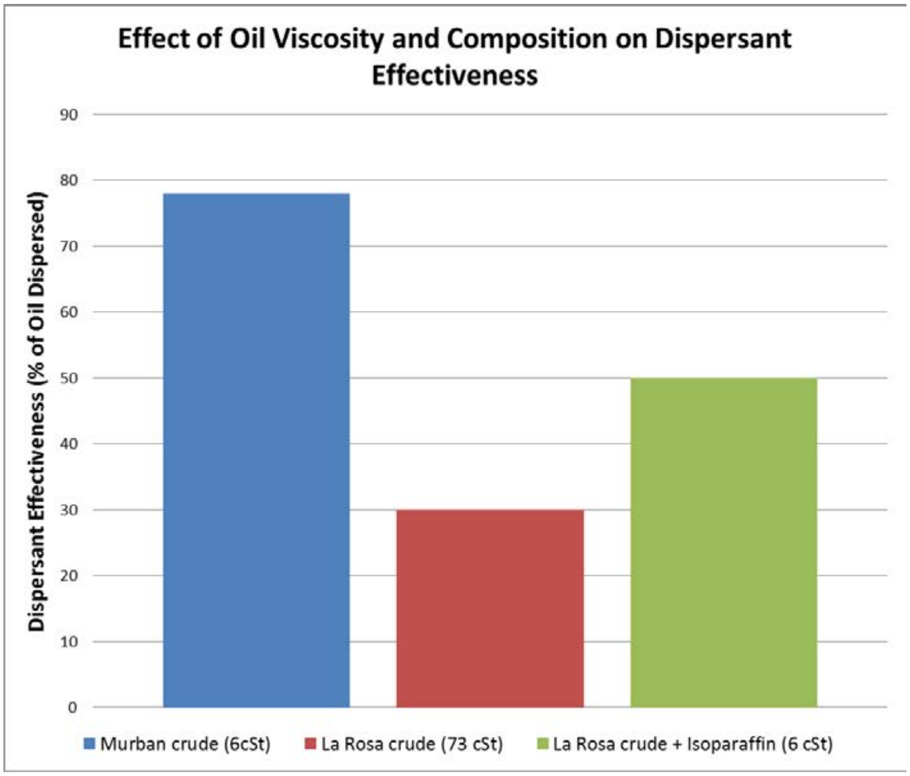

Figure 4-1. Effect of Composition and Viscosity on Dispersant Effectiveness.

Canevari[21] used two crude oils and a mixture of pure isoparaffin oil to demonstrate that, while viscosity has an effect on dispersant effectiveness, oil composition can be the dominant factor.

Fingas[35] examined the dispersability of 15 oils with Corexit 9500 in swirling flask tests. Oil composition was evaluated as saturate, aromatic, resin, and asphaltene (SARA) fractions, as well as alkane content, PAH content, naphthalene content, fraction whose boiling point was under 200°C, and fraction whose boiling point was under 250°C. A model was proposed for predicting dispersibility of an oil based on alkane content, naphthalene content, PAH content, and percentage of oil whose boiling point was under 250°C. Twelve other models were evaluated, but were found to be less accurate and/or include redundant parameters.

Mukherjee[68] modified 14 crude oil samples to contain specific SARA fractions. Corexit 9500 was used in baffled flask tests to measure dispersant effectiveness. A generalized linear model was used to evaluate the effects of individual SARA components and component pair interactions. Increased aromatic fractions were associated with increased effectiveness. Effectiveness was also increased when both saturates and resins were present in high concentration.

Although physical properties such as viscosity are significant factors, oil composition seems to be directly tied to dispersant effectiveness. Future work could include more testing similar to that performed by Fingas,[41] utilizing more dispersants and more oils to establish which components most control dispersant effectiveness. By identifying these components, future dispersant formulations could be designed to either target these components or to include other ingredients, targeting other major components in crude oil to encourage droplet formation.

It is also known that crude oils contain various amounts of "natural" surfactants that stabilize water-in-oil emulsions. These oil-in-water emulsion stabilizing tendencies have been exploited in multiphase production systems to disperse water into oil phases to prevent hydrate agglomeration and plugging of production flow lines.[53] It is postulated that the existence of such natural surfactants can interfere with chemical oil spill dispersants by affecting the packing of dispersant surfactants at the oil-water interface.

Canevari[21] investigated the natural surfactant issue by performing dispersant effectiveness experiments in a Labofina test apparatus. In this study, ten crude oils and one "clean," processed hydrocarbon (tetradecane) were tested with four (unspecified) dispersant formulations. Additionally, the natural surfactant phases from five of the crude oils were extracted, and added to tetradecane samples in proportions similar to those found in each of the crude oils to form "spiked" tetradecane samples. These "spiked" tetradecane samples were then tested for effectiveness with a single dispersant (referred to as Dispersant A). These experiments showed that addition of the natural surfactant extracts to a clean tetradecane sample reduced the effectiveness of the tested dispersant in all cases tested.

5. EFFECTS OF THE ENVIRONMENT ON DISPERSANT EFFECTIVENESS

Dispersant effectiveness is additionally a function of the environment in which the dispersant is applied. The effects of application environment on dispersant effectiveness (which should not be confused with the effects of the dispersant or dispersed oil on environmental health) are discussed in this section.

5.1 Salinity Effects

Many traditional dispersants have been formulated for use in temperate seas conditions (i.e., temperatures above 10°C and a salinity around 3.5% by mass). The effect of varying water salinity on dispersant effectiveness has been studied by several investigators, particularly for applications in estuaries and arctic environments. Historical literature on this topic has been summarized by Fingas,[40] Lewis et al.,[54] and S.L. Ross Environmental Research.[80]

5.1.1 Oil Recovery in Freshwaters

Formulation of dispersants for low salinity environments has not been a concern in the past with most oil exploration occurring at typical seawater salinities, around 35 parts per thousand (ppt). As previously mentioned, traditional commercially-available dispersants are made for marine waters with maximum effectiveness occurring between 20 and 40 ppt as discussed by S.L. Ross Environmental Research.[80] The same maximum effectiveness salinity range was also seen by Fingas.[40] Other experimental reports, such as Blondina et al.,[12] found a more specific salinity value of 33 ppt for maximum effectiveness. Dispersants were formulated with this salinity range in mind because it reflects typical salinities in marine environments. However, there has recently been an increased demand for dispersants capable of dispersing oil effectively in a wider range of salinities. Freshwater dispersants are formulated for maximum effectiveness between 10 to 20 ppt. Arctic applications for dispersants have increased due to increased discovery and transport of oil products through arctic waters. For example, the Barents Sea has been reopened for exploratory drilling and tanker traffic through the region.[16] Therefore, the importance of effectively dispersing oil in salinities lower than the typical salinity range targeted in marine dispersant formulation is growing.

Salinity ranges will vary significantly in arctic environments due to the degree of ice coverage. Additionally, the freezing of fresh bodies of water that feed into arctic waters can vary the salinity range. This results in a large salinity variation throughout arctic bodies of water, such as a variation from very low salinity up to 33 ppt in Prince William Sound due to smaller bay regions and creek outflows as documented by Fingas.[40]

Salinity effects on dispersant effectiveness can be explained by examining the HLB. The dispersant is effective only when located at the water-oil interface. If the water salinity is too low, the hydrophilic part of the dispersant is too strongly attracted and will dissolve in the water. Consequently, very high salinity could cause the dispersant to dissolve in the oil due to a weak water attraction, according to Canevari.[20]

The lack of commercially-available freshwater dispersants has led to the utilization of alternative oil spill response methods. Mechanical recovery has been used extensively in the past involving the use of skimmers and booms to collect oil from the water surface. In-situ burning has also been used in less saline waters, with ice coverage aiding in the process by making a thicker oil slick at the water surface.

Currently, dispersant guidelines developed during the Helinski Commission (HELCOM) still hold true for oil spill recovery in the Baltic Sea. The current policy states that mechanical recovery should be used in the Baltic Sea with the use of chemical dispersants being limited as much as possible as described in S.L. Ross Environmental Research.[80] Approved freshwater dispersants are not common. In fact, S.L. Ross Environmental Research[80] also states France is the only country that currently has a list of approved dispersants for freshwater use. Canada, the U.S., the U.K., and other countries that have coasts along arctic waters do not have an approved freshwater dispersant list or specific criteria listing decision-making guidelines or integration procedures for the use of freshwater dispersants.

Limitations exist in the use of mechanical recovery and in-situ burning. There is an increased risk of exposure to hydrocarbons leading to health risks of oil recovery personnel, limited hours during which the method can be applied, and a greater chance of weather interferences. With increased oil exploration and traffic through arctic and freshwaters, limitations of currently-used spill response options, and the wide range of salinities in these environments, freshwater dispersant formulation is becoming an active area of research. The following section will describe this research by reviewing tests conducted on marine dispersants in a wide range of salinity conditions.

5.1.2 Testing Traditional Marine Dispersant Effectiveness in Low Salinity Waters

Many experiments and literature reviews have been conducted analyzing the performance of marine dispersants with water salinity variation. These experiments range from laboratory methods to large-scale tests with variation in oil type, dispersant type, and other testing conditions in order to fully analyze the effect of salinity on dispersant effectiveness.

Mackay and Hossain[62] performed spinning drop tests to characterize the interfacial tensions of oil, water, and dispersant systems under varying temperature and salinity conditions. This technique provides a more fundamental approach to characterizing the factors affecting dispersant effectiveness, but does not give any information regarding the efficiency with which the dispersant migrates through the oil (or water) to reach the oil-water interface and, thus, does not constitute a complete effectiveness test. Mackay and Hossain found that interfacial tension values were lower in synthetic salt water (3.5% NaCl in distilled water) than those in fresh (distilled) water systems, both with and without dispersant. The reduction in interfacial tension at the oil-water interface is most likely due to accumulation of sodium salts or organic acids present at the interface. Mackay and Hossain also found that surfactants partition more readily into distilled water than salt water due to a reduction in solubility of dispersants with salt addition. This indicates the effect of salinity on dispersion is due to altered partitioning and interfacial tension of the dispersant-free solution.

In 1991, Fingas et al.[35] conducted a study on the physical and chemical behavior of oil and dispersant mixtures. Along with analyzing the effect of oil bulk components on effectiveness, environmental effects were also studied, including temperature and salinity. A swirling flask test method was used and salinity ranged from approximately 0 to 90 ppt using ASMB, Norman Wells, and Adgo crude oils and Corexit 9527, Enersperse 700, and Citrikleen dispersants. Dispersant effectiveness was at a maximum at salinities between 40 to 45 ppt based on data processing that used a least squares procedure to fit the data to polynomial curves with two variables. This trend was consistent with all oil dispersant combinations tested. The authors concluded for the dispersants tested, ionic interaction was necessary for dispersion. The decrease in effectiveness at salinity values higher than 45 ppt was attributed to surfactants in the dispersants tested being nonionic, with HLB depending strongly on ionic strength of the dispersant/water system.

Blondina et al.[12] studied the influence of salinity on petroleum accommodation using dispersants Corexit 9500 and Corexit 9527, a modified swirling flask test, ten different oils, and salinity ranging from 0 to 35 ppt. In addition to reviewing the potential for salinity to affect dispersant performance, oil characteristics were reviewed including API gravity, TPH value, PAH content, volatile hydrocarbon content, density, and viscosity. Using a wide range of oil properties, the authors hoped to generalize the effect of salinity for all oil types. The results were statistically significant and indicated decreased dispersant effectiveness in low salinity waters. Corexit 9500 performed better for a wider range of salinities than Corexit 9527, which reached maximum effectiveness at 35 ppt for all but one oil type. Corexit 9500 was selected as the preferred dispersant for areas with salinity fluctuations due to a less hydrophilic formulation that created a larger impact on the oil-water interface at lower salinities and better oil penetration due to hydrocarbon-based solvents. Conversely, Corexit 9527 contains surfactants in a water matrix, not a hydrocarbon matrix, which may explain its poorer performance. Blondina et al.[12] concluded that dispersant effectiveness is influenced by water salinity, but the interaction is dependent on the specific dispersant and oil used.

Moles et al.[66] conducted 60 experiments using Corexit 9527 and Corexit 9500 with fresh, weathered, and emulsified Alaska North Slope crude oil at varying temperatures and salinities of 2.2% and 3.2%. The authors concluded that these dispersants exhibited decreased effectiveness at lower salinities.

In 2004, Fingas et al.[35] published a technical report for the Prince William Sound Regional Citizens' Advisory Council (PWSRCAC) on the effect of salinity on dispersant effectiveness. The objective of the report was to explore the potential for dispersant use in Prince William Sound, with salinities ranging from very low at creek outflows and smaller bays up to 33 ppt near the center. The report reviewed older laboratory methods, recent laboratory methods, surfactant literature, and field studies to observe dispersant effectiveness at various salinities. In this report, the author noted that dispersants were less effective at lower salinities as discovered from his previous work. The older laboratory methods completed before the mid-1990s used calorimetric measures and exhibited largely inflated effectiveness values without the use of gas chromatography. Consequently, recent laboratory results were analyzed more closely, using various dispersants and oils at multiple salinities with a variety of current testing methods. The reviewed field studies were conducted in ponds, lakes, and artificial streambeds. All studies showed peak dispersant effectiveness between 20 to 40 ppt. All commercially-available dispersants were largely ineffective in low salinity waters, around 0 ppt. The effect of salinity on dispersant effectiveness fits a Gaussian distribution since effectiveness increases with salinity until a maximum value and decreases rapidly after. Decreased effectiveness, at very high and low salinities, is a result of salinity affecting the HLB and stability of the surfactant due to changes in the ionic strength of the water. The salinity at which a dispersant shows maximum effectiveness will vary based on the specific dispersant and oil. Fingas et al.[35] concluded to PWSRCAC that Prince William Sound had areas that would exhibit decreased dispersant effectiveness due to less saline waters.

A full factorial experiment was conducted by Chandrasekar et al.[25] to study the effects of salinity, temperature, oil type, oil weathering, dispersant type, and rotating speed on dispersant effectiveness. South Louisiana Crude, Prudhoe Bay Crude, and Number 2 Fuel Oil were tested with a baffled flask tests at salinities of 10, 20, and 34 ppt and temperatures of 5, 22, and 35°C. Two different dispersants were used for this test, but their identities were not released. This experiment determined salinity increased dispersion for most oil-dispersant pairs. Interestingly, it was also concluded that salinity had an effect on how significantly temperature impacted dispersant effectiveness.

In conjunction with the U.S. Environmental Protection Agency, Nagarajan et al.[68] analyzed empirical correlations of dispersant effectiveness on oil spills. Three oils were tested using the baffled flask method at three levels of weathering with dispersants Corexit 9500 and Dispersit SPC 1000. Three different salinities were chosen to represent the range from average ocean levels to estuaries. Six different temperatures and three mixing speeds were tested. From testing results, dispersant effectiveness was modeled as a function of viscosity, salinity, and mixing speed. Nagarajan concluded that salinity had a significant effect on dispersant effectiveness for each oil dispersant pair.

Under contract with the Minerals Management Service (MMS), S.L. Ross Environmental Research[80] summarized the trends in data collected by Fingas et al.,[35] Blondina,[6] Byford,[18] and Belk[6] for the commonly-studied dispersants Corexit 9527 and Corexit 9500. Since the test methods used by the investigators (and, undoubtedly, the accuracy of the results) varied from study to study across this 25-year period, absolute values of effectiveness were difficult to compare, but S.L. Ross compared the normalized values of dispersant effectiveness to identify trends in the performance of these two dispersant formulations. They identified that, in almost every case tested, the effectiveness of both Corexit 9500 and Corexit 9527 achieved a maximum value of effectiveness at a certain salinity value in the range of 2.0% to 4.0%. An increase or decrease in salinity from this value was always accompanied by a decrease in effectiveness, although the rate at which the effectiveness fell was a function of the oil being tested, the test method, and other parameters of the experiments. In general, Corexit 9500 maintained its peak effectiveness levels over a wider range of salinities than did Corexit 9527. S.L. Ross Environmental Research[80] states more testing on dispersants in a range of salinity conditions is required if current policy has a chance of becoming more accepting of chemical dispersant use in fresh and brackish waters.

As demonstrated by multiple laboratory tests, large-scale tests, field studies, and literature reviews, traditional marine dispersants are ineffective at low salinities. Understanding that the reason behind this ineffectiveness lies at the molecular level is imperative. Dispersion is affected by the HLB of the surfactants and migration of the dispersants to the oil-water interface. Surfactant stability is largely affected by changes in the ionic strength of the water. This indicates the need to develop freshwater dispersants that can perform optimally at low salinities and remain effective through a wider range of salinity. Tests already confirmed that a hydrocarbon-based solvent, used in dispersants such as Corexit 9500, works better at a wider range of salinities. This information, along with knowledge of the working mechanism behind chemical dispersion, can be utilized to develop freshwater dispersants. The following section will discuss freshwater dispersants, along with tests conducted to aid in their development.

5.1.3 Testing and Development of Freshwater Dispersants

The potential benefits of freshwater dispersants would aid in situations where large freshwater bodies experience a transfer pipe rupture or similar disaster that leads to a significant amount of spilled oil. They could also be utilized in ocean waters with smaller areas of low salinity due to freshwater river and creek outflows into the region. Lastly, there are special arctic applications for freshwater dispersants due to low salinity bay regions and decreased local salinity in the upper water layers caused by ice formation. Traditional marine dispersants have proved to be ineffective at salinities below 20 ppt. Several researchers have responded to the growing demand on freshwater dispersants, conducting experiments to help in developing a chemical formulation that is effective in a wide salinity range.

Belk[6] presented a report at the 1989 Oil Spill Conference on comparative dispersant effectiveness in fresh and low salinity waters. This was one of the few reviewed salinity studies that tested freshwater dispersants. A Labofina laboratory test with Prudhoe Bay Crude and Warren Spring Laboratory Test oils was performed using four marine dispersants, one commercially-available freshwater dispersant, and one developmental freshwater dispersant. The specific names of the dispersants were not disclosed. Salinity values ranged from 0 to35 ppt during testing using different salts. The five different salts used to test dispersant efficiency at different cation concentrations were sodium chloride, sodium sulphate, calcium chloride, calcium acetate, and magnesium chloride. Prudhoe Bay crude oil showed lower efficiency with all dispersant types and salinity percentages. The hydrocarbon solvent type marine dispersant was the most effective. Most marine dispersants tested showed a rapid increase in efficiency with an increase in salinity above 10%. Above 20% salinity, two marine dispersants showed a decrease in efficiency with Prudhoe Bay crude oil. The developmental freshwater dispersant was more effective than the commercially-available freshwater dispersant at all tested salinity percentages. To compare dispersant effectiveness and different electrolyte solutions, the hydrocarbon solvent type marine dispersant and the two freshwater dispersants were further analyzed using a temperature of 10°C and Warren Spring test oil. From this test, it was found that changing the anion of the electrolyte solution had little effect on dispersant effectiveness. However, a higher efficiency index was seen in low-strength calcium ion solutions for the marine dispersant, accompanied by a rapid decrease as calcium content was further increased. Additionally, for the marine dispersant, calcium chloride resulted in lower efficiencies than calcium acetate. The marine hydrocarbon solvent dispersant showed increased effectiveness in high hardness water with 400 ppm calcium chloride. Freshwater dispersant effectiveness was less affected by electrolyte concentration and type than marine dispersant effectiveness. However, the freshwater dispersants also showed increased effectiveness at 400 ppm calcium chloride with reduced performance at 200 ppm. As the salinity was further reduced to 0 ppm, the two freshwater dispersants showed different behaviors. As expected, the commercially-available freshwater dispersant suffered a drop in effectiveness as salinity was further decreased, but the developmental freshwater dispersant had an increase in effectiveness in distilled water compared to 200 ppm salt water. Salinity and cation strength were plotted against the dispersant efficiency index for all Labofina tests. Belk et al.[6] concluded that effectiveness behavior in calcium and magnesium salt solutions was markedly different from sodium salt solutions. Consequently, the detailed water composition must be accounted for in designing future test procedures to evaluate dispersant effectiveness in freshwater. It is important to note that the test method used here used a higher oil-to-water ratio and mixing energy than found in the field, so this data is strictly comparative and is difficult to correlate with field results from real-world applications.

George-Ares et al.[40] demonstrated that the addition of calcium chloride to Corexit 9500 resulted in an increased effectiveness (with respect to stock Corexit 9500) under freshwater conditions for three crude oils. The study used the Exxon Dispersant Effectiveness Testing (EXDET) laboratory method to evaluate the stock Corexit 9500, modified Corexit 9500, and several freshwater dispersant formulations on three crude oils (one Alaskan North Slope and two Argentine crudes). In addition to the data showing the increased effectiveness of the modified Corexit 9500, the authors observed that an optimum level of calcium chloride addition was observed in the testing; that is, the addition of too much calcium chloride prevented the dispersion of the lightest crude oil in the study (Hydra Alaskan North Slope crude oil), although no supporting data were provided.

Lehtinen and Vesala[52] conducted dispersant effectiveness experiments using the MNS method over a variety of temperatures and water salinities. A single marine dispersant (referred to as Dispersant A) and two "low-salinity" dispersants (Dispersants B and C) were tested – details of the varying compositions of the formulations were not given. Experiments were conducted using a single, "light Russian" crude oil in both fresh and weathered states, at salinity levels of 0.3%, 0.7%, and 1.2%, and at temperatures of 4°C, 10°C, and 15°C. Dispersant performance trends with respect to salinity levels were mixed. For instance, the marine dispersant (Dispersant A) showed increasing dispersant performance with increasing salinity (within the range tested) for all temperatures and with both fresh crude and weathered crude. Dispersant B was influenced less by salinity, and Dispersant C showed no significant dependence on salinity for fresh crude and even an inversed dependence (i.e., effectiveness decreases as salinity increases) for weathered crude. Clearly, dispersant effectiveness is a strong function of oil and dispersant composition and (in some cases) a complicated function of temperature and salinity. Without additional details of dispersant composition, it is difficult to draw additional conclusions from this study regarding the effects of salinity.

Wrenn et al.[99] formulated known, experimental dispersant compositions from available surfactants in a known solvent in order to investigate the effects of dispersant composition and HLB on dispersant effectiveness in freshwater. The motivation for this study was the lack of work regarding dispersant performance in freshwater and no released information on the chemical composition of freshwater dispersants, specifically how they differ from traditional marine dispersants. Three HLB values were tested with nine distinct chemical formulations per HLB value, and results led the authors to claim that, at least for the one crude oil/synthetic lake water combination tested, dispersants could be formulated for freshwater that performed as well as the leading commercially-available dispersants performed in salt water. The authors noted, as previously noted by Belk et al.,[6] that the detailed water composition must be taken into account while analyzing freshwater dispersant effectiveness. In fact, minor ions such as calcium and magnesium have proven to have a greater impact on dispersant effectiveness than sodium and chloride ions which currently dominate dispersant salinity testing since most are conducted by diluting natural or artificial seawater.

Relatively few tests have been conducted on freshwater dispersant formulations, compared to the number of tests on salinity effects of marine dispersants. There must be an increase in tests on freshwater dispersant formulations to fully-understand their effectiveness. Once freshwater dispersant formulations have been adequately tested and refined, the products can be made commercially-available. Governing bodies of countries that deal with a potential for freshwater oil spills can come up with an approved list of dispersants. Further research can be utilized to determine decision-making guidelines regarding the use of freshwater dispersants, limiting the potential for biological harm. Lastly, integration methods can be better understood in order to utilize multiple oil spill response options in a given area, allowing incorporation of traditional marine dispersants with freshwater dispersants without any harmful repercussions. This may be particularly useful in marine environments that have local areas of low salinity or arctic environments. However, freshwater dispersants must account for the effect of temperature on performance since many applications will involve low temperature ranges, such as arctic waters. The following section focuses on the effect temperature has on chemical dispersant performance.

5.2 Effect of Temperature

Another application environment aspect that affects dispersant performance is temperature. It is necessary to fully-understand the effect of temperature on chemical dispersion with current oil production in diverse climate conditions. This section describes the effect water temperature has on oil properties and dispersion, reviewing experiments conducted using dispersants as an oil recovery method in a range of temperatures.

5.2.1 Water Temperature Effect on Oil Properties

Surface seawater temperatures can range from approximately -2°C to 33°C around the globe. Before examining the use of dispersants in this large temperature range, it is important to note the effect this range of temperature will have on the properties of the spilled oil. Oil viscosity will increase as a result of decreasing temperatures. A change in viscosity is a direct result of a change in oil properties that are caused by a change in temperature. Therefore, temperature has an indirect effect on dispersant effectiveness through changes in the oil properties. The rate of viscosity change and the range of oil viscosities due to changes in temperature are specific to each oil. Light, low-viscosity oil has been more commonly tested with the use of chemical dispersants. Heavy oils add a higher level of complication to dispersion and have not been tested as thoroughly in low temperature environments. Temperature will affect dispersion indirectly through its effect on oil viscosity, but the direct effect of temperature on dispersion must also be considered.

5.2.2 Effect of Temperature on Dispersion

Temperature affects dispersant effectiveness in several general ways. The solubility of certain surfactants in water, for instance, increases at lower temperatures.[20] This increase in water solubility can result in a loss of surfactants into the water from the oil-water interface and could decrease overall dispersant effectiveness. This relates back to the HLB of surfactants and differences between the polar and nonpolar ends of the surfactant molecule being affected by temperature according to Rewick et al.[78] Additionally, cold temperatures can significantly increase viscosities of both the oil and dispersant phases, potentially limiting the penetration and mixing rates at which the dispersant interacts with the oil. No conclusive relationship between oil viscosity and dispersant effectiveness has been found. However, if the oil is so viscous it becomes semi-solid, the penetration and mixing of the dispersant with the oil will be severely impacted, with the potential for dispersants to simply roll off the top of the oil slick.[20] Finally, temperature can affect the kinetics of surfactant packing at the oil-water interface.[78] Interfacial tension between the water and oil will decrease as temperature increases. Since reducing interfacial tension increases dispersion, this implies that dispersion will decrease at lower temperatures.

The effect of temperature on dispersion is going to differ between different oil and dispersant types due to changes in viscosity and solubility being very dependent on oil and dispersant types. Therefore, it is important to test the effect of temperature on dispersant effectiveness, with a range of oils and dispersants to fully-understand the effect. It is also important to test temperature effects because thermal effects are difficult to individually assess. Temperature is correlated with other factors such as viscosity, solubility, oil weathering, and mixing energy which can make it difficult to reliably separate and predict thermal effects.[78]

There have been many tests on chemical dispersants in a range of temperature conditions, from -5°up to 35°C. However, the results have varied significantly between the tests. The following section will review these tests and significant conclusions drawn from them.

5.2.3 Testing the Effect of Temperature on Dispersant Effectiveness

While covering salinity effects, a 1991 study conducted by Fingas et al.[35] on the physical and chemical behavior of oil and dispersant mixtures was mentioned. Along with analyzing the effect of oil bulk components on effectiveness, environmental effects were also studied, including temperature and salinity. A swirling flask test method was used with ASMB crude oil and Corexit 9527. Temperature was varied between approximately 0°C and 50°C. Fingas concluded increasing temperature has a positive effect on dispersion, increasing dispersant effectiveness. The data were best fit with an exponential relationship. Analyzing the effect of oil bulk components on effectiveness, Fingas found that there is no direct correlation with viscosity and effectiveness. However, saturate content had a strong positive correlation with dispersant effectiveness. Conversely, negative correlations with dispersant effectiveness were found for aromatic content, asphaltene content, and polar compound content. This indicates temperature has an impact on dispersant effectiveness which may be attributed to changes in oil properties, other than the change in viscosity. In conclusion, this study found that dispersant effectiveness, in general, can rise with increasing temperature, although published data were limited.

Moles et al.[66] conducted experiments using Corexit 9527 and Corexit 9500 with fresh, weathered, and emulsified Alaska North Slope crude oil under at temperatures of 3°C, 10°C, and 22°C and salinities of 2.2% and 3.2%. The results from this study were also discussed in the salinity section of this report. The authors concluded dispersants were ineffective at temperatures found in Alaskan waters.

Chandrasekar et al.[23] tested dispersant effectiveness for a range of environmental conditions in 2003, specifically testing three different temperatures, levels of weathering, and mixing speeds. The three temperatures tested were 4°C, 25°C, and 35°C. The objective of this study was to collect empirical data for the EPA Research Object-Oriented Oil Spill Model. A factorial experiment was conducted using a baffled flask test method, two dispersants (Corexit 9500 and Dispersit SPC 1000), and three different oils (South Louisiana Crude, Prudhoe Bay Crude, and Number 2 Fuel Oil). After conducting an analysis of variance to validate the statistical significance of the test results, it was concluded that temperature has a significant interaction with dispersant type. However, dispersant effectiveness was not found to have a consistent relationship with temperature.

As discussed previously, Lehtinen and Vesala[52] conducted dispersant effectiveness experiments using the MNS method over a variety of temperatures and water salinities. A single marine dispersant (referred to as Dispersant A) and two "low-salinity" dispersants (Dispersants B and C) were tested – details of the varying compositions of the formulations were not given. Experiments were conducted using a single, "light Russian" crude oil in both fresh and weathered states, at salinity levels of 0.3%, 0.7%, and 1.2%, and at temperatures of 4°C, 10°C, and 15°C. For each dispersant tested, increasing temperature resulted in increasing dispersant effectiveness values in all salinities in both fresh and weathered crude oil cases. Furthermore, Lehtinen and Vesala[52] referred to a test in which a "colder" dispersant (4°C) was used in a warmer water (15°C). They found that the "cold" dispersant effectiveness (40%) was reduced when compared to a case in which the dispersant was added was at 15°C (56% effectiveness).

Abdelrahim[1] conducted experiments to measure interfacial tension of oil-water-dispersant systems at varying temperatures. At subsea pressures (2,225 psi), Abdelrahim found that the interfacial tension of these systems (with both the crude oil and n-Octane fluids tested) decreased as temperature increased (in the range of 4.4°C to 21.1°C).

In 2006, expanding on previous research, Chandrasekar et al.[25] used the baffled flask test to complete a large factorial experiment on three oils (South Louisiana crude, Prudhoe Bay crude, and Number 2 fuel oil), three levels of weathering, three temperatures (5°C, 22°C, and 35°C), and three salinities (1.0%, 2.0%, and 3.4%). Results from this experiment pertaining to salinity were also mentioned in the salinity section of this report. Results from these experiments did not consistently show effectiveness to be a monotonically increasing function of increasing temperature. In some cases, dispersant effectiveness increased with each level of increasing temperature. In other cases, effectiveness values increased with an increase in temperature from 5°C to 22°C, but decreased at 35°C. Furthermore, they found that the effect of salinity was more pronounced at the highest temperature (35°C) than it was at the lower temperatures tested. Consequently, the salinity affected the significance of temperature on dispersant effectiveness.

As mentioned in the salinity section of this report, Nagarajan[68] utilized Baffled Flask Test data[23, 25] to derive correlations of dispersant effectiveness of two dispersants (Corexit 9500 and Dispersit SPC 1000) for three oils (Prudhoe Bay Crude oil, South Louisiana Crude oil, and Number 2 Fuel Oil) across a range of temperatures, three levels of salinity representative of estuaries, three levels of oil weathering, and three levels of mixing energy. In this study, the temperature and weathering factors were correlated to oil viscosity for inclusion in the effectiveness correlation. Nagarajan[69] concluded that temperature had a significant effect on dispersant effectiveness for each oil dispersant pair.

Belore et al.[10] tested four Alaskan crude oils (Alaska North Slope, Endicott, Northstar, and Pt. McIntyre) with Corexit 9500 and Corexit 9527 to observe dispersant effectiveness in cold water. The testing was conducted at Ohmsett, a large-scale testing facility with water temperatures ranging from -4.4°C to 9.4°C. The testing found that both dispersants were effective in cold water applications. In addition, weathering of the oil did not have a significant impact on dispersant effectiveness. Corexit 9500 outperformed Corexit 9527 in a significant number of tests.

Li et al.[56] performed a study to determine the effect of temperature and wave conditions on dispersion of heavy oil using IFO 180 Fuel Oil. A flow-through tank test was conducted with two different simulated wave conditions, breaking waves and regular sea surface waves. The effect of water temperature on dispersion was observed under both wave conditions, with a 10°C to 17°C window. Two dispersants, Corexit 9500 and SPC 1000, were tested. The dynamic dispersant effectiveness was found to be higher under breaking waves than regular waves, with maximum values occurring for both dispersants under breaking waves at the highest temperature, 17°C. At low temperatures under breaking wave conditions and at all temperatures under regular wave conditions, dispersion was ineffective. Higher interfacial tension and oil viscosity resulted in poorer dispersion for the tested heavy oil compared to the lighter crude oils under the same wave conditions. It is important to note that very few tests on the effect of temperature on chemical dispersion have been performed using heavy oil. Overall, the observed mixing energy effect is consistent with that seen in previous tests, indicating feasible chemical dispersion of heavy oil under appropriate environmental conditions.

Venosa and Holder[95] used a baffled flask test to evaluate the performance of eight dispersants on South Louisiana Crude Oil at two temperatures, 5°C and 25°C. The temperatures were chosen to represent surface and ocean-bed temperatures near the Deepwater Horizon well. Although this test did produce very repeatable results and determined the best and worst dispersant under the given test conditions, no general relationship was found between temperature and effectiveness. Some dispersants showed decreasing effectiveness with increases in temperature. This trend is opposite of the trend typically seen in most experiments. However, some dispersants showed the more often seen trend with effectiveness increasing with increases in temperature.

Wang et al.[96] tested three oils (Alaska North Slope Crude, Arabian Light Crude, and IFO-40 Fuel Oil) with two dispersants (Corexit 9500 and Corexit 9527) at one oil concentration (800 ppm) and one water salinity (30 g/L). A full factorial experiment was conducted at two different dispersant-to-oil ratios and five mineral-to-oil ratios to investigate the effect of oil-mineral-aggregate formation on the dispersion of oil. This experiment was conducted at two temperatures, a low temperature between 0 and 4°C and a high temperature of 20°C, to investigate the effect of temperature on oil dispersion. Wang et al. concluded that lower test temperatures resulted in a decreased oil removal percentage that was proportional to the increase in viscosity of each oil as a function of lowering temperature. Therefore, the temperature affected the oil dispersion indirectly through its effect on oil viscosity.

Fingas[39] conducted experiments with Corexit 9500 and Alberta Sweet Mixed Blend (ASMB) crude oil across a range of temperature and salinity conditions. The results were surprising, namely that the dispersant/oil combination tested showed increasing effectiveness with increasing temperature from 5°C to 10°C, but then a decreasing trend for most salinities from 15°C and 20°C. Dispersant effectiveness was observed to decrease at all salinities tested when temperature was increased from 20°C to 25°C.

Both Chandrasekar[25] and Fingas[39] suggest that a more complex interaction between temperature and salinity is possible, depending on the oil/dispersant system tested. Neither author presents a comprehensive theory explaining this interaction, but full experimental evaluation at the temperature/salinity requirements for future use are suggested. Fingas[39] was able to find a three-way correlation between temperature, salinity, and effectiveness that could yield a predictive model with good reliability. This will be covered in more detail in the following section, relating to arctic environments with temperature and salinity variations.

5.3 Arctic Environment

Oil exploratory drilling and tanker traffic have recently increased in arctic waters. The following section will describe characteristics of an arctic environment, briefly review current oil spill recovery methods, and comment on the potential use of chemical dispersants in arctic waters based on experimental testing.

5.3.1 Properties of an Arctic Environment

The Arctic Ocean contains 45,000 kilometers of coastline, almost completely surrounded by North American, Europe, and Asia. Ice coverage in the Arctic Ocean changes based on season, with maximum ice coverage reaching approximately 15 million square kilometers in recent years and a minimum of approximately four million square kilometers. There are several arctic water bodies that are completely ice-free in late summer, and even two water bodies that have no ice year-round, the Labrador and Norwegian Seas.

Ice coverage will vary due to fluctuation in temperature relating to weather conditions. Additionally, ice coverage varies due to a gyre that circulates the Arctic Ocean in a clockwise rotation, driven by currents and winds. This rotation causes ice to drift through the ocean. Seasonal melting of ice changes local salinity of the surface water. When ice coverage increases, the salinity of the surrounding water increases to varying degrees based on ice thickness. Conversely, as ice melts, salinity of the surrounding water decreases which ultimately decreases the density of the surface water. This can result in a salinity gradient throughout the water column.[54] The salinity of arctic waters will also decrease with seasonal ice melting as a result of restored outflows from local freshwater bodies that have recently thawed.[38] Consequently, the salinity in the Arctic Ocean can range from an average of 28 to 34 ppt in the water level that extends from the surface to a depth of 650 feet. However, as previously mentioned, smaller areas, such as Prince William Sound, have seen extremely low salinities in smaller bay regions and creek outflows while there are up to 33 ppt in the center.[38] Considering seasonal salinity fluctuations, the Arctic Ocean has the lowest salinity of all the world’s oceans. This low salinity is caused by limited outflows to neighboring oceans, low evaporation, and freshwater river inflows.

The Arctic Ocean is also characterized as having extremely low water temperatures. A common temperature range found in the arctic is between -1.5°C and -1.8°C. However, minor temperature fluctuations also occur due to seasonal weather conditions. During the summer, water is heated in the Barents, Norwegian, and Chukchi seas by inflows from the Pacific Ocean and North Atlantic Current which results in water temperatures ranging from 8°C to 12°C. These are the warmest waters in the arctic region. Extreme environmental conditions have led to the use of alternative oil spill recovery options rather than chemical dispersants in the arctic.

5.3.2 Current Oil Spill Recovery Methods used in the Arctic

The use of chemical dispersants in arctic waters is currently very limited. An example of this limitation is seen for the Baltic Sea region by the HELCOM recommendation adopted March 21, 2001. The HELCOM Recommendation 22/2 of the 1992 Helsinki Convention is still in effect, stating the “restricted use of chemical agents and other non-mechanical means in oil combatting operations in the Baltic Sea area." It goes on to note that, "Mechanical means are the preferred response measure, and chemical agents may only be used in exceptional cases, after authorization has been granted in each individual case." This decision reflects the difficulty associated with chemical dispersant application in waters with properties similar to those found in the Arctic Ocean, such as the Baltic Sea.

One currently-used oil spill recovery method in arctic waters is mechanical recovery. Mechanical recovery involves using booms and skimmers to physically collect and remove the spilled oil from the water surface. Since more spills are small and close to the shoreline, mechanical recovery is the most widely-used oil spill response method. Although widely-used, mechanical recovery does have its limitations. The equipment must be able to reach the spilled oil which can be made more difficult by inclement weather conditions or thick ice coverage. All necessary equipment and personnel must be able to reach the spilled oil. This results in increased exposure of personnel to the spilled oil, which increases the risk of adverse health effects. Additionally, the oil response can only continue by means of equipment controlled by personnel which is limited to working hours, becoming very difficult in darkness. This is especially of concern in arctic regions, since days of constant darkness or light can occur.

Another oil spill response option currently used in the arctic is in-situ burning. In-situ burning is a controlled burn of the oil from the water or ice surface. A common limitation to this method is that an adequate oil slick thickness must be reached. Ice can actually improve the effectiveness of in-situ burning by creating a barrier for the oil to spread along the water surface, creating a thicker oil slick. However, waves can make ignition of surface slicks very difficult. This was observed through a series of burning experiments that studied the effect of waves, wind, and currents on in-situ oil recovery in broken ice conditions. It was found that the fresh oil was ignited with little impact from the waves, but oil emulsions were nearly impossible to ignite in the wave conditions. In-situ burning in broken ice conditions was also studied by the University Centre at Svalbard (UNIS) in cooperation with SINTEF between 1997 and 2004 to test a variety of oil products at multiple weathering degrees and the effect on oil recovery effectiveness.[16] Although in-situ burning is a viable option for arctic oil spill recovery, the presence of waves and emulsified oil make it difficult. Additionally, although ice may act as a shield to thicken an oil slick, if the ice isn't thick enough to prevent spreading, booms will need to be utilized which can be difficult in ice-infested waters.

Despite the existence of current oil recovery methods, there may be major challenges to applying these methods in the future. It is important to investigate the use of dispersants in arctic environments due to limitations on current methods including variable ice coverage, extended periods of darkness, increased health risks to personnel, and inclement weather that can cause wave action and poor visibility. The following discussion will describe the potential for use of chemical dispersants in arctic waters as observed through experimental testing.

Brandvik et al.[15] used an IFP dilution test to study the effectiveness of dispersants under arctic conditions. Initial screening tests consisted of 14 dispersants on two types of North Sea weathered oils during which the temperature was kept constant at 0°C and two discrete salinity values were tested, 0.5% to 3.5%. The effect of salinity was further investigated by sampling the effectiveness of two dispersant types in increments of 0.75% salinity from 0.5% up to 3.5% on a single crude oil. Brandvik et al.[15] found that several other commercial dispersant formulations for general marine use (with nominal 3.5% salinities) suffered from lowered effectiveness in low-salinity conditions (down to 0.5%), when compared to the nominal 3.5% salinity waters.

They additionally showed that some alternative products, which were (in 1995) newly designed for improved low-salinity effectiveness, suffered from significantly lower effectiveness across a broader range of salinities (0.5% to 3.5%). Two theories are stated for possible explanations of this behavior. First, a salinity variation may cause a change in the electric field at the oil-water interface due to ions caused by surface activity of ionic surfactants being salinity-dependent. Second, salinity variation may cause surfactants to leach from the oil into the water phase. The authors noted an interesting observation occurred when a dispersant exhibited high effectiveness at test temperatures 10°C to 15°C below the pour point of the oil. This observation was opposite of what had been seen in previous studies and was explained by a stabilization of the water droplet in the emulsion caused by a gathering of wax particles at the oil-water interface.

As previously mentioned, Moles et al.[66] conducted experiments using Corexit 9527 and Corexit 9500 with fresh, weathered, and emulsified Alaska North Slope crude oil under varying temperatures and salinities of 2.2% and 3.2%. The authors concluded dispersants exhibited decreased effectiveness at lower salinities and temperatures common in Alaskan waters. The main objective was to determine dispersant effectiveness in Subarctic conditions. The authors found temperature and salinity had an interactive effect on dispersant performance. An effectiveness of less than 10% was found using simulated environmental conditions of Alaska. To increase effectiveness of dispersants in arctic waters, the authors attempted to form a relationship by correlating temperature, salinity, and effectiveness using data analysis. Moles et al. was able to fit a simple linear equation for fresh oil data with good correlation, but weathered and emulsified oil data fit poorly with the same linear equation. The authors concluded that more experimental testing should be conducted to validate the three-way correlation found between temperature, salinity, and effectiveness. Specifically, the correlation for weathered and emulsified oil leaves great potential for improvement.

In addition to the interactions between salinity temperature variations and increased viscosities associated with conditions found in arctic locations, the presence of ice in arctic environments can affect the effectiveness of dispersants. Consequently, several of the studies conducted took into account the effect of ice on dispersion.

In 2004, Brandvik et al.[16] wrote a paper on oil spill research and development in Norwegian Arctic waters. Two large-scale experimental crude oil release tests were compared to understand arctic weathering processes. One experiment was conducted in open water with no ice at 10°C while the other was in broken ice conditions at -1.8°C. Weathering properties were compared, including evaporative loss on the crude oil, density of water-free oil after breaking the water-in-oil emulsion, water uptake, and emulsified oil viscosity. They found significant differences for all weathering properties due to ice preventing oil spreading and reducing wave action. The evaporative loss of the crude oil was much higher in open water than in broken ice, with 40% after a 3.5 day period compared to 25% after a 7 day period. This is due to ice floes restricting oil spreading at the water surface, increasing oil slick thickness. Lower temperature may have also restricted evaporative loss by reducing diffusion of the oil components and creating a gradient into the bulk oil phase. The density of the water-free crude oil was higher in open water than broken ice. The volume percent of water uptake in the crude oil was much greater in open water, 70% to 80%, than broken ice, 20%, due to interference with wave input energy caused by high ice coverage. As ice coverage reduced, more wave action occurred between ice floes, increasing water uptake at the end of the testing period. The viscosity of the water-in-oil emulsion was approximately 400-600 cP in broken ice compared to 15,000-

18,000 cP in open water after a 3.5 day period. This was expected since the viscosity is influenced by the difference in water content, temperature, and evaporative loss of oil.

An experiment conducted by Fingas et al.[39] in 2005 was covered previously in the temperature section of this report because it tested dispersant effectiveness in a variety of temperatures. While evaluating the effect of arctic conditions on dispersant effectiveness, it is important to further discuss results of this experiment, since the objective of the study was to use more data points to validate the three-way interaction between temperature, salinity, and effectiveness seen in Moles et al. As previously mentioned, an ASTM standard test was conducted using Corexit 9500 and Alberta Sweet Mixed Blend. Temperatures varied from 5°C to 25°C, and eight different salinity values were used, ranging from 0 to 35 ppt. From the results of this experiment, an interrelationship between temperature, salinity, and effectiveness was observed. Since arctic waters have low temperatures and a range of salinities, it's important to understand how these variables interact and effect dispersion in order to maximize effectiveness. The interrelationship between the three variables was clear due to maximum effectiveness occurring at 10°C with a salinity of 25 ppt, not the expected highest temperature and salinity values. Therefore, peak salinity that is based on surfactant content and a three-way trade-off between temperature, salinity, and effectiveness exists that is dependent on the specific dispersant applied. A possible explanation for this interaction is the increased effectiveness at higher temperatures causes the ionic strength to match with surfactant polarity. The results from this study were similar to those shown by the Moles et al.[66] study that was also discussed in Fingas[38] with a maximum effectiveness between 20 to 30 ppt. Any slight differences between the two studies can be explained by differences in oil type. Therefore, the interrelation is clear, but the salinity at which peak effectiveness occurs is dependent on specific dispersant and oil type.

Lewis et al.[54] wrote a report in 2007 that reviewed oil spill dispersant effectiveness studies in arctic conditions. The arctic environment was described as having low temperature, ice presence, and salinity variations. Lewis explains that low temperatures will significantly decrease dispersant effectiveness due to an increase in oil viscosity above a certain value, and lower salinities will decrease dispersion which is common due to seasonal melting or river estuaries. He also mentions how ice formations can suppress wave action, reducing mixing energy and decreasing dispersion. The report goes on to summarize a series of laboratory tests, large-scale tank tests, and tests conducted at the Oil and Hazardous Materials Simulated Environment Test Tank (OHMSETT) in New Jersey. Lewis found that temperature, salinity, and ice formation are all related, so individual assessment of each factor is difficult. Although low temperatures reduce effectiveness, they also suppress the oil weathering rate which increases the window of opportunity during which dispersants can be applied. Lewis also concluded that ice may cause an out-of-phase movement that actually increases mixing energy at the surface, enabling dispersion in small-amplitude wave conditions. However, these results were seen in a tank test that added wall shearing which is not indicative of field results. Therefore, this may not accurately represent conditions at sea. This report called for further investigation on the effect of dispersion due to localized low-salinity areas caused by melted ice.

In 2010, Brandvik et al.[18] released results from another SINTEF study on oil weathering, in-situ burning, and dispersant application as a function of ice conditions. Further experiments within a "meso-scale" (20 L of oil) flume basin showed that while high ice coverage and low energy (due to ice) result in lower evaporation and water uptake rates for some oils, other oil compositions (in this case napthenic/asphaltenic crudes) form stable emulsions, even in ice coverage. In this same study, SINTEF conducted dispersibility testing of the weathered oils. A similar MNS test was conducted, adding Corexit 9500 to test dispersant effectiveness. No general trend was found for the effect of ice on dispersion for the specific dispersant and oil type tested. However, the amount of time after a spill while a dispersant can be applied is increased due to a reduced weathering rate in icy waters. This is consistent with the results found by Lewis et al.[54] Additional mixing energy may be necessary for dispersion with ice coverage above 50% to 70%. In conclusion, field data showed that the presence of ice can result in larger slick thicknesses, lower weathering rates, and slower water uptake rates when compared to the open water.

The trends summarized by S.L. Ross Environmental Research,[80] under contract with MMS, were previously mentioned in the salinity section of this report with a maximum value of dispersant effectiveness achieved between 2.0% to 4.0% salinity. Effectiveness of traditional marine dispersants will decrease in arctic waters due to salinity fluctuation. This indicates the need to create freshwater dispersant formulations for fresh, brackish, and arctic waters. Another important conclusion from this report is chemical herders are not affected by water salinity or ice presence. The use of chemical herders can create a thicker oil slick, aiding in utilization of in-situ burning as an oil recovery method. This report highlights the limitations of dispersants for use in arctic waters due to salinity variation and states that previously-used oil recovery methods can be improved through chemical herders.

6. MIXING ENERGY, DISPERSANT APPLICATION, AND SUBSEA EFFECTS

6.1 Mixing Energy Effects

Recall that chemical dispersants function by lowering the interfacial surface tension (IFT) sufficiently to allow an oil slick to break into droplets for dispersal into the water column. However, even with very low IFT, film breakup does not occur without the addition of some mixing energy. Wind and current energy at sea act to provide this energy. The effect of mixing energy on dispersant effectiveness continues to be a topic of research in both laboratory and open sea settings.

Even after oil film breakup, oil droplets dispersed into the water column undergo advection transport and dilution. Dispersion in the vertical plane is countered by the natural buoyancy of the oil droplets in water. The size of the oil droplets determines rise velocity, and smaller droplets have a better chance of remaining suspended within the water column. Classical theory of droplet breakup in stationary turbulence predicts the maximum stable droplet size as $d_{max} = \alpha(\sigma/\rho)^{3/5}\varepsilon^{-2/5}$, where α represents a constant of proportionality, ρ represents density of the continuous phase (water), σ is a interfacial tension, and ε is the turbulent dissipation rate.[44] Droplet size distribution and drop coalescence is an important parameter not only for surface oil spill research, but also for investigation into dispersant effectiveness in subsea oil release.[47]

As will be discussed in the Section 7, many test methods exist for evaluating dispersant performance. However, no single method has been agreed upon as the best representation of open sea conditions. Considerable work, therefore, has been done to quantify the levels of mixing energy present in various experimental setups, although comparison of the data between the sea and different laboratory settings remains challenging.

Li et al.[56] suggest that the energy dissipation rate of waves plays a major role in the effectiveness of a dispersant, and may be used to scale different wave-energy conditions from the laboratory to the field. Using a wave tank, they examined “deep water” waves, defined as when the ratio of water depth to wave length is greater than 0.5. Their data showed that breaking (high-energy) waves provided smaller dispersed oil droplets and higher dispersant effectiveness values than did regular (lower energy) waves.

Wickley-Olsen et al.[96] provide a detailed discussion of wave kinematics in their recent work, also stressing the importance of energy dissipation rate as a parameter to gauge mixing energy. As expected, energy dissipation was observed to be highest at the surface and decreased with depth. Breaking waves showed two orders of magnitude higher energy dissipation compared to the regular waves, indicating the importance of breaking waves in dispersion of oil for spill response.

Trudel et al.[86] presented a comparison of wave tank test results with “at-sea” results using comparable oil species, dispersant types, dispersant-to-oil ratios (DORs), and mixing energies. Mixing energy of the wave tank tests were matched to sea trials through scoping experiments to identify the wave frequency that produced an effectiveness similar to the sea trials. Comparison of wave tank and at-sea results showed good qualitative agreement. However, due to uneven distribution of the dispersant at-sea, precise matching of DORs was difficult for quantitative comparison with laboratory tests. This example of problematic variable control at-sea was identified by the authors as a reason for studying dispersant effectiveness in wave tanks.

In the study of Venosa, et al.,[92] the authors present a comparison of mixing energy results between the wave tank and laboratory tests (swirling flask test and baffled flask test). The dissipation of kinetic energy has been measured and used as the basis of comparison between test types. Justification for this stems from reasoning that energy dissipation is due to turbulent and laminar shears within the water, and shear in turn is directly proportional to velocity gradients that define the mixing intensity of chemicals. Mixing energy comparison in laboratory flask testing showed that dissipation was consistently much higher in the baffled flask test (BFT) compared to the swirling flask test (SFT). Additionally, the dissipation rates in the BFT were shown to be similar in magnitude to typical breaking wave conditions generated in the wave tank. Wave tank testing was conducted at two different breaking-wave energies, and conservation of dissipation between the wave tank scale and the field-testing scale indicated to the authors that wave tank testing is sufficient to accurately evaluate the effectiveness of a dispersant.

Kaku et al.[49] also compared the mixing characteristics of fluid using the SFT method versus the BFT method. Small-scale structures of turbulence are generally understood to be independent of the system or orientation effects (locally isotropic). Thus, the authors postulated that laboratory experiments may be used to extrapolate dispersion effects of oil on a much larger scale. Hot wire anemometry was used in this study to measure the azimuthal and radial water speeds at five speeds. The average Kolmogorov scale (K-scale) measured in laboratory experiments was used to correlate to the expected oil droplet size in an oil spill. Justification for this comes from the fact that the K-scale represents the smallest eddy size. If the smallest eddies are smaller than an oil droplet, it would be expected that they would stretch and eventually break it apart. Conversely, if eddies were larger, they would tend to entrain oil droplets without breaking them. An assumption in the study is that energy dissipation occurs predominately due to turbulent shear, neglecting effects of laminar shear. The authors state that this is a common state for most environmental flows. It was found that the K-scale for SFT at 150 rpm was about 400 microns, while it was about 50 microns for the BFT at 200 rpms. Note that the size distribution of dispersed oil at sea has been observed to be in the range of 50 to 400 microns. Thus, it has been concluded by the authors that mixing in standardized SFT is not representative of dispersant mixing that occurs at sea, while the standardized BFT more closely replicates the physics. More study is needed to quantify and define energy dissipation rate at different sea states.

6.2 Dispersant Application Effects

Historically, the effects of dispersant type, oil composition, environmental effects, and mixing energy levels have been discussed in terms of their influence on dispersant effectiveness. An area that receives less attention from the research community, but can greatly affect the performance of dispersants in the field is the application method of dispersants. At a basic level, ideal application of dispersant will provide the maximum contact area between the oil and surfactant. From a logistical standpoint, however, this is very hard to achieve in an open sea environment where oil slicks are of uneven thickness, and dispersant application is difficult to control.

After a surface oil spill event, dispersants are normally sprayed onto the oil slick from either an aircraft (airplane/helicopter) or a ship. Dispersants may be applied either “neat” (undiluted) or diluted with seawater. For aerial application, dispersants are generally applied neat due to aircraft capacity restraints. Field trials of neat versus diluted application methods conducted in 1984 suggest that neat application may be most effective.[29] Potential disadvantages for ship application include washing of the dispersant off the slick from ship bow-waves,[29] as well as greater difficulty and time to reach all areas of the slick. Aerial applications do not suffer from these challenges. However, they are prone to problems with atmospheric transport of the dispersant droplets. This includes atmospheric conditions such as wind and turbulence causing the droplets to miss the slick, unexpected aircraft vortex effects on the terminal settling velocities of the droplets, and changes to droplet size by the time of impact.[58, 83] Since oil slicks do not spread evenly from spills, aerial treatment of patchy slicks often results in dispersant being sprayed into the open sea. This can lead to slicks being under-dosed[86] and oil herding issues. Herding occurs when surfactant molecules on the water surface follow their tendency to orient themselves based on their hydrophilic-lipophilic components. Molecules at the water surface act to herd/push the oil aside, congregating the oil to create thicker slicks that reduce dispersant access to the oil.[26]

Aside from macro-scale application considerations, dispersant application has also been studied from the fundamental physics perspective of droplet size. Early dispersant testing has suggested that dispersal effectiveness is better with smaller drop sizes.[7, 63, 83] This makes sense from the standpoint that surface area contact between dispersant and oil is maximized with smaller droplets. However, larger droplet sizes may lead to more effective dispersion with viscous or weathered oils because the drops are less likely to be washed off the slick. Nedwed et al.[72] presented test results comparing performance of a gelled dispersant against the more conventional Corexit 9500. Whereas conventional dispersants are sprayed with a 300-700 micron droplet size to reduce loss of dispersant to the water column, the new gel was delivered in much larger droplets (up to 0.5 cm) that are positively buoyant and adhere to oil slicks (oleophilic). Over one hundred tests were performed in a wave basin facility to provide side-by-side comparison data between dispersants. While both dispersants appeared to work well for medium-to-light crude oils at high DORs, the new dispersant outperformed Corexit 9500 for lower DORs, heavy oils, and lower mixing energies. Four main improvements were noted for the gelled dispersant: (1) reduced spray drift due to use of larger buoyant droplets that can re-contact a slick if they penetrate into the water or miss the slick, (2) provided visual feedback on dispersant coverage since it could be clearly seen when applied to oil, (3) effective on heavier oils due to olephilic gel delivery that adheres to the oil slick without washing off, and (4) utilizes 90% active surfactant in gel compared to traditional 40% to 50% active ingredients.

In summary, the application method for oil spill treatment is an important consideration for predicting dispersant performance. Aerial and ship applications each have their own set of advantages and disadvantages that should be considered on a case-by-case basis for remediation efforts. In addition, while the conventional thought process holds that smaller droplets sprayed onto an oil slick will result in better effectiveness, new studies have shown that larger gel droplets may have better performance for cases with highly viscous oils. This remains an active area of research, particularly for arctic conditions. In addition to evaluating performance of gelled dispersants, development of aerial delivery systems to meet arctic environment challenges is needed. Finally, concern about subsea oil leaks from wellheads has led to increased interest in research on dispersant injection subsea. This topic is discussed more in the following section.

6.3 Subsea Environment

During the response to the Deepwater Horizon oil spill release, dispersants were injected subsea, directly at the source of the leak. Approximately 771,000 gallons of dispersant (Corexit 9500) were injected into the wellhead and within the ejected plume. Intuitively, this method shows considerable promise for increasing dispersant effectiveness and application efficiency, as the mixing energies and concentration of oil within the plume at the source of the leak are both highest at the leak source. Both long-term environmental effects and actual dispersant effectiveness of the actions are still debated.

Nedwed et al.[74] showed that cessation of subsea injection of dispersants near the Macondo wellhead correlated to higher levels of volatile organic compounds (VOCs) measured by surface vessels during the intervention effort, implying that subsea injection of dispersants kept the oil slicks from forming near the surface vessels. Additionally, aerial photographs, as shown in Figure 6-1, present further evidence that subsea injection of dispersants during the Macondo intervention changed the fundamental behavior of the oil in the water column by reducing the appearance of slicks near the surface intervention vessels.

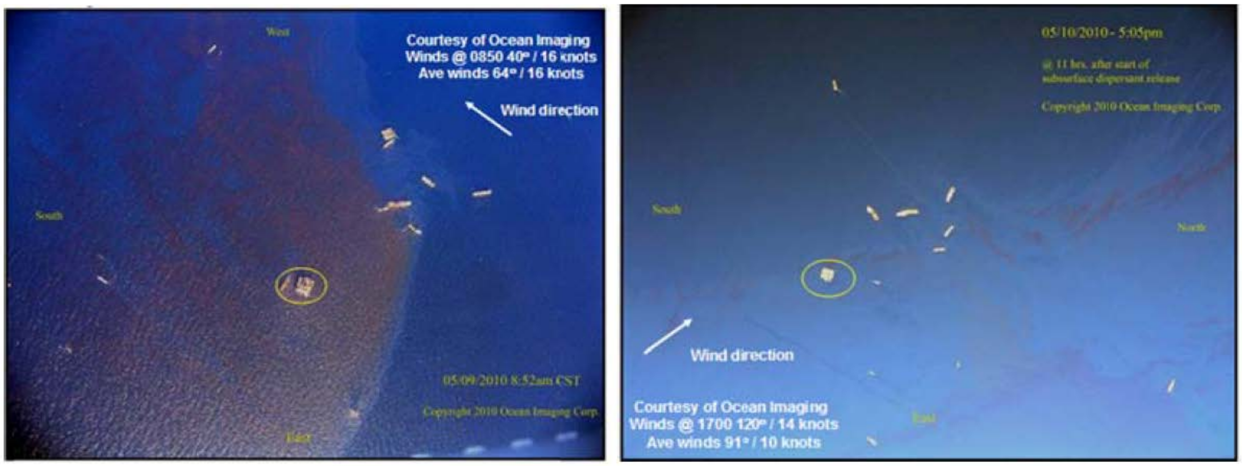

Figure 6-1. Aerial Photos Taken over Macondo Well.
The left photograph was taken before (May 9, 2010), and the right photograph (May 10, 2010) was taken after 11 hours of subsea dispersant injection. Copyright 2012, OTC. Reproduced with permission of OTC. Further reproduction prohibited without permission.

The ultimate fate of oil droplets released from a subsea spill is determined by their buoyancy in the water column. Small oil droplets which are neutrally buoyant can persist as diluted deepwater plumes in the water column for some time. Kujawinksi et al.[51] tracked deepwater plumes of oil by measuring the concentrations of the anionic surfactant dioctyl sodium sulfosuccinate (DOSS), a compound within Corexit 9500 and Corext 9527 (surface application), within the water column during the spill and one month after the spill. Elevated DOSS concentrations were detected in the water column between 1,000 and 1,200 meters in depth indicating that dispersants remained within the subsea oil plume.

The visual observations at the surface and the ocean oil plume previously described in this section suggest that the use of dispersants in deepwater conditions was effective in minimizing the quantity of oil rising to the surface. However, a key component in determining if dispersant use in deepwater conditions is effective would be to characterize the oil droplet size distribution (DSD) with and without dispersant use. Unfortunately, the DSD near the release point was not measured during the Deepwater Horizon spill.

6.4 Simulation and Testing of Dispersants for Subsea Use

This section discusses the simulated and experimental tests that have been conducted to replicate fluid behavior for subsea oil spill conditions. Methods are generally centered on understanding the mechanisms that lead to smaller droplet formation.

6.4.1 Models and Simulations of Subsea Blowout Conditions

Paris et al.[76] conducted a numerical study using the Macondo blowout conditions and concluded that "applying Corexit 9500 at the wellhead may not have significantly changed the amount of crude oil rising to the surface," suggesting that the ejection velocity and associated turbulence-generated oil droplet sizes were already almost neutrally buoyant. The model produced in this study stochastically tracked simulated oil particles released in Macondo blowout conditions from a droplet distribution of 1-300 µm (mean droplet size of 100 µm) for untreated Macondo crude. The DSD shifts when dispersant is applied because of the reduction in interfacial surface tension (IFT). The simulated DSD used for dispersant application was between 20-100 µm. Simulation results indicated that only a 1% to 2% reduction in surface mass can be attributed to the use of Corexit 9500. The authors do suggest that there are likely multiple contributing factors which affect the DSD from subsea blowout conditions that are not captured in their study.

A published comment by Adams et al.[2] on the Paris study argued that the original authors' model assumptions on initial droplet size were not realistic and suggested that the models generated by Johansen et al.[47] would yield droplet sizes on the order of 3-10 mm. Adams et al. also suggested that data collected during a controlled release of hydrocarbons (the DeepSpill project) in 2000 showed droplet sizes in the 1-10 mm range for marine diesel. Paris and Aman responded to the comment provided by Adams et al. stating that further experimental data is needed before scaling the droplet diameter model published by Johansen et al. to uncontrolled deepwater blowout conditions. Paris and Aman suggested that the discharge velocity and shear rates experienced by the oil, as well as dissolved methane content, would likely lead to reduced droplet sizes for untreated crude.

Effective dispersant use is centered on reducing oil droplet size which is directly related to reducing the IFT between oil and its surrounding medium. Simulations conducted by Lindersen[59] using SINTEF's Marine Environmental Modelling Workbench (MEMW) studied the effects that flow rate, gas-to-oil ratio (GOR), and DOR have on droplet size distributions from subsea releases of crude oil from a well in the Norne field. Simulation results showed that increasing the flow rate, increasing the GOR, and increasing the DOR all independently shifted the DSD towards smaller peak droplet sizes. It is important to note that the simulated results modeled the effect of increasing DOR by reducing the IFT.

6.4.2 Experimental Methods for Replicating Subsea Blowout Conditions

Lindersen[59] also conducted subsurface release experiments in SINTEF's MiniTower (open top tank) with Norwegian crude oils, seawater, and Corexit 9500 to determine the particle sizes/distributions with and without dispersant injection. The tank size is 40 cm in diameter and 80 cm tall. The 0.5 mm ejection point was fixed near the bottom of the tank to create a jet and plume. The dispersant was injected into the crude oil nozzle six diameters upstream of the ejection point. Oil droplet sizes were measured near the top of the tank using laser in-situ scattering. The experimental results for droplet size distribution were compared to the simulation outputs from MEMW with good agreement for a fixed DOR of 1:100. IFT measurements of the crude oils and the crude oil/dispersant mixtures were performed by the spinning drop method. A summary of the experimental results are shown in Table 6-1. Lindersen suggests that MEMW could be a useful tool to determine droplet size distribution from a subsea blowout which could help allocate the quantity of dispersant needed for effective oil dispersal. Lindersen also acknowledged that the relationship between viscosity and shear rate, and its effect on oil droplet size distributions, should be further explored for future experiments.

Table 6-1. Lindersen Experimental Results from the MiniTower Tests.[59]

Lindersen conducted experiments to determine the sizes of oil droplets with and without dispersant. The dispersant used was Corexit at a DOR of 1:100, and IFT was measured by the spinning drop method.

Crude Oil	d_{50}, Oil [microns]	d_{50}, Oil+Dispersant [microns]	Viscosity [mPa-s]	IFT Oil [mN/m]	IFT Oil+Dispersant [mN/m]
Alve	259	157	12.5	13 ± 0.7	0.09 ± 0.05
Norne	219	88.2	1968	18.2 ± 0.2	0.007 ± 0.003
Svale	219	128	257	13.3 ± 0.1	0.4 ± 0.2

In a related experiment, Brandvik et al.[17] conducted scaled release tests with crude oil and air in a large (6-m high, 3-m diameter cylindrical) atmospheric "tower" basin filled with seawater. Similarly in this study, crude oil was injected through a nozzle into a stationary volume of seawater within the tower basin. However, this experiment varied the DOR and studied the effect that air injection had on the droplet sizes. Dispersants in this study were injected into the oil flow line 1.5 m upstream of the nozzle. This study reported data for oil droplet size distributions with varying injection rates, nozzle diameters, and DORs. The crude oil used in this study was an Oseberg Blend with a viscosity of 5 cP. While droplet breakup without dispersant addition appeared to follow a Weber number scaling law, dispersant experiments were shown not to adhere to the same scaling. The results showed that droplet sizes were reduced by dispersant injection and that increasing DOR from zero to 1:25 resulted in continuous reduction in droplet size. The results of the experiment are shown in Table 6-2 and Table 6-3.

Table 6-2. SINTEF "Tower" Basin Flow Rate Experiments.[17]

In general the droplet sizes from the flow rate experiments followed the Weber number scaling law.

Nozzle Diameter [mm]	Oil Flow [L/min] (± 0.02)	Air Flow [L/min]	DOR	Exit Velocity [m/s]	IFT [mN/m] (± 0.2)	Peak Diameter [micron]
0.5	0.2	--	--	17	15.5	74.5
0.5	0.5	--	--	42.4	15.5	16.8
1.5	1	--	--	9.4	15.5	280
1.5	1.5	--	--	14.1	15.5	201
2	5	--	--	26.5	15.5	87.9
2	2.5	2.5	--	18.8	15.5	170
2	2.5	2.5	1:150	18.8	N/A	53.5
3	5	--	--	11.8	15.5	280

Table 6-3. SINTEF "Tower" Basin DOR Experiments.[17]

For DORs greater than 1:500 the peak droplet diameter was reduced due to the injection of dispersant.

Nozzle Diameter [mm]	Oil Flow [L/min] (± 0.02)	DOR	Exit Velocity [m/s]	IFT [mN/m]	Peak Droplet Diameter [micron]
1.5	1.2	--	11.3	15.5 ± 0.2	237
1.5	1.2	1:1000	11.3	15.3 ± 0.2	280
1.5	1.2	1:500	11.3	15 ± 0.2	280
1.5	1.2	1:250	11.3	1.7 ± 0.01	237
1.5	1.2	1:100	11.3	0.5 ± 0.01	237
1.5	1.5	1:50	14.1	0.05 ± 0.01	170
1.5	1.5	1:25	14.1	0.09 ± 0.01	87.9

Additional tests conducted within the "tower" basin experiments, with unreported data, were reported to show that pre-mixing of the oil and dispersant (rather than dispersant injection 1.5 m upstream of the nozzle) resulted in further decreased droplet sizes, showing that the dispersant injection method itself is important. Further experiments are currently being conducted in the same apparatus and under a pressurized environment at other facilities in work sponsored by the American Petroleum Institute (API).[30]

Johansen et al.[47] used the results from the "tower" basin experiment to construct correlations for predicting droplet size distributions with and without dispersants. Previous experiments used the Weber number to predict mean droplet size from oil releases but the results did not apply to cases with dispersant injection. A viscosity term was added to the Weber number to account for the use of dispersant and subsequent reduction in IFT. This model has shown to match the volume median droplet sizes from the liquid-only "tower" basin experiments quite well and could also be further modified to account for releases with gas. The use of dispersants in this experiment resulted in Weber number reduction factors from four to eight, with the largest reduction occurring at the highest exit velocity. These large reductions contrast the field-scale DeepSpill data which suggest a reduction factor of only 1.3; however, the velocity in the field experiment was much lower than the laboratory tests. The authors state that the viscosity term has the largest effect on the droplet size distributions in the laboratory tests while gas void fraction and buoyancy are more important in the field-scale experiments.

6.4.3 *Effect of Pressure on Interfacial Surface Tension*

With a historical focus on dispersion of surface slicks, investigation of high-pressure (in deepwater environments) effects on dispersant effectiveness have only recently become of interest in the area of subsea dispersant injection. Abdelrahim[1] reported on work sponsored by BP and the Gulf of Mexico Research Initiative. This study used the pendant drop method to characterize the interfacial tension (IFT) between water/oil/dispersant systems at various pressures (0 to 2,210 psig), temperatures (4.4°C to 24.4°C), water salinities (0%, 1.3%, 2.5%, and 3.7%), and concentrations of dispersant (Corexit 9500) dissolved into the water or the oil phases. The oil used in this experiment was "dead" Macondo crude.

Abdelrahim's results showed that, with dispersant dissolved into a 2.5% salt water phase at 4.4°C, IFT reduction by 1,000-ppm dispersant was somewhat reduced as pressure increased.

That is, the IFT value of the dispersant+water and crude oil interface increased slightly as pressure was increased from 0 to 2,200 psig, as shown below in Figure 6-2. This same trend was not observed when tested with n-Octane and 1,000 ppm dispersant dissolved into 2.5% salt water. The author does not provide an explanation for the differences between the crude oil and n-Octane IFT measurements as a function of pressure.

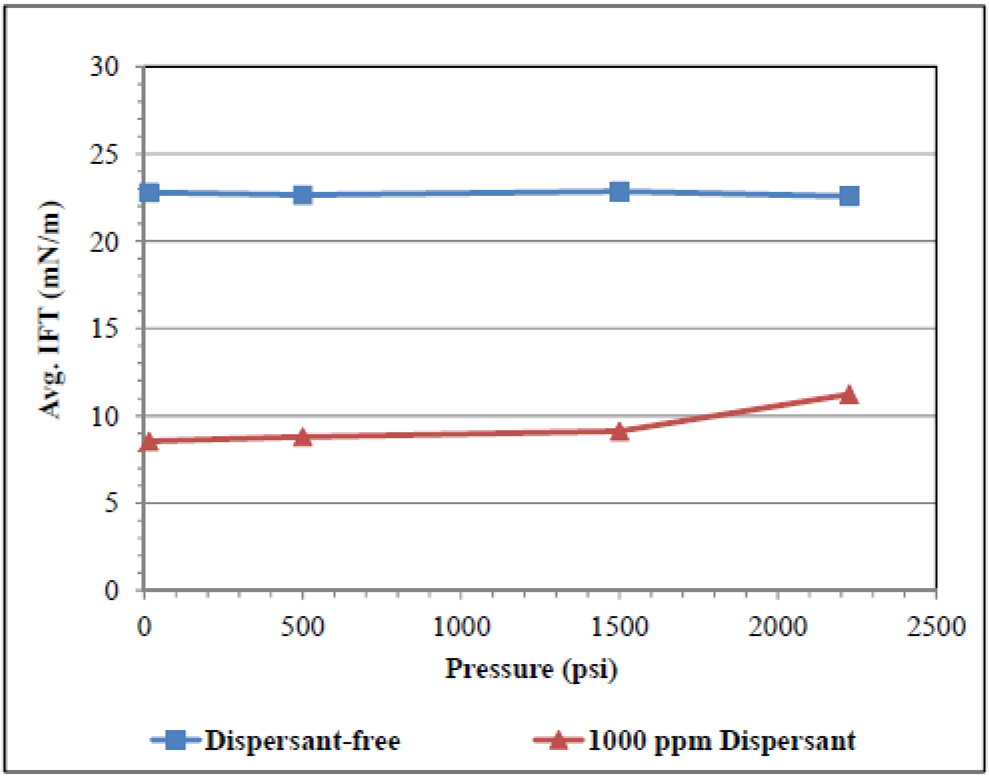

Figure 6-2. Effect of Pressure on IFT Between Crude Oil and 2.5% Salt Water at 4.4°C.
Abdelrahim[1] conducted interfacial tension (IFT) measurements using the pendant drop method in pressurized oil-water-dispersant systems with Corexit 9500.

It should be noted that, due to limitations on the pendant drop apparatus used, Abdelrahim was unable to take measurements at interfacial tension valves lower than 8 mN/m (i.e., DORs above 1:1,000). This is one to two orders of magnitude lower dispersant concentration than other authors have expected to be used in subsea applications. Similar experiments (IFT vs. pressure) should be conducted at lower interfacial tension values (higher DOR).

Abdelrahim additionally acknowledges the fact that measurements of IFT are sensitive to the light ends (live oil from a subsea blowout) which would likely improve dispersant effectiveness. The effect of pressure on IFT when dispersant was dissolved into the oil phase was not studied. Another area which was not studied is the effect that salinity has on measurements of IFT at subsea pressures. Another interesting outcome from a similar experiment would be to better understand the relationship between IFT, DOR, and dispersant types at different pressures.

6.4.4 *Effect of Solution Gas and/or Free Gas*

The presence of "live" oil solution gas (light ends of crude oil only present as liquids at high-pressure conditions such as those present at a subsea blowout) ensures that the chemical makeup and physical properties of a live fluid vary drastically from those of the "dead" oil at the surface. This aspect of subsea dispersant effectiveness is yet to be investigated.

Brandvik et. al.[17] was not able to draw any conclusions with the combined gas and oil release experiments because the air contributed very little to the momentum of the fluid because its density is much less than the oil used. The addition of a flowing gas content (free gas) in the areas of subsea dispersant injection, dispersant mixing, or effluent discharge in a subsea blowout could additionally affect the effectiveness of dispersants injected subsea. Research efforts in this area are ongoing.[17]

With the presence of free gas, or even live oil solution gas, in a subsea oil discharge, the potential for hydrate formation exists. Preliminary research conducted in high-pressure water tunnels at the Colorado School of the Mines[43] and the Department of Energy's National Energy Technology Laboratory (NETL)[3] have shown, however, that hydrate formation is delayed until a certain condition of gas saturation within the surrounding seawater is met. It is expected that this condition will not be easily met in most subsea releases (which include large volumes of seawater) and that hydrate formation processes are not likely to interfere with dispersant application. The complete effects of free gas, solution gas, and/or hydrate formation are currently unknown. Current research projects are attempting to assess dispersant/hydrate interactions, including a project sponsored by BSEE (BSEE TAP Project Number 698).

6.5 Future Research for Subsea

Dispersant application in deepwater subsea environments is not well understood in terms of its effectiveness in reducing oil droplet size and subsequent particle buoyancy in the water column. Visual results for dispersant effectiveness in the Deepwater Horizon spill contradict simulations based on predicted oil droplet sizes suggesting that physical mechanisms which affect droplet size distribution have yet to be correlated. Most of the subsea application field data collected from the Macondo incident is visual or qualitative and does not provide information for model development or verification. Measurements of IFT and DSD from the Macondo ejection flow would have provided valuable data for oil spill research and subsea dispersant injection strategies.

The ultimate goal in the use of dispersants in subsea conditions is to reduce the interfacial surface tension of oil in the water column which would lead to smaller neutrally buoyant droplets that could be broken down through natural processes. However, the term dispersant effectiveness has not been standardized in subsea applications. Correlations for the relationship of droplet size to DOR have yet to be developed experimentally for subsea applications. In particular, the effect of oil type, varying DOR, the effect of dissolved and free gases, and dispersant type are topics of ongoing research. Published dispersant effectiveness studies are mostly centered on the use of Corexit 9500 and liquid-only releases in atmospheric tanks. Future studies could benefit from pressurized testing in using multiple oil types, dispersants types, and the introduction of gas.

The relationship between IFT and DOR is also not well established and may vary with application method and for different oils and dispersants. Laboratory experiments determine IFT from oil samples taken from within the plume which in real cases may be impractical. Predicting IFT to a given DOR for subsea conditions would likely be very useful in spill mitigation strategies. Therefore, IFT measurements with a variety of oils premixed with different DORs could help establish general operating guidelines for dispersant use in subsea deepwater multiphase conditions.

Dispersant mixing and pretreatment is another area of research which is likely to bear easy fruit. Brandvik et al.[17] stated that much lower droplet sizes have been observed for oil that is sufficiently premixed with a dispersant, suggesting that more development length is needed for maximum dispersant effectiveness. Therefore, studying different dispersant types and mixing strategies would likely yield valuable results for future spill mitigation in terms of DOR and injection location. Researchers have also noted the importance of the relationship between fluid shearing mechanisms and droplet size due to choked flow, free-gas within the release, and ocean currents at the ejection point. Experimental results for liquid-only tests have shown that increasing the ejection velocity leads to a reduction in the mean oil droplet size in a subsea blowout. Verification of droplet size models that incorporate these turbulent mixing mechanisms could better predict the proper DOR given the spill conditions.

BSEE's Oil Spill Response Research (OSRR) Program has funded several research projects for Fiscal Year 2013 regarding subsea dispersant effectiveness. OSRR Project 1001 (contracted by the U.S. Environmental Protection Agency and Center for Offshore Oil, Gas, and Energy Research – COOGER, Canada) is intended to study the effects of dispersant on droplet-size distributions and evaluate dispersion effectiveness as a function of oil type, flow rate, and DOR. OSRR Project 1003 (Contracted to S.L. Ross Environmental Research Ltd. and Applied Research Associates, Inc.) is intended to conduct bench-small-scale experiments to investigate the role of natural gas in the gas-dispersant-water-oil system and conduct large-scale dispersant effectiveness testing at Ohmsett. OSRR Project 1011 (contracted to S.L. Ross Environmental Research Ltd.) is intended to identify subsea dispersant injection research needs and the feasibility of conducting such research at Ohmsett. Currently no public reports are available for these projects to be summarized in this report.

7. TESTING METHODS FOR DISPERSANT EFFECTIVENESS

Many methods have been devised for testing the effectiveness of dispersants. These include both quantitative as well as qualitative “ranking” methods. No consensus on a single best-practice test method has yet been reached by government or industry. In part, this is due to poor understanding at present of the important factors that influence effectiveness, as well as the interrelation of these factors. The definition of effectiveness itself has not been firmly established either, and different test methods use different ways of characterizing this parameter. This can include basing effectiveness on the:

- Interfacial surface tension value,
- Quantity of oil remaining in a slick,
- Water column concentration of dispersed oil, or
- Dispersed oil droplet size.

These measurements may be taken at a pre-specified time, periodic intervals, or followed as a function of time. In addition, they may be measured in dynamic system states in order to determine the effect of mixing energy on the results.

The following chapter provides an outline and brief description of various testing methods that have been used since the early 1980s to gauge the effectiveness of chemical dispersants. These have been grouped into bench-scale laboratory methods, mid-to-large facility methods, field-testing, and numerical simulation. The chapter closes with a summary and comparison of the test methods discussed.

7.1 Bench-Scale Laboratory Test Methods

As the name implies, bench-scale laboratory testing includes dispersant performance evaluations that can be conducted on a small scale, without major investment in capital equipment or facilities. Apparatus for testing generally includes some type of small container that is filled with either premixed water/oil, or with the oil added to the top of the water to emulate a slick. Dispersant may be added premixed or directly to the oil. Mixing energy is generally applied to the system prior to effectiveness measurement, though not for all bench methods. The following section outlines the various test methods.

7.1.1 Interfacial Surface Tension Measurement

It is well-known that dispersants operate by reducing the oil-water interfacial tension (IFT), which allows mixing energy to break up the oil into small droplets that can be subsequently dispersed into the water phase. Thus, a simplistic approach to defining effectiveness is simply to measure the IFT, and then compare dispersants based on this value. The drop-weight test and spinning drop test operate under this assumption. Such tests do not attempt to directly include the effects of mixing energy in ranking dispersants.

In the drop-weight test,[1, 78] dispersant is premixed with water in a vial. A pre-weighed amount of oil is then placed in a syringe, and the end of the syringe tube is submersed in the dispersant/water mixture. Gas pressure is then applied to the top of the syringe, causing injection of a drop of the oil into the mixture. The oil drops are allowed to grow slowly prior to detachment. Following detachment, the remaining oil is weighed to determine the drop weight.

Drop weight versus dispersant concentration is plotted to generate a Critical Micelle Concentration (CMC) curve. The CMC point is defined as the intersection where the slope changes between two linear lines drawn through the data. The oil drop weight differences up to the CMC are proportional to the interfacial tension (IFT) of the oil-water.

In the spinning drop test for dispersants,[1, 62] dispersant, oil, and water are premeasured and placed in a separatory funnel. This is shaken, and then allowed to settle for at least 6 hours. Samples of the oil layer and water layer are subsequently taken and the IFT measured using a spinning drop test apparatus. The apparatus operates by injecting an oil drop into a glass tube filled with water and observing its shape while spinning in the horizontal water column. Length and diameter of the drop are controlled by centrifugal and interfacial tension forces. Measurement of droplet length and predetermination of the droplet volume allow calculation of the IFT.

7.1.2 Rotating Flask

The rotating flask test is one of the earliest lab-scale tests that attempts to include mixing energy effects. The apparatus consists of flasks resembling separatory funnels, which are filled with a small volume of seawater. Oil is added to the surface of the water, followed by the dispersant added drop-wise to the surface of the oil. The flask opening is closed and then placed in a rotating machine. After a period of agitation, a sample of the water is extracted and the oil content measured. Various adaptations of the rotating flask test exist. Some of the most well-known include the Labofina test,[6, 21] Warren Spring Laboratory (WSL) test,[82, 85] and the Exxon Dispersant Effectiveness Test (EXDET).[5, 22]

The Labofina and WSL tests are comparable, with slight modifications for geometry of the flasks. These tests use 250 ml of seawater, to which is added 5 ml of oil, and then 0.2 ml of dispersant (resulting in a 1:25 DOR). The flask is rotated for two minutes at 33 rpm and then uncorked. Note that the rotational trajectory is about the horizontal axis at right angles to the longitudinal axis. After a one-minute standing period, 50 ml of oily water is extracted from the bottom of the flask. The oil is then extracted into chloroform and the amount of oil determined spectrophotometrically. The efficiency index is expressed as a percentage of the oil that would be present if it were uniformly distributed throughout the water at the time of sampling.

While the EXDET test is similar to the Labofina/WSL tests, several important changes to the procedure should be noted. Four flasks are used for this test, all filled with 250 ml of seawater. To each of these is added 1 ml of oil and dispersant premixed to the desired DOR. The flasks are then agitated on a wrist-action shaker for 15 minutes. While still shaking, sorbent pads are added and allowed to remain for five minutes. The water is then drained and the dispersed oil extracted with chloroform. Non-dispersed oil remaining in the flask and pad is then extracted and the oil filtered out. The percentage of dispersed/undispersed oil is then calculated based on spectrophotometric measurements of the oil.

Unlike the Labofina/WSL testing, the EXDET test allows for a mass balance of the oil to be obtained and eliminates the need for an extraction curve for each oil sample. In addition, the creators of this test claim the wrist-action shaker to be more realistic of sea states than the Labofina/WSL vessel motion.[5] Finally, since the sample is collected under dynamic conditions, this eliminates the uncertainty associated with settling time. Uncertainty is also bounded by the fact that the four tests are conducted simultaneously, and standard deviation of results may be computed.

7.1.3 Swirling Flask

The swirling flask test (SFT) apparatus consists of a 125-ml Erlenmeyer flask with a side spout, as shown in Figure 7-1. The side spout allows for removal of sub-surface sample volumes at the bottom without disturbance of the top surface oil layer. The original procedure[31] formulated by Environment Canada for dispersant evaluation with SFT prescribed the addition of 120 ml of seawater to the flask, followed by 0.1 ml of a premixed dispersant/oil solution with a DOR of 1:25. Agitation was then performed for 20 minutes on an orbital shaker table at a specified shaking rate (e.g., 150 rpm) to induce a swirling motion in the flask. After shaking, the flask was allowed to settle for ten minutes, and then a 30 ml water sample was collected through the side spout. Oil concentration in the water was then analyzed via spectrophotometer.

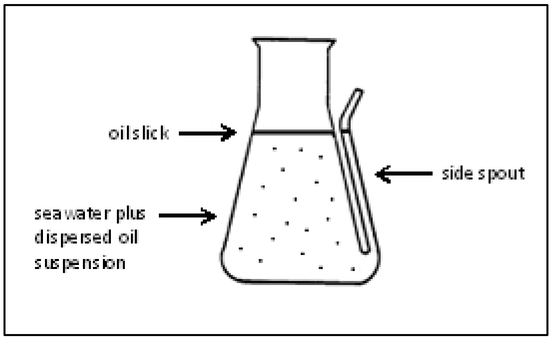

Figure 7-1. Swirling Flask Testing Apparatus. Adapted from 40 CFR 300.[70]
The sided spout on the flask allows for removal of sub-surface sample volumes without disturbance of the top oil surface layer.

Modifications to the initially-proposed SFT have been recommended over the years. These include the addition of unmixed oil first to the water, followed by one to two drops of dispersant on the oil slick.[34] This was suggested as more representative of actual herding effects of the oil by the dispersant, where surfactant molecules orient at the liquid surface and push aside the oil, thus reducing the interaction between the surfactant molecules and the oil.

A formal effectiveness measurement protocol was adopted by the EPA in 1994,[87] which required dispersants to pass a version of the SFT for eligibility to be listed on the NCP Product Schedule. Acceptance was based on dispersants showing at least 45% efficiency in dispersing South Louisiana crude and Prudhoe Bay crude oils. However, the official SFT was reexamined after the first year of use due to complaints that large discrepancies were being observed between test data of dispersant manufacturers and EPA contract laboratories.[37, 46] Some of the problems identified included: calibration standards outside detection limits of analytical instruments, inappropriate settling time, too stringent pass/fail criterion, insufficient energy addition by the shaker, and movement of the flask side arm tube causing variable results.

In 1997, the California Office of Spill Prevention and Response (OSPR) undertook a further modification of the EPA's standard SFT.[10] The side arm was removed from the bottom sampling location, and stopcocks were placed at the flask top and at the bottom sampling opening. In addition, dispersant was not premixed with oil for this protocol, but added drop-wise to the top of the oil slick. Samples were stored at -10˚C until analysis could be performed via gas chromatographs equipped with flame ionization detectors. Results showed the OSPR method to have substantially higher percent efficacy estimates compared to those of the EPA SFT.

7.1.4 Baffled Flask

Due to the problems described in the previous section with the EPA swirling flask test,[46] a new protocol with better reproducibility was sought. A sensitivity study of the various factors impacting SFT variability was carried out,[83] and a new testing method was proposed based on redesign of the flask. The new flask design consisted of a 150 ml baffled trypsinizing flask similar to those used in biological science research and clinical laboratory testing.

The procedure itself for the new Baffled Flask Test (BFT),[91] is similar to the SFT – 120 ml of seawater is first added to the flask, followed by 0.1 ml of oil, and then 0.004 ml of dispersant onto the top of the oil slick (DOR of 1:25). The flask is then placed on an orbital shaker for ten minutes at a speed of 200 rpm and then allowed to settle for ten minutes. Sampling is then conducted by draining and discarding the first 2 ml of water and then collecting the next 30 ml. The sample is subsequently analyzed for oil concentration via spectrophotometer.

Studies have shown the BFT to be an improvement on the former SFT as a measure of dispersant effectiveness. When the SFT flask is rotated on an orbital shaker at 150 rpm, very little mixing occurs, which is uncharacteristic of the over-and-under type of wave action at sea. Kaku et al.[49] used hot wire anemometry to characterize the mixing dynamics occurring in SFT versus BFT over five rotational speeds. It was found that movement in SFT is two-dimensional in nature, changing from horizontal at low speed to axisymmetric at high speed. However, the BFT fluid movement was three-dimensional at all speeds, which is more representative of flow at sea. Venosa et al.[91] performed a detailed round robin evaluation of the BFT for reproducibility and repeatability. This was funded as part of a qualification study to replace the SFT with the BFT for EPA acceptance testing. Nine independent analysts were used to conduct testing on 18 dispersants and two crude oils. This showed that the BFT gave much more reliable data than the SFT. The repeatability error was composed primarily of experimental error, instead of inherent error of the method.

7.1.5 IFP Dilution

The Institute Francais du Petrole (IFP) test is a dynamic flow-through test developed for assessing the effectiveness of dispersants.[13] A ring beating up and down in the test vessel at a prescribed frequency of 15 cycles/min is used to transmit energy into the water column. The transmitted mixing energy is thought to be representative of low wave energies (2-5 m/s wind speed) for open sea conditions.[18]

Figure 7-2 shows the components that make up the IFP testing apparatus. This includes an experimental beaker, which contains the beater that supplies the mixing energy. An electo-magnet is used to power this beater and is set with a programmable timer. Upstream of the experimental beaker is the pure water storage container, which can be fed to the beaker via a peristaltic pump.

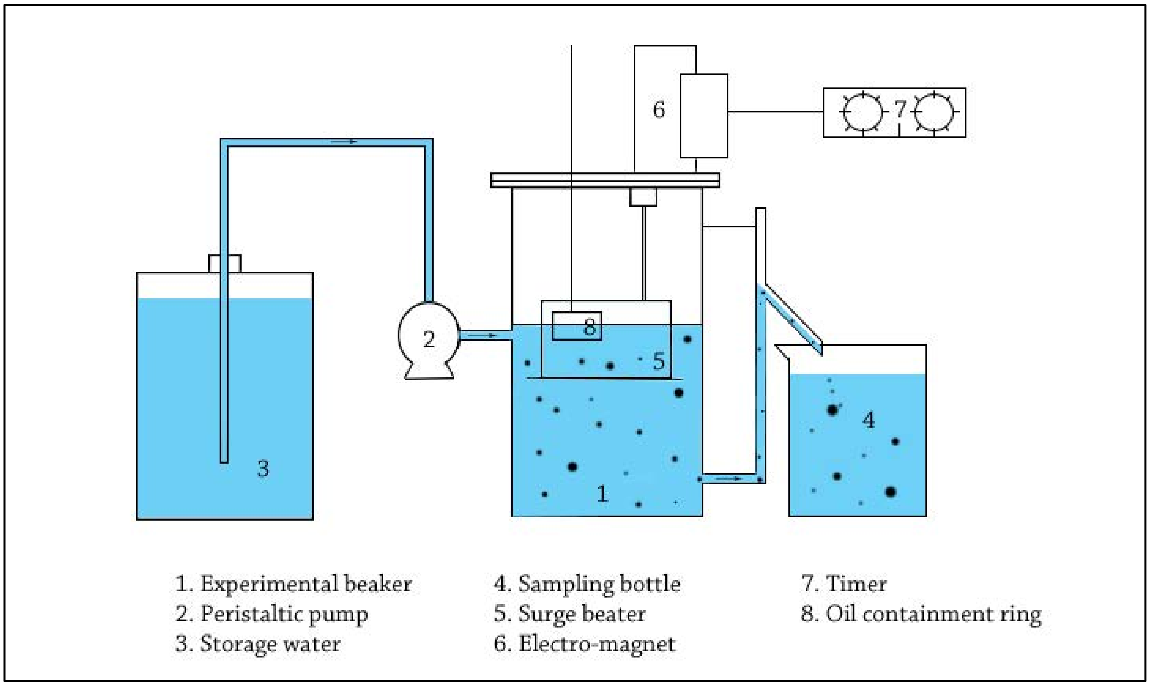

Figure 7-2. IFP Testing Apparatus. Adapted from Brandvik.[18]
Effectiveness of the IFP test is based on the percentage of oil washed out in a given period of time relative to the maximum amount of recoverable oil in the same time.

The test begins by filling the experimental beaker with 4.5 liters of seawater and then starting the pump with a flow rate of 2.5 ltr/hr. Once the beaker reaches 5 liters of volume, offtake through the overflow pipe is started. The system is allowed to equilibrate for ten minutes, after which the containment ring is submerged to half its depth. Four grams of oil are then deposited on the water surface inside the ring and allowed to stand for three minutes. The dispersant is then added to the oil surface as evenly as possible. One minute after start of the dispersant addition, the containment ring is removed, and the beater is simultaneously started. A sample bottle is placed at the outlet of the overflow pipe to recover water and dispersed oil. After collecting water for 60 minutes, the flow is stopped and the sampling container removed. Oil within the sample container is filtered out and weighed. Effectiveness of the dispersant is then computed as the percentage of oil washed out relative to the maximum amount of recoverable oil in the same time under theoretical conditions of an immediate pseudo-solubilization.

The IFP dilution test continues to be used as an effectiveness measurement for dispersants. It is a relatively simplistic and cost-effective test that allows a realistic approach to dynamic conditions found offshore. The 1995 work of Brandvik et al.[15] used the test to study 14 dispersants under arctic conditions with water salinity variation between 0.5% and 3.5% at 0˚C. Such testing would be very difficult to control in mid-to-large facility testing, but was achievable with this bench-scale test apparatus. Similarly, dispersant testing over a wide salinity range was also conducted more recently in the 2010 “Oil on Ice” JIP study.[18]

7.1.6 MNS

The Mackay-Nadeau-Steelman (MNS) test[60] has been designed to provide realistic mixing energy in the form of wave action, while retaining a simple procedure and minimizing the necessary equipment. Mixing energy in this method is supplied by forcing air across the oil-water surface to produce a circular wave motion. Wave heights typically range from one to six centimeters. The test has been said to correspond with a medium to high sea-state condition.[18]

Apparatus for the test consists of equipment shown in Figure 7-3 The test is performed using a glass tank inside a temperature-controlled water bath. The Plexiglas lid on the tank has ports for (1) oil collection, (2) oil addition, (3) thermometer insertion, (4) dispersant addition, (5) inflow of air, and (6) outflow of air. Air is precooled by passage through an ice-water bath. Pressure drop in a pressure plate manometer upstream of the inlet to the test chamber is monitored in order to reproduce agitation levels between the tests.

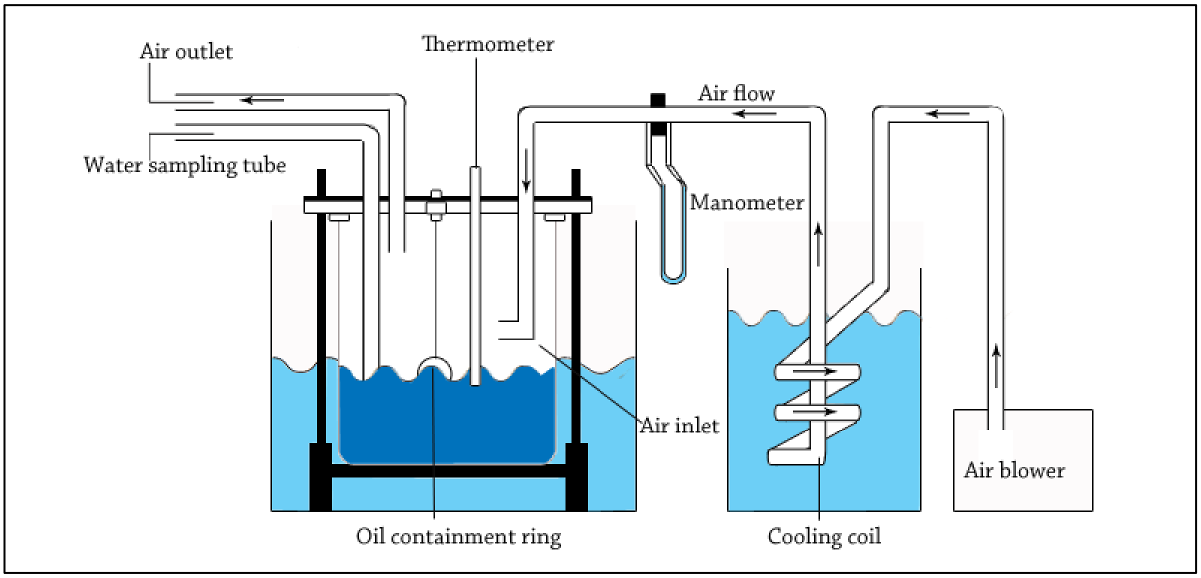

Figure 7-3. MNS Testing Apparatus. Adapted from Brandvik.[18]

Through a bench-scale test, the MNS procedure uses wave action generated by a forced air current for mixing energy addition – similar to open sea.

The test is performed by first adding a volume of seawater to the tank, followed by oil and either diluted or undiluted dispersant. A one-minute soak period is allowed for the dispersant to penetrate the oil, after which the oil containment ring is removed and the air flow is turned on. After ten minutes of wave agitation, a 500 ml sample of water is acquired and analyzed for oil concentration via spectrophotometry.

Comparison of MNS tests using two different protocols showed very different results in the laboratory studies of Daling and Lichtenthaler.[29] Testing was performed at the first laboratory with a DOR ratio of 1:10 and sampling after a five-minute static period. At the second laboratory, a DOR of 1:100 was used, and all of the sampling occurred under dynamic conditions. Results indicated no correlation between the two testing methods, independent of oil type. The authors noted that even small changes in previous works have led to major differences in results. The two procedures produced results that are thought to reflect different mechanisms of dispersion. Under static conditions, much of the oil had formed larger droplets that rose to the surface by the time of sampling. Thus, the mixing energy parameter was far different compared to the case of sampling under dynamic conditions.

7.2 Mid-to-Large Facility Test Methods

Much discussion has surrounded the validity of bench-scale testing of dispersant effectiveness. While relatively simple and cost-effective, replication of sea state oil spreading, mixing energy mechanisms, and dispersant application are limited. Therefore, mid-to-large facility test methods have been designed to address these concerns. This section provides a discussion of basin/mesocosm, standard EPA, flume, and wave tank testing methods.

7.2.1 Basin Test/Mesocosm

Basin and mesocosm tests are the simplest dispersant effectiveness measures among the facility-scale methods. Essentially, basin testing involves containing a large volume of static seawater and either pouring or spraying oil on the surface. After the oil layer is established, dispersant is added either in neat or diluted form. Like the bench-scale interfacial surface tension tests discussed in Section 7.1.1, mixing energy effects are not considered in the dispersant effectiveness measure. Rather, oil spreading and weathering effects are the primary focus. A major disadvantage of outdoor basin and mesocosm tests is that they do not allow for any control of environmental conditions.

In the recent work of King et al.,[50] lab basin testing has been used to address interfacial film formation and its effects on the spreading rates of oil. Previous studies had reported the presence of surface films that formed in test facilities as an artifice of the bounded/confined nature of the methods. It was thought that walls restrict the spreading of surfactants on the surface of the water, which results in the surface film formation. The study of Nedwed and Coolbaugh[73] showed such unwanted surface films affect the thermodynamics of oil spreading on seawater, and thus, may interfere with the controlled testing of chemical dispersants in a facility environment. King et al. confirmed that lab basin seawater contaminated with oil under static conditions does produce an interfacial film. Film formation was driven by molecular diffusion, and was seen to affect the kinetics of oil spreading on the water. The films produced thicker oil slicks that required greater energy to disperse. As noted by the authors, when oil is naturally dispersed, there appears to be no interfacial film formed.

Experiments by Joo et al.[48] were carried out in a mesocosm, where nine bags 5 meters in depth and 0.5 meters in diameter were first filled with 1,000 liters of seawater. Three of the bags then had 1 liter of oil added, and three bags had 1 liter of premixed oil and dispersant added. The bags were placed in the ocean attached to a floating pier for 77 days. Evaporation, dissolution, and dispersion were all identified as major weathering processes for the oil, though evaporation was by far the most significant. Comparison of mass balance data from laboratory studies and the mesocosm experiment showed laboratory testing to severely under-predict water column hydrocarbon concentrations. The authors suggest that more studies are needed to resolve these differences between mid-scale facility testing and bench-scale testing.

7.2.2 Revised Standard EPA Test

Prior to adoption of the Swirling Flask Test (SFT), the US Environmental Protection Agency listed the Revised Standard EPA as the approved acceptance method for dispersant testing on the Federal Register.[87] Thus, much of the test data prior to 1994 is based on this method. As depicted in Figure 7-4, the test utilizes a large stainless steel tank. A total of 130 liters of 25 ppt seawater is first added to the tank, followed by 100 ml of oil placed within the containment cylinder at the center of the vessel. Dispersant (3, 10, or 25 ml) is then added in a fine stream over a one-minute period. Mixing energy is added by using a centrifugal pump to spray water onto the dispersant/oil mixture for a one-minute period as the containment ring is removed. After initial mixing, the tank water continues to recirculate from the top to the bottom of the tank. Oil samples are removed from the bottom of the tank after (a) ten minutes and (b) two hours of recirculation. Oil concentration in the water is analyzed using spectrophotometry for gauging dispersant effectiveness.

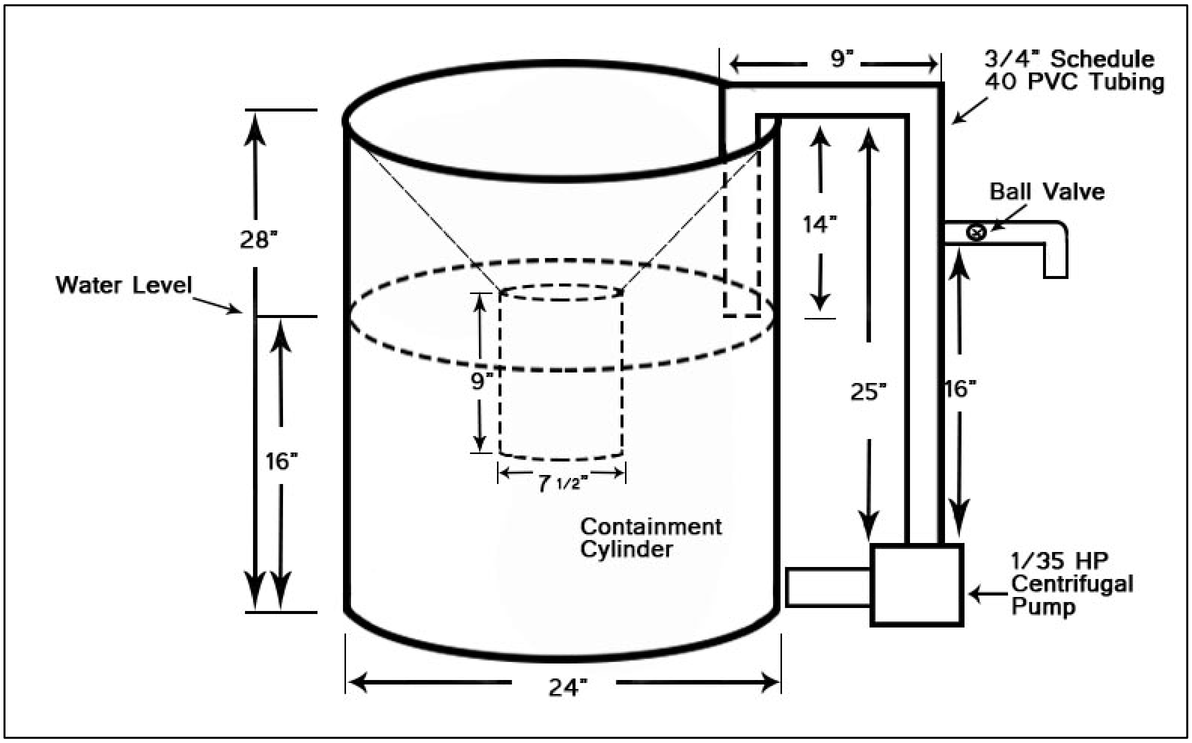

Figure 7-4. Revised Standard EPA Testing Apparatus. Adapted from Clayton.[27]
As shown in the figure, mixing energy is applied to the system by recirculating the liquid from bottom to top using a centrifugal pump.

After the EPA adoption of the test in 1984, various problems with the test were identified, including a need for (1) better reproducibility of the mixing energy application method, (2) use of a mixing energy source that more closely simulates wave and tidal action, since the circulating pump creates additional interfaces via shear effects, and (3) development of a sampling method that eliminates the need for the circulation pump and associated tubing.[26] Modifications to the test proposed by Woodward-Clyde Consultants and SRI International[98] included using a low shear paddle stirrer to replace the circulation pump and adding sampling ports to the tank wall. Shum[79] further proposed changing the shape of the tank from round to square, while reducing the overall capacity to 38 liters. The dimensions of the proposed tank were based on sizes of the largest turbulent eddies estimated to occur for small-scale turbulence structures in the ocean. The square design was intended to minimize vortex formation during propeller operation. Overall, the revised standard EPA testing method is no longer widely-employed for dispersant effectiveness testing.

7.2.3 *Flume*

The flume test was one of the first methods attempting to replicate field tests using wave and current action. Essentially, it consists of a looped system in which water is continuously circulated and waves generated. One of the earliest systems was designed with a system of cascading weirs, as shown in Figure 7-5. Depending on flow rate and the angle of inclination, either regular or breaking waves can be generated. In the testing conducted by Mackay et al.,[61] weir slopes of 20:1 up to 100:1 were used on their flume.

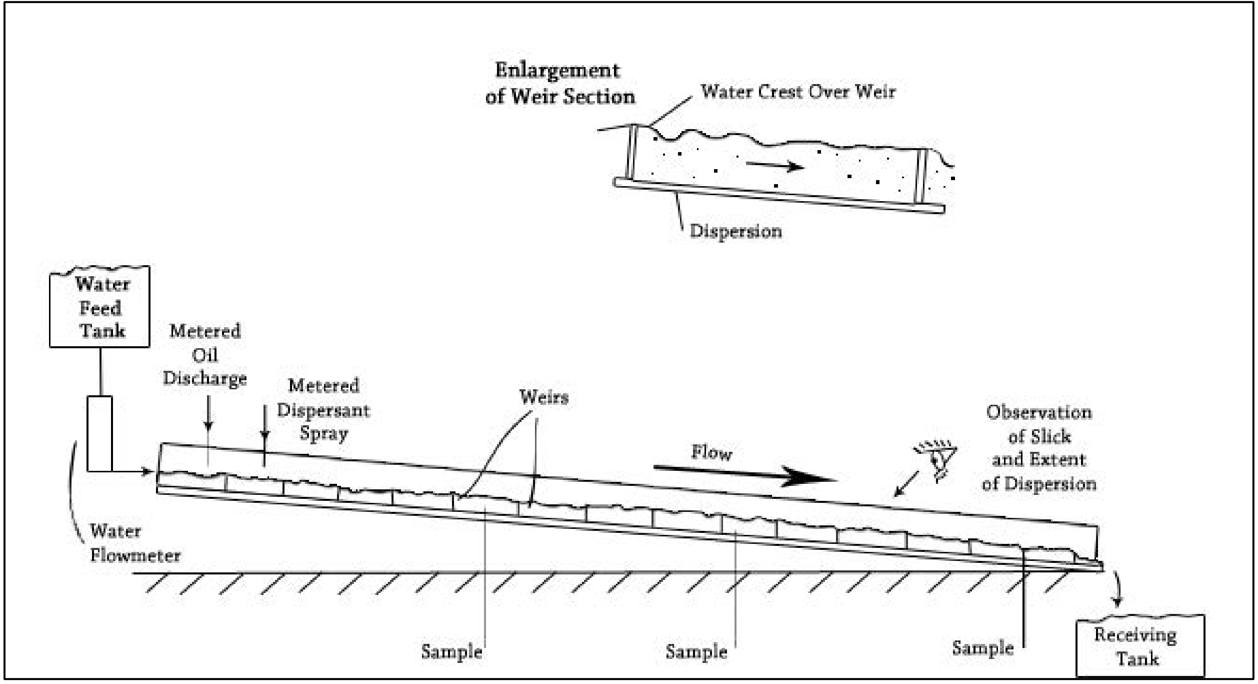

Figure 7-5. Flume Testing Apparatus. Adapted from Clayton.[27]
This flume setup uses a system of cascading weirs to generate waves as water flows.

For testing of dispersants, oil is discharged on the water surface at a continuous rate to produce a slick that is carried down the flume. Dispersant is sprayed onto the oil at a prescribed rate to achieve the desired DOR. This spray action is similar to that performed from a ship. Analysis of dispersant effectiveness is performed using a variety of techniques. Water samples are collected at various points along the flume and analyzed for oil content and drop size. The oil slick is visually observed and photographed to study changes along the length of the flume in relation to mixing time after dispersant addition. Turbulence measurements using laser Doppler velocimetry may also be made in order to relate these to local mixing energy. Daling and Lichtenthaler[29] compared results from the flume testing with those of the MNS method and field-test data. Relatively good correlations between results were found. However, it is noted that the energy level in the flume test is thought to be closer to that of actual sea conditions (lower turbulence) compared to the MNS test.

7.2.4 *Wave Tank*

Researchers are continually seeking better ways to study dispersant effectiveness under controlled conditions in a laboratory setting. The ability to reproduce conditions at sea is very challenging due to the many variables involved and their interdependencies. Wave tanks are an increasingly popular option for dispersant study, since the wave motion can be controlled to reproduce both the plunging and breaking waves observed at sea. There are multiple wave tank facilities that have been used for dispersant effectiveness study. These include the Shoreline Environmental Research Facility (SERF) of Texas A&M University,[14] the EPA/BIO facility at the Bedford Institute of Oceanography in Nova Scotia[50, 55, 56, 92, 96], the National Oil Spill Response Research and Renewable Energy Test Facility (Ohmsett) of BSEE[7, 81, 86], and the S.L. Ross indoor wave tank facility in Ottawa.[72]

Wave tanks are generally long, rectangular, and shallow (1 to 3.5 meters) in comparison to the open sea. Some type of paddle/flapper is located at one end that can be programmed to generate waves at reproducible frequency and amplitude. Often, wave absorbers are located at the far end to dampen waves in order to prevent reflections from affecting experiments. A common procedure for dispersant effectiveness experiments is to place oil within a containment ring a short distance from the wave generator.[50] Dispersant is then sprayed onto the surface of the oil to achieve the desired DOR. Oil thickness is maintained inside the containment ring until the approach of the first wave. At this point, the containment ring is removed, and the experiment officially begins. The mixing zone is generally located about midway down the tank.

The mixing energy imparted to the waves controls whether the waves become plunging or breaking in nature. Early wave tank studies used a "dispersive-focusing" technique to create breaking waves, where wave frequencies were decreased until achieving breaking wave convergence at a single point. This resulted in a single dramatic breaker that could not be reproduced until the system was brought back to quiescent equilibrium. However, the "frequency sweep" method is now commonly employed, which generates breaking waves at regular intervals to better mimic wave action at sea.

Effectiveness determination in wave tank testing can be based on a variety of techniques, since the wave tank offers a high level of versatility. Water samples for analysis of oil concentration are often obtained at multiple depths and distances from the wave maker. Dispersed oil droplet size distributions can also be measured using a laser in-situ scattering and transmissometry (LISST) particle size analyzer.[55,56,72] High accuracy wave gauges can be used to measure water level in response to wave height changes.[96] In addition, acoustic Doppler velocimetry[96] or hot wire anemometry[92] can be used to gain information on local turbulence levels.

The primary disadvantage of wave tanks is the fact that they are closed environments with wall effects that are not representative of open sea conditions. Mechanisms have been developed to minimize these effects. For instance, bubble curtains have been constructed with tiny perforated holes along tank walls to prevent oil adherence to the sides of the tank during testing.[92] Also, flow-through tanks have been designed to prevent back-flowing underwater currents that have been shown to arise when operating a wave tank in batch mode.[56] King et al.[50] investigated the potential for interfacial film formation in wave tanks, which was shown to be a problem in lab basin testing. Basin testing revealed surface films affect the thermodynamics of oil spreading, and can interfere with dispersant effectiveness results. The authors found that the higher surface area-to-volume ratios of water and higher wave energy of wave tank tests reduced the probability of interfacial film formation compared to lab basin tests. However, the results indicated one hour was needed before the mixing energy in the wave tank negated all influence of the interfacial film on the chemical dispersant effectiveness. Thus, interpretation of data from closed wave tanks may be difficult, since the time required to wait until dissipation of surface film effects will be dependent on the system design and mixing energy of each particular test. In conclusion, the authors advocate using surface tension measurements to detect the presence of surface films for quality assurance purposes in closed system laboratory testing.

7.3 Field-Testing

Field-testing is often seen as the paradigm of dispersant effectiveness measurement, since it is directly representative of oil spills at sea – unlike laboratory testing, which attempts to correlate data using similarity assumptions. However, major disadvantages to the field-testing have been acknowledged to include the high cost and complexity for carrying out experiments, environmental concerns over the intentional release of oil and dispersant, and lack of control over environmental variables. The last point is especially important, since it means an experiment can never be truly replicated.

While field trials are unlikely to be part of any standard dispersant effectiveness testing requirement, they do provide valuable insights into the assumptions and scalability of other laboratory approximation methods. The data have been widely-used for calibration/ benchmarking of laboratory and mesoscale experiments.[29, 38, 86] Field trials generally consist of a controlled release of a pre-specified volume of oil into the sea. Dispersant (neat or diluted) is then sprayed onto the surface, and its effectiveness monitored.

In 1989, Fingas[33] provided a review of 106 field studies that had been conducted with dispersant applications. Though field trials have continued since then, evaluation techniques of dispersant effectiveness remain much the same. According to Colcomb et al.,[28] there are two basic ways of quantitatively measuring effectiveness at sea – (1) measure the total amount of oil that remains on the sea surface as a function of time, or (2) measure the amount of oil dispersed into the water column as a function of time. However, the author states in his 2005 work that, "Unfortunately, it is impossible to accurately conduct these quantifications with currently available techniques, or attempting to do so will unduly influence the dispersion process." Complications for estimating dispersant performance in field trials can include: uneven application of the dispersant, differential spreading of oil into varying thicknesses, irregular patterns of dispersed oil plumes beneath the slicks, and herding of surface oil by dispersants.[26] Visual estimation of dispersant performance is often used in field trials, which is subject to the varied experience and skills of the "trained observers."[9, 28, 86]

In addition to deliberate field-testing carried out to assess dispersants, field data has also been gathered from "spills of opportunity." These are true unplanned oils spills that require implementation of emergency response plans. In such instances, researchers frequently record details about remediation efforts and their results in order to learn more about how dispersants react under actual sea state conditions. However, information gathered in such circumstances can be difficult due to the following considerations[26]:

- Minor spills do not allow time to adequately monitor dispersant performance.
- Obtaining surface and subsurface measurements for oil in the water column is complicated and not always possible under challenging environmental conditions.
- Mass-balance and estimates for the oil are often difficult to achieve.

- It is generally impossible to determine what percentage of dispersant is successfully applied to the slick, at what concentration, and at what droplet size range due to the greater need for rapid response compared to carefully-controlled observations.

Field test kits are available for qualitative assessment of dispersant effectiveness for "spill of opportunity" cases. These tests are much simpler than laboratory methods, and are limited in the scope of information they can provide. However, because they can be performed onsite real-time, evaluation of dispersant reaction to oil prior to any weathering effects can be made. Examples of test kits include[26]: EPA field dispersant effectiveness test, API field dispersant effectiveness test, Mackay simple field test, Pelletier screen test, and the Fina spill test kit.

7.4 Numerical Simulation

Numerical simulation and other modeling efforts are not, *per se*, true dispersant testing methods. Rather, they represent an extrapolation of empirical data combined with knowledge of physical mixing and chemical processes. Models can be valuable tools for predicting dispersant effectiveness through sensitivity studies. Some models allow multiple variables and their interdependencies to be quickly examined to support decision-making processes for experimental design, or even for dispersant selection in remediation efforts after an oil spill.

The EPA has funded numerous studies in recent years to collect data to be used for developing a simulation technique called the EPA Research Object- Oriented Oil Spill (ERO^{3}S) model. Experiments have been carried out, and statistical analysis of data performed to develop empirical relations for use in the model.[23, 24, 68] Variables studied include oil composition, oil weathering, dispersant type, temperature, and mixing energy. Other dispersant modeling tools have also been developed based on empirical data. For instance, the SINTEF Oil Weathering Model has been designed for prediction of weathering properties of oil at selected temperatures, wind speeds, and spill scenario.[16] While progress continues to be made on the formation of predictive models for dispersant effectiveness, this area is still in its infancy. Efforts are ongoing for use of computational fluid mechanics for modeling oil drop breakup. In addition, relationships between energy dissipation rate and effectiveness/particle size distribution need better definition to support predictive modeling efforts.[56]

A relatively new topic of interest for dispersant modeling is in the area of subsea oil releases. For this application, researchers study droplet formation and plume theory in an effort to understand the hydrodynamics of multiphase fluids in subsea releases within medium and deep waters. The droplet size directly determines the ultimate fate of hydrocarbon particles in a subsea release. Droplet size for oil rising to the surface is usually dependent on release depth, gas-to-oil ratio, release velocity, and oil type. The following paragraphs outline some of the recent advances in subsea predictive modeling.

A 3D stochastic model for oil droplet transport was created for simulating the effects that synthetic dispersants had on the uncontrolled-release of crude oil from the subsea Macondo well blowout in 2010.[76] During the Macondo blowout, there was uncertainty in the formation of oil droplets and their sizes, which is the largest contributor to droplet rise velocity. Corexit 9500 was injected into the plume in order to break up the larger droplets and prevent the oil from rising to the surface. Numerical experiments were conducted that evaluated the effects of particle size distribution, chemical dispersion, vertical currents, and oil droplet rise velocities.

Johansen et al.[47] also recently presented a new method for estimation of droplet size distributions from subsea blowouts. This is important from the standpoint of predicting the type of oil film, and thus, the necessary type of oil spill response. The study focused on the turbulent breakup regime, as determined by the non-dimensional Ohnesorge number (We^0.5/Re). While empirical results from a meso-scale tower basin test facility were used to develop the predictive model, the model has also been validated against the large-scale DeepSpill field experimental data. At present, the model applies only to single-phase (liquid-only) releases. However, the authors suggest that the model applicability may be expanded using their proposed void fraction correction for gas.

Last year, Lindersen[59] published work on a new algorithm to predict droplet size formation from subsurface blowouts of oil and gas. This was implemented as a submodel in SINTEF's Marine Environmental Modelling Workbench (MEMW) simulation tool. The author modified an existing algorithm to include the viscosity number effect with a modified Weber number, which improved simulation results to correlate more closely with existing theory. The IFT was varied to simulate the effect of different dispersant-to-oil ratios (DORs).

7.5 Summary and Comparison of Testing Methods

The effectiveness of dispersants for oil spills has been considered since their early use in remediation efforts.[63] However, it was not until the mid-90s that reliable quantitative methods began to appear.[38] This chapter has outlined some of the most common testing methods that have been used for dispersant assessment. A list of the methods is provided in Table 7.1. Also indicated in the table is the testing scale (e.g., bench, facility, or open sea), how the dispersant is applied (e.g., premixed, drop, spray), and what source is used to simulate mixing energy. As mentioned previously, there is currently no consensus on how to define effectiveness in terms of a measurement quantity. Thus, Table 7.1 also indicates the effectiveness measure used for ranking dispersants in each test. Finally, a list of references for each of the testing methods is shown. It should be noted that these references are merely representative, not comprehensive. For further references, the searchable database provided as part of this project can be used to filter publications based on testing method.

The primary motivation for development of the dispersant evaluation techniques discussed herein is to predict the effectiveness of dispersants operating under real-world conditions for oil spill remediation. Bench-scale testing is the most widely-used technique due to the lower cost and complexity for carrying out the tests. However, facility-scale testing is generally acknowledged to be more representative of an actual oils spill environment. Field-testing is, of course, highly applicable to accidental oil spill scenarios, but suffers from high cost, environmental concerns, and the inability to control the test conditions. Each method has distinct advantages, as well as disadvantages – which is the reason no agreement has been reached on a single "best practice" technique. Some of these issues are discussed more in the following paragraphs.

The drop-weight and spinning drop tests are simple in that they directly relate lowering of interfacial surface tension to improved dispersant effectiveness. They also avoid any uncertainty related to variable mixing energy in the testing, wall-effects, variability among sampling methodologies, or unintended wave dampening. However, disadvantages include the fact that the method offers no way to estimate mixing energy effects, performance testing results can be

Table 7.1. Dispersant Effectiveness Testing Method Comparison.
The various testing methods discussed in this chapter are compared by testing scale, dispersant application, mixing energy source, and method of measuring effectiveness.

Method	Scale	References	Dispersant Application	Energy Source	Effectiveness Measure
drop-weight	bench	1, 78	premixed	N/A	interfacial surface tension
spinning drop	bench	1, 62	premixed	N/A	interfacial surface tension
Labofina/WSL	bench	6, 21, 82, 85	drop	rotating vessel	oil concentration in water column
EXDET	bench	5, 22	premixed	wrist action shaker	oil concentration in water column
swirling flask	bench	10, 31, 34, 37, 46	premixed/drop	orbital shaker table	oil concentration in water column
baffled flask	bench	23, 45, 49, 91	premixed/drop	orbital shaker table	oil concentration in water column
IFP dilution	bench	13, 15, 18	drop	beating ring	oil concentration in water column
MNS	bench	18, 29, 60	premixed/drop	wave action	oil concentration in water column
basin/ mesocosm	facility	48, 50, 73	pour/spray	N/A	interfacial surface tension
revised standard EPA	facility	79, 87, 98	pour	recirculating tank fluid	oil concentration in water column
flume	facility	29, 61	spray	wave/ current action	mixing energy analysis/ oil droplet size/ oil concentration in water column
wave tank	facility	7, 14, 50, 55, 56, 72, 81, 86, 92, 96	spray	wave action (batch and flow-through)/ current action (flow-through only)	mixing energy analysis/ oil droplet size/ oil concentration in water column
field-testing	sea	9, 16, 28, 29, 33, 38, 74, 86	neat or diluted spray	wave/ current action	remaining oil in slick/ oil concentration in water column
modeling	N/A	16, 23, 24, 47, 56, 59, 68, 75	premixed/drop	simulated	application-specific

operator-dependent, and dispersants are being judged under use circumstances far from those intended by their manufacturers.

Agitated flask testing (Labofina, WSL, EXDET, swirling flask, and baffled flask) is carried out by combining small amounts of water, oil, and dispersant in a closed container and then applying a mixing energy source to agitate the contents. Water samples are removed after a period of time to analyze for oil concentration as a measure of dispersant effectiveness. The container design, dispersant application method, mixing energy source, settling time, and sampling method are varied among the different tests. However, they all retain advantages of simplicity in the test procedure, relatively low cost for the testing apparatus, and the speed at which multiple tests can be completed. A major disadvantage includes the fact that samples are generally taken under static conditions, and effectiveness measurement becomes very sensitive to settling time. In addition, wall effects from oil adherence to flask walls have the potential to bias dispersion estimates. Finally, relating flask agitation levels to open sea mixing energy remains problematic and controversial. Despite this, the baffled flask test (BFT) is expected to be adopted soon as the EPA-approved method for dispersant evaluation for inclusion on the National Contingency Product Plan Schedule for use during an oil spill event.[45, 90] The swirling flask test (SFT) remains the currently approved method until then.

It should be noted that, according to Fingas,[36] early spectrophotometry methods used for oil concentration analysis in many of the flask tests were flawed. This was because the addition of water for preparing benchmark curves produced some coloration. This inflated effectiveness values of the samples, leading to errors of a few percent for typical medium oils, but up to 300% for heavy oils. Thus, much of the data from effectiveness tests using spectrophotometry have been called in question. Gas chromatography is suggested as the most accurate way to analyze dispersant effectiveness in terms of oil concentration in water samples.

While still bench scale, the IFP dilution and MNS tests use mixing energy sources that mimic the wave and current action of the sea more closely than flask testing. However, the complexity of the testing apparatus and procedure is much greater. Repeatability of experiments and variability in results can be high when changing operators. Wave dampening has also been shown to be problematic with the MNS test.

Basin/mesocosm testing has the advantage of providing weathering data on oils and dispersed oils under real environmental conditions. However, the cost for large-scale facilities and disposal of contaminated oil can be high. Also, like the bench-scale interfacial surface tension tests, the effect of mixing energy on dispersant performance cannot be investigated using this technique.

The revised standard EPA test was formerly the approved method for dispersant acceptance into the National Contingency Product Plan Schedule. However, due to its disadvantages, the method was replaced in 1994 with the swirling flask test. These disadvantages included results that were very operator-dependent due to the extreme care needed to apply dispersant uniformly, avoid splashing of oil onto tank walls, control the water recirculation spray, etc. Also, a much larger volume of oil-contaminated water is generated for this method compared to agitated flask methods. Finally, the tank and associated apparatus is large, expensive, and difficult to clean.

Flume and wave tank methods allow dispersants to be tested with much greater realism compared to bench-scale techniques. The hydrodynamic scale is also much closer to ocean conditions, and realistic waves can be generated instead of only small-scale turbulence. Dynamic dispersant effectiveness testing in flow-through wave tanks incorporates both dispersion of oil into the water column and transport/dilution of the dispersed oil droplets through the water column. Bench-scale tests incorporate only contact efficiency effects between oil and dispersant under very enclosed conditions that may influence transport and dilution effects.

Wave tanks have advantages over field-testing in that much better variable control is possible,[86] and detailed measurements of mixing energy, oil droplet size, and oil concentration can be made at predetermined locations within the tank. Like all techniques that use boundaries to contain the experiment though, oil can adhere to walls and lead to overestimation of dispersant effectiveness. Hydrodynamic wall effects may also influence dispersant effectiveness measurement. Despite these complications, flume and wave tank testing remain the best option for both realistic and repeatable testing. Their use for expansive evaluation of dispersants is limited though, due to the complexity and expense of operation.

In summary, bench-scale tests offer simplicity, speed, and low cost for operation, yet their mixing energy methods are far removed from the wind and currents of the open sea. Field-testing provides a highly realistic environment, but cannot be well-controlled or replicated for study. Wave tanks represent a solution for realistic, yet repeatable testing of dispersant effectiveness. However, due to the limited number of facilities available and the cost, wave tanks alone cannot meet the need for dispersant effectiveness study. Thus, efforts are underway to relate wave tank data to bench-scale testing. One proposed solution for this is to use energy dissipation rate as a parameter to relate results between different types of laboratory and sea tests. Turbulence analyses in flask testing and wave tanks have focused on this parameter as a way to bridge different testing tecniques.[49, 55, 92, 96] Further study is needed to quantify and define the energy dissipation rate at different sea states.[49, 91]

8. GAP ANALYSIS

Certain gaps within existing knowledge and previously compiled experimental data were identified during the course of this literature synthesis. Although these gaps are addressed in greater detail through the discussion in the preceding sections, this report section compiles this analysis to identify the specific gaps in existing studies and, in some cases, suggests recommendations for future work to address these gaps.

At the fundamental level, there still seems to be no sweeping consensus on the effects of complex crude oil chemical composition and dispersant effectiveness. Traditionally, crude oils have been characterized in the literature by physical properties (viscosity or density). More recently, closer attention has been paid to characterization of the tested crude oils chemical compositions, through SARA analysis, for instance. It is suggested that any future work continue to characterize crude oil compositions and publish these data for each study.

In many of the experiments reviewed (both surface and subsurface applications), the dispersant-to-oil ratio (DOR) was either held at a fixed value and not included as part of the investigated variables or only tested at a handful of varying values. Particularly for subsea injection applications, the effects of varying DOR should be investigated directly.

The study of subsea dispersant use is, admittedly, in an early stage. Neither comparative test methods for dispersant evaluation nor the specific meaning of the term “dispersant effectiveness” has been standardized for subsea applications. The limited data already published has focused on a single dispersant formulation (Corexit 9500). Once the methods and analysis techniques have reached a reasonable level of consistency and acceptance, additional dispersant formulations must certainly be investigated for subsea applications. As stated in the previous sections of this report and in numerous other references, the effects of elevated static pressure, solution gas, free gas, and hydrate formation on the effectiveness of subsea dispersant use remain unknown. Additional testing in field-like environments should be conducted to better understand the effects of these phenomena on dispersant effectiveness.

The literature is so far unable to agree on proper techniques to correlate shear mechanisms on droplet breakup behavior in subsea releases of oil, water, and gas. These fundamental flow relationships need to be better understood if effective subsea dispersant use recommendations are expected to be provided under varying subsea blowout conditions (i.e., different flow rates, pressures, fluid contents, and discharge geometries). Additional research should be conducted in this area in order to identify areas in which dispersants can be successfully deployed and enhance application by determining the proper injection location and DOR to maximize dispersant effectiveness. It is further noted that the research needed in this area is likely to overlap with similar needs from industrial communities focused on subsea blowout containment, leak detection, and worst-case discharge planning.

Spills of opportunity provide the most field-realistic conditions for dispersant testing. However, they are also, perhaps, the most difficult test to instrument. For instance, during the Macondo incident, aerial photographs and subsea remotely-operated vehicle (ROV) video provided unique qualitative information regarding the action and effectiveness of subsea dispersant injection. However, if technology had been implemented to conduct subsea measurements of droplet size and ejection flow rates, this data would be instrumental in moving forward the debate in subsea droplet breakup. Technologies or techniques for clamp-on flow measurement and droplet/bubble sizing exist in industry for various applications and could likely be adapted for use in subsea oil spill response. These technologies should be investigated and qualified in anticipation of use in future research efforts.

The correlation of laboratory-scale-and field-scale tests for dispersant effectiveness remains challenging and unproven in the general case. Specifically, a better technique than visual observation is needed to relate effectiveness at-sea to wave tank results. Additional study of dispersant effectiveness as a function of energy dissipation rate across different oil and dispersant types will also provide a useful addition to the available dataset, with the goal of using energy dissipation rates to relate results between different types of laboratory tests and at-sea results. To this end, there is also a need to define and quantify energy dissipation rates at different sea states.

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APPENDIX A

Single-Page Literature Summary Forms

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Interfacial Tensions of Oil Water Chemical Dispersant Systems
Author(s):	Donald Mackay and Khon Hossain
Publication Date:	August 1982
Publication Source:	The Canadian Journal of Chemical Engineering, Volume 60

SUMMARY

This article described a test conducted using the spinning drop technique and various mixtures of oils and dispersants in salt and distilled water to observe the oil-water interfacial surface tension without measuring dispersant migration efficiency to the oil-water interface. A full effectiveness test was not conducted because migration efficiency wasn't discussed, and a change in the amount of dispersant that reaches the oil-water interface may significantly affect overall performance. A theoretical analysis was conducted along with the experimental analysis, focusing on concentrations below the critical micelle concentration (CMC) in which the effective oil-water partition coefficient (K) is constant, interfacial tensions are sensitive to concentrations, and no emulsions form. The volumetric ratio of oil to water and the amount of dispersant was varied to determine the K value and deduce an exponential relationship between dispersant concentration and reduction in interfacial tension. The ability of the relationship to assess dispersant effectiveness was discussed.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

The oil-water interfacial surface tension is consistently higher for distilled water mixtures than saltwater mixtures, most likely due to the accumulation of sodium salts of organic acids present at the oil-water interface. Surfactants partition more readily into distilled water than saltwater, which is probably due to a reduction in solubility of dispersants due to salt addition. Determination of K implies that oil concentrations of interfacial tension reducing substances are higher for saltwater than distilled water. Different oils and dispersants will have different K values, so this doesn't truly reflect the partitioning behavior of solvents. The effects of salinity on dispersion are due to altered partitioning and dispersant-free interfacial tension. Only a few percent of dispersant can be effective at a time, due to a large reduction in interfacial tension occurring at a lower dispersant-to-oil ratio than is typically found in real -world applications. Dispersion decreases at lower temperatures, due to a reduction in interfacial tension as temperature increases. The effect of oil type on interfacial tension was not found by only testing four oils. Dispersion is more difficult for oils with higher dispersant-free interfacial tensions.

OTHER INFORMATION

Dispersants Tested:	Corexit 9527, BP 1100 WD
Oil Species Tested:	La Rosa, Murban, Alberta Mixed Sour Blend, Kuwait Crude Oils
Oil Classifications/Properties:	Densities (kg/m^3) at 20°C: Murban - 823, Kuwait - 866, La Rosa - 910, Alberta Mixed Sour Blend - 824
Testing Method Used:	Spinning Drop Technique
Organizations/Venues Involved:	Department of Chemical Engineering and Applied Chemistry, University of Toronto; Imperial Oil Ltd.; Exxon Research and Engineering Co.; Environment Canada
Effectiveness Factors Discussed:	Dispersant Type, Oil Type, Salinity, Temperature
Keywords:	Oil-water interfacial surface tension, critical micelle concentration (CMC), dispersant-free interfacial tension, volume ratio dispersant to oil, volume ratio dispersant to water
Suggested Future Work	Acquire data to better understand transient nature of dispersant migration to oil-water interface, focusing on the effect of solvents. Determine temperature effects on E value (dimensionless constant characteristic of oil and dispersant), K value, oil viscosity, and dispersant-oil mixing. Acquire data on oil-water mixing and oil droplet separation processes as influenced by ocean turbulence to create a quantitative description of dispersion in the ocean.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	The Drop-Weight Interfacial Tension Method for Predicting Dispersant Performance
Author(s):	Robert T. Rewick; Karen A. Sabo; James H. Smith
Publication Date:	1983
Publication Source:	Industrial and Engineering Chemistry Product Research and Development

SUMMARY

This paper investigated the use of three different test methods to determine dispersant effectiveness ranking. These included the drop-weight method, a new drop-time method, and oil penetration testing. A total of 17 dispersants were tested using two different oils. Temperature and salinity effects were also considered. Temperature effects are important and influence dispersant performance through (1) kinetics of surfactant packing at the oil/water interface, (2) diffusion of the surfactant through the oil slick, and (3) solubility differences between the polar and nonpolar ends of the surfactant molecule. The authors felt it was important to test dispersant effectiveness as a function of temperature because the individual contribution of thermal effects can be difficult to reliably separate and predict. Similarly, salinity effects are significant since increased salinity is known to increase the interfacial tension, thereby affecting dispersant effectiveness.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

Product ranking orders of the tested dispersants were presented by the authors with respect to oil type, temperature, and salinity. Effectiveness rankings were based on whether the dispersant (1) reached full surface coverage at the oil/water interface at the lowest concentration, (2) promoted the largest reduction in interfacial tension per unit concentration, and (3) displayed the largest reduction in interfacial tension. The latter criterion was recommended by the authors as the key measure of performance. A comparison of results among the three different testing methods (drop-weight, drop-time, and oil penetration) suggested that a single dispersant effectiveness test is generally insufficient to meet all effectiveness testing requirements.

OTHER INFORMATION

Dispersants Tested:	17 unnamed dispersants were tested
Oil Species Tested:	Light Arabian Crude Oil and No. 6 Fuel Oil
Oil Classifications/Properties:	Not Provided
Testing Method Used:	Drop-Weight Method, Modified Drop-Weight Method (Drop Time), Oil Penetration Test
Organizations/Venues Involved:	SRI International
Effectiveness Factors Discussed:	Temperature, Salinity, Dispersant Type
Keywords:	Interfacial Tension, Critical Micelle Concentration
Suggested Future Work	The authors suggest that oil penetration testing could be improved to provide more accurate results if the drop time was significantly reduced to more accurately represent the first appearance of drop-weight test, interfacial tension, or oil penetration surfactant at the oil/water interface. Further testing of their new end-time measure is recommended.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	The Effect of Crude Oil Composition on Dispersant Performance
Author(s):	Gerard Canevari
Publication Date:	1985
Publication Source:	1985 Oil Spill Conference

SUMMARY

This was a literature review. The author first gave a preference to the Mackay-Nadeau-Steelman test. Salinity effects were explained through the hydrophilic-lipophilic balance: the dispersant only is effective when it remains at the interface of the oil and water. If the salinity is too low, the hydrophilic part of the dispersant is too strongly attracted and dissolves in the water. Conversely, too much salinity causes the dispersant to dissolve in the oil. Temperature similarly affects solubility, with lower temperatures increasing ethoxylated surfactant solubility in water. No conclusive relationship between viscosity and effectiveness was found with one exception. When oil becomes so viscous as to become semi-solid, the dispersant rolls off of the oil and is ineffective. The author identified the presence of indigenous surfactants in the crude oil as the primary component of oil composition affecting dispersant effectiveness. These natural surfactants can form films that support the production of water-in-oil emulsifications. Water-in-oil emulsifications drive effectiveness down by increasing interfacial area between oil and water, leaving a much larger area on which a dispersant will act.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

Dispersant effectiveness is driven largely by oil composition, specifically the amount and type of naturally-occurring surfactants in the oil. These surfactants help form water-in-oil emulsions, lowering dispersant effectiveness through the increase in interfacial area.

OTHER INFORMATION

Dispersants Tested:	N/A
Oil Species Tested:	N/A
Oil Classifications/Properties:	N/A
Testing Method Used:	N/A
Organizations/Venues Involved:	Exxon Research and Engineering Company
Effectiveness Factors Discussed:	Salinity, Temperature, Viscosity, Composition, Indigenous Surfactants
Keywords:	Surfactants
Suggested Future Work	Research dispersant interaction with chemical makeup of oil, specifically natural surfactant is suggested.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Chemical Dispersion of Oil. Comparison of the Effectiveness Results Obtained in Laboratory and Small-Scale Field Tests
Author(s):	Per S. Daling; Rainer G. Lichtenthaler
Publication Date:	1986
Publication Source:	Oil & Chemical Pollution

SUMMARY

This paper provided a comparison between results obtained in small-scale field testing versus three laboratory test methods. The use of six different dispersants was investigated on four types of oils. Both diluted and neat applications of dispersants were considered in the field testing. Laboratory techniques included the Mackay-Nadeau-Steelman (MNS) test and the flume test. The MNS test was applied with sampling of the suspension under either dynamic or static conditions. Correlation between result sets of different tests were analyzed, and recommendations given for increasing reliability of testing methods.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

Results between the three laboratory testing techniques exhibited poor correlation. Correlation between field tests and laboratory tests was also poor. Interestingly though, taking the combined mean results of all of the laboratory tests in comparison with the field testing provided more reasonable agreement. This suggests that the test methods produce results that reflect different properties/mechanisms of dispersion. Thus, while one method alone is not sufficient to represent full-scale open sea conditions, the correct combination may have this potential. The last finding from the study was that neat application in field testing showed an effectiveness 2-8 times higher compared to diluted dispersant application. However, it is not clear whether this may be due at least in part to variation in environmental conditions between the tests.

OTHER INFORMATION

Dispersants Tested:	BP 1100 WD, R-OD-1, Finasol OSR 5, Dispolene 34S, Corexit 9527, Corexit 9550
Oil Species Tested:	Ekofisk Crude, IF-30 Bunker Oil, Statfjord Crude, Topped Statfjord (Light Fuel Oil)
Oil Classifications/Properties:	Ekofisk Crude: viscosity=10 cSt, rho=0.805 g/ml; IF-30: viscosity=635 or 200 cSt, rho=0.941 or 0.943 g/ml; Statfjord Crude: viscosity=6.5 cSt, rho=0.83 g/ml; Topped Statfjord: viscosity=10 cSt, rho=0.852 g/ml
Testing Method Used:	Small-Scale Field Trials, Mackay-Nadeau-Steelman (MSN) Lab Test, Flume Test
Organizations/Venues Involved:	Center for Industrial Research, Norway; Norwegian Oil Pollution Control – Research and Development Program
Effectiveness Factors Discussed:	Undiluted vs. Neat Application of Dispersant, Wind/Current Effects, Static vs. Dynamic Sampling in Laboratory Testing
Keywords:	Laboratory testing, field-testing, Mackay-Nadeau-Steelman (MNS) test, flume test, neat application
Suggested Future Work	The authors note a need to improve predictive capabilities of laboratory tests to correlate with field testing under defined environmental conditions. They suggest droplet-size distribution measurements may be used to relate results between the two scales. A second area of improvement suggested is in methods for determining effectiveness in field testing. They suggest higher reproducibility may be achieved by quantifying remaining surface oil, as opposed to measuring dispersed oil.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Basic Study Reveals How Different Crude Oils Influence Dispersant Performance
Author(s):	G. Canevari
Publication Date:	1987
Publication Source:	International Oil Spill Conference

SUMMARY

Ten crude oils, as well as a clean hydrocarbon (tetradecane), were tested for dispersant effectiveness with four dispersants. The ten oils were chosen for their range in tendencies to form water-in-oil emulsions. Tetradecane was used as a baseline, as it is processed to contain no surfactants that would enhance the formation of water-in-oil emulsions. The Labofina dispersant effectiveness test was used for all oil-dispersant pairs and dispersant effectiveness was reported. For each of the crude oils, the indigenous surfactant was extracted and measured. For five of the crude oils, this surfactant was then mixed at the same weight concentration with tetradecane. The mixtures were then tested for dispersant effectiveness using a single dispersant.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

No correlation was found between the tendency of an oil to form a water-in-oil emulsion and its dispersibility, although all oils were less dispersible than tetradecane. Dispersant type significantly affected dispersibility. Tetradecane was proposed as a test “oil” to illustrate maximum dispersant effectiveness. The weight percent of indigenous surfactant extracted from each oil was found to correlate with each crude oil’s dispersibility. When the extracted surfactants were mixed with tetradecane, reductions in dispersibility were noted, but no clear relationship was found.

OTHER INFORMATION

Dispersants Tested:	Not Disclosed
Oil Species Tested:	Crude Oils: Kuwait, La Rosa, North Slope, Guanipa, Loudon, Murban, South Louisiana, Ekofisk, Saharan Blend, Goose Creek
Oil Classifications/Properties:	Water-In-Oil Emulsion Tendency – Extremely Strong-Very Weak, Viscosity – Not Listed, Density – Not Listed
Testing Method Used:	Labofina
Organizations/Venues Involved:	Exxon Research and Engineering Company
Effectiveness Factors Discussed:	Oil Properties
Keywords:	Indigenous surfactants, pure hydrocarbon
Suggested Future Work	N/A

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	The Comparative Effectiveness of Dispersants in Fresh and Low Salinity Waters
Author(s):	John L. Belk; Deborah J. Elliott; L. Michael Flaherty
Publication Date:	1989
Publication Source:	1989 Oil Spill Conference

SUMMARY

This article described a Labofina laboratory test conducted to observe the effectiveness of four marine dispersants and two freshwater dispersants at salinity values ranging from zero to 35 percent. It also observed the effect of changing the electrolyte solutions, and testing calcium and magnesium salt solutions and sodium salt solutions. The article began with an introduction stating the need to develop a freshwater dispersant, since current dispersants are less effective in lower salinities. It then described the Labofina test method and gave details on data collection with a description of the dispersants and oils used. The tests were conducted at 10 degrees C and 20 degrees C. The five salts used to test dispersant efficiency indices at different cation concentrations were also described. Salinity and cation strength were plotted against the dispersant efficiency index for all Labofina tests, followed by discussion and conclusions.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

Prudhoe Bay Crude Oil showed lower efficiency with all dispersant types and salinity percentages. The hydrocarbon solvent type marine dispersant was the most effective. Most marine dispersants tested showed a rapid increase in efficiency with an increase in salinity above 10%. Above 20% salinity, two marine dispersants showed a decrease in efficiency with Prudhoe Bay Crude Oil. The Dasic developmental freshwater dispersant was more effective than the commercially-available freshwater dispersant at all tested salinity percentages. Changing the anion of the electrolyte solution had little effect on dispersant effectiveness. However, a higher efficiency index was seen in low-strength calcium ion solutions for one marine dispersant, accompanied by a rapid decrease as calcium content was further increased. Calcium chloride resulted in lower efficiencies than calcium acetate. Freshwater dispersant effectiveness was less affected by electrolyte concentration and type than marine dispersant effectiveness. One of the marine hydrocarbon solvent dispersants showed increased effectiveness in high hardness water with 400-ppm calcium chloride. The freshwater dispersants also showed increased effectiveness at 400-ppm calcium chloride with reduced performance at 200 ppm.

OTHER INFORMATION

Dispersants Tested:	Four Marine Dispersants - Type 3 Concentrates, Hydrocarbon Solvent or Glycol Ether Solvent Type; Two Freshwater Dispersants – Commercially-Available and Dasic Developmental
Oil Species Tested:	Prudhoe Bay Crude, Warren Spring Laboratory Test Oil
Oil Classifications/Properties:	Prudhoe Bay Crude - U.S. EPA-API Reference Oil, Warren Spring – viscosity of 2,000 mPas at 10°C
Testing Method Used:	Labofina
Organizations/Venues Involved:	Dasic International, Ltd.
Effectiveness Factors Discussed:	Salinity, Dispersant Type, Oil Type, Electrolyte Solutions (Calcium And Magnesium Salt Solutions, Sodium Salt Solutions), Temperature
Keywords:	Salinity, marine dispersant, freshwater dispersant, calcium hardness, cation
Suggested Future Work	Test to see if the positive effects of calcium ion content in freshwater can improve freshwater dispersant effectiveness. Develop new testing procedures for freshwater dispersants that apply a higher oil-to-dispersant ratio and lower mixing energy to better replicate freshwater conditions.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	A Method for Evaluating Oil Spill Dispersants - Exxon Dispersant Effectiveness Test (EXDET)
Author(s):	K.W. Becker; L.G. Coker; M.A. Walsh
Publication Date:	1991
Publication Source:	Ocean Technologies and Opportunities in the Pacific for the 90s – Proceedings

SUMMARY

This paper presented a new laboratory testing method for evaluating the effectiveness of dispersants. The authors stated a need for this due to lack of correlation among current tests in agitation level and in the time interval between the stop of mixing and sampling. Advantages of the new method were said to include: (1) improved/standardized agitation method, (2) enhanced sample collection, (3) mass balance capability for dispersed/undispersed oil, (4) better inter-laboratory correlation technique, and (5) greater insensitivity to oil/water ratio. Testing with a single dispersant was carried out at various oil/water ratios.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

Testing showed high-performance dispersants to be insensitive to agitation time after five minutes. Therefore, 15 minutes was chosen as the standard for the EXDET method to ensure that slower-acting dispersants would be given opportunity to reach their maximum effectiveness. Examination of oil/water ratio sensitivity showed there to be insignificant effect on dispersant effectiveness for ratios between 1:250 and 1:2500 using the new method. Enhanced mass balance techniques eliminated common sample-measuring errors of other testing methods, because the new method used only the actual amount of oil on the water for calculation of dispersed percentage of oil. Overall, the EXDET method was stated by the authors to objectively judge dispersant effectiveness, and to be convenient for use, since it employs standard laboratory equipment and small volumes of water and chemicals.

OTHER INFORMATION

Dispersants Tested:	Corexit 9527
Oil Species Tested:	Middle East Crude, NWC Crude, EUG.IS.191 Crude, S.LA.MP306E Crude, CA.Monterey Crude
Oil Classifications/Properties:	N/A
Testing Method Used:	Exxon Dispersant Effectiveness Test (EXDET)
Organizations/Venues Involved:	Exxon
Effectiveness Factors Discussed:	Mixing Energy, Oil Composition, Dispersant Type
Keywords:	Laboratory testing, agitation level, effectiveness
Suggested Future Work	N/A

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Studies on the Physical and Chemical Behavior of Oil and Dispersant Mixtures
Author(s):	Mervin Fingas; Ian Bier; Mark Bobra; Sandra Callaghan
Publication Date:	1991
Publication Source:	1991 Oil Spill Conference

SUMMARY

The swirling flask method is used to determine environmental effects on dispersant effectiveness and to analyze dispersant effectiveness as affected by oil bulk components, i.e., asphaltenes, aromatics, polar compounds, saturate compounds, and waxes. The swirling flask tests indicated an increase in temperature would cause an increase in effectiveness, while an increase in the oil-to-dispersant ratio (decrease in dosing) consistently decreased effectiveness. Salinity was also investigated, with a peak effectiveness reported at a salinity of 40%-45%. A large array of experiments was performed using Corexit 9527, Enersperse 700, and Citrikleen combined with 25 oils. Saturate content, “the percentage of the oil that constitutes hydrocarbon compounds with only singly bonded carbon,” was found to have a strong positive correlation with dispersant effectiveness (as saturate content went up, effectiveness increased). Aromatic content, asphaltene content, and polar compound content were all found to have strong negative correlations with dispersant effectiveness (as these quantities went up, effectiveness decreased). No correlation was found with effectiveness and either wax content or viscosity.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

Increasing temperature and dosage increases dispersant effectiveness. Maximum effectiveness is observed at a salinity of ~45%. Dispersant effectiveness is largely controlled by oil composition, having a strong positive correlation with saturate content and a strong negative correlation with aromatic, asphaltene, and polar compound content. Wax content and viscosity have no direct correlation with effectiveness.

OTHER INFORMATION

Dispersants Tested:	Corexit 9527, Enersperse 700, Citrikleen
Oil Species Tested:	Adgo, Amuligak, Arabina Light, ASMB, Atkinson, Avalon J-34, Bent Horn, Bunker C, California API=11, California API=15, Cohasset A-52, Cold Lake Heavy, Endicott, Federated, Hibernia, Issungnak, Lago Medio, Norman Wells, Panuke F-99, Prudhoe Bay, South Louisiana, Syncrude, Terra Nova, Transmountain
Oil Classifications/Properties:	SARA, Adgo (66 cSt), Amauligak (16 cSt), ASMB (16 cSt), Atkinson (57 cSt), Avalon J-34 (14 cSt), Bent Horn (24cSt), Bunker C (48,000 cSt), California API=11 (34,000 cSt), California API=15 (6,400 cSt), Cohasset A-52(2 cSt), Cold Lake Heavy (235,000 cSt), Endicott (92 cSt), Federated (4.5 cSt), Hibernia (92 cSt), Issungnak (4 cSt), Lago Medio (47cSt), Norman Wells (6 cSt)
Testing Method Used:	Swirling Flask
Organizations/Venues Involved:	Environment Canada
Effectiveness Factors Discussed:	Temperature, Oil Composition
Keywords:	Oil properties, swirling flask, flowing cylinder, salinity, temperature, doseage
Suggested Future Work	Further study is suggested on the effect of viscosity on the mixing of oil and dispersant.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Laboratory Testing of Dispersants under Arctic Conditions
Author(s):	P.J. Brandvik; O. Knudsen; M. Moldestad; P.S. Daling
Publication Date:	1995
Publication Source:	The Use of Chemicals in Oil Spill Response (STP 1252)

SUMMARY

This paper presented results from effectiveness testing of dispersants under Arctic conditions (0 degrees C and 0.5% to 3.5% salinity) using the IFP dilution test. Note that the IFP test is considered a low energy test, where an effectiveness of 40% is considered low, while 60-80% is considered high. A total of 14 different dispersants were employed in an initial screening study using two types of North Sea weathered oils. Temperature was held at the freezing point, while discrete salinities of 0.5% and 3.5% were tested. Five dispersants with high levels of effectiveness were then chosen to proceed to a second study examining effectiveness with four types of oils, both weathered water-free and water-in-oil emulsions. Finally, the effect of salinity was investigated further by sampling effectiveness of two dispersant types in increments of 0.75%, from 0.5% up to 3.5%, on a single type of crude oil.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

Data from the initial screening study indicated that many of the dispersants that performed well at high salinity (3.5%) showed poor effectiveness at low salinity (0.5%). This trend was repeated for the follow-on extended dispersant testing. The authors state two theories from the literature as possible explanations for this behavior. First, surface activity of ionic surfactants may be salinity-dependent, leading to ions in the water changing the electric field at the water/oil interface. Second, surfactants may leach from the oil into the water phase as a result of salinity variation. An interesting observation from the extended testing was a dispersant that exhibited high effectiveness while test temperatures were 10-15 degrees C lower than the pour point of the oil. This is opposite of what earlier studies have shown. The authors explained this as being the result of wax particles gathering at the water/oil interface to stabilize the water droplet in the emulsion. They further suggest that the ability to form wax crystal structures in the emulsion may be reduced, since some of the wax particles are bound at the water/oil interface.

OTHER INFORMATION

Dispersants Tested:	Corexit 9527; Corexit 9550; Dasic Slick Gone FW; Dasic Slick Gone LTS; Dasic Slick Gone NS; Dispolene 36S, Dispolene 38S, Enersperse 700; Enersperse 1037; Finasol OSR-5; Finasol OSR-52; IKU-9; Inipol IPC; Inipol IPF
Oil Species Tested:	Oseberg; Gullfaks; Veslefrikk; IF-30 Bunker
Oil Classifications/Properties:	Oseberg (100 cP, 0.853 kg/l); Gullfaks (810 cP, 0.882 kg/l); Veslefrikk (90 cP, 0.839 kg/l); IF-30 Bunker (3200 cP, 0.936 kg/l)
Testing Method Used:	IFP Dilution Test
Organizations/Venues Involved:	American Society for Testing and Materials (ASTM)
Effectiveness Factors Discussed:	Temperature, Salinity, Dispersant Type, Oil Type
Keywords:	Oil weathering, optimization, effectiveness testing, Arctic conditions, salinity
Suggested Future Work	The authors state a need for further fundamental work to explore the different interfacial phenomena occurring with dispersants used at varying salinities. Furthermore, they point out a need for future development of dispersants that have a high effectiveness at both low temperature and over a wide range of salinities for combating Arctic spills. Other logistical areas of concern specific to Arctic conditions include: low-temperature dispersant application systems, and necessary levels of mixing/turbulence required for dispersion in ice-filled waters.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	The Effect of Energy, Settling Time and Shaking Time on the Swirling Flask Dispersant Apparatus
Author(s):	Merv F. Fingas; Eleanor Huang; Ben Fieldhouse; Lei Wang; Joseph V Mullin
Publication Date:	1996
Publication Source:	Spill Science and Technology Bulletin

SUMMARY

This paper investigated the effect of varying the rotational speed, settling time, and shaking time on swirling flask test (SFT) effectiveness results. Rotational speeds from 50 to 250 rpm were studied, settling times from one to 80 minutes, and shaking times from 10 to 160 minutes. All three variables were tested using three different types of oils with a single dispersant. Effectiveness of the dispersant was taken as the percentage of oil in the water column versus a control sample.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

Results from rotational speed tests showed rapid onset of dispersion between 100 to 150 rpm, indicating a mixing energy threshold process. Beyond 150 rpm, the effectiveness was observed to increase significantly at a constant rate. The authors note that the specified speed of 150 rpm for standardized SFT falls in a region of relatively little change – which promotes repeatability of results. Dispersion effectiveness has been observed to decrease rapidly with settling time. While changes at five minutes were large, the effectiveness nearly stabilized by 80 minutes. Standardized SFT specifies sampling at 10 minutes. However, the authors noted that since not all samples can be taken at once and the effectiveness is still rapidly changing at 10 minutes, repeatability of results is problematic. Finally, shaking time is shown to have little effect on effectiveness. While data show a slow rise in effectiveness with increased shaking time, it is not significant. The authors state that, like the rotational speed effect results, this is indicative of a threshold process.

OTHER INFORMATION

Dispersants Tested:	Corexit 9500
Oil Species Tested:	Prudhoe Bay Crude; Alberta Sweet Mixed Blend, Thevenard Island
Oil Classifications/Properties:	Not Provided
Testing Method Used:	Swirling Flask Method
Organizations/Venues Involved:	Environment Canada, U.S. Department of the Interior, Minerals Management Service
Effectiveness Factors Discussed:	Oil Type, Mixing Energy
Keywords:	Effectiveness testing, swirling flask
Suggested Future Work	The authors suggest that the current specification of 10-minute settling time for standardized swirling flask tests be reconsidered. They recommend investigating the possibility of changing this to 20 minutes, or creating a novel way to improve repeatability and precision of sampling.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	A Modified Swirling Flask Efficacy Test for Oil Spill Dispersants
Author(s):	Gloria J. Blondina; Michael L. Sowby; Maria T. Ouano; Michael M. Singer; Ronald S. Tjeerdema
Publication Date:	1997
Publication Source:	Spill Science and Technology Bulletin

SUMMARY

This paper presented justification for modifying the standard EPA-approved swirling flask test used to gauge dispersant performance. A direct comparison of the standard and modified test results was provided. Main differences between the two tests included: (1) the modified test used a closed flask to inhibit loss of volatile compounds through evaporation, (2) the modified test applied dispersant in a single drop to the surface of the oil, whereas the standard test premixed the oil and dispersant, (3) an emulsion inhibitor was used in the modified test to reduce variability among samples, and (4) sample analysis was performed using gas chromatography (GC) for the modified test instead of UV spectrometry.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

While GC analysis provided a detailed profile of crude oil composition not possible with UV analysis, its use did require further modification of the standard test. First, while UV analysis may be completed immediately after extraction, GC analysis requires 1-1.5 hours holding time. In order to reduce volatilization and degradation during that time, GC samples were held at -10 degrees C until analyses. Second, standard test extraction volumes produced concentrations below GC detection limits. Thus, extract volumes were changed to 15 mL (from 5 mL). Encouragingly, it was found that the high precision of seawater and dispersant blanks made extensive replication unnecessary, unlike using UV analysis with the standard test method. In conclusion, comparison of the EPA standard method with the modified method showed the latter had much higher precision among results. While the standard test indicated 39% and 57% efficacy for the two dispersants, the modified method showed only 16% and 22% efficacy. This suggests that the standard test generates substantially higher percent efficacy estimates, likely due to premixing of the oil and dispersant, which does not reflect “real-world” conditions.

OTHER INFORMATION

Dispersants Tested:	Corexit 9500 and Corexit 9527
Oil Species Tested:	Prudhoe Bay Crude
Oil Classifications/Properties:	API Gravity 29.0-deg
Testing Method Used:	Swirling Flask Test (Modified)
Organizations/Venues Involved:	California Department of Fish and Game; University of California
Effectiveness Factors Discussed:	Temperature, Salinity
Keywords:	Efficacy, swirling flask test, gas chromotography
Suggested Future Work	N/A

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Influence of Salinity on Petroleum Accommodation by Dispersants
Author(s):	G.J. Blondina; M.M. Singer; I. Lee; M.T. Ouano; M. Hodgins; R.S. Tjeerdema; M.L. Sowby
Publication Date:	1999
Publication Source:	Spill Science & Technology Bulletin

SUMMARY

The effect of water salinity on dispersant effectiveness was studied using a modified swirling flask test (SFT), dispersants Corexit 9500 and 9527, 10 different oils, and salinity ranging from 0 to 35 ppt. The chemical composition of dispersants was reviewed, along with the potential for salinity and oil properties to affect dispersant performance. The test method was described as adding oil and dispersant with 10:1 oil-to-dispersant ratio to water and swirling the mixture on a rotary shaker table before settling and later sampling. Treatments included oil and seawater, oil with dispersant and seawater, and both seawater and dispersant alone for experimental controls. The sample was analyzed using a gas chromatograph (GC) with a flame ionization detector. Effectiveness was calculated to represent the proportion of oil entering the water column through chemical and natural processes. The GC and mass spectrometry was used to analyze oil characteristics and observe their effect on dispersant effectiveness with changing salinity, including API gravity, TPH value, PAH content, volatile hydrocarbon content, density, and viscosity. A one-way analysis of variance was conducted to ensure statistically-significant results.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

This study observed similar trends as previous studies in that dispersant effectiveness decreased with low-salinity water. The maximum effectiveness for Corexit 9527 was seen at 35 ppt for all but one oil, Forcados Crude, which was unique in its chemical composition with a high TPH content and low VPH content. Corexit 9500 performed better on most oils at most salinities than Corexit 9527. Its better performance for a wider range of salinities was attributed to a less hydrophilic formulation that created a larger impact on the oil-water interface at lower salinities and better oil penetration due to hydrocarbon-based solvents. Therefore, Corexit 9500 was the preferred dispersant for areas with salinity fluctuations. The correlations between dispersant effectiveness and oil composition parameters were determined for both dispersants indicating chemical and physical oil properties may affect dispersant performance with changes in the receiving water's ionic strength. Dispersant effectiveness was influenced by water salinity, but the interaction was dependent on the specific dispersant and oil used.

OTHER INFORMATION

Dispersants Tested:	Corexit 9500 & 9527
Oil Species Tested:	Arabian Light & Medium, Bunker C, Prudhoe Bay, Forcados, Kern Ridge, Kuwait, Maya, Oman, South Elwood Crudes
Oil Classifications/Properties:	ALC (35.8 API), Arabian Med. (28.3 API), Bunker C (12.1 API), Forcados (36.3 API), Kern ridge (9.8 API), Kuwait (34.7 API), Maya (20.2 API), Oman (38.3 API), PBC (29.0 API), South Elwood (25.5 API)
Testing Method Used:	Modified Swirling Flask Test (SFT)
Organizations/Venues Involved:	California Department of Fish and Game, University of California
Effectiveness Factors Discussed:	Salinity, Oil Properties
Keywords:	Dispersants, efficacy, salinity effects, crude oil
Suggested Future Work	Obtain results that are better indicative of field results to help in the dispersant decision-making process for real-world applications.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Key Parameters Affecting the Dispersion of Viscous Oil
Author(s):	G. Canevari; P. Cacavecchio; K. Becker; R. Lessard; R. Fiocco
Publication Date:	2001
Publication Source:	International Oil Spill Conference

SUMMARY

The goal of this study was to determine what affected dispersant effectiveness in viscous oils. Although increasing viscosity typically indicated decreasing effectiveness, studies have shown that two oils with the same viscosity can have very different effectiveness. Fourteen heavy fuel oils were used in these tests, with viscosities ranging from 1,100 to 20,000 centistokes. The dispersant Corexit 9500 was used at a dosage ratio of 1:20. The EXDET method was used for measuring dispersant effectiveness. IATROSCAN analyses were performed to quantify saturate, aromatic, resin, and polar content of the oils. Gas chromatography was used to measure the amount of paraffin in each oil.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

No correlation was found between the physical properties of the oils and the dispersability of the oils, although it was noted that high-viscosity oils resist droplet formation. Saturate content did have a correlation with dispersant effectiveness, with increasing saturate content correlated with decreasing effectiveness. n-paraffin content was also found to have a correlation with effectiveness. The authors posited that the long chain paraffins increase cohesion in the oils, decreasing the ability to form droplets.

OTHER INFORMATION

Dispersants Tested:	Corexit 9500
Oil Species Tested:	IFO 180, IFO 380
Oil Classifications/Properties:	SARA
Testing Method Used:	EXDET
Organizations/Venues Involved:	ExxonMobil
Effectiveness Factors Discussed:	Oil Properties
Keywords:	Viscosity, density, paraffins
Suggested Future Work	none

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	The Baffled Flask Test for Dispersant Effectiveness: A Round Robin Evaluation of Reproducibility and Repeatability
Author(s):	Albert D. Venosa; Dennis W. King; George A Sorial
Publication Date:	2002
Publication Source:	Spill Science & Technology Bulletin

SUMMARY

This paper began by providing justification for insufficient reliability of the current swirling flask test (SFT) as a method for EPA screening of dispersant effectiveness. The authors then proceeded to describe the baffled flask test (BFT), which had been suggested to have superior effectiveness and reproducibility over the SFT. In order to quantitatively determine the reproducibility and repeatability of the new test, independent analyses were conducted by nine different laboratories. Six dispersants were selected for use in the experiments, based on previous effectiveness measurements. Two high (>80%), two medium (30-79%), and two low (<30%) effectiveness dispersants were chosen to provide a range of data for the study. In addition, two reference oils were chosen to compare effects of light versus medium crude. Four samples have been run for each combination of dispersant/oil at each of the nine labs. Results were then used to provide guidance on establishing a pass/fail criterion for listing of a dispersant on the national contingency plan product schedule.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

Analysis of data from the independent testing facilities suggested that all error associated with the BFT was due to the test method itself, rather than due to differences among the laboratories. This encouraging reproducibility was noted to be superior to the SFT. Furthermore, the test provided mixing conditions more reflective of the moderately energetic environments where dispersants will be employed (as opposed to SFT, which uses oil/dispersant premixing). While a precise pass/fail threshold determination will ultimately be the responsibility of EPA Headquarters, the authors suggested a value somewhere between 65-80%, based on their outlined 95% lower confidence limit formula.

OTHER INFORMATION

Dispersants Tested:	6 dispersants, not identified by name
Oil Species Tested:	Prudhoe Bay Crude (PBC) and South Louisiana Crude (SLC)
Oil Classifications/Properties:	Light to Medium Crude, Properties Not Reported
Testing Method Used:	Baffled Flask Test, Swirling Flask Test
Organizations/Venues Involved:	U.S. Environmental Protection Agency; Statking Consulting Inc.; University of Cincinnati
Effectiveness Factors Discussed:	Test Type (BFT vs SFT), Oil Type, Dispersant Type
Keywords:	Baffled flask test, swirling flask test, dispersants, round robin test, inter-laboratory test, dispersion effectiveness, crude oil
Suggested Future Work	Further research for establishing a correlation between energy dissipation in the BFT versus energy dissipation at different sea states is needed. According to the authors, calibration of laboratory test conditions with field conditions (mixing energy or weathering processes) may allow extrapolation of lab results to real-world expectations.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Determining Dispersant Effectiveness Data for a Suite of Environmental Conditions
Author(s):	S. Chandrasekar; G. Sorial; J. Weaver
Publication Date:	2003
Publication Source:	International Oil Spill Conference

SUMMARY

The goal of this series of experiments was to collect empirical data for the EPA Research Object-Oriented Oil Spill model. Two dispersants were tested on three oils at three levels of weathering, three mixing speeds, and three temperatures. The baffled flask test was used to evaluate dispersant effectiveness. The effect of each of these factors was measured using analysis of variance and linear regression modelling.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

The analysis of variance indicated that weathering, mixing speed, and temperature all had significant interactions with the dispersant type. A linear regression model was built using the collected data. The model matched the data well. The authors noted that “dispersant effectiveness increases with increase in mixing energy,” “decreases with increase in weathering,” and does not have a consistent relationship with temperature.

OTHER INFORMATION

Dispersants Tested:	Corexit 9500, Dispersit-SPC 1000
Oil Species Tested:	South Louisiana Crude, Prudhoe Bay Crude, Number 2 Fuel Oil
Oil Classifications/Properties:	Weathering – 0%, 10%, 20% Weathering by Volume
Testing Method Used:	Baffled Flask Test
Organizations/Venues Involved:	University of Cincinnati; U.S. Environmental Protection Agency
Effectiveness Factors Discussed:	Environmental Effects
Keywords:	Factorial experiment, baffled flask, statistics
Suggested Future Work	N/A

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Dispersant Effectiveness on Heavy Fuel Oil and Crude Oil in New Zealand
Author(s):	L. Stevens; J. Roberts
Publication Date:	2003
Publication Source:	International Oil Spill Conference

SUMMARY

The dispersants kept in stock in New Zealand for oil spill response were tested on fresh crude oils and fresh fuel oils most likely to be accidently spilled. Fuel oils were used from nine sources. Two potential dispersants were also tested. The Warren Spring Lab test was used to measure dispersant effectiveness. All initial tests were performed at 15 degrees C and at a dispersant-to-oil ratio of 1:25. A dispersant effectiveness of 15% or greater was considered as an indication that the dispersant would be able to disperse the oil at sea. After the initial tests, Corexit 9500 and Slickgone EW, the potential dispersants, were tested on three fuel oils at varying dispersant-to-oil ratios and varying temperatures.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

Corexit 9500 and Slickgone EW performed better than the then currently-stocked dispersants. The heavy fuel oils were less likely to disperse than the fresh crude oils. Neither decreases in viscosity nor increases in temperature consistently indicated increased dispersant effectiveness.

OTHER INFORMATION

Dispersants Tested:	Corexit 9500, Slickgone EW, Corexit 9527, Gamlen OSD L/T, Slickgone LTSW, Tergo R40
Oil Species Tested:	Arab Light, Barrow Island, Kutubu, Kuwait, Labuan, Oman, Oman Residue, IFO-380
Oil Classifications/Properties:	Viscosity – 31 cP (AL), 12 cP (BI), 11 cP (Kut), 38 cP (Kuw), 47 cP (Oman), 2908-90325 for IFOs
Testing Method Used:	Warren Spring Lab test
Organizations/Venues Involved:	Cawthron Institute; Maritime Safety Authority of New Zealand
Effectiveness Factors Discussed:	Oil Properties, Weathering
Keywords:	Warren Spring Lab, New Zealand
Suggested Future Work	Investigate effects of weathering and application method.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Dispersants, Salinity, and Prince William Sound
Author(s):	Merv Fingas
Publication Date:	December 2004
Publication Source:	Report

SUMMARY

The objective of this article was to observe dispersant effectiveness at various salinities, similar to the various salinities found in Prince William Sound. It began with a review of the general relationship between salinity and dispersant effectiveness, with dispersants being less effective at lower salinities. It then reviewed some older laboratory testing methods completed before the mid-1990s using colorimetric measures, but data values were largely inflated without the use of gas chromatography. Next, recent laboratory methods were described for multiple experiments testing various dispersants and oils at multiple salinities with current testing methods. The author then briefly reviewed salinity effects described in surfactant literature. The effect of salinity on dispersant effectiveness was also discussed from a review of field studies conducted on dispersants in ponds, lakes, and artificial stream beds. Lastly, the author described the various salinity conditions found in Prince William Sound, ranging from 33 o/oo in the center to very low salinities found at creek outflows and smaller bay regions.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

Then currently-available dispersants were largely ineffective in low-salinity waters, around 0 o/oo. The peak of dispersant effectiveness typically occurred around 20 to 40 o/oo. The type of dispersant used will determine the salinity at which it reaches maximum effectiveness. Corexit 9500 was found to be less sensitive to salinity, while Corexit 9527 was more sensitive, with peaks at 35 o/oo and 25 o/oo, respectively. Most then-recent tests were performed using Corexit 9527 and 9500, so results varied with dispersants containing different surfactant packages. The oil type also affected the peak salinity value. The effect of salinity on dispersant effectiveness fit a Gaussian distribution, since effectiveness increases with salinity until a maximum value and then decreases rapidly after. Decreased effectiveness, at very high and low salinities, was a result of salinity affecting the hydrophilic/lipophilic balance (HLB) and stability of the surfactant due to changes in the ionic strength of the water. There was not enough data to make solid conclusions about the reaction between temperature and salinity, although high correlation between these variables was found in some then-recent laboratory tests. Field trials conducted in freshwater also indicated low dispersant effectiveness with less saline environments. Prince William Sound had some low-salinity areas that could experience lower dispersant effectiveness.

OTHER INFORMATION

Dispersants Tested:	Corexit 9527 and 9500
Oil Species Tested:	Prudhoe Bay Crude, Light Arabian Crude, Alaska North Slope (ANS), Alberta Sweet Mixed Blend (ASMB), Norman Wells Crude
Oil Classifications/Properties:	Numerous
Testing Method Used:	Labofina Laboratory Apparatus, Mackay, Exdet, Warren Springs, Swirling Flask Test, Field Studies
Organizations/Venues Involved:	Environmental Technology Centre; Prince William Sound Regional Citizens' Advisory Council (PWSRCAC)
Effectiveness Factors Discussed:	Salinity
Keywords:	Hydrophilic, lipophilic, salinity, surfactants
Suggested Future Work	Study the temperature-salinity interaction and its effect on dispersants. Vary oil exposure and salinity and draw conclusions on biological effects. Validate salinity and effectiveness correlations using laboratory testing with more data points.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Oil Spill R&D in Norwegian Arctic Waters with Special Focus on Large-Scale Oil Weathering Experiments
Author(s):	P.J. Brandvik; I. Singsaas; P.S. Daling
Publication Date:	2004
Publication Source:	Interspill Conference

SUMMARY

This paper began by reviewing the oil spill response options that were researched for use in Norwegian waters after the Ekofisk blowout in 1977, including mechanical skimmers, in-situ burning, chemical dispersants, and bioremediation. Recent increases in tanker traffic and the reopening of the Barents Sea for exploratory drilling have recently increased interest in oil spill response options leading to this study, which compared two large-scale experimental crude oil release tests to understand Arctic weathering processes. The Haltenbank Experiment was conducted in open water with no ice at 10 degrees C. The Marginal Ice Zone Experiment was conducted in broken ice conditions at -1.8 degrees C. Both tests involved surface application of oil and sampling taken over a 3.5 to seven-day period. Compared weathering properties included evaporative loss on the crude oil, density of water-free oil after breaking the water-in-oil emulsion, water uptake, and emulsified oil viscosity.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

Significant differences were seen for all weathering properties, due to reduced wave action and oil spreading with ice. The evaporative loss of the crude oil was much higher in open water than in broken ice, with 40% after a 3.5-day period compared to 25% after a seven-day period. This is due to ice floes restricting oil spreading at the water surface, increasing oil slick thickness. Lower temperature may have also restricted evaporative loss by reducing diffusion of the oil components and creating a gradient into the bulk oil phase. The density of the water-free crude oil was higher in open water than broken ice. The volume percent of water uptake in the crude oil was much greater in open water, 70-80%, than broken ice, 20%, due to interference with wave input energy caused by high ice coverage. As ice coverage reduced, more wave action occurred between ice floes, increasing water uptake at the end of the testing period. The viscosity of the water-in-oil emulsion was approximately 400-600 cP in broken ice compared to 15,000-18,000 cP in open water after a 3.5-day period. This was expected, since the viscosity is influenced by difference in water content, temperature, and evaporative loss of oil.

OTHER INFORMATION

Dispersants Tested:	None
Oil Species Tested:	Oseberg and Sture Blend Crudes
Oil Classifications/Properties:	Sture Blend has higher pour point (-3 v. -22°C), higher wax content (4.3 v. 2.8 wt.%), lower density (0.847 v. 0.855 g/ml), higher viscosity (32 v. 12 cP), and lower asphaltene content (0.07 v. 0.10 wt.%) than Oseberg Crude
Testing Method Used:	Large-Scale Experimental Oil Spill
Organizations/Venues Involved:	Norwegian Oceanographic Research Company (OCEANOR); SINTEF; Norwegian Institute for Nature Research (NINA); Norwegian Clean Seas Association for Operating Companies (NOFO)
Effectiveness Factors Discussed:	Arctic Conditions (Low Temperatures [0-20 degrees C] and Ice Presence), No Ice vs. Broken Ice, Weathering Processes (Wind, Waves, Drift, Spreading)
Keywords:	Arctic, weathering, water-in-oil emulsion, North Sea, Barents Sea, bioremediation, mechanical recovery, in-situ burning, dispersants
Suggested Future Work	Obtain more data through laboratory studies and full-scale field experiments under a variation of ice conditions to better understand oil weathering in Arctic environments and create corresponding predictive models.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Determination of the Limiting Oil Viscosity for Chemical Dispersion at Sea
Author(s):	K. Colcomb; D. Salt; M. Peddar; A. Lewis
Publication Date:	2005
Publication Source:	International Oil Spill Conference

SUMMARY

Twenty-one tests were performed in the English Channel to establish effects of viscosity and dosage ratio on dispersion. Two fuel oils and three chemical dispersants were used during testing. The test originally included four fuel oils, but testing was limited by weather. Dispersant brands used were not disclosed. Nominal dosage ratios of 1:25, 1:50, and 1:100 were used. For each test, 10 or 20 L of fuel oil were sprayed on the sea surface. The fuel oil was then sprayed with dispersant, minimizing time for natural dispersion. The slick was observed for 10 minutes. Dispersion was graded by expert observers at two, five, and 10 minutes.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

The IFO 180 used in this test had a viscosity of 2,075 cP at 15 degrees C; the IFO 380 had a viscosity of 7,100 cP at the same temperature. Rapid dispersion of the IFO 180 was observed with two of the three dispersants, while the more viscous IFO 380 was not dispersed quickly by any dispersants. Wind speed played a significant role, with higher wind speeds aiding dispersion. Higher dosage ratios were also observed to aid in dispersion.

OTHER INFORMATION

Dispersants Tested:	Not Disclosed
Oil Species Tested:	IFO 180, IFO 380
Oil Classifications/Properties:	IFO 180: (density 0.970 g/mL at 20C, viscosity: 2,075 cP at 15C), IFO-380: (density: 0.983 g/mL at 20C, viscosity: 7,100 cP at 15C)
Testing Method Used:	At Sea / Field Trial
Organizations/Venues Involved:	Maritime and Coastguard Agency; Oil Spill Response Limited; Department for Environment, Food, and Rural Affairs
Effectiveness Factors Discussed:	Oil Composition
Keywords:	Oil composition, mesoscale, viscosity, field trial
Suggested Future Work	N/A

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Determining the Viscosity Limits for Effective Chemical Dispersion: Relating OHMSETT Results to those from Tests At-Sea
Author(s):	B.K. Trudel; R.C. Belore; A. Lewis; A. Guarino; J. Mullin
Publication Date:	2005
Publication Source:	International Oil Spill Conference Proceedings

SUMMARY

This paper presented a comparison of wave tank test results with “at-sea” results with comparable oil species, dispersant types, dispersant-to-oil ratios (DORs), and mixing energies. Two intermediate fuel oils with high viscosity were tested, along with three dispersant formulations. Mixing energy of the wave tank tests were matched to sea trials through scoping experiments to identify the wave frequency that produced an effectiveness similar to sea trials. Effectiveness was defined based on 1) the difference between the amount of oil spilled and collected, and 2) visual observations by trained observers. Marine salinity and 16 degree C water was used in wave tank testing to simulate Arctic conditions.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

Wave tank testing showed that while the dispersant Corexit 9500 had high effectiveness when applied to the lower viscosity oil, a much lower effectiveness was observed with the higher viscosity oil. The authors stated that this is consistent with previous conclusions that the viscosity limit for dispersion lies between the viscosities of the two oils tested in this paper. However, they also pointed out that “limiting viscosity” is a variable influenced by both mixing energy and dispersant type. Comparison of wave tank and at-sea results showed good qualitative agreement. Both Corexit and SD 25 proved more effective than the Agma dispersant in the sea and wave tank trials on the two oil types. However, due to uneven distribution of the dispersant at-sea, precise matching of DORs was difficult for quantitative comparison with laboratory tests. This example of problematic variable control at-sea was identified by the authors as a reason for studying dispersant effectiveness in wave tanks.

OTHER INFORMATION

Dispersants Tested:	Corexit 9500, Superdispersant 25, Agma DR 379
Oil Species Tested:	IFO 180; IFO 380
Oil Classifications/Properties:	IFO 180 (mu=2075 cP @ 16 C); IFO 380 (mu=7100 cP @ 16 C)
Testing Method Used:	Wave Tank; At-Sea Testing
Organizations/Venues Involved:	SL Ross Environmental Research Ltd.; MAR Inc.; U.S. Department of the Interior, Minerals Management Service (MMS); OHMSETT
Effectiveness Factors Discussed:	Mixing Energy, Dispersant Type, Oil Properties
Keywords:	Sea trials, wave tank, mixing energy, effectiveness measurement, Arctic conditions
Suggested Future Work	[1.] The authors point out that since effectiveness was based in part on visual observations, argument could be made that wave tank testing will produce consistently higher rankings based purely on better visibility. However, sufficient data are not available to test this theory, and could be the subject of future work. [2.] The conclusion from wave tank testing that only control level dispersibility is achieved for the IFO 380 oil was pointed out as suspect by the authors, due to a significantly lower dispersant treatment as compared to the IFO 180 oil. This occurred as a result of slower spreading of the higher viscosity oil. Repeating this test with better control is recommended.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Dispersant Effectiveness on Three Oils under Various Simulated Environmental Conditions
Author(s):	S. Chandrasekar; G. Sorial; J. Weaver
Publication Date:	2005
Publication Source:	Environmental Engineering Science

SUMMARY

A full factorial experiment was used to evaluate the effects of temperature, oil type, weathering, dispersant type, and rotational speed (mixing energy) on dispersant effectiveness. The baffled flask test was used to evaluate dispersant effectiveness. Three temperatures, three oils, three rotational speeds, and two dispersants were tested. ANOVA was used to identify significant factors affecting dispersant effectiveness and linear regression models were developed for each oil-dispersant pair, with dispersant effectiveness as a function of significant factors.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

The linear regression models matched well with the experiments, with R^2 values above 90% in all cases. The authors noted that increased mixing energy and decreased weathering both led to increased dispersant effectiveness. They also noted that a consistent trend between dispersant effectiveness and temperature was not found.

OTHER INFORMATION

Dispersants Tested:	Not Given
Oil Species Tested:	South Louisiana Crude, Prudhoe Bay Crude, Number 2 Fuel Oil
Oil Classifications/Properties:	Weathering – 0%, 10%, 20% (SLC and PBC), 0%, 3.8%, 7.6% (2FO)
Testing Method Used:	Baffled Flask Test
Organizations/Venues Involved:	University of Cincinnati, U.S. Environmental Protection Agency
Effectiveness Factors Discussed:	Oil Properties, Temperature, Mixing Energy, Weathering
Keywords:	Baffled flask, statistics
Suggested Future Work	N/A

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Measuring Energy Dissipation Rates in a Wave Tank
Author(s):	A.D. Venosa; V.J. Kaku; M.C. Boufadel; K. Lee
Publication Date:	2005
Publication Source:	International Oil Spill Conference Proceedings

SUMMARY

This paper provided information on a new wave tank facility constructed at the Bedford Institute of Oceanography. Comparison of mixing energy results between the wave tank and laboratory tests (swirling flask test and baffled flask test) were presented. The dissipation of kinetic energy was measured, and used as the basis of comparison between test types. Justification for this stems from reasoning that dissipation is due to turbulent and laminar shears within the water, and shear in turn, is directly proportional to velocity gradients that define the mixing intensity of chemicals.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

Mixing energy comparison in laboratory flask testing showed that dissipation was consistently much higher in the baffled flask test (BFT) compared to the swirling flask test (SFT). While the SFT exhibited solid body motion of the fluid, the BFT displayed high and low velocity values throughout the flask to provide overall better mixing. Additionally, the dissipation rates in the BFT were shown to be similar in magnitude to typical breaking wave conditions generated in the wave tank. Wave tank testing was conducted at two different breaking-wave energies, and conservation of dissipation between the wave tank scale and the field-testing scale indicated wave tank testing is sufficient to accurately evaluate the effectiveness of a dispersants.

OTHER INFORMATION

Dispersants Tested:	Corexit 9500
Oil Species Tested:	Mesa Light Crude
Oil Classifications/Properties:	Not Provided.
Testing Method Used:	Batch Wave Tank, Swirling Flask Test, Baffled Flask Test
Organizations/Venues Involved:	U.S. Environmental Protection Agency; Temple University; Bedford Institute of Oceanography, Fisheries, and Oceans (DFO);
Effectiveness Factors Discussed:	Mixing Energy
Keywords:	Wave tank, breaking waves, mixing energy
Suggested Future Work	The authors intend to perform follow-on work to quantify the effectiveness of dispersants under various mixing energies. In addition, upgrades to the wave tank to allow for flow-through conditions will be completed. Future research is also planned by the authors in the area of toxicity effects on caged pelagic fish species at various locations within the wave tank.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	The Effectiveness of Dispersants under Various Temperature and Salinity Regimes
Author(s):	Merv Fingas; Ben Fieldhouse; Zhendi Wang
Publication Date:	2005
Publication Source:	Arctic Marine Oil Spill Program Technical Seminar (AMOP)

SUMMARY

This study was conducted as a result of a conclusion drawn from a previous publication (Fingas and Ka'aihue, 2005) stating there is not enough data to observe the effect of temperature-salinity interaction on dispersant effectiveness. Therefore, a study was conducted using the ASTM standard test with Corexit 9500 and ASMB oil at five different temperatures, ranging from 5-25 degrees C, and eight different salinities, ranging from 0-35 o/oo. Two different calibration methods, RPH and TPH, were used to analyze the oil-water mixture with a gas chromatograph. A separate temperature calibration curve was created at each specific temperature, as well as a composite temperature calibration curve from all five temperatures. Old (1998) and new (2003) batches of Corexit 9500 were tested to see if the effect of salinity and temperature on dispersant effectiveness varies due to different processing conditions or feed stock, affecting surfactant properties. The results of these tests were compared with an earlier salinity-temperature interaction test explained in literature, Moles et al.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

It was found that using RPH or TPH calibration methods does not affect the temperature-salinity interaction and only affects the calculated dispersant effectiveness value by 1-3%, with the TPH values being slightly higher. Using a calibration curve created at specific temperatures or a composite calibration curve also only affects the calculated effectiveness value by a few percent. Therefore, analytical variation due to the calibration method is insignificant, close to being within the standard deviation. An interrelationship between temperature, salinity, and effectiveness was observed because the maximum effectiveness occurred at 10 degrees C and 25 o/oo, not the expected highest temperature and salinity values. This indicates there may be a peak salinity based on surfactant content, indicating a three-way trade off between temperature, salinity, and effectiveness that is dependent on the specific dispersant. A possible explanation is the increase in effectiveness at higher temperatures causes the ionic strength to match with the surfactant polarity. The results were similar to that shown by Moles et al. with maximum effectiveness occurring between 20 to 30 o/oo, and slight differences explained by oil type (ASMB vs. Prudhoe Bay). In comparing the two different dispersant batches, a very large effectiveness difference occurred, and even the temperature-effectiveness curve was somewhat different from 10-20 degrees C.

OTHER INFORMATION

Dispersants Tested:	Corexit 9500, Corexit 9527
Oil Species Tested:	Alberta Sweet Mixed Blend (ASMB)
Oil Classifications/Properties:	Not Confirmed In Paper
Testing Method Used:	ASTM Standard Test, GC with Flame Ionization Detector using Resolved Peak Method (RPH) and Total Petroleum Hydrocarbons (TBH) Calibration Methods
Organizations/Venues Involved:	Environmental Technology Center
Effectiveness Factors Discussed:	Temperature, Salinity, Temperature-Salinity Interaction, Old vs. New Batches, RPH vs. TPH Methods, Specific vs. General Temperature Calibration Curves, Manual vs. Automatic Baseline Placement
Keywords:	Salinity-Temperature Interaction, Calibration Curve, TPH, RPH
Suggested Future Work	Use the three-way correlation between temperature, salinity, and effectiveness to create a predictive model.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Dispersant Effectiveness on Oil Spills - Impact of Salinity
Author(s):	S. Chandrasekar; G. Sorial; J. Weaver
Publication Date:	2006
Publication Source:	ICES Journal of Marine Science

SUMMARY

A full factorial experiment was performed to study the effects of salinity, temperature, oil type, oil weathering, dispersant type, and rotating speed on dispersant effectiveness. Three salinities, temperatures, oil types, levels of weathering, and rotating speeds were used in this experiment, and two dispersants were used. The baffled flask test was used to measure dispersant effectiveness. A very large number of tests were performed, with each data point repeated four times.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

Salinity increased dispersion for most oil-dispersant pairs. Salinity also had an effect on “the significance of temperature on dispersant effectiveness.”

OTHER INFORMATION

Dispersants Tested:	Not Given
Oil Species Tested:	South Louisiana Crude, Prudhoe Bay Crude, Number 2 Fuel Oil
Oil Classifications/Properties:	Weathering – 0%, 10%, 20% (SLC and PBC), 0%, 3.8%, 7.6% (2FO)
Testing Method Used:	Baffled Flask Test
Organizations/Venues Involved:	University of Cincinnati, U.S. Environmental Protection Agency
Effectiveness Factors Discussed:	Oil Properties, Temperature, Salinity, Mixing Energy, Weathering
Keywords:	Baffled flask, statistics, salinity
Suggested Future Work	N/A

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Flow Dynamics in Eccentrically Rotating Flasks used for Dispersant Effectiveness Testing
Author(s):	Vikram J. Kaku; Michel Boufadel; Albert D. Venosa; James Weaver
Publication Date:	2006
Publication Source:	Environmental Fluid Mechanics

SUMMARY

This study compared the mixing characteristics of fluid using the swirling flask test (SFT) method versus the baffled flask test (BFT) method. Small-scale structures of turbulence are generally understood to be independent of the system or orientation effects (locally isotropic). Thus, laboratory experiments may be used to extrapolate dispersion effects of oil on a much larger scale. Hotwire anemometry was used in this study to measure the azimuthal and radial water speeds at five speeds, ranging from 50 to 200 rpm. Note that for standardized testing, SFT is conducted at 150 rpm, while the BFT is conducted at 200 rpm. The average Kolmogorov scale (K-scale) measured in laboratory experiments was used to correlate to the expected oil droplet size in an oil spill. Justification for this comes from the fact that the K-scale represents the smallest eddy size. If the smallest eddies are smaller than an oil droplet, it would be expected that they would stretch and eventually break it apart. Conversely, if they were larger, they would tend to entrain oil droplets without breaking them. An assumption in the study is that energy dissipation occurs predominately due to turbulent shear, neglecting effects of laminar shear. The authors stated that this is a common state for most environmental flows.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

Velocity measurements for the SFT method indicated that flow is primarily two-dimensional, with a stagnant core above 150 rpm. While flow appeared predominantly horizontal at low speeds, it switched to axi-symmetric for high speeds. Measurements with the BFT method showed the flow to be consistently three-dimensional in nature, with the zone of highest velocity at the center of the flask for all speeds. This zone moved downward as the rotational speed was increased. Above 150 rpm, a sudden increase in radial and azimuthal speeds was noted. The authors stated that this was likely due to reaching the fully-turbulent regime at that point. The fact that BFT mixing is three-dimensional, while SFT is two-dimensional, suggests that the BFT test more closely approximated open sea conditions. In addition, the K-scale for SFT at 150 rpm was about 400 microns, while it was about 50 microns for the BFT at 200 rpms. Note that the size distribution of dispersed oil at sea was observed to be in the range of 50 to 400 microns. Thus, it was concluded by the authors that mixing in standardized SFT is not representative of dispersant mixing that occurs at sea, while the standardized BFT more closely replicates the physics.

OTHER INFORMATION

Dispersants Tested:	None
Oil Species Tested:	None
Oil Classifications/Properties:	N/A
Testing Method Used:	Swirling Flask Test, Baffled Flask Test
Organizations/Venues Involved:	Temple University, U.S. Environmental Protection Agency
Effectiveness Factors Discussed:	Testing Methods
Keywords:	Anemometer, Eccentric, Energy Dissipation, Rotating Flasks, Time Series Analysis, Turbulence, Velocity Gradient
Suggested Future Work	The authors suggest further study is needed to define the relationship between rotational speeds in BFT methods and various actual sea states. Similarly, they also state the need to quantify and define the energy dissipation rates at different sea states.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	A Review of Studies of Oil Spill Dispersant Effectiveness in Arctic Conditions
Author(s):	Alun Lewis and Per S. Daling
Publication Date:	2007
Publication Source:	SINTEF

SUMMARY

This article discussed the effect of Arctic conditions on dispersant effectiveness observed through several studies. It began with an introduction to the conditions in an Arctic environment, including low temperatures, ice presence, and salinity variations. Low temperatures increase oil viscosity, which will significantly decrease dispersant effectiveness above a certain value. Ice formations will vary based on season and location and can suppress wave action, reducing mixing energy and decreasing dispersion. Lower salinity also decreases dispersion and is common at enclosed areas and river estuaries due to seasonal melting. Ice formation also tends to increase salinity of surrounding water to varying degrees based on ice thickness. After the ice melts, salinity of the water will decrease causing a decrease in the density of the surface water. The article went on to discuss several laboratory tests, large-scale tank tests, and tests conducted at the Oil and Hazardous Materials Simulated Environment Test Tank (OHMSETT) in New Jersey. Generally, most tests only observe the effects of low temperature on dispersion, but some observe the effect of ice, and a few observe salinity effects.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

Temperature, salinity, and ice formation are all connected, so it is difficult to assess the individual contribution of each condition. Low temperatures will reduce effectiveness by increasing viscosity, but it also suppresses the weathering rate of the oil, which leads to a longer “window of opportunity” during which dispersants can be used. Ice causes out-of-phase movement at the oil/water interface that enables dispersion at low frequency and small amplitude wave conditions that wouldn’t be possible without ice. However, this was observed in tank tests that may not accurately represent conditions at sea due to wall shearing and paddle-induced waves. Melted ice will temporarily decrease salinity in upper water layers, but the effect of small, low-salinity areas at the oil/water interface on dispersion is unknown and future testing should be conducted.

OTHER INFORMATION

Dispersants Tested:	Corexit 9527, 9500, 8666, and 9550; Oilsperse 43; BP 1100X; Drew OSE 71; IKU-9; Dasic-LTS and NS; Inipol-IPC, IPF, and IFP; Enersperse 700 & 1037; Dispolene 36S & 38S; Finasol OSR-52 and OSR-5
Oil Species Tested:	Alaska North Slope (ANS), Hibernia, Endicott, North Star, Point McIntyre, Chayvo, Prudhoe Bay Crude Oils; Russian Export Blend Crude Oil (REBCO); Oseberg Blend 150°C+; Oseberg Blend 150°C+/50% w/o-Emulsion
Oil Classifications/Properties:	Temperature – 0-22 degrees C, Viscosity – not listed, Weathering – values not listed, Pour Point - ?-27 degrees C
Testing Method Used:	Mackay/Nadeau/Steelman (MNS), WSL, EPA Test Protocol, IFP, Swirling Flask Test (SFT), Modified SFT, ExDet, Oscillating Hoop, Tank Tests with Paddle Wave-Maker, Large-Scale Testing (10,000 ton) at OHMSETT
Organizations/Venues Involved:	SINTEF; SL Ross Environmental Research Ltd.; DF Dickens Associates; AGIP KCO; Chevron; ConocoPhillips; Shell; Statoil; Total
Effectiveness Factors Discussed:	Temperature, Ice Presence, and Salinity
Keywords:	Arctic, salinity, mixing energy
Suggested Future Work	Study the effect of sea ice on dispersion by observing the effect of spring thawing conditions on salinity at various ice and energy conditions

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Effects of Chemical Dispersants and Mineral Fines on Crude Oil Dispersion in a Wave Tank Under Breaking Waves
Author(s):	Z. Li; P. Kepkay; K. Lee; T. King; M. Boufadel; A. Venosa
Publication Date:	2007
Publication Source:	Marine Pollution Bulletin

SUMMARY

Four tests were run to investigate the effects of dispersants and mineral fines on particle sizes and distributions in a wave tank. A control test was run with just oil, then one test with dispersant and mineral fines individually, then a test with both. The wave tank was 16-m long, 0.6-m wide, and 2-m high and filled with filtered seawater. For each test, oil and the prescribed fines or dispersant were added to ~2 L of seawater and mixed for two hours. Test conditions were set such that breaking waves were created in the middle of the tank where the oil mix was applied. The test was run for five hours. Samples were taken to measure oil distribution in the tank and a LISST-100x was used to measure particle size and particle volume concentration.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

The tests showed that both mineral fines and dispersant promoted dispersion of the oil. Together the two additives were the most effective. The combination also produced the smallest particles. The authors explained this through three factors. First, the reduced interfacial tension via the dispersant allowed the fines to attach to oil droplets and further break them down. Second, this interaction reduced the amount of time necessary to produce small droplets. This time is usually limited by the amount of time the dispersant is present before it is washed into the seawater. Third, the mineral fines increased the density of the particles, preventing them from resurfacing.

OTHER INFORMATION

Dispersants Tested:	Corexit 9500
Oil Species Tested:	Scotia Shelf Condensate, Weathered
Oil Classifications/Properties:	Density = 0.869 mg/L, Viscosity = 6 mPa*s
Testing Method Used:	Wave Tank
Organizations/Venues Involved:	Bedford Institute of Oceanography, Fisheries, and Oceans (DFO); Temple University; U.S. Environmental Protection Agency
Effectiveness Factors Discussed:	Oil Composition
Keywords:	Oil composition, mesoscale, viscosity
Suggested Future Work	Other factors in OMA and dispersant interaction, such as oil types, weathering state, and surface properties of mineral fines should be evaluated further. Further research is warranted to model interactions between crude oil, suspended sediments, and dispersants.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Assessment of Chemical Dispersant Effectiveness in a Wave Tank Under Regular Non-Breaking And Breaking Wave Conditions
Author(s):	Zhengkai Li; Kenneth Lee; Thomas King; Michel C. Boufadel; Albert D. Venosa
Publication Date:	2008
Publication Source:	Marine Pollution Bulletin

SUMMARY

This paper investigated the effect of mixing energy on dispersant effectiveness using wave tank tests. The authors postulated these tests to be superior to bench-scale testing, due to inclusion of transport and dilution effects. Three energy dissipation rates of waves were considered: (1) non-breaking waves of constant frequency and wave height, (2) spilling breaking waves generated by alternating high-frequency and low-frequency waves, and (3) plunging breaking waves of alternating frequencies with higher wave heights compared to the spilling waves. Dispersant effectiveness was determined through sampling the dispersed oil concentration at various locations, and by analyzing the oil-droplet size distribution in the wave tank.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

Oil concentration results indicated that natural oil dispersion was low under non-breaking wave conditions. While surface spreading of oil was enhanced by the addition of the dispersant, concentrations in the bulk phase remained sufficiently low to suggest application of dispersants under calm seas is unlikely to be effective at low mixing energies. Concentration results for spilling breaking waves showed increased dispersion of oil due to the presence of dispersant. However, insufficient penetration depth of the dispersed oil was noted near the bottom of the tank. Concentration results for plunging breaking waves resulted in increased natural dispersion of the oil, with dramatically increased dispersion with the addition of the chemical dispersant. Overall, the intrusion depth of the oil was noted to be strongly correlated to the energy dissipation rate. Oil droplet measurements under regular non-breaking wave conditions showed droplet sizes of the order of 200 microns. This reduced (without the addition of a dispersant) to 100 and 70 microns for spilling and plunging breaking waves, respectively. Addition of the dispersant to non-breaking waves lowered the droplet size to 50 microns. Interestingly, addition of the dispersant to the higher energy waves led to comparable droplet sizes (~ 50 microns). Thus, the effect of the dispersant was noted to be less pronounced for higher energy waves with regard to oil-droplet breakup.

OTHER INFORMATION

Dispersants Tested:	Corexit EC9500A
Oil Species Tested:	MESA Crude Oil (Petro-Canada, Montreal, QC)
Oil Classifications/Properties:	API Gravity 29.7-deg.; Weathered by Aeration to 86.2% of Original Weight
Testing Method Used:	Wave Tank (Batch)
Organizations/Venues Involved:	Bedford Institute of Oceanography, Fisheries, and Oceans (DFO); Temple University; U.S. Environmental Protection Agency (EPA)
Effectiveness Factors Discussed:	Mixing Energy
Keywords:	Oil spill; droplet size distribution; energy dissipation rate; breaking waves
Suggested Future Work	The authors suggest expansion of their current investigation to include the effect of various crude oils and dispersant formulations on dispersant effectiveness as a function of energy dissipation rate. Also, the wave tank facility recently underwent an upgrade to extend its length and incorporate a flow-through system. It is suggested that additional experimental studies be conducted in the upgraded facility. Finally, modeling of oil-drop breakage with computational fluid mechanics was being pursued by the authors at the time of the paper publication.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Calm Seas Application and Dispersant Wash-Out
Author(s):	Not Listed
Publication Date:	2008
Publication Source:	SL Ross Environmental Ltd.

SUMMARY

This series of tests investigated the effects on dispersion of water currents without the presence of breaking waves. The tests were performed at the OHMSETT facility, a 203-m long, 20-m wide, 3.3-m deep tank with a wave generator that is filled with seawater and used as a mesoscale test facility for dispersion studies. Oil that was premixed with Corexit 9500 at a dispersant-to-oil ratio of 1:20 was applied to the surface. Its location was kept constant through the use of floating barriers. A bubble barrier was used to generate small currents in each test. Three oils were tested: weathered Alaska North Slope, IFO 30, and IFO180. Tests lasted from two to four days. As controls, oil mixed with dispersant was also applied to trays of seawater that were kept still. Periodically, samples were taken from the slicks and tested using the Warren Spring Lab test for dispersion. At the conclusion of each test, breaking waves were generated and a LISST system was used to measure particle diameter and oil concentration. Due to the nature of the experiment, dispersion effectiveness was not calculated or estimated. Measured values were used as relative indicators of dispersion.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

The IFO 180 appeared to lose dispersant very quickly. The authors attributed this to the temperature, which was near the pour point for the oil. The IFO-30 and Alaska North Slope both illustrated similar behaviors, with the currents leaching dispersant away from the oil. This was indicated by the LISST system and Warren Spring Lab tests.

OTHER INFORMATION

Dispersants Tested:	Corexit 9500
Oil Species Tested:	Alaska North Slope, IFO 30, IFO 180
Oil Classifications/Properties:	Viscosity – 60 cP (ANS), 260 cP (IFO-30), 1,800 cP (IFO-180) all at 15 degrees C, Weathering – 0, 10, 25% by volume, Density – 0.892 g/mL (ANS), 0.935 g/mL (IFO-30), 0.962 g/mL (IFO-180), Pour Point
Testing Method Used:	Mesoscale at OHMSETT, LISST, Warren Spring Lab
Organizations/Venues Involved:	SL Ross Environmental Research Ltd.; OHMSETT
Effectiveness Factors Discussed:	Mixing Energy
Keywords:	Currents, calm seas
Suggested Future Work	Additional testing at OHMSETT should be designed to elucidate a relationship between the WSL test and the wave tank testing.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Dispersant Effectiveness on Oil Spills - Empirical Correlations
Author(s):	K. Nagarajan; N. Deshpande; G. Sorial; J. Weaver
Publication Date:	2008
Publication Source:	International Oil Spill Conference

SUMMARY

Multiple tests were run evaluating dispersant effectiveness using the baffled flask test. South Louisiana and Prudhoe Bay Crudes, as well as Number 2 Fuel Oil, were tested at three different levels of weathering. Corexit 9500 and Dispersit-SPC 1000 were used as dispersants in these tests. Three salinities were chosen as ranging from estuary to average ocean levels. Six temperatures and three mixing speeds were tested. Viscosity measurements were taken for each oil at each level of weathering and at each tested temperature. A correlation identifying viscosity as a function of weathering and temperature was used and a linear regression model was developed for the full data set, with dispersant effectiveness modeled as a function of viscosity, salinity, and mixing speed.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

All of the factors included in this experiment (viscosity, temperature, weathering, salinity, mixing speed) had significant effects on dispersant effectiveness for each oil-dispersant pair.

OTHER INFORMATION

Dispersants Tested:	Corexit 9500, Dispersit-SPC 1000
Oil Species Tested:	South Louisiana Crude, Prudhoe Bay Crude, Number 2 Fuel Oil
Oil Classifications/Properties:	Weathering – 0%, 10%, 20% by volume, Viscosity (all at 22 degrees C) – 5.445 cSt (SLC 0%), 8.691 cSt (SLC 10%), 13.756 cSt (SLC 20%), 32.548 cSt (PBC 0%), 91.649 cSt (PBC 10%), 248.394 cSt (PBC 20%), 3.58 (2FO 0%), 3.781 cSt (2FO 3.8%), 3.917 cSt (2FO 7.6%)
Testing Method Used:	Baffled Flask Test
Organizations/Venues Involved:	University of Cincinnati, U.S. Environmental Protection Agency
Effectiveness Factors Discussed:	Oil Properties, Temperature, Salinity, Mixing Energy, Weathering
Keywords:	Baffled flask, statistics, salinity, estuary
Suggested Future Work	N/A

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Dispersant Effectiveness Testing On Viscous, U.S. Outer Continental Shelf Crude Oils and Water-in-Oil Emulsions at OHMSETT
Author(s):	R. Belore; A. Lewis; A. Guarino; J. Mullin
Publication Date:	2008
Publication Source:	International Oil Spill Conference

SUMMARY

Two sets of tests were performed at the OHMSETT facility, a 203-m long, 20-m wide, 3.3-m deep tank with a wave generator that is filled with seawater and used as a mesoscale test facility for dispersion studies. The first evaluated the effect of viscosity on dispersability of crude oils. For each test, the wave generator was adjusted until the desired wave conditions were achieved. The crude oil was then applied, immediately followed by the dispersant. After application, the test was run for 20 minutes. The wave generator was turned off and the water allowed to settle. Oil that remained on the surface was then collected and measured for dispersion effectiveness calculation. In the second set of tests, the fresh oil was replaced with a water-in-oil emulsion.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

Oils with viscosities less than 6,500 cP resulted in dispersion effectiveness between 40% and 90%. The dispersion effectiveness for oils with viscosity greater than 33,000 cP was less than 10%. Emulsions with viscosity above 10,000 cP resulted in dispersion effectiveness less than 12%, while emulsions with viscosity below 10,000 cP resulted in dispersion effectiveness up to 40%. Corexit 9527 performed slightly better than Corexit 9500 in most emulsion test cases.

OTHER INFORMATION

Dispersants Tested:	Corexit 9500, Corexit 9527
Oil Species Tested:	Elly, Gilda, Gina, Harmony, Heritage, Irene, Sockeye, Endicott, IFO 30, IFO 120
Oil Classifications/Properties:	All Heavy Crude Oils, Viscosities Ranging from 80 to 30,000 cP
Testing Method Used:	OHMSETT Mesoscale
Organizations/Venues Involved:	SL Ross Environmental Research Ltd.; U.S. Department of the Interior, Minerals Management Service (MMS); MAR Inc.; Oil Spill Consultancy
Effectiveness Factors Discussed:	Oil Composition
Keywords:	Oil composition, mesoscale, viscosity, water-in-oil emulsion
Suggested Future Work	The authors noted that the experiment lacked a test oil between 10,000-12,000 cP and another gap existed at around 20,000 cP.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Dispersant Effectiveness as a Function of Energy Dissipation Rate in an Experimental Wave Tank
Author(s):	A.D. Venosa; M. Boufadel; Z. Li.; E. Wickley-Olson; T. King
Publication Date:	2008
Publication Source:	2008 International Oil Spill Conference

SUMMARY

Dispersant effectiveness testing was conducted in a wave tank with seawater on Unweathered Alaska North Slope Crude and Weathered MESA Light Crude Oil using Corexit 9500, SPC 1000, and no dispersant application over a three different energy dissipation rates (regular non-breaking waves, spilling breakers, and plunging breakers). Energy dissipation rate was measured using wave gauges that record wavelength and amplitude. Oil volumetric concentration in the water column was measured using a spectrophotometer at three different wavelengths. The tested dispersant-to-oil ratio was 1:25 with an initial oil volume of 300 mL.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

The authors suggested that mixing energy is one of the most important factors in oil dispersion. Results were determined by measuring the oil concentrations at the surface, at a median depth, and near the bottom of the tank through syringe ports in the tank. Dispersion occurs more readily with high-energy dissipation rates while non-breaking waves just transport the oil on the surface. Corexit 9500 performed better than SPC 1000 in low-energy breaking waves and SPC 1000 performed better in high-energy dissipation rates. The findings from this study suggest that dispersant use in a deepwater environment with moderately energetic wave conditions could lead to less oil rising to the surface.

OTHER INFORMATION

Dispersants Tested:	Corexit 9500, SPC 1000
Oil Species Tested:	Unweathered Alaska North Slope and Weathered MESA Light
Oil Classifications/Properties:	Alaska North Slope (API 32), MESA Light (API 30)
Testing Method Used:	Wave Tank
Organizations/Venues Involved:	Government & University Research
Effectiveness Factors Discussed:	Mixing Energy
Keywords:	Wave tank, effectiveness, energy dissipation rate, oil concentration
Suggested Future Work	This study was conducted under batch conditions, but future work should consider continuous flowing oil into the water column.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Effect of Mixing Energy, Mixing Time and Settling Time on Dispersion Effectiveness in Two Bench-Scale Testing Systems
Author(s):	Biplab Mukherjee
Publication Date:	May 2008
Publication Source:	International Oil Spill Conference

SUMMARY

Dispersion experiments were conducted to study the effect that mixing energy, mixing time, and settling time have on dispersant effectiveness and droplet size distribution on Weathered Mars Crude Oil. The dispersants tested were a mixture of n-dodecane as a solvent and Tween 80 or Span 80 as the surfactant. These fluids were mixed to obtain hydrophile-lipohile balances (HLB) of 10 and 12. Test runs were conducted with baffled flasks and paddle jar mixing systems by premixing the oil and dispersant. The droplet sizes were measured with an optical particle counter and the dispersion effectiveness was measured as a percentage of floating surface oil that remained in the flask after a 20-minute settling time. Small, medium, and large droplets where quantified by particle diameters of less than seven microns, between seven and 18 microns, and greater than 18 microns, respectively.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

For all cases studied within this experimental program, it was found that the dispersion effectiveness increased with mixing energy added to the system and that dispersion effectiveness reached a maximum value and then leveled off regardless of additional energy dissipation. The baffled flask system generated similar behavior for both HLB 10 and 12 mixtures, but the paddle jar system results indicated that dispersion effectiveness was more sensitive to oil-dispersant properties. The paddle jar results showed that HLB 12 dispersed the oil into medium-sized droplets and that HLB 10 resulted in large droplets. Mixing time did not seem to have a significant effect on dispersion effectiveness when compared to the effects of energy dissipation rates and oil-dispersant combination. Both the paddle jar and baffled flask experiments resulted in multimodal distributions of droplet size, which suggests more than one mechanism for dispersion, which was not identified in this study.

OTHER INFORMATION

Dispersants Tested:	Dispersants with a HLB of 10 and 12
Oil Species Tested:	Elaborately Weathered Mars Crude Oil, API >30
Oil Classifications/Properties:	0T
Testing Method Used:	Baffled Flask and Paddle Jar Mixing Systems
Organizations/Venues Involved:	University Research
Effectiveness Factors Discussed:	Mixing Energy
Keywords:	Paddle-jar, baffled-flask, mixing energy, mixing time, settling time, energy dissipation, dispersant effectiveness, droplet size
Suggested Future Work	The author suggested that a detailed study on the effect of flow dynamics in dispersion would provide more information on the mechanism of droplet formation to explain the differences in results from different bench-scale systems and multimodal size distributions.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	New Dispersant Delivered as a Gel
Author(s):	Tim Nedwed; Gerard P Canevari; James R Clark; Randy Belore
Publication Date:	2008
Publication Source:	International Oil Spill Conference Proceedings

SUMMARY

This paper presented initial laboratory test results comparing effectiveness of a new ExxonMobil gel dispersant to that of a conventional dispersant. Whereas conventional dispersants are sprayed with a 300-700 micron droplet size to reduce loss of dispersant to the water column, the new gel will be delivered in much larger droplets (up to 0.5 cm) that are positively buoyant and adhere to oil slicks (oleophilic). One hundred and ten tests were performed in a wave basin facility to provide side-by-side comparison data between dispersants. Dispersant-to-oil ratios (DORs) ranging from 1:20 to 1:200 were studied using nine oils with a wide range of viscosities. In addition, a single comparison test was conducted using a rotating flask with heavy oil collected from the 2002 Prestige spill off the coast of Spain.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

Wave basin testing showed both dispersants worked well for medium to light crude oils at high DORs. However, the new dispersant outperformed Corexit 9500 for lower DORs, heavy oils, and lower mixing energies. Four main improvements were noted for the new dispersant: (1) reduces spray drift due to use of larger buoyant droplets that can re-contact a slick if they penetrate into the water or miss the slick, (2) provides visual feedback on dispersant coverage since it may be clearly seen when applied to oil, (3) effective on heavier oils due to olephilic gel delivery that adheres to oil slick without washing off, and (4) utilizes 90% active surfactant in gel compared to traditional 40-50% active ingredients. Wave basin tests suggest the new formulation may more than triple the capacity of airborne response platforms to treat light to medium oil spills. In addition, rotating flask tests showed the new dispersant was able to disperse the highly viscous Prestige oil sample, whereas the Corexit 9500 was not effective.

OTHER INFORMATION

Dispersants Tested:	New ExxonMobil Dispersant (10,100 cP @ 15 C; 0.921 g/cc); Corexit 9500 (107 cP @ 15C; 0.968 g/cc)
Oil Species Tested:	Gilda, Elly, Gina, IFO 580, Doba, Terra Nova, Hibernia, Edicott, Alaska North Slope, Prestige 2002 Oil Spill Sample
Oil Classifications/Properties:	Density and Viscosity Information for Nine Test Oils are Provided In Table 1; Prestige Oil Had a Viscosity of 30,000 at 15C.
Testing Method Used:	Wave Basin, Rotating Flask
Organizations/Venues Involved:	ExxonMobil; GP Canevari and Associates; SL Ross Environmental Research Ltd.
Effectiveness Factors Discussed:	Dispersant Type, DOR, Oil Viscosity
Keywords:	Dispersant gel, wave tank, heavy oil
Suggested Future Work	Due to the very different fluid properties of the new dispersant compared to traditional formulations, a new delivery system must be designed and a prototype built. Once completed, field testing of the delivery efficiency for the new dispersant will commence. Final toxicity testing of the new dispersant also had not been completed at the time of this paper.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Oil Droplet Size Distribution as a Function of Energy Dissipation Rate in an Experimental Wave Tank
Author(s):	Zhengkai Li; Kenneth Lee; Thomas King; Michel C. Boufadel; Albert D. Venosa
Publication Date:	2008
Publication Source:	2008 International Oil Spill Conference

SUMMARY

Dispersant effectiveness testing was conducted in a wave tank with seawater on Unweathered Alaska North Slope Crude and Weathered MESA Light Crude Oil using Corexit 9500, SPC 1000 and no dispersant application over a three different energy dissipation rates (regular non-breaking waves, spilling breakers, and plunging breakers). Energy dissipation rate was measured using an acoustic Doppler velocimeter at different locations within the tank. Oil droplet size in the water column was measured using a laser in-situ scattering and transmissiometer (LISST-100X, Type C). The tested dispersant-to-oil ratio was 1:25 with an initial oil volume of 300 mL.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

Dispersant effectiveness is directly related to oil concentration and the droplet size distribution within the water column. A high dispersant effectiveness is associated with smaller oil droplets and vice versa. In this study, dispersant effectiveness was evaluated by determining the oil concentration in the water column after two hours of dispersion. Chemical dispersants, as well as wave energy, were used to disperse the oil in this study. The wave energy for non-breaking, spilling breaker, and plunging breaker was measured to be 0.005, 0.1, and 1 m2/s3, respectively. Without chemical dispersants, the MESA was dispersed up to 20% in the low to medium energy waves and up to 30% for the high energy. With SPC 1000, the dispersant effectiveness was 30% at the low energy and increased to about 50% with the medium and high energies. Using Corexit 9500, the dispersant effectiveness was 50% at the low energy and up to 70% at the higher wave energies. The Alaskan North Crude demonstrated similar results with slightly more dispersability due to lower viscosity and interfacial oil-water surface tension. Droplet sizes measured during the start of experiments was around 150 microns and was reduced to about 20 microns 90 minutes into the experiment with high-energy dissipation rates. At low-energy dissipation rates, Corexit 9500 was able to reduce the droplet size significantly more than SPC 1000, while with the medium energy rates the results were statistically similar.

OTHER INFORMATION

Dispersants Tested:	Corexit 9500, SPC 1000
Oil Species Tested:	Unweathered Alaska North Slope and Weathered MESA Light
Oil Classifications/Properties:	Alaska North Slope (API 32), MESA Light (API 30)
Testing Method Used:	Wave Tank
Organizations/Venues Involved:	Government & University Research
Effectiveness Factors Discussed:	Up to 70% with Corexit 9500
Keywords:	Wave tank, effectiveness, energy dissipation rate, oil concentration
Suggested Future Work	This study was conducted under batch conditions, but future work should consider continuous flowing oil into the water column.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Evaluating Crude Oil Chemical Dispersion Efficacy in a Flow-Through Wave Tank under Regular Non-Breaking Wave and Breaking Wave Conditions
Author(s):	Zhengkai Li; Kenneth Lee; Thomas King; Michel C. Boufadel; Albert D. Venosa
Publication Date:	2009
Publication Source:	Marine Pollution Bulletin

SUMMARY

This paper introduced a new experimental method for studying the effectiveness of dispersants using a wave tank. Earlier closed volume tank facilities suffered from back-flowing underwater currents and artificially enhanced dispersant exposure levels. However, the facility described in this paper was built as a flow-through system that more closely simulates an open sea environment with ocean currents. Both low-energy non-breaking waves and high-energy plunging breaking waves were studied by the authors. Effectiveness of two dispersants on two different crude oils was investigated. An equivalent oil concentration parameter was proposed and used for comparison of results among different study conditions.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

The authors presented data indicating significantly increased oil concentration in the water column as a result of dispersant addition under high wave energy conditions. Reduced oil droplet size distribution and accelerated dilution rates were also observed. Breaking waves led to much higher oil concentrations than non-breaking waves. Interestingly, the effectiveness of the two dispersants tested herein were very different in the batch system, but showed similar effectiveness in the present flow-through system. This demonstrates the superiority of the flow-through system in mimicking real-world conditions that prevent artificial re-coalescence of dispersed droplets.

OTHER INFORMATION

Dispersants Tested:	Corexit EC9500A (hydrocarbon-based reformulation of water-based Corexit 9527 – meant for use on higher viscosity oils and emulsions), SPC 1000 (water-based formulation)
Oil Species Tested:	Medium South American Crude (MESA), Alaska North Slope Crude (ANS)
Oil Classifications/Properties:	MESA: viscosity=42.3 cP at 21 C; ANS: viscosity=50.1 cP at 21 C. (Note MESA oil was weathered by evaporation to simulate approximately 14% loss of volatile components at sea after spill.)
Testing Method Used:	Wave Tank (breaking and regular non-breaking conditions)
Organizations/Venues Involved:	Bedford Institute of Oceanography, Fisheries, and Oceans (DFO); Temple University; National Risk Management Research Lab (US EPA)
Effectiveness Factors Discussed:	The concept of dynamic dispersant effectiveness (DDE) unique to the flow-through wave tank was presented here as an improved technique to compare dispersants. DDE incorporates both dispersion of oil into the water column and transport/dilution of the dispersed oil droplets through the water column. Traditional dispersant effectiveness (DE) obtained in bench-scale tests incorporates only contact efficiency effects between oil and dispersant under very enclosed conditions that influence transport and dilution effects.
Keywords:	Waves, currents, dynamic dispersant effectiveness, particle size distribution
Suggested Future Work	The flow-through wave tank system could be used for exposure studies on the toxicity of dispersed oil on sensitive marine species. This would more closely simulate the actual conditions of environmental concern. In addition, improved understanding of functional relationships between energy dissipation rate and dispersant effectiveness/particle size distribution could be used to improve predictive models for real-world scenarios.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Large-Scale Cold Water Dispersant Effectiveness Experiments with Alaskan Crude Oils and Corexit 9500 and 9527 Dispersants
Author(s):	Randy Belore; Ken Trudel; Joseph Mullin; Alan Guarino
Publication Date:	2009
Publication Source:	Marine Pollution Bulletin

SUMMARY

Four Alaskan Crude Oils in several states of weathering were tested in cold water conditions at OHMSETT, a large-scale testing facility. Water temperatures ranged from -4.4 to 9.4 degrees C. Corexit 9500 and 9527 were applied to oil slicks. Waves were then generated and the test was run for 45 minutes. During testing, oil concentration and droplet size were measured in the water. After the test was finished, oil remaining on the surface was collected and measured, and estimates of oil evaporation were made. It was assumed that the remainder of the oil had been dispersed. Dispersant effectiveness was then corrected by the fraction of observed droplets whose volume mean diameter was less than 70 microns, allowing for larger droplets that would otherwise move to the surface over time.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

Both dispersants were effective in cold water applications. Corexit 9500 performed better than Corexit 9527 in a significant number of tests. Weathering of the oil did not have a significant impact.

OTHER INFORMATION

Dispersants Tested:	Corexit 9500, Corexit 9527
Oil Species Tested:	Alaska North Slope, Endicott, Northstar, Pt. Mcintyre
Oil Classifications/Properties:	ANS (0.863-0.903 mg/L, 22-203 cP), Endicott (0.901-0.917 mg/L, 270-644 cP), Northstar (0.802-0.843 mg/L, 7.6-143 cP), Pt. McIntyre (0.861-0.898 mg/L, 34-695 cP)
Testing Method Used:	OHMSETT mesoscale
Organizations/Venues Involved:	SL Ross Environment Research Ltd.; U.S. Department of the Interior, Minerals Management Service; MAR Inc.
Effectiveness Factors Discussed:	Oil Properties, Temperature, Arctic Conditions
Keywords:	Cold water, Alaska, Corexit
Suggested Future Work	N/A

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Dispersibility of Crude Oil in Fresh Water
Author(s):	B.A. Wrenn; A. Virku;, B. Mukherjee; A.D. Venosa
Publication Date:	2009
Publication Source:	Environmental Pollution

SUMMARY

In this study, experimental dispersants were formulated to investigate the relationship between dispersant effectiveness in freshwater and dispersant composition. Limited work regarding dispersant performance in freshwaters has been conducted, and no information regarding the actual chemical composition of the dispersants has been reported. This study was intended to address this issue by formulating several “experimental” dispersants with known chemical compositions. Several dispersants were formulated with similar HLBs, but varying chemical compositions, to test the hypothesis that dispersants can be designed for low-salinity waters based on the HLB. Three HLB levels (8, 10, and 12) were tested with nine distinct formulations at each HLB level. These formulations were tested against a single, weathered crude oil (Mars GOM Crude, weathered while stirring under nitrogen for three days, resulting in an 18.5% mass loss) with a single synthetic lake water.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

Interestingly, the authors point out that, while most salinity investigations on dispersants have been conducted by diluting natural or artificial seawater, which is dominated by sodium and chloride ions, minor ions such as magnesium and calcium may be more important in determining dispersion effectiveness – this implies that any comparisons being made for freshwater dispersant effectiveness must take the detailed water composition into account. The authors conclude that the results from this study show that, at least with the GOM crude oil tested in the artificial lake water, dispersants can be formulated to be as effective in freshwater as the best commercially-available dispersants

OTHER INFORMATION

Dispersants Tested:	Custom, Experimental Formulations
Oil Types Tested:	GOM Crude Oil (“Mars”) 30 degrees API
Laboratory Testing Method Used:	Baffled Flask Test
Effectiveness Factors Discussed:	Salinity, Dispersant Composition
Keywords:	Freshwater
Suggested Future Work	Considerably more oils and freshwater formulations must be tested before determining that dispersants are an effective option for use in freshwaters.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Dispersant Studies of the Deepwater Horizon Oil Spill Response, Volume 2
Author(s):	Don Aurand; Randy Belore; Gina Coelho; Alun Lewis; Oliver Peltz
Publication Date:	June 17, 2010
Publication Source:	BP

SUMMARY

Prior to dispersant use for the Deepwater Horizon spill, BP conducted a literature review of dispersant use, laboratory effectiveness studies for dispersing MC 252 Crude, field studies for dispersing MC 252 Crude, and toxicity effects of dispersant release. The results from these experiments were presented in “Volume 1” of this series and summarized within “Volume 2.” In “Volume 2,” BP continued to study dispersant effectiveness in controlled wave tank and swirling flask tests, as well as toxicity screening tests.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

The results presented in “Volume 1” of this series indicated that the use of dispersants on large oil spills is uncommon. There are two notable spills (Braer spill in 1993, Sea Empress spill in 1996) in which dispersants that were used in large quantity were able to prevent some oil from reaching the shoreline. Exxon Dispersant Effectiveness Tests (EXDET) were conducted with MC 252 Crude with the Environmental Protection Agency’s endorsed dispersants. In these tests, Biodispers performed the best, and Corexit EC95500A, Nokomis 3-AA, and JD2000 achieved an intermediate level of effectiveness, while Sea Brat #4, Dispersant SPC 1000, and SAF-RON Gold performed poorly. Field studies indicated that Corexit EC9500A was the only dispersant that effectively dispersed the oil through visual observations, oil concentrations, and particle size determination. “Volume 2” testing was conducted with high-energy (DOR 1:250) and low-energy (DOR 1:200) wave tank and swirling flask tests. A water-oil control test was also completed to study the oil’s natural dispersant response. Corexit EC9500A, Corexit EC9527A, and Finasol OS 52 all performed well in the wave tank and swirling flask tests. Dispersion of the oil was achieved within six to 10 minutes in wave tank tests. In low-energy tests, Corexit EC9527A and Finasol OSR dispersant effectiveness declined, but still achieved high levels of dispersion. Nokomis 3-AA, Nokomis 3-F4, SAF-RON Gold, and Sea Brat #4 did not achieve dispersant effectiveness any higher than the water-oil control experiments. Similar results for the Corexit and Finasol products were present in the swirling flask tests. Results of the toxicity testing were inconclusive because of the rapid deployment of the test and because of contamination of the sample crude used in the test.

OTHER INFORMATION

Dispersants Tested:	Corexit 9500, Corexit 9527, Dispersit SPC 1000, Finasol OSR 52, JD 2000, Nokomis 3-AA, Nokomis 3-F4, Saf-Ron Gold, Sea Brat
Oil Species Tested:	MC 252 Crude
Oil Classifications/Properties:	MC252
Testing Method Used:	Wave Tank, Swirling Flask
Organizations/Venues Involved:	BP; Ecosystem Management & Associates; SL Ross Environmental Research Ltd.
Effectiveness Factors Discussed:	Wave Tank and Swirling Flask Tests Indicated Dispersion up to 99% for Corexit EC9500A.
Keywords:	Wave tank, mixing energy, surface effectiveness,
Suggested Future Work	Conduct similar tests with crude oil that has been significantly weathered or has emulsified after being exposed to the water column. Further toxicity testing is required for Corexit EC9500A.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Effects of Temperature and Wave Conditions on Chemical Dispersion Efficacy of Heavy Fuel Oil in an Experimental Flow-Through Wave Tank
Author(s):	Z. Li; K. Lee; T. King; M.C. Boufadel; A.D. Venosa
Publication Date:	2010
Publication Source:	Marine Pollution Bulletin

SUMMARY

This study evaluated the effectiveness of two chemical dispersants on heavy fuel oil in a flow-through tank test under two different wave conditions, regular waves found at the sea surface and breaking waves. Effectiveness was related to the oil concentration in the water column and the droplet size distribution of the oil. The water temperature effect on dispersion was observed under both wave conditions, within a 10- to 17-degree C window. The flow-through tank was designed to simulate field conditions with waves and an underwater current flow. The experiment added oil to seawater, followed by dispersant with a dispersant-to-oil ratio of 1:25. Wave conditions were maintained for one hour before sampling at multiple locations downstream of the wave maker, at three different water column depths, and through the effluent sampling port. The data were analyzed using an analysis of covariance (ANCOVA) for statistical significance.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

The dynamic dispersant effectiveness (DDE) was higher under breaking waves than regular waves. The maximum DDE, 90% for Corexit 9500 and 50% for SPC 1000, occurred under breaking waves at the highest temperature, 16 degrees C. Dispersion was ineffective at all temperatures for regular wave conditions and at low temperatures for breaking wave conditions, indicating high DDE dependence on temperature under breaking waves only. Small droplet size, less than 200 µm, is associated with effective dispersion. Reduced droplet diameters were observed under breaking waves compared to regular waves, regardless of dispersant presence. Under breaking wave conditions, the addition of either dispersant further reduced droplet size, as observed in previous studies with Unweathered MESA and ANS Crude Oils. Relatively large droplet size and poor DDE under both wave conditions for heavy oil compared to crude oil was attributed to higher interfacial tension and oil viscosity. Droplet size distribution and DDE was relatively the same for IFO180 as crude oils by means of natural dispersion. The observed mixing energy effect was consistent with that seen in previous tests, indicating feasible chemical dispersion of heavy oil under appropriate environmental conditions.

OTHER INFORMATION

Dispersants Tested:	Corexit 9500, SPC 1000
Oil Species Tested:	IFO180 Fuel Oil
Oil Classifications/Properties:	Heavy, specific gravity = 0.96, dynamic viscosity = 2,471 mPa s, Oil-seawater interfacial tension = 21 mN/m (at 15 degrees C)
Testing Method Used:	Experimental Flow-Through Wave Tank
Organizations/Venues Involved:	Bedford Institute of Oceanography, Fisheries, and Oceans (DFO); Program of Energy Research and Development (PERD); U.S. Environmental Protection Agency; NOAA/UNH Coastal Response Research Center; U.S. Department of the Interior, Minerals Management Service; Temple University
Effectiveness Factors Discussed:	Wave Conditions (Regular or Breaking), Mixing Energy, Temperature, Dispersant Type, Oil Type, Droplet Size Distribution, DDE
Keywords:	Heavy fuel oil, temperature effect, wave effect, DDE, droplet size distribution
Suggested Future Work	Perform similar tests for a variety of heavy oils and multiple batches of IFO180 fuel oil to be able to generalize findings for all heavy oils.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION	
Title:	Literature Review of Chemical Oil Spill Dispersants and Herders in Fresh and Brackish Waters
Author(s):	SL Ross Environmental Research Ltd.
Publication Date:	January 2010
Publication Source:	SL Ross Environmental Research Ltd.

SUMMARY

The objective of this report was to assist decision makers when confronted with oil spills in fresh and brackish waters by documenting what was then known about the use of dispersants and chemical herders in this type of environment due to laboratory, large-scale, and field tests. The research included reviewing scientific journals that studied the effect of salinity on dispersant effectiveness. Laboratory tests that were reviewed observed salinity effects using a variety of test methods, oil types, salinities, temperatures, and dispersant types, including marine and freshwater dispersants. The effect of salinity on chemical herder performance was also reviewed. Existing policies and guidelines that were then in effect for dispersant use in fresh and brackish waters were studied for France, the U.S., the U.K., Canada, the Caspian Sea, and the Baltic Sea.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

Dispersants that are formulated for use in marine waters are less effective at water salinities above 40 ppt and below 20 ppt. Dispersants formulated for use in freshwater show better performance than marine dispersants, with maximum effectiveness occurring between salinities of 10 to 20 ppt. Chemical herders are not affected by water salinity or ice presence and are useful to create thicker slicks for in-situ burning. The only country that has a list of approved dispersants for freshwater use is France. Freshwater oil spill recovery practices are published in the U.K. with no mention of dispersants. Canada and the U.S. have freshwater recovery guidelines that vaguely mention dispersants, but don’t include a decision-making guide, specific criteria, or integration procedures. The Caspian Sea recommends dispersants as a primary spill response option only in water depths greater than 10 m at distances greater than 5 km from the shore after evaluation of dispersant toxicity, effectiveness, and environmental effects and a secondary response option elsewhere. The Baltic Sea dispersant guidelines state that mechanical recovery should be used, while chemical dispersant use should be limited as much as possible.

OTHER INFORMATION	
Dispersants Tested:	Corexit 9500, 9527, 7664, 9600, 8667, 9550, 8666, 9580; Enersperse 700; Citrikleen; Dasic FW; Inipol-IPF; MP 900; W-1911; BP1100X; Oilsperse 43; Drew OSE 71; OFD D-60
Oil Species Tested:	Adgo, IFO 30, Warren Spring; Alberta Sweet Mixed Blend (ASMB), Alaska North Slope (ANS), Lago Medio, Prudhoe Bay, Oseberg, Gullfaks, Veslefrikk, MARS, Norman Wells Crudes
Oil Classifications/Properties:	ANS and Lago Medio Crudes Tested Fresh and Weathered; Oseberg, Gullfaks, and Veslefrikk Crudes Tested Weathered and Emulsified (50% Water)
Testing Method Used:	Baffled, Swirling, and Rotating Flask; EXDET; Mackay-Nadeau-Steelman (MNS), Large-Scale (Freshwater Sloughs, Streambeds, Fen Lakes)
Organizations/Venues Involved:	U.S. Department of the Interior, Minerals Management Service (MMS)
Effectiveness Factors Discussed:	Salinity (Fresh and Brackish Waters), Temperature, Dispersant Type, Oil Type, Testing Method; Salinity and Ice Presence on Chemical Herders
Keywords:	Fresh and brackish waters, chemical herders, Caspian Sea, Baltic Sea
Suggested Future Work	Obtain more information on the use of dispersants in the Baltic Sea so that the Helinski Commission (HELCOM) changes its recommendation to stick to mechanical recovery and avoid the use of chemical agents. Develop freshwater dispersant decision-making guidelines and integration methods for use with other countermeasures in the U.S., U.K., and Canada.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Oil in Ice - JIP Report No. 19: Mesoscale Weathering of Oil as a Function of Ice Conditions. Oil Properties, Dispersibility and In-Situ Burnability of Weathered Oil as a Function of Time
Author(s):	Per Johan Brandvik; Janne Lise Myrhaug Resby; Per Snorre Daling; Janne Fritt-Rasmussen; Frode Leirvik
Publication Date:	2010
Publication Source:	SINTEF JIP

SUMMARY

This report covered a large joint industry project studying the effects of weathering, dispersant application, and in-situ burning after an oil spill in icy waters. A controlled weathering process was produced by cutting a flow loop into ice and filling it with seawater and crude oil. Propellers and a wave generator were used to induce flow in the loop, while fans and lamps were used to simulate wind and solar effects. Large chunks of hard ice were added to the flow loop such that the desired surface coverage was reached. Weathering experiments lasted 72 hours. At several points through each experiment, the resulting water-in-oil emulsion was sampled for water content, viscosity, and evaporation. High ice levels inhibited water uptake by decreasing the mixing energy at the surface. This inhibition was less pronounced in oils with high levels of waxes, resins, and asphaltenes as these compounds tend to stabilize emulsions. No general trend was found for the effect of ice on viscosity or evaporation. A similar set of tests was performed to study dispersibility. The resulting emulsion was sampled and tested using Corexit 9500 in an MNS test. Tests were also performed where dispersant was applied to the whole flow loop. No general trends were found for the effects of ice on dispersibility with these oils and this dispersant. The authors did note that the decreased weathering of the oil tends to increase the amount of time after a spill when dispersant use is effective. It was also noted that when ice coverage is above 50% to 70%, additional mixing energy may be necessary to enhance dispersion.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

Oil spills in icy conditions are dispersible and weather slower than in temperate conditions. The window of time during which dispersants may be applied is lengthened in icy conditions due to lower weathering rates.

OTHER INFORMATION

Dispersants Tested:	Corexit 9500
Oil Species Tested:	Statfjord, Grane, Troll B, Norne, Kobbe
Oil Classifications/Properties:	Density, Pour Point, Wax %, Asphaltene %
Testing Method Used:	IFP, MNS
Organizations/Venues Involved:	SINTEF
Effectiveness Factors Discussed:	Oil Properties, Salinity, Temperature, Arctic Conditions
Keywords:	Review, density, viscosity
Suggested Future Work	Procedural – apply a test application to a spill to check dispersibility of the oil/dispersant pair at an oil spill.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Oil Viscosity Limitation on Dispersibility of Crude Oil under Simulated At-Sea Conditions in a Large Wave Tank
Author(s):	K. Trudel; R. Belore; J. Mullin; A. Guarino
Publication Date:	2010
Publication Source:	Marine Pollution Bulletin

SUMMARY

This set of tests sought to find an upper limit on viscosity for dispersant application. Thirteen oils with viscosities ranging from 67 to 40,100 cP were used in the tests. Temperatures ranged from nine to 27 degrees C. Corexit 9500 was used as the dispersant. The article is not clear on dosage ratio, listing multiple values in two tables, but stating that the dosage ratio was a constant 1:20. The test facility is 203-m long, 20-m wide, and 3.3-m deep and is filled with filtered seawater. Each test began by generating waves. The oil and dispersant were then applied and exposed to the waves for 30 minutes. During testing, droplet size and oil concentration were monitored. The wave generator was then turned off, the liquid allowed to settle, and the oil remaining on the surface was collected and measured. Control tests were also performed with oil and seawater with no dispersant. The reported dispersion effectiveness was corrected by the natural dispersion measured in the control tests.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

Dispersion effectiveness is shown to fall with increasing viscosity. Oils > 33,000 cP reported corrected dispersion effectiveness of less than 13%. A viscosity between 18,690 and 33,400 cP is proposed as an upper limit past which dispersants are not effective.

OTHER INFORMATION

Dispersants Tested:	Corexit 9500
Oil Species Tested:	Crude Oils – Hondo, Beta, Hueneme, Santa Clara, Pt Pedernales, Pescado, Carpinteria
Oil Classifications/Properties:	Harmony (1,530 cP), Elly (4,980 cP), Gina (5,500 cP), Gilda (6,530 cP), Irene (33,400 cP), Heritage 2005 (40,100 cP), Henry (67 cP), Edith (290 cP), Gina H14 (1,393 cP), Heritage (1,408 cP), Eureka (2,565 cP), Heritage 2005 (10,610 cP), Gina H7 (18,690 cP)
Testing Method Used:	OHMSETT Mesoscale
Organizations/Venues Involved:	SL Ross Environmental Research Ld.; U.S. Department of the Interior, Minerals Management Service; MAR Inc.
Effectiveness Factors Discussed:	Oil Composition
Keywords:	Oil composition, mesoscale, viscosity
Suggested Future Work	N/A

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Effect of Oil Composition on Chemical Dispersion of Crude Oil
Author(s):	B. Mukherjee; J. Turner; B. Wrenn
Publication Date:	2011
Publication Source:	Environmental Engineering Science

SUMMARY

Dispersion effectiveness was studied for an array of oil blends adjusted to have specific ratios of saturates, aromatics, resins, and asphaltenes (SARA). Although crude oil is composed of many different chemicals, most can be classified as one of the SARA components and will react similarly to dispersants. The blends were based on Weathered Arabian Light Crude, which then had SARA components extracted from Lloyd Crude added and mixed. Corexit 9500 was used as the dispersant. The baffled flask test was used to measure dispersed oil, as well as oil droplet size. Each test was performed three times for repeatability. Fourteen different blends were tested with points at the maxima and minima of the SARA ratios, as well as points between. The dispersion effectiveness and average particle diameter were both analyzed using a generalized linear model, which accounts for individual SARA component effects and SARA component pair interactions.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

The results indicated an increased aromatic level was associated with increased dispersion effectiveness. A positive interaction between saturates and resins was also noted, as dispersion effectiveness increased when both components were present in high concentration. A proposed mechanism was “high concentrations of the saturates fraction may enhance dispersion of the oil as small droplets in water by facilitating the formation of favorable associations between the lipophilic surfactants of the resins fraction and the hydrophilic surfactants of the dispersant.” Droplet sizes were gathered around three modes for all tests: < 7 micron, 7 – 20 micron, and > 20 micron. SARA component ratios did not affect the droplet sizes encountered, but did affect the volume of oil found in each droplet size bin. High concentration of saturates and interactions between saturates and asphaltenes promoted small and medium-sized droplets. Aromatics and asphaltenes interacted to promote large-sized droplets.

OTHER INFORMATION

Dispersants Tested:	Corexit 9500
Oil Species Tested:	Arabian Light modified to have specific SARA ratios
Oil Classifications/Properties:	SARA
Testing Method Used:	Baffled Flask
Organizations/Venues Involved:	Washington University, Temple University
Effectiveness Factors Discussed:	Oil Composition
Keywords:	Oil composition, baffled flask, viscosity
Suggested Future Work	Better characterization of SARA fractions including viscosity is suggested.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Fate of Dispersants Associated with the Deepwater Horizon Oil Spill
Author(s):	Elizabeth B. Kujawinski; Melissa C. Kido Soule; David L. Valentine; Angela K. Boysen; Krista Longnecker; Molly C. Redmond
Publication Date:	2011
Publication Source:	Environmental Science and Technology

SUMMARY

Both Corexit 9527 (surface application) and Corexit 9500A (surface and subsea application), were used during the Deepwater Horizon blowout. Both dispersants contain the anionic surfactant dioctyl sodium sulfosuccinate (DOSS) that was used in this study as a tracer to model the deepwater plume and to determine the long-term toxicological effects. Chromatography and mass spectrometry were used to determine the DOSS concentrations in the water column samples. Most samples in this study were taken from subsea locations, rather than from the surface.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

The bulk of elevated DOSS concentrations was detected in water between 1,000 and 1,200 meters in depth and represents the deepwater plume that contains droplets that lack the buoyancy to rise to the surface. This plume traveled laterally at this depth and was carried by currents in the Gulf of Mexico. The data collected from this study suggests that the dispersant applied at the surface did not substantially intermingle within the water column and the deepwater injections appear to have stayed within the subsea plumes. The authors went on to state that observations associated with the DOSS concentrations cannot determine if dispersant application in subsea conditions is successful in reducing the oil droplet size or keeping the oil in deepwater; only that the DOSS compounds, and presumably other Corexit 9500A components did enter and stay with the deepwater plumes. Concentrations of DOSS within samples near the actively-flowing wellhead did indicate that the dispersant was applied at an effective dispersant-to-oil ratio of 0.05% based on published volume estimates for the spill.

OTHER INFORMATION

Dispersants Tested:	Corexit 9500A (surface/subsea application), Corexit 9527 (surface application)
Oil Species Tested:	N/A
Oil Classifications/Properties:	N/A
Testing Method Used:	Chromatography and Mass Spectrometry
Organizations/Venues Involved:	Woods Hole Oceanographic Institute, University Research
Effectiveness Factors Discussed:	Subsea
Keywords:	Solvent, dispersant, DOSS, subsea, tracers
Suggested Future Work	The authors suggest studying other molecules to assess the long-term transportability of these nonpolar surfactants and solvents from Corexit application.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Chapter 15 - Oil Spill Dispersants: A Technical Summary
Author(s):	Mervin Fingas
Publication Date:	2011
Publication Source:	Oil Spill Science and Technology

SUMMARY

This book chapter summarized many aspects related to oil dispersion. With respect to oil composition, Fingas noted that viscosity was not a reliable indicator of dispersibility. He noted that C12, C14, naphthalene, and other contents were good predictors of dispersibility, while physical characteristics were poor predictors.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

Paper is a Summary Text.

OTHER INFORMATION

Dispersants Tested:	N/A
Oil Species Tested:	N/A
Oil Classifications/Properties:	N/A
Testing Method Used:	N/A
Organizations/Venues Involved:	N/A
Effectiveness Factors Discussed:	N/A
Keywords:	Summary, book, chapter
Suggested Future Work	N/A

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Use of the BFT to Evaluate Eight Oil Dispersant Products and to Compare Dispersibility Of Twenty-Three Crude Oils – Chapter 3
Author(s):	Edith Holder
Publication Date:	July 2011
Publication Source:	University of Cincinnati

SUMMARY

The baffled flask test method was used to determine the dispersant effectiveness of Corexit 9500 when applied to 23 crude oils. These data are then compared to effectiveness data collected with the same oils and dispersant, but tested at the OHMSETT test facility.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

The baffled flask test effectiveness was shown to have a linear correlation with the OHMSETT effectiveness with R^2 = .48. For Corexit 9500, increasing viscosity was found to decrease effectiveness.

OTHER INFORMATION

Dispersants Tested:	Corexit 9500, SPC1000, JD-2000, Nokomis 3F4, Nokomis 3AA, SafRon Gold, ZI400, SeaBrat #4
Oil Species Tested:	Anadarko, ANS (20% evaporated), ANS (fresh), BHP Billiton, Doba, Elly, Endicott (18% evap), Endicott (fresh), Hamony, IFO 120, IFO 380, North Star, PER 038, PER 040, PXP 01, PXP 02, Rock, Terra Nova, Venoco e-10, Venoco E-19, South Louisiana, Arabian Light, Prudhoe Bay
Oil Classifications/Properties:	SLC (37 API, 4.8-9.1 cSt), Anadarko (24API, 11 cSt), ANS (20% evaporated 27 API, 58 cSt), ANS (fresh – 28 API, 40 cSt), BHP Billiton (API 21, 420 cSt), Doba (22 API, 2130 cSt), Elly (15.9 API, 10,125 cSt), Endicott (18% evap – 21.7 API, 560 cSt), Endicott (fresh – 21.7 API, 560 cSt), Hamony (18.4 API, 3809 cSt), IFO 120 (17.46 API, 1519 cSt), IFO 380 (14.69 API, 10859 cSt), North Star (35 API, 9 cSt), PER 038 (16.22 API, 3,114 cSt), PER 040 (14.4 API, 19,112 cSt), PXP 01 (16.99 API, 9,884 cSt), PXP 02 (14.84 API, 31,195 cSt), Rock (16.06 API, 3,438 cSt), Terra Nova (31.4 API, 438 cSt), Venoco e-10 (15.45 API, 12,389 cSt), Venoco E-19 (26.8 API, 72 cSt), Arabian Light (31.95 API, 8 cSt), Prudhoe Bay (26.46 API, 44 cSt)
Testing Method Used:	Baffled Flask
Organizations/Venues Involved:	University of Cincinnati, BOEMRE
Effectiveness Factors Discussed:	Oil Properties, Test Methods
Keywords:	Oil properties, baffled flask, viscosity, density
Suggested Future Work	None.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Evolution of the Macondo Well Blowout: Simulating the Effects of the Circulation and Synthetic Dispersants on the Subsea Oil Transport
Author(s):	Claire B. Paris; Matthieu Le Henaff; Zachary M. Aman; Ajit Subramaniam; Judith Helgers; Dong-Ping Wang; Vassiliki H. Kourafalou; and Ashwanth Srinivasan
Publication Date:	November 20, 2012
Publication Source:	Environmental Science and Technology

SUMMARY

A 3D stochastic model for oil droplet transport was created for simulating the effects that synthetic dispersants had on the uncontrolled release of crude oil from the Macondo well blowout in 2010. During the Macondo blowout, there was uncertainty in the formation of oil droplets and their size, which is the largest contributor to droplet rise velocity. Corexit 9500 was injected into the plume in order to break up the larger droplets and prevent the oil from rising to the surface. The dispersant-to-oil ratio was not known because of the unknown volumetric output from the blowout. Numerical experiments were conducted that evaluated the effects of particle size distribution, chemical dispersion, vertical currents, and oil droplet rise velocities.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

The authors' main conclusion from this numerical study was that the dispersant Corexit 9500 did not have a large effect on reducing droplet size for the oil that rose to the surface due to droplet size in the plume. The droplet size distribution has the largest effect on the transportability of the oil particles and dispersant effectiveness. Droplet size distribution depends on three factors: the chemistry of the crude oil, the shear rate, and the temperature at the ejection point. The assumed droplet size distribution from this study (one to 300 microns without dispersant) indicates that the majority of the particles were already close to being neutrally-buoyant due to the particular conditions of the blowout (relatively small riser pipe diameter and large ejection velocity). This study estimates that 1-2% less oil mass was transported to the surface with the use of Corexit 9500.

OTHER INFORMATION

Dispersants Tested:	Corexit 9500
Oil Species Tested:	Macondo Crude (MC-252)
Oil Classifications/Properties:	Oil Water Surface Tension of 20 mN/m.
Testing Method Used:	Numerical Simulation
Organizations/Venues Involved:	University Research, National Science Foundation
Effectiveness Factors Discussed:	Subsea
Keywords:	Numerical Simulation, Subsea, Droplet size
Suggested Future Work	Numerical and experimental methods should concentrate on determining the droplet size distribution from a subsea release. The droplet size distribution has the largest effect on subsea dispersant effectiveness.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Measurement of Interfacial Tension in Hydrocarbon/Water/Dispersant Systems at Deepwater Conditions
Author(s):	Mahmed Abdelrahim
Publication Date:	May 2012
Publication Source:	Louisiana State University

SUMMARY

Macondo Crude Oil and n-octance were mixed with synthetic seawater in this study to measure the oil/water interfacial surface tension (IFT) by the Pendant Drop method for deepwater conditions. The effectiveness of Corexit 9500 was evaluated through the reduction in IFT. Pressure, temperature, water salinity, and dispersant concentration were varied to independently determine their effect on IFT.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

The measured IFT was decreased from 25.69 to 22.55 mN/m from surface to seafloor conditions at the Macondo well (2,225 psi, 40F. 2.5 wt% salinity). Corexit 9500 was capable of reducing the IFT by 70% at the water surface and a 50% reduction was observed at seafloor conditions for a 1,000-ppm dispersant concentration that was dissolved into the water. A 58% reduction in IFT was observed for seafloor conditions when the dispersant was dissolved into the crude oil at 1,000 ppm. A reduction in the IFT of 90% was observed for the n-octane experiments; the author indicated that indigenous surfactants in the crude oil will likely lead to different dispersion processes. The low temperature at the seafloor is the primary factor that contributed to a reduction in dispersant effectiveness due to the increase in oil viscosity. Pressure had a smaller effect on the dispersant effectiveness when compared to temperature. At 10,000 ppm, the oil in this experiment at seafloor conditions took the shape of a continuous stream, rather than separating into smaller particles. Changes in dispersant effectiveness recorded in this study due to variations in water salinity were noted as being specific to the experimental setup and conclusions could not be drawn from the data.

OTHER INFORMATION

Dispersants Tested:	Corexit 9500
Oil Species Tested:	MC252 Crude (Macondo)
Oil Classifications/Properties:	API 36.2, Kinematic Viscosity 5.067 cSt
Testing Method Used:	Pendant Drop Method for IFT
Organizations/Venues Involved:	University Research, BP/The Gulf of Mexico Research Initiative
Effectiveness Factors Discussed:	Subsea
Keywords:	Salinity, Temperature, Pressure, Dispersant Effectiveness, Interfacial Surface Tension, Subsea
Suggested Future Work	Perform similar experiments with methods that can measure IFT lower than 1.0 mN/m. The crude oil used in this study was a “dead” sample without its dissolved light ends and this may contribute to dispersant effectiveness. A more accurate representation of seawater should be used to better understand the effect that salinity has on dispersant effectiveness.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Relationship Between Size of Oil Droplet Generated during Chemical Dispersion of Crude Oil and Energy Dissipation Rate: Dimensionless, Scaling, and Experimental Analysis.
Author(s):	Biplab Mukherjee; Brian A. Wrenn; Palghat Ramachandran
Publication Date:	October 12, 2011
Publication Source:	Chemical Engineering Science

SUMMARY

Dimensional and scaling analysis was performed on the various forces and physical properties of crude oils that effect the formation of droplets in flow fields. The scaling factors identified for the dimensionless mechanisms of droplet formation were compared to baffled flask mixing experiments.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

The study identified that there is not a simple one-to-one correlation with the size of the oil droplets during dispersion because of the differences in physical properties of oil and water (i.e., viscosity, oil/water interfacial tension, density); hence the need for a dimensionless and scaling analysis. The dimensionless and force balance analysis on droplet formation identified four energy dissipation scaling parameters based on the initial droplet size and their relationship to the Kolmogorov length scale. For droplets greater than the Kolmogorov length scale, the external force that deforms the droplets is the pressure difference across the droplet diameter. For droplets less than the Kolmogorov length scale, the viscous shear can deform the droplets. The energy scaling parameters for droplet formation identified in the analysis were experimentally verified against baffled flask mixing studies and against experimental data in a separate study for droplet formation of Prudhoe Bay Crudes. The results of this analytical model can be used to identify the most effective dispersant-to-oil ratio based on the specific physiochemical factors at the spill location.

OTHER INFORMATION

Dispersants Tested:	Corexit 9500, Laboratory Made HLB 10 & 12
Oil Species Tested:	Weathered Crudes (% Weathered): Arabian Light (23%), Mars (21%), Lloyd (17%)
Oil Classifications/Properties:	Arabian Light (API 32.8), Mars (API 30), Lloyd (API 22)
Testing Method Used:	Analytical and Baffled Flask
Organizations/Venues Involved:	University Research
Effectiveness Factors Discussed:	Mixing Energy
Keywords:	Baffled Flask, Energy Dissipation Rate, Mixing Energy, Droplet Size
Suggested Future Work	Large-scale dispersant testing with uneven flow fields and their effect on droplet formation is suggested.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	The Value of Dispersants for Offshore Oil Spill Response
Author(s):	Tim Nedwed; Tom Coolbaugh; Greg Demarco
Publication Date:	2012
Publication Source:	Offshore Technology Conference

SUMMARY

This paper began by briefly discussing oil behavior during a subsea release noting rapid dispersion is common with low-viscosity oils and high wave action. It then reviewed oil spill response options, including mechanical recovery, in-situ burning, and dispersants with a brief description of each method, along with respective advantages and disadvantages. Mechanical recovery physically removes oil form the surface using booms and skimmers. In-situ burning rapidly removes large quantities of thick oil layers from the surface using controlled burning. Dispersants enhance natural biodegradation to rapidly remove oil through the application of surfactants. The science behind dispersants was explained in more detail to confront popular misperceptions. This section included a description of dispersant chemistry, toxicity, effectiveness testing, the biodegradation process, and the potential effects on human health from dispersant exposure. The use of dispersants during the Deepwater Horizon incident was discussed to analyze dispersant effectiveness through both surface and subsea application methods.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

Dispersants effectively removed oil during the Deepwater Horizon incident. For large offshore spills, dispersants should be used as the primary response tool. Application by aircraft is most efficient for surface dispersant use. Subsea injection is the preferred application method because it reduces oil at the surface decreasing safety risks, less dispersant can be used for equal efficiency, mixing between dispersant and oil occurs before spreading, relatively no weather limitations exist, application can take place both day and night, and all oil is treated easier due to a single release point. Mechanical recovery is less effective, but should still be used for small spills near the shore because it is the only method that physically removes the spilled oil from the environment. In-situ burning was used for the first time offshore during the Deepwater Horizon spill because continuous spilling oil created a thick enough layer for burning without the use of booms. In-situ burning proved another effective response method for deepwater release.

OTHER INFORMATION

Dispersants Tested:	Dispersants used during Deepwater Horizon Incident
Oil Species Tested:	Macondo Well Oil
Oil Classifications/Properties:	Light (approximate viscosity of 1 cP)
Testing Method Used:	Field Application during Deepwater Horizon Incident Including Surface and Subsea Dispersant Injection
Organizations/Venues Involved:	ExxonMobil
Effectiveness Factors Discussed:	Oil Spill Response Options (Mechanical Recovery, In-Situ Burning, Dispersants), Surface Dispersant Application, Subsea Dispersant Injection
Keywords:	Mechanical recovery, in-situ burning, subsea dispersant injection, surface dispersant application, Deepwater Horizon, biodegradation, VOCs, toxicity
Suggested Future Work	Conduct studies on deepwater ecology, including linkages between ecosystems and interaction between dispersed oil and microbial communities. Increase understanding of biodegradation of crude oil by deepwater microbes. Use Deepwater Horizon incident to study dispersant effect on long-term environmental impacts.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Determining the Dispersibility of South Louisiana Crude Oil by Eight Oil Dispersant Products Listed on the NCP Product Schedule
Author(s):	Albert Venosa; Edith Holder
Publication Date:	2013
Publication Source:	Marine Pollution Bulletin

SUMMARY

Eight dispersants were tested using the baffled flask test on South Louisiana Crude (SLC) at two temperatures, five degrees C and 25 degrees C. These were chosen as typical ocean bed and surface temperatures near the Deepwater Horizon well; SLC was chosen as similar to the oil leaked from the well. Six tests were performed with each dispersant at each temperature, as well as six tests at each temperature with oil alone. Aquarium Systems "Instant Ocean" was used for saltwater. The baffled flask test was used as it has been shown to be more repeatable than the swirling flask test. Dispersit SPC1000, Corexit 9500, and JD 2000 were reported as effective for SLC, with dispersant effectiveness ranging from 78% to 83%. Sea Brat #4 was found to perform the worst. No general relationship between temperature and effectiveness was found, with effectiveness decreasing with increasing temperatures for some dispersants, while others increased with increasing temperatures.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

The baffled flask test is very repeatable, with more repeatability than the swirling flask test. Dispersit SPC1000 was found to perform best out of the eight dispersants tested at dispersing SLC. Sea Brat #4 was found to perform the worst. No general relationship between temperature and effectiveness was found.

OTHER INFORMATION

Dispersants Tested:	Corexit 9500A, Dispersit SPC1000, JD-2000, Nokomis 3-AA, Nokomis 3-F4, Saf-Ron Gold, Sea Brat #4, ZI-400
Oil Species Tested:	South Louisiana Crude
Oil Classifications/Properties:	Density – 0.84 kg/L (15 degrees C), API gravity – 37 degrees (15 degrees C), Pour point - -32 degrees C, Kinematic viscosity – 9.14 cSt (5 degrees C)
Testing Method Used:	Baffled Flask Test
Organizations/Venues Involved:	U.S. Environmental Protection Agency; Pegasus Technical Services
Effectiveness Factors Discussed:	Dispersant Type
Keywords:	South Louisiana Crude, baffled flask test
Suggested Future Work	Evaluate baffled flask test for applicability to real-world conditions.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Droplet Breakup in Subsea Oil Releases – Part 2: Predictions of Droplet Size Distributions With and Without Injection of Chemical Dispersants
Author(s):	Oistein Johansen; Per Johan Brandvik; Umer Farooq
Publication Date:	2013
Publication Source:	Marine Pollution Bulletin

SUMMARY

The objective of this paper was to present a new method for prediction of droplet size distributions from subsea blowouts. This is important from the standpoint of predicting the type of oil film, and thus the necessary type of oil spill response. The study focused on the turbulent breakup regime, as determined by the non-dimensional Ohnesorge number (We^0.5/Re). While empirical results from a mesoscale tower basin test facility were used to develop the predictive model, the model was also validated against the large-scale DeepSpill field experimental data. At present, the model applies only to single-phase (liquid-only) releases. However, the authors suggested that the model applicability may be expanded using their proposed void fraction correction for gas.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

The authors' model for prediction of turbulent drop breakup for oil (both untreated and with dispersant additive) was successfully developed. For coefficients of the dispersant/oil model, a modified Weber number was computed from experimental data. This Weber number is significantly reduced compared with standard Weber numbers of untreated oil. Reduction factors range from four to eight based on tower basin tests, with the largest reduction occurring at the highest exit velocity. Interestingly, the field-scale DeepSpill data suggested a reduction factor of only about 1.3 – though the exit velocity was much smaller than laboratory tests. The authors concluded that the viscosity term in the model played a larger role in laboratory tests on untreated oil, while void fraction and buoyancy effects are more important in field-scale experiments.

OTHER INFORMATION

Dispersants Tested:	Corexit C9500 (Nalco)
Oil Species Tested:	Oseberg Blend (Norwegian Crude)
Oil Classifications/Properties:	SG=0.8393, viscosity=5 mPa s, asphaltenes wt%=0.2, wax wt%=2.7 (typical light paraffinic blend with low viscosity and high evaporative losses)
Testing Method Used:	Mesoscale Test Facility; Dispersant Injected into Rising Oil Plume from Bottom of Tower Basin
Organizations/Venues Involved:	SINTEF Materials and Chemistry
Effectiveness Factors Discussed:	N/A
Keywords:	Subsea blowouts, droplet size distribution, chemical dispersants, model predictions
Suggested Future Work	The authors point out that the relationship between dispersant-to-oil ratio (DOR) and interfacial tension is not well established. They suggest that further study of interfacial tension measurements with a wider variety of oils premixed with different DORs could provide clarity on this point.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Droplet Breakup in Subsurface Oil Releases – Part 1: Experimental Study of Droplet Breakup and Effectiveness of Dispersant Injection
Author(s):	Per Johan Brandvik; Oistein Johansen; Frode Leirvik; Umer Farooq; Per S Daling
Publication Date:	2013
Publication Source:	Marine Pollution Bulletin

SUMMARY

This paper presented oil droplet size measurement data from experiments conducted in a mesoscale test facility meant to simulate subsea blowouts. The facility consisted of a tower basin, where pressurized oil and gas were injected from the bottom of the tank, while dispersant was injected upstream of the release. Three different methods were employed for determination of oil droplet sizes: a laser diffractometer, a macro camera, and in-line particle visual microscopy. Turbulent drop breakup experiments were divided into two categories: varying release conditions (velocity and gas ratio) and dispersant testing (dispersant-to-oil ratio).

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

While droplet breakup without dispersant addition appeared to follow a Weber number scaling law, dispersant experiments were shown not to adhere to the same scaling. Reductions in droplet size were not as large as expected. Lack of correlation with Weber scaling implies other factors limit droplet breakup in cases with significant reduction in interfacial tension (possibly viscous forces). Additionally, for very small dispersant-to-oil ratios (1:250), very little reduction in interfacial tension was observed.

OTHER INFORMATION

Dispersants Tested:	Corexit C9500 (Nalco)
Oil Species Tested:	Oseberg Blend (Norwegian Crude)
Oil Classifications/Properties:	SG=0.8393, viscosity=5 mPa s, asphaltenes wt%=0.2, wax wt%=2.7 (typical light paraffinic blend with low viscosity and high evaporative losses)
Testing Method Used:	Mesoscale Test Facility; Dispersant Injected into Rising Oil Plume from Bottom of Tower Basin
Organizations/Venues Involved:	SINTEF Materials and Chemistry
Effectiveness Factors Discussed:	Dispersant-to-Oil Ratio, Subsea
Keywords:	Subsurface blowouts, droplet size distribution, chemical dispersants, laboratory study
Suggested Future Work	Continue investigation of oil droplet breakup/sizing looking at influence of different injection methods, dispersant types, and oil types.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Interfacial Film Formation: Influence on Oil Spreading Rates in Lab Basin Tests and Dispersant Effectiveness Testing in a Wave Tank
Author(s):	Thomas L King; Jason A.C. Clyburne; Kenneth Lee; Brian J. Robinson
Publication Date:	2013
Publication Source:	Marine Pollution Bulletin

SUMMARY

The objective of this paper was to analyze the effect of surface films in lab basin and wave tanks on dispersant effectiveness testing. Both types of tests were conducted in an artificially closed/bounded environment, unlike the open sea where oil spills actually occur. Wall boundaries tend to restrict the spread of surfactants on the surface of the water, resulting in film formation. Earlier studies have shown surface films affect the thermodynamics of oil spreading, and can interfere with dispersant testing. A single dispersant type was used for both the lab basin and wave tank studies. A single oil was tested in the wave tank experiments, while three oil types were used in lab basin experiments. Generated waves simulated high-energy plunging breaking waves (1.0e-2 W/kg at surface, 5.0e-4 W/kg at 20-cm depth). Dispersant effectiveness was evaluated using a combination of hydrocarbon values and interfacial tension measurements. Surface films were generated using a syringe to deposit dispersant inside the initial oil ring to achieve a controlled 0.4-mm film thickness prior to start.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

Lab basin results indicated that contamination of seawater with a surface film greatly impeded oil spreading. The authors note that while oils initially spread quickly, as the oil layer thins and approaches walls, the rate of spreading on the seawater slows as an artifice of the closed system setup. Thus, it was concluded that surface films present during dispersant testing under static conditions in small-scale lab basin testing would probably affect test results. Wave tank testing indicated that compared to lab basin tests, higher surface area-to-volume ratios of water and high wave energy reduce the probability of interfacial film formation. However, test results indicated one hour was needed before the mixing energy in the wave tank negated all influence of the interfacial film on the chemical dispersant effectiveness. Thus, interpretation of data from closed wave tanks may be difficult, since the time required to wait until dissipation of surface film effects will be dependent on the system design and mixing energy of each particular test. In conclusion, the authors advocated using surface tension measurements to detect the presence of surface films for quality assurance purposes in closed-system laboratory testing for dispersant effectiveness.

OTHER INFORMATION

Dispersants Tested:	Corexit 9500A (0.948 g/mL density)
Oil Species Tested:	Arabian Light Crude (ALC); Alaskan North Slope Crude (ANS), Intermediate Fuel Oil 120 (IFO 120)
Oil Classifications/Properties:	ALC: weathered to remove volatiles by aeration to 93% by volume, 31-33 API gravity, 15.5 cP @ 20C; ANS: weathered by aeration to 90% by volume, 27-30 API gravity, 17.5 cP @ 20C; IFO 120: 15 API gravity, 1177 cP @ 50C
Testing Method Used:	Wave Tank, Lab Basin
Organizations/Venues Involved:	Centre for Offshore Oil, Gas, and Energy Research (COOGER - Canada); St. Mary's University; National Resources Research Centre (Australia)
Effectiveness Factors Discussed:	Effect of Artificial Surface Films Created in Closed-Laboratory Systems
Keywords:	Interfacial tension, surface film, kinetics, wave tanks
Suggested Future Work	Repeat studies of film surface measurements in a flow-through wave tank for comparison to a closed system are suggested.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Mesocosm Study on Weathering Characteristics of Iranian Heavy Crude Oil With and Without Dispersants
Author(s):	Changkyu Joo; Won Joon Shim; Gi Beum Kim; Sung Yong Ha; Moonkoo Kim; Joon Geon An; Eunsic Kim; Beom Kim; Seung Won Jung; Young-Ok Kim; Un Hyuk Yim
Publication Date:	2013
Publication Source:	Journal of Hazardous Materials

SUMMARY

Nine large “bags” were used to store 1,000 L of seawater each. These bags were .5 m in diameter and 5 m in height and were stored outside and exposed to the elements. Three contained just seawater as a control, three had 1 L of oil added, and three had a mixture of 1 L of oil and 100 mL of dispersant added. This study focused on the chemical degradation of the oil and did not report a dispersant effectiveness. “As this study only considered truly dispersed oil that gained neutral buoyancy over a longer time period, the output of the conventional OSD effectiveness test methods, such as the swirling flask, the baffled flask, and the field test, are not compatible with this study.”

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

The oil retained its chemical “fingerprint” throughout the 77-day test. Evaporation, dissolution, and dispersion contributed significantly to weathering.

OTHER INFORMATION

Dispersants Tested:	Hi-Clean
Oil Species Tested:	Iranian Heavy Crude
Oil Classifications/Properties:	API = 30
Testing Method Used:	Mesocosm
Organizations/Venues Involved:	Korea Institute of Ocean Science and Technology, Institute of Marine Industry
Effectiveness Factors Discussed:	none
Keywords:	Weathering, outdoor experiment, hi-clean
Suggested Future Work	None

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION	
Title:	Modelling of Subsurface Releases of Oil and Gas
Author(s):	Peter Johan Bergh Lindersen
Publication Date:	June 2013
Publication Source:	Norwegian University of Science and Technology

SUMMARY

This master's thesis studied droplet formation and plume theory in an effort to understand the hydrodynamics of multiphase fluids subsea releases in medium and deepwaters. The droplet size directly determines the ultimate fate of hydrocarbon particles in a subsea release. Oil that rises to the surface is usually dependent on release depth, gas-to-oil ratio, release velocity, and oil type. Simulations were performed on three Norwegian crude oils using SINTEF's Marine Environmental Modelling Workbench (MEMW) in order to study the droplet sizes with and without dispersant. Simulations were conducted over a 12-hour period with a fixed release rate of 4,800 m3/d for Alve, Norne, and Svale. The release diameter was 120 mm and the GOR was varied between 0, 100, 200, and 400. The interfacial oil surface tension (IFT) was assumed to be 20 mN/m without dispersant and 0.1 mN/m with dispersant. This IFT was also varied to simulate the effect of different dispersant-to-oil ratios (DORs). Experimental subsurface releases were also conducted in SINTEF's MiniTower (open top tank) and particle sizes/distributions were measured with a LISST-100X particle analyzer. Corexit 9500 was injected into each crude oil stream at a "tee" mixing location.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

Simulation results show that the average particle diameter for Alve was reduced from 568 microns to 38 microns with an assumed IFT of 0.1 mN/m. The simulations also showed that droplet size is strongly dependent on IFT, as expected. A reduction in IFT from 20 mN/m to 5 mN/m reduced the average droplet size from 405 to 147 microns. With an IFT of one mN/m the average droplet size was reduced to 75 microns within the simulation. Experimental results showed that the average droplet size was reduced for each oil type with injected dispersant (with a DOR of 100) and was also reduced with increasing oil flow rate due to the shear force at the nozzle. The measured IFTs for Alve, Norne, and Svale were 13, 18, 13 mN/m, respectively. The Alve and Svale measurements were performed at 13 degrees C, but the Norne was performed at 25 degrees C. With a DOR of 100, the IFTs for Alve, Norne, and Svale were measured as 0.09, 0.007, 0.4 mN/m, respectively with the same temperature as reported above with negligible change in density. There was good agreement between droplet size distributions between the simulation and experimental results, which suggests that MEMW could be a useful tool in the event of a subsea blowout with subsequent oil release.

OTHER INFORMATION	
Dispersants Tested:	Corexit 9500
Oil Species Tested:	Alve, Norne, Svale
Oil Classifications/Properties:	Alve (API 46, 12.5 cP @ five degrees C); Norne (API 32, 1,968 cP @ 13 degrees C); Svale (API 23, 257 cP @ five degrees C)
Testing Method Used:	Numerical Modeling, Experimental Droplet Measurement
Organizations/Venues Involved:	Norwegian University of Science and Technology
Effectiveness Factors Discussed:	Subsea
Keywords:	Numerical modeling, droplet size
Suggested Future Work	The author indicates that further work should vary viscosity as a function of shear rate to understand its effect on oil droplet size distributions. Also more simulations should be run with the latest version of MEMW to validate its robustness across other input conditions. Because of the limited amount of crude oil used in this experiment, a set of new experiments with the Mini-Tower should be repeated to confirm droplet size distributions.

REVIEWED LITERATURE

One-Page Summary

SOURCE INFORMATION

Title:	Chemical Dispersion of Oil With Mineral Fines in a Low Temperature Environment
Author(s):	Weizhi Wang; Ying Zheng; Kenneth Lee
Publication Date:	2013
Publication Source:	Marine Pollution Bulletin

SUMMARY

Baffled flask experiments were conducted with three test oils (Alaska North Slope Crude, Arabian Light Crude, and IFO-40 Fuel Oil), two dispersants (Corexit 9500 and Corexit 9527), one oil concentration (800 ppm), and one water salinity (30 g/L). In addition to dispersants, these experiments used fine particles (Kaolin) to induce the formation of oil-mineral-aggregates (OMAs) to investigate their effect on the dispersion of oil A full factorial matrix investigation of the three oils, two dispersant types, two dispersant-to-oil ratios (1:25 and 1:50), and five mineral-to-oil ratios (1:1.5, 1:2, 1:3, 1:6, and 1:12) was conducted. Experiments were conducted at two temperatures of 0-4 degrees C and 20 degrees C to investigate the effect of temperature. Oil content from baffled flask samples was determined using a UV spectrometer (UV-1800 Mapada). A Leica DM4000M microscope was used to determine particle size distribution on samples from the baffled flask.

CONCLUSIONS AND SIGNIFICANT CONTRIBUTIONS

Lower test temperatures resulted in decreased oil removal percentage (ORP) – the authors noted that the decrease was proportional to the increase in viscosity of each oil as a function of lowering temperature. The size frequency peaks for OMA shifted towards larger diameters when temperature decreased from 20 degrees C to two degrees C. The addition of dispersants to tests conducted with mineral fines (MOR of 1:3) in tests conducted at two degrees C showed improved oil removal percentages in all cases shown. The authors noted that optimal ratios of MOR and DOR exist and seem to be a function of oil type or viscosity. Corexit 9500 performed slightly better than Corexit 9527 in most cases tested.

OTHER INFORMATION

Dispersants Tested:	Corexit 9500, Corexit 9527
Oil Species Tested:	Alaska North Slope, Arabian Light Crude, IFO-40 Fuel Oil
Oil Classifications/Properties:	Alaska North Slope (Density: 0.8607 g/mL, Viscosity 66.11 mPaS at two degrees C); Arabian Light Crude (Density: 0.8691 g/mL, Viscosity 80.06 mPaS at two degrees C; IFO-40 (Density: 0.9393 g/mL, Viscosity: 8804.5 mPaS at two degrees C)
Testing Method Used:	Baffled Flask Test
Organizations/Venues Involved:	University of New Brunswick, Bedford Institute of Oceanography, Fisheries, and Oceans (DFO)
Effectiveness Factors Discussed:	Dispersant type, Oil type, Temperature
Keywords:	Mineral fines
Suggested Future Work	N/A