15 October 2013
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ARCTIC RESPONSE TECHNOLOGY
OIL SPILL PREPAREDNESS

DISPERSANT TESTING UNDER REALISTIC CONDITIONS

FINAL REPORT 2.1

Report from Joint Industry Programme to identify and summarise the state-of-the-art on research conducted to date on the effectiveness of dispersant and mineral fines in ice.

ABOUT THE JIP

Over the past four decades, the oil and gas industry has made significant advances in being able to detect, contain and clean up spills in Arctic environments. To further build on existing research, increase understanding of potential impacts of oil on the Arctic marine environment, and improve the technologies and methodologies for oil spill response, in January 2012, the international oil and gas industry launched a collaborative four-year effort – the **Arctic Oil Spill Response Technology Joint Industry Programme (JIP)**.

Over the course of the programme, the JIP will carry out a series of advanced research projects on six key areas: dispersants, environmental effects, trajectory modeling, remote sensing, mechanical recovery and in-situ burning. Expert technical working groups for each project are populated by the top researchers from each of the member companies.

JIP MEMBERS

The JIP is managed under the auspices of the International Association of Oil and Gas Producers (OGP) and is supported by nine international oil and gas companies – BP, Chevron, ConocoPhillips, Eni, ExxonMobil, North Caspian Operating Company (NCOC), Shell, Statoil, and Total – making it the largest pan-industry programme dedicated to this area of research and development.

EXECUTIVE SUMMARY

Introduction

This review has been prepared to identify and summarise the state-of-the-art on research conducted to date on the effectiveness of dispersant and mineral fines in ice, research describing Arctic-capable dispersant delivery systems and new experimental dispersant technologies. The review has focused on studies conducted in wave tanks with ice present where the effectiveness of dispersants was quantitatively determined. This aim has been to identify the test oils and test conditions that have already undergone study in an attempt to guide and minimise the testing in later Tasks in the project.

What we learned - Key findings

The past studies have produced some common conclusions:

1. *The presence of ice pieces on the water surface in wave tanks increases dispersant effectiveness, compared to the same test oil/dispersant DOR/wave energy combination without ice.*
2. *While a slight wave-breaking action is a requirement for rapid dispersion of dispersant-treated oil in the absence of ice, wave conditions that would produce breaking waves if ice was not present are not required for effective dispersion of oil with ice. Very low wave energy with ice present is insufficient to cause dispersion of oil, but moderate swells of non-breaking waves plus sufficient ice coverage causes dispersion of many dispersant-treated oils.*
3. *As with dispersant use on oils in open water, the oil dispersion process with ice present is resisted by the flow behaviour of the dispersant-treated oil and promoted by mixing energy input. Increased weathering of oil increasingly resists dispersion, but this resistance can be overcome in part by increased mixing energy input.*
4. *Studies in flume basins and at sea have demonstrated that the weathering processes are slowed down when ice is present, enabling a longer "time window" for dispersant application.*
5. *Highly weathered oils that are not dispersed by the addition of dispersant in waves with ice can be dispersed by the application of additionally mixing energy such as that supplied by ASD (Azimuthal Stern Drive) units or other sources such as water thrusters.*

Recommendations on areas for further research

1. *The selection of crude oils, and the method used to artificially weather the oil to a particular extent, will be a very important consideration for future work. The test oils used in future work needs to be adequately characterized so that the testing will be repeatable and reproducible.*
2. *Only two dispersants have been used in past work; Corexits 9527 and 9500. The use of Corexit 9500 in future work has some justification; unless dispersant brand is to be a variable investigated in future work.*

3. *The wave conditions produced in wave tanks cannot be rigorously correlated with waves at sea. The addition of ice to water in the wave tanks adds another level of simulation that requires experimental justification.*

PURPOSE

This review has been prepared to identify and summarise the state of the art reports and research conducted to date on:

- The effectiveness of dispersant and mineral fines in ice.
- Research describing Arctic capable delivery systems.
- New "experimental" dispersant technologies.

The review has focused on studies conducted in wave tanks with ice present where the effectiveness of dispersants was quantitatively determined. This aim has been to identify the test oils and test conditions that have already undergone study in an attempt to guide and minimise the testing in later Tasks in the project.

An Excel spreadsheet (DispEffectInIce.xlxs) accompanies this report. The Excel spreadsheet contains a summary of the major independent variables altered to affect the dependent variable of dispersant effectiveness, plus details of the independent variable parameters for each study.

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CHAPTER 1. OVERVIEW OF DISPERSANT EFFECTIVENESS IN THE OPEN SEA

The overall aim of using dispersants on spilled oil is to reduce the environmental impact of spilled oil by removing the oil from the sea surface and transferring it into the water column. Spilled oil drifting into shallow water and drifting ashore can contaminate habitats of oil-sensitive organisms. Oil dispersed at sea is rapidly diluted to low concentrations in the water column and is biodegraded to large extent. Any use of dispersant should be the subject of an evaluation in the form of NEBA (Net Environmental Benefit Analysis). The effect of using dispersants on spilled oil is to break the oil down into very small oil droplets that are dispersed in the water column. The effectiveness of a dispersant applied to spilled oil can be defined as *the proportion (percentage) of a spilled oil that is permanently dispersed by the application of dispersant to the oil under the prevailing conditions.*

1.1 Natural dispersion

In flat calm sea conditions a layer of spilled oil floating on the sea surface will not be disrupted or broken up and the oil slick will drift with the prevailing current. The principal source of mixing energy that causes rapid natural dispersion of spilled oil in open water at sea is breaking waves. Breaking waves start to occur in open-water when the wind speed exceeds 7 to 10 knots and this is the onset of rapid natural dispersion of low viscosity oils. Even a small amount of wave-breaking at the crest of a wave has sufficient shearing action to locally disrupt the oil layer and convert the oil into droplets with a wide range of sizes. Dispersion of the larger oil droplets will be only temporary. Larger oil droplets, possessing higher buoyancy by virtue of their greater size, will rapidly float upwards through the water column and reach the water surface where they will rapidly spread out to reform an oil layer on the sea surface. Nevertheless, a small proportion of the oil may be converted into oil droplets that are small enough to be maintained in the water column by the turbulence present in the upper water column.

Permanently dispersed oil is the oil that has been converted into oil droplets that are sufficiently small to be retained in the water column by the prevailing turbulence. The eventual fate of dispersed oil is to be substantially biodegraded. The size of oil droplets that will be permanently dispersed is defined by their buoyancy (and therefore oil density) and the level of turbulence that is constantly present in the water column. The level of turbulence in the upper water column fluctuates with wave action and varies with the prevailing sea-state. The prevailing turbulence declines with increasing water depth. An often quoted value of the required oil droplet diameter for permanent dispersion is 70 microns (Lunel, 1995). This was measured in moderate sea states by dispersing a light crude oil from the sea surface and into the upper (10 to 20 metres) water column by the use of dispersants. The oil droplet diameter required for permanent dispersion will be higher for more dense oils in rougher seas and lower for less dense oils in calmer seas.

Dispersion of oil is the outcome of two opposing factors:

Dispersion of oil is <u>promoted</u> by the level of mixing action applied to the oil layer floating on the sea surface. In most cases this is provided by the prevailing wave action, but additional mixing from other sources such as propeller-wash from vessels can also be used.
Dispersion of oil is <u>resisted</u> by the physicochemical properties of the oil:

1. The oil/water interfacial tension (IFT), or interfacial surface free energy, resists the formation of increased interfacial area by the applied agitation and results in larger oil droplets being formed.

2. The bulk physical properties of oil can also resist the deformation of the oil and the break-up into droplets caused by the applied mixing energy.

1.2 Using dispersants to enhance dispersion of oil

The application of dispersant enhances dispersion because the blends of surfactants used in dispersants can cause a very marked reduction in the oil/water interfacial tension. This promotes the rapid formation of smaller oil droplets for a given mixing energy input. The addition of dispersant to oil allows the prevailing mixing energy, from the prevailing waves or other additional sources of agitation, to convert a much greater proportion of oil more rapidly into smaller oil droplets that will be permanently dispersed by the prevailing turbulence in the water column. The majority of the volume of these oil droplets will be subsequently biodegraded by microorganisms that occur naturally in the sea.

1.3 Oil flow behaviour limiting dispersant-enhanced dispersion

While the successful application of dispersant to a spilled oil will cause a very marked drop in oil/water IFT (interfacial tension, or interfacial free energy), this may not be sufficient under the prevailing mixing conditions to cause rapid dispersion of the dispersant-treated oil, because the dispersion can still be resisted by the bulk physical properties of the oil.

The flow properties of oil are often simplified and described by a single viscosity value at the relevant temperature. This has led to the concept of a 'limiting oil viscosity' for successful dispersion. No justifiable, single viscosity value that is applicable to all oils has been found. Instead, there are various estimates of viscosity ranges that have been proposed.

The reasons for there being no universally applicable viscosity value to define the limits of dispersant use are many. If oil viscosity was the only factor limiting dispersant performance, there would need to be a different limiting oil viscosity value for the prevailing sea state; higher viscosity oils would be dispersible in rougher seas. However, a much broader problem is that most weathered oils and the water-in-oil emulsions formed by these oils exhibit non-Newtonian flow behaviour. One aspect of non-Newtonian flow behaviour is that the viscosity decreases with increasing shear rate used to measure it. This has been addressed by standardizing the shear rate at a common value such as $10s^{-1}$, but this only partially addresses the complexities of non-Newtonian flow.

1.4 Factors influencing dispersant effectiveness in the open sea

From the previous overview it can be seen that the major factors influencing dispersant effectiveness are:

1) Physicochemical properties of the oil / emulsion under the prevailing conditions.
2) Dispersant formulation (brand) and treatment rate achieved by its application to the spilled oil.
3) Mixing energy. This includes (i) the mixing energy supplied to cause dispersion of the oil, and (ii) the prevailing turbulence in the water column available to maintain the oil droplets as being permanently dispersed.

Many subsidiary factors that contribute to each of these major factors have been identified and some are interrelated. For example, the flow properties of oil that can resist dispersion will be a function of the degree of oil weathering, the prevailing air / water temperatures and the shear stress that the oil is exposed by the imposed mixing action of waves or additional mixing.

1.5 Effect of ice on waves and the effects of waves and ice on the dispersion of oil

The presence of ice as pieces on the sea surface suppresses wave action at sea. The formation of capillary waves by wind action is suppressed by the presence of ice pieces on the sea surface. Longer wavelength swell can penetrate some distance into large ice fields. Breaking waves do not generally occur in ice fields. However, another possible mechanism for the initial dispersion of the oil layer exists when ice is present on the sea surface. Oil spilled amongst ice pieces on the sea surface will congregate on the water surface in between the ice pieces. The oil will be partially corralled by the ice into thicker layers than would occur in open water and this slows down the weathering processes (i.e. evaporation rate and w/o emulsification), compared to the rate on the open sea.

Any prevailing wind will cause the ice pieces to drift. The oil, being partially contained by the ice will also drift with the ice. Any prevailing wave action, such as swell, will cause the ice to move up and down. This movement of the ice is often slightly out of phase with the motion of the water due to the inertia of the ice pieces. This differential movement of the ice with respect to the water exerts a shearing action on the oil on the water at the edges of the ice pieces. Experience from previous observations made at sea (and reported in SINTEF JIP Oil-in-ice reports available from http://www.sintef.no/Projectweb/JIP-Oil-In-Ice/Publications/) and the wave-tank studies described in more detail in this report indicate that, if dispersant has been added to the oil, enhanced dispersion of the oil will occur along the ice/water edges under sea states where less dispersion would occur if ice were not present.

1.6 References

Lunel, T. 1995. Understanding the mechanism of dispersion through oil droplet size measurements at sea. In Lane, P. (ed.). The Use of Chemicals in Oil Spill Response. Philadelphia, Pa.: American Society for Testing and Materials. pp. 240-285. ISBN:0803119992.

CHAPTER 2. STUDIES OF DISPERSANT EFFECTIVENESS THAT HAVE BEEN CONDUCTED WITH ICE

Compared to the huge number of laboratory tests that have been conducted to determine the effectiveness of various dispersants on different oils without the presence of ice, studies of dispersant effectiveness in the presence of ice are few.

Simply added pieces of ice to the seawater used in almost all bench-scale laboratory tests for measuring dispersant effectiveness would not be a realistic simulation of the use of dispersants on spilled oil in ice at sea. Adding pieces of ice to the seawater in the WSL (Warren Spring Laboratory) rotating flask, Swirling Flask, Baffled Swirling Flask, IFP (Insitut Français du Pétrole), or MNS (Mackay-Nadeau-Steelman) or EXDET (Exxon Dispersant Effectiveness Test) dispersant effectiveness test methods would create a substantial increase in the mixing energy at the spilled oil/ice/water interfaces as the ice was tumbled, oscillated, blown around or shaken with the water and dispersant-treated oil by the primary mixing energy input method.

2.1 Dispersant effectiveness testing conducted in wave tanks

The reports and papers considered in this review are given in Table 1.

Table 1. Reports and papers reviewed

Abbreviation	Authors	Title	Reference
Owens and Belore. 2004	Owens, C. K and R. S. Belore 2004	Dispersant effectiveness testing in Cold water and Brash Ice.	27th AMOP 2004. pp 819-841
SL Ross, 2005	SL Ross, 2005	Phase 1 Tests to Evaluate the Effectiveness of Vessel Assisted Chemical Dispersion in Ice.	April 2005
Spring et al. 2006	Spring, W., T. Nedwed and R. Belore, 2006	Icebreaker Enhanced Chemical Dispersion of oil Spills.	29th AMOP, 2006 pp 711-727
SL Ross. 2006	SL Ross and MAR Inc. 2006	Dispersant Effectiveness Testing in Cold Water and Ice On Chayvo Z6 crude Oils for ExxonMobil Upstream Research.	June 2006
SL Ross. 2007	SL Ross July 2007	Scale Model Testing of Diversion Boom & Prop-Wash Assisted Oil Slick Dispersion in Simulated Ice.	
SINTEF JIP 19	Brandvik, P. J., J. L. M. Resby, P. S. Daling, F. Leirvik and J. Fritt-Rasmussen, 2010	Meso-Scale Weathering of Oil as a Function of Ice Conditions. Oil Properties, Dispersibility and In Situ Burnability of Weathered Oil as a Function of Time. JIP report no: 19	SINTEF A15563 ISBN 978-82-14-04772-1

In some cases, the work described in the reports has also been presented in other papers at conferences. These have not been included in the review. Earlier work, such as that conducted by Brown, H.M. and R.H. Goodman in 1996 (The Use of Dispersants in Broken Ice. 19th AMOP 1996 pp. 453-460) concluded that a 'fresh crude' oil treated with dispersant could be substantially dispersed when ice was present with wave generator settings that did not produce breaking waves. This work established the principle, but only later work explored the effect of variables and these are summarised in this report.

2.2 Purpose of testing, variables and findings

The purpose of conducting the testing and the variables used, classified into four categories; (i) Test Oils, (ii) Dispersant, (iii) Waves (plus Additional Mixing if used) and (iv) Ice are presented here for the six studies. Only major variables and results are included in the summaries of these studies.

2.2.1 Owens and Belore. 2004

Purpose

Tests were conducted at Ohmsett as a logical extension of previous testing of dispersant effectiveness on oils in cold water. Ohmsett had been used for testing of skimmers in ice (MORICE project) and the water-chillers were installed and ice was available.

Test oils

Oil to be tested was Chayvo crude oil from Sakhalin, but was in limited supply, so Hibernia crude oil was used as a surrogate for Chayvo crude oil on basis of similar density and Pour Point (ASTM D5853 – 11). ANS crude oil also subject of limited testing to show effect of oil type.

Dispersant

Corexit 9527 dispersant used as being available at Sakhalin and known to be effective on Hibernia from previous testing.

Waves

Three-metre diameter boomed areas of oil and ice subjected to long period, low height waves as breaking waves known not expected in ice-covered water.

'Low energy' waves (with 17cm average height and 5.5 second period) used for 30 minutes followed by 'higher energy' waves (with 33 cm average height and 4 second period) for another 30 minutes. 'Very low energy' waves of 15 cm height and 6 second period did not cause dispersion of oil.

Ice

Ice as "blocks" (~0.6m x ~0.6m) and "fragments" (small fragments less than 0.3m x 0.3m). Tests performed with mixtures of "blocks" and "fragments" of ice at 0/10, 4/10 and 8/10 ice coverage.

Findings

- Presence of ice increased amount of mixing for dispersion of oil. Higher ice concentration (8/10) produced higher effectiveness than4/10 ice coverage. No ice present led to less dispersion.
- Dispersant-treated fresh Chayvo, Hibernia and ANS crude oils substantially (>95%) dispersed with ice, less (92%) when no ice present. Weathered oils less dispersed than fresh crude oils.

2.2.2 *SL Ross. 2005*

Purpose

Tests conducted at SL Ross wave tank to determine if propeller wash from azimuthal stern drive (ASD) ice-breaking vessel would provide sufficient agitation in an ice field to cause dispersion of oil treated with dispersant.

Test oils

Chayvo Z6 crude oil was used in all tests. The oil was evaporated 9% and 12.3% by volume using air sparging to simulate 12 hours and 24 hours of weathering in 0ºC temperatures and 5 knot winds.

Dispersant

Corexit 9527 used in all tests, but water-diluted in one.

Waves and additional mixing

In all of the tests completed with ice present surface agitation was supplied using a Minn Kota Endura 46 electric trolling motor with its propeller shaft positioned at 35 cm below the water surface and directed parallel to the water surface. Waves with a 20 cm height and a period of 1.4 seconds were used in the open water tests.

Ice

The ice block dimensions used in the tests were 0.3m x 0.3m x 15mm thick Ice field with 80 to 90% ice cover was used in the testing.

Findings

- Weathered Chayvo Z-6 crude oil (9 to 12% evaporated by volume) was only about 50% dispersed when spilled on open ~0ºC water, treated with Corexit 9527 dispersant at a DOR of 1:20 and subjected to the maximum wave energy possible in the SL Ross test tank without the loss of containment of the oil.
- When weathered and dispersant-treated crude oil was subjected to the propeller wash from a trolling motor and the oil was completely dispersed in both open water and ice covered situations.
- A control test indicated that the mixing energy from the trolling motor alone was not adequate to disperse the oil and that the chemical dispersant was required to achieve complete dispersion.

2.2.3 *Spring et al. 2006*

Purpose

Tests using SL Ross wave tank (Phase 1 and Phase 2) and much larger AAT (Aker Arctic Technology, Finland) test basin with a scale model of FESCO Sakhalin ice breaker (Phase 3) used for further investigation of use of ASD on ice-breaker to disperse dispersant-treated oil in ice.

Test oils

Chayvo Z6 crude oil was used in all tests, both Phase 1 and Phase 2. “Pre-weathered” to 9% and 12% vol. evaporative loss in Phase 1 tests, weathered on tank for 4 days in Phase 2 tests.

Dispersant

Corexit 9527 used in all tests, but water-diluted in one Phase 1 test (as in SL Ross 2005).

Waves and additional mixing

In Phase 1 and 2 tests, Minn Kota Endura 46 electric trolling motor provided surface agitation. Waves with a 20 cm height and a period of 1.4 seconds were used in the open water tests. Scale model of FESCO Sakhalin ice breaker provided agitation in Phase 3 tests.

Ice

Phase 1 & 2: The ice block dimensions used in the tests were 0.3m x 0.3m x 15mm thick. In Phase 1, ice field with 80 to 90% ice cover was used and in Phase 2, ice coverage of 25%, 0% and 75% was used, plus open water (no ice) tests.

Findings

- Propeller wash resulted in >90% dispersion of oil in most tests with ice concentrations of 4/10 to 9.5/10. This was twice as much dispersion as in tests with dispersant treatment but with only non-breaking wave action.
- No dispersant controls produced 51% and 27% dispersion in Phase 1 and 2 tests.
- Tests in large ice basin with scale model ice-breaker confirmed >90% dispersion of oil.

2.2.4 SL Ross. 2006

Purpose

Tests were conducted at Ohmsett to further investigate the dispersibility of Chayvo Z6 crude oil in ice.

Test oils

Fresh, weathered and emulsified Chayvo Z6 crude oils were used. Weathering was simulated by air-sparging the crude oil to 8%, 14% and 20% loss by weight. Emulsified oils with water contents of 25% and 50% were prepared using a paint stirrer.

Dispersant

Corexit 9527 was used in all tests.

Waves

In most tests, the Ohmsett wave paddle was operated at 10 cycles per minute for 15 minutes, increased to 12 cycles per minute for another 15 minutes and then operated at 16 cycles per minute for an additional 30 minutes.

Ice

Four different sizes of ice pieces, designated from EL (Extra Large, 1.2m x 1.2m) to ES (Extra Small, 0.2m X 0.2m) were used. Mixtures of the different sized ice pieces were used at ice coverage of 25%, 65%, 90% and 95%.

Findings

- Measured dispersant effectiveness values ranged from 30.2% to 99.5%. The lowest dispersant effectiveness (30.2%) was measured on a test of 8% weathered oil in low ice cover (25%) with a low dispersant to oil ratio (1:80).
- Five tests resulted in 99.5% dispersant effectiveness and each used somewhat different conditions, but each test had 90+% ice concentration and a dispersant to oil ratio of 1:20.
  - Mixing energy is the most important parameter in the chemical dispersion of oil in ice cover conditions.
  - Oil thickness and dispersant-to-oil ratio had little or no effect on the test outcomes over the range of values tested in this study.
  - The ice concentration or ice cover clearly affected the dispersants effectiveness. Higher dispersion occurred in higher ice concentrations. The ice trapped the oil so that the prop-wash exerted higher mixing energy on the oil. In lower ice coverage, the oil was pushed away and out of range of the prop-wash.
  - The effect of ice piece size on dispersion was inconclusive. In most tests, ice piece size appeared to have no effect.

2.2.5 SL Ross. 2007

Purpose

The objective of this study conducted at Ohmsett was to determine if boom and vessel combination could be used to direct dispersant treated oil to the prop-wash of vessel in open water and up to 25% ice-covered waters in manner that would result in the dispersion of the oil by the turbulence created by the vessels' prop-wash.

Test oils

Hibernia crude oil as fresh and 10% weight loss by evaporation was used. A single test was conducted with fresh Chayvo Z6 crude oil.

Dispersant

Corexit 9527 was used in all tests.

Waves and additional mixing

A 1:25th scale model of typical offshore workboat was used to provide propeller wash. All but two of the tests were completed with no artificially generated waves.

Ice

One-inch thick sheets of low-density polyethylene plastic were used as artificial ice in the tests.

Findings

- Dispersant effectiveness estimates of 40 to 80% were measured for the tests completed. The primary causes for the lower effectiveness tests appeared to be the inability of the scale model boom system to prevent the loss of oil under the boom. This effect and the inflexibility of the boom were scaling effects. The scaling up of this system to full-scale would have been challenging to construct a full-size boom system capable of operating in broken ice.

2.2.6 SINTEF JIP 19

Purpose

The purpose of the meso-scale experiments in SINTEF's flume was to study how different oils weathered in the presence of ice on the water surface. The properties of the oils were monitored as they weathered and dispersant effectiveness testing using the MNS test method was conducted on samples taken during the weathering. The weathered oils were sprayed with dispersant after a period of 3- 7 days of weathering in the flume basin.

Test oils

Five different crude oil types were used: Statfjord (paraffinic), Troll (naphthenic), Grane (asphaltenic), Norne (waxy) and Kobbe (light oil).

Dispersant

Corexit 9500 was used in all the tests where oils weathered in the meso-scale flume were sprayed with dispersant.

Waves

The waves in the meso-scale flume were generated by different settings for the different ice cover conditions based on earlier field experiences/observations of energy/movements of ice under different ice-conditions in the field:

- Open water and 30% ice: 30cm breaking waves and 15 cm/sec current
- 50% ice: 20cm non-breaking waves and 10 cm/sec current
- 70% ice: 15cm swell and 5cm/sec current
- 90% ice: 10 cm swell and 5 cm/sec current

Ice

Ice coverage of 0% (open water), 30%, 50%, 70% and 90% were achieved by adding the requisite number of ice sheets (20cm x 30) to the flume

Findings

- The rate of oil weathering (rate of evaporation of volatile components and water uptake to form stable w/o emulsions) depended on oil type and ice coverage.
- Dispersant effectiveness was measured in two ways:
  1. Removing samples during the weathering period and determining ex-situ the dispersant effectiveness in the MNS method using Corexit 9500. This gives an indication of dispersant effectiveness under relatively high energy mixing conditions in the absence of ice.
  2. *In-situ* dispersion in the flume by spraying remaining oil residue (in many cases, the emulsified oil residue) with Corexit 9500 and measuring the effectiveness of dispersion under the prevailing wave conditions and presence of ice.
- A summary of the results is presented in Table 2. Three oils (Grane, Norne and Kobbe) were dispersed to only a slight degree by the addition of dispersant to the

emulsified oil residues in the flume, while two oils (Statfjord and Troll B) were dispersed to a much higher degree.

The dispersant effectiveness is related, but not directly, to the viscosity of the weathered oil. The Grane oil residue has the highest viscosities and low dispersant effectiveness, but the Norne residue and Troll B residue have similar viscosities, but very different levels of dispersion. The reasons for this are discussed in the report.

The MNS (adjusted) results indicate that some oils that were only dispersed to a low level by dispersant addition in the flume would have been dispersed to a higher level if they had been exposed to more intensive mixing.

Table 2. Summary of dispersant effectiveness results in SINTEF JIP 19 report

Oil	Days weathering	Evap loss %wt	Water content (% vol.)	Emulsion visc (cP)	Dispersant effectiveness (%)	
					in-situ in flume	MNS adj
Statfjord						
0% ice	3	38.8	63	3,850	91	100
30% ice	3	40.8	27	3,340	59	68
50% ice	3	40.4	57	3,730	70	67
70% ice	3	40.0	42	4,630	67	NA
90% ice	3	33.6	6		15	38
Grane						
0% ice	3	13.5	67	26,753	5	11
50% ice	3	12.1	68	35,894	3	4
90% ice	3	10.6	72	13,871	7	NA
Troll B						
0% ice	3	22.4	81	9,070	32	NA
30% ice	4	21.6	72	4,730	63	82
50% ice	4	24.5	77	8,050	78	NA
70% ice	7	23.0	65	4,686	100	90
90% ice	7	20.7	31	2,210	59	94
Norne						
0% ice	3	13.5	20	8,410	0	23
50% ice	3	13.1	20	5,670	0	14
90% ice	2.97	12.4	8	6,170	3	26
Kobbe						
0% ice	3	44.0	61	1,954	0	36
50% ice	3	47.0	42	2,450	0	56
90% ice	3	37.0	7	911	0	78

- The extensive test studies in the SINTEF flume basin (more than 20 meso-scale experiments, each following the weathering of the oil up to 3-7- days) showed that the weathering rate and processes will be slowed down when ice is present. This resulted into a higher dispersibility for many (but not all) of the oils tested as a function of weathering time vs. no ice present, enabling a longer "time window" for dispersant application. Some of the oils spilled in high ice concentrations remained dispersible for a period of several days.

- Due to the wave damping in high ice coverage experiments, the limited mixing energy available became the limiting factor for dispersant effectiveness. Under such conditions, it became clearly apparent that additional mixing energy would need to be applied after dispersant application in order to achieve dispersion of the oil. These findings from the flume basin experiments were very useful when designing the large-scale dispersant field testing in the Barents Sea in 2009, both with respect to choice of oil type, weathering time and dispersant treatment strategy (including use of artificial turbulence).

2.3 Comparison and consideration of results obtained in the studies

An Excel spreadsheet (DispEffectInIce.xlxs) accompanies this report. The Excel spreadsheet contains a summary of the major independent variables altered to affect the dependent variable of dispersant effectiveness, plus details of the independent variable parameters for each study.

The major independent variable altered where:

1. Tests oils used
2. Dispersant used
3. Mixing conditions
4. Presence of ice

Each of these major independent variables has associated minor variables. For example:

- The degree of weathering of a particular test oil is a subsidiary variable with the major “Test oil used variable”.
- The treatment rate (Dispersant to Oil Ratio (DOR)) used is a subsidiary variable within the major “Dispersant Used” variable
- The intensity and duration of agitation used is a subsidiary of the major “Mixing conditions” variable.

The studies reviewed were not all conducted as part of a coherent and consistent data-set. Some studies were connected to each other, while others were not. The entire matrix of all possible permutations and combinations of major and minor independent variables were therefore not investigated in the studies.

The primary reason for this was that most of the studies were conducted to study one or two specific aspects of dispersant effectiveness on spilled oils in the presence of ice. These are described in the previous section under the “Purpose” heading.

As with the experimental design of any scientific study, the effect of altering one or two independent variables of specific interest on the dispersant effectiveness was studied, while holding all other variables as constant as possible, was the approach followed in most of the studies. The studies that investigated additional mixing from ship’s prop-wash (SL Ross 2005 and SL Ross 2007) clearly have different purposes from studies with no additional mixing, other than that of the waves in the wave tanks.

Attempts to retrospectively assess and compare the results of the studies are somewhat confounded by the variables being quantified in a way that is no consistent across all of the studies. Some variables are easily quantified and can be compared between studies while others cannot be easily compared.

1. **Test oils used**

   While the identity of a crude oil is clear enough from its name, the degree of weathering (evaporation and water-in-oil emulsification, if any) is not reported in a consistent way that allows the results from all of the studies to be compared. The studies conducted by SL Ross describe weathering in terms of the percentage evaporative loss with only very limited viscosity and density data. This is discussed further in Sections 2.3.1.2 and 2.3.1.3 of this report.

2. **Dispersant used**

   Only Corexit 9527 was used in five studies with only Corexit 9500 being used in the sixth study described in the SINTEF JIP 19 report. The DORs in the different studies are expressed on different bases; sometimes as treatment rate of actual oil treated with dispersant and in others as the proportion of dispersant to oil before weathering during the test.

3. **Mixing conditions**

   There is no quantifiable data on the intensity of mixing to allow a comparison of the mixing conditions used in the different studies.

4. **Presence of ice**

   The presence of ice is the most consistently reported major variables across all of the studies, being reported as either percentage or tenths.

Direct comparisons between all of the dispersant effectiveness results obtained in the different studies is not easy because the studies were conducted to study the effects of different variables under different conditions. However, some trends are evident in the results from all the studies.

2.3.1 Test oils

The dispersant effectiveness result obtained in a particular test will be dependent on the properties of the test oil used and how these properties were modified during weathering of the oil.

2.3.1.1 Types of crude oil used in tests

The studies conducted at Ohmsett and in the SL Ross wave tank used Chayvo Z6 crude oil or Hibernia crude oil as a surrogate. Alaska North Slope crude oil was used in a limited number of tests. Chayvo Z6 crude oil is a medium density crude oil with a Pour Point of 0°C. Hibernia crude oil has a Pour Point of 3°C to 7°C. The Statfjord crude oil used in the SINTEF JIP 19 test matrix has similar properties to Chayvo Z6 crude oil.

The majority of dispersant effectiveness tests conducted in wave tanks with ice to date have used light to medium density, paraffinic crude oils with the Pour Points of the fresh crude oils being close to 0°C. While this is especially relevant for the Sakhalin project, there is no particular reason to consider that only light or medium crude oils could be spilled in waters where ice is present. A coherent rationale for using the same, or different, crude oils in future testing needs to be developed.

2.3.1.2 Weathering of crude oils

Weathering of the crude oils was simulated by varying the degree of evaporative loss in the tests conducted at Ohmsett and in the SL Ross wave tank, with only a very limited number of results being obtained with emulsified oils. In some cases, the test oils emulsified to some degree during the testing. The primary purpose SINTEF JIP 19 work programme was to study the weathering of different oils in the presence of ice and comprehensive characterisation of five oils was conducted. The presence of ice modified the weathering behaviour to varying degrees.

Dispersant effectiveness in tests with ice present was generally very high for the fresh crude oils and lower with weathered oils. However, comparisons of past results from different studies are complicated because testing has been conducted with different crude oils at different stages of weathering.

Once again, a clear rationale for testing with fresh crude oils or crude oils weathered to a particular degree needs to be established in any future testing work. The weathering degree (evaporative loss and formation of w/o emulsions) should be based on previous weathering studies, suitably modified to reflect the presence of ice. The degree of weathering should not be an arbitrary level designed merely to 'standardize' the results, but should reflect operational realities, such as the likely time that would pass before dispersant spraying could start. Many past dispersant effectiveness studies have concentrated on defining the limits of dispersant performance or the time "window of opportunity" for dispersant use.

2.3.1.3 Characterisation of weathered crude oils

Weathered crude oils have been characterised, as in the standard SINTEF methodology, by determining the viscosities of the distillation residues that simulate evaporative loss and the w/o emulsions produced by mixing these residues with water to various water contents.

Many weathered oils and w/o emulsions will contain precipitated asphaltenes and waxes that modify the flow behaviour by forming structure within the oil. In the case of precipitated waxes, this is made evident by the Pour Point of the oil. Oils at temperature around or below their Pour Points will exhibit other aspects of non-Newtonian flow. This manifests itself as thixotropy, a shear-thinning property with an attendant yield stress. This was expressly noted in the Spring et al. 2006 study for Chayvo Z6 crude oil. It is also evident from the results of the SINTEF JIP 19 study that many of the emulsified oils that were tested with dispersant at temperatures far below the Pour Point of the oil residue of which they were composed (Table 3).

In such a situation, the viscosity of an oil residue, or of the w/o formed from this oil residue, is not a sufficient description of the flow properties. A more rigorous description of the rheology of the weathered oils that are treated with dispersant is required.

Non-Newtonian flow behaviour can be difficult to quantify, but relying viscosity alone can produce misleading impressions of the flow behaviour of a weathered oil. In addition, the flow properties of a sample of a weathered oil will be strongly dependent on the "shear history" and "thermal history" that the particular sample has been exposed to. In order that future dispersant effectiveness studies are repeatable and reproducible, some effort should be devoted to adequately characterizing the oils in the condition that they are when dispersant is applied.

Table 3. Oils, Densities and Pour Points of oils used in tests

Oil type	Residue	Density (Kg/m^3)	Evaporative Loss (Vol. %)	Pour Point (°C)
Hibernia	Fresh	0.860	0	3
Chayvo Z6	Fresh	0.848*	0	0
		0.846	8	
		0.851	14	
		0.851	20	
		0.878*	29	15
		0.890*	40	21
Statfjord	Fresh	0.835	0	-6
	150°C+	0.870	19.8	9
	200°C+	0.884	31.4	18
	250°C+	0.896	42.4	21
Grane	Fresh	0.941	0	-24
	250°C+	0.968	13	-6
Troll B	Fresh	0.900	0	-36
	250°C+	0.930	25.5	-27
Norne	Fresh	0.868	0	21
	250°C+	0.888	23	30
Kobbe	Fresh	0.797	0	-39
	250°C+	0.875	53.6	21

*Determined at 0°C

2.3.2 Dispersant used and DOR

Corexit 9527 was used in the SL Ross and Ohmsett studies, while Corexit 9500 was used in the SINTEF JIP 19 studies for reasons that are made clear in the reports. Although these two dispersants have similar surfactant packages, there are known differences in performance. Other dispersants are commercially available, but broadening any future studies to test multiple dispersants might not be cost-effective at this stage.

The normally recommended DOR (Dispersant to Oil Ratio) of 1:20 was used in the majority of the tests, but lower DORs (down to 1:100) were found to be effective in some instances such as fresh or lightly weathered oils and with higher mixing energies.

There is clearly a ‘triangular’ arrangement of factors that determine dispersant effectiveness:

1) The flow properties of the test oil that resist physical dispersion, with more resistance being exhibited by oils with some characteristics that include, but are not limited to, high viscosity.

The treatment rate (DOR) of applied dispersant.

The intensity of the mixing applied to the dispersant-treated oil on water.

The results show that a DOR of 1:20 is more than sufficient to cause high dispersion of some oils in some cases, but insufficient in other cases. Moving away from the often used DOR of 1:20 could be justified once general trends have been established, but conducting future work at other DORs would be of little obvious benefit.

2.3.3 Waves used in tank tests

Correlating the mixing energy in different wave tanks with each other, or correlating the mixing energy in wave tanks with that occurring at different sea conditions has not yet proved to be possible or rigorous.

Previous studies conducted at Ohmsett on dispersant effectiveness with no ice present have established that some cresting or breaking wave action is needed for rapid dispersion to occur. Slower dispersion may occur over a period of days for low viscosity oils at low sea states with infrequent cresting waves.

All of the studies conducted with ice (at Ohmsett, in the SL Ross wave tank and in the SINTEF meso-scale flume) have shown that a less energetic wave action is needed to disperse oil when ice is present that when it is not. The results from the tests with ice consistently show that the dispersion of oil is much lower when the same wave conditions are used without ice.

2.3.4 Presence of ice and ice coverage

All of the studies show that the presence of ice intensifies the mixing action experienced by the dispersant-treated oil in a wave tank and this produces higher dispersant effectiveness when ice is present than when it is not. Increasing the ice coverage generally increased the dispersant effectiveness, unless offset by the flow properties of the weathered oil.

The questions to be addressed are:

- “Is this “intensification effect” of ice due to the method of wave production in a tank test, as compared to that of waves and ice at sea?” or
- “Are wave tank tests with ice a good simulation of the action of waves and ice on oil at sea?”

In the wave tank tests, the wave action is generated by a mechanical wave-maker, often a plunging wedge, or oscillating wave-board, which rhythmically displaces water to produce a wave action throughout, along or around the tank. The addition of ice pieces to the water surface generates shearing action at the water surface as the ice is moved by the wave action. When oil is placed on the water surface and treated with dispersant, it is subjected to much more shearing action along the oil/ice contact lines than if ice were not present.

At sea, the prevailing wave action is damped by the presence of ice to a degree that depends on ice coverage, ice type (frazil, grease etc.) and distance of the ice-field from open water. The action of waves on ice near the edge of the MIZ (Marginal Ice Zone) seems similar to that observed in wave tanks with ice. However, at other places in different prevailing conditions the presence of ice may reduce the wave action to practically zero.

The difficulty in correlating wave condition produced in wave tank with those at sea at different sea states, and the effect that this will have on the dispersion of oil, is well known. Adding ice to waves created in wave tanks adds a further level of difficulty in making comparisons or correlations.

The waves used at Ohmsett in the Owens and Belore 2004 study were varied over a range that produced from no dispersion to rapid dispersion when ice was present. The 15 cm height and 6 second period waves did not cause dispersion of oil at 4/10 or 8/10 ice coverage. Most tests at Ohmsett and in the other wave tanks and flume have been conducted under wave and ice conditions that produce some degree of dispersion. This is very understandable from an experimental point of view, but defining the wave/ice conditions when dispersion does not occur will also yield useful information for operational use of dispersants on oil spills in ice.

2.3.5 Use of additional mixing such as prop-wash or ASD

Three of the six studies, SL Ross. 2005, Spring et al. 2006 and SL Ross. 2007, were specifically conducted to study the effect of additional mixing in situations where the wave/ice combination was unlikely to produce sufficient dispersion of oil. Information regarding the effect of waves alone and waves plus ice was generated during the studies, but was not the primary purpose of conducting the work.

Experience gained from the large-scale field testing in the Barents Sea in 2009 (Sørstrøm et al. 2010) into the use of additional mixing energy after dispersant treatment on Troll crude oil that had been weathered for 6 days in high ice coverage was very significant. The strategy used was dispersant treatment followed by artificial energy/turbulence using (i) propeller/thruster washing; and/or (ii) MOB (Man Overboard) boat water jets. This caused dispersion of the oil as very small droplets.

The resistance to dispersion presented by the flow behaviour of dispersant-treated oils could be totally overcome by the application of sufficiently intense mixing energy. Oils far below their Pour Point, on ice or water, could be totally dispersed with the use of ASD thrusters. The use of dispersant was necessary, as evidenced by less than total dispersion of untreated oil. The use of such intense mixing sources may be required in some oil spill response situations, but may be unavailable in others. The rationale of conducting future studies on this aspect, perhaps as additional to work to studies conducted in the first place with additional mixing, needs to be examined.

2.4 Conclusions about dispersant effectiveness in ice

The studies that have been conducted on dispersant effectiveness of dispersants used on spilled oil in ice have produced some common conclusions:

1. The presence of ice pieces on the water surface in wave tanks increases dispersant effectiveness, compared to the same test oil/dispersant DOR/wave energy combination without ice.

2. While a slight wave-breaking action is a requirement for rapid dispersion of dispersant-treated oil in the absence of ice, wave conditions that would produce breaking waves if ice was not present are not required for effective dispersion of oil with ice. Very low wave energy with ice present is insufficient to cause dispersion of oil, but moderate swells of non-breaking waves plus sufficient ice coverage causes dispersion of many dispersant-treated oils.
3. As with dispersant use on oils in open water, the oil dispersion process with ice present is resisted by the flow behaviour of the dispersant-treated oil and promoted by mixing energy input. Increased weathering of oil increasingly resists dispersion, but this resistance can be overcome in part by increased mixing energy input. The flow behaviour of many weathered crudes oils, particularly those tested at far below their Pour Points is not adequately described by the viscosity alone.
4. Both test studies in the SINTEF's flume basin (SINTEF JIP-19) and experimental field studies (SINTEF Oil-in-the-Northern-Area program studies in the MIZ (Marginal Ice Zone) in 1993 (Vefsnno eta al, 1996)) and in the Barents Sea in 2009 (Sørstrøm et al. 2010) have demonstrated that the weathering processes are slowed down when ice is present, enabling a longer ”time window" for dispersant application. Some oils spilled in ice may remain dispersible over a period of several days.
5. Highly weathered oils that are not dispersed by the addition of dispersant in waves with ice can be dispersed by the application of additionally mixing energy such as that supplied by ASD (Azimuthal Stern Drive) units or other sources such as water thrusters.

In terms of past work guiding future work, the following conclusions can also be reached:

1. The majority of past studies have been conducted with Chayvo Z6 crude oil or a surrogate, Hibernia crude oil. These are low to medium density, paraffinic crude oils with the Pour Point of the fresh crude oil being close to 0°C. The fresh crude oils have similar properties to Statfjord crude oil. The oils became resistant to dispersant as they weathered. The SINTEF JIP 19 study documented the weathering behaviour and dispersibility of four other oil types in ice. High wax content, high Pour Point crude oils (such as Norne) and high density, asphaltenic oils (such as Grane) and light oils with a high wax content (such as Kobbe) are unlikely to be dispersible under the effects of waves plus ice. The selection of crude oils, and the method used to artificially weather the oil to a particular extent, will be a very important consideration for future work.
2. The test oils used in future work needs to be adequately characterized so that the testing will be repeatable and reproducible. The test oil needs to be characterized in the state that it will be when dispersant is applied. More information than oil density, amount evaporated and oil or w/o emulsion viscosity will be required to describe the oil.
3. Only two dispersants have been used in past work; Corexits 9527 and 9500. The use of Corexit 9500 in future work has some justification; unless dispersant brand is to be a variable investigated in future work.
4. The wave conditions produced in wave tanks cannot be rigorously correlated with waves at sea. The addition of ice to water in the wave tanks adds another level of simulation that could need to be justified.

2.5 References

Sørstrøm, S.E., P.J. Brandvik, I. Buist, P.S. Daling, D. Dickins, L-G. Faksness, S. Potter, J.F. Rasmussen and I. Singsaas, "Joint Industry Program. Oil Spill Response for Arctic and Ice-covered Waters". Summary Report – Oil in Ice JIP, SINTEF report A14181, ISBN no. 978-82-14-04759-2. 2010.

Vefsnmo S., Jensen, H., Singsaas, I. and Guenette, C. 1996: Oil Spill Response in Ice Infested waters. SINTEF report STF22 F96202. SINTEF Trondheim. Norway.

CHAPTER 3. STUDIES OF MINERAL FINES EFFECTIVENESS ON OIL IN ICE

Suspended particulate matter (SPM) has long been recognized as an important factor in the transport of spilled oil from one environmental compartment to another. This interaction includes both the adsorption of hydrocarbons and the association of dispersed oil droplets with organic and inorganic SPM (Bassin and Ichiye, 1977; Boehm, 1987; Karickhoff, 1981; Payne et al., 1989). The active generation of oil-mineral-aggregates (OMA) as an oil spill countermeasure in the field has been used under the term “surf-washing” (Lee et al., 1999; Owens, 1999). The method employs shoreline wave energy to promote interaction between mineral fines and oil stranded onshore. The operational efficacy of surf-washing was demonstrated in the 1996 Sea Empress spill (Lee et al., 1997) and at a large-scale field experiment conducted in 1997 under Arctic conditions in Svalbard (Lee et al., 2003).

3.1 The use of mineral fines in ice

The use of OMA as a spill countermeasure in ice-packed waters was illustrated in the late 1990s following an accidental release of oil onto ice from the tanker Saraband in the Saguenay Fjord, Canada (Canadian Coast Guard, 2002). A decision was made to apply mineral fines to the oil during a scheduled ice-breaking operation to open a shipping channel. The crew on the ice-breaker observed that the oil was rapidly dispersed into the water column along with the mineral fines and there was no observed residual oil reaching the shore (Blouin, 2001).

3.2 Studies of the effectiveness’s of mineral fines on oil in ice

Although a lot of studies have been conducted on the effect of mineral fines on spilled oil, the amount of work that has been conducted on the effectiveness of mineral fines on spilled oil in ice is very limited.

A field study was conducted with a Canadian Coast Guard (CCG) ice-breaker in the St. Lawrence River Estuary (offshore of Matane, Quebec, Canada) (Lee et al. 2011). Three field tests were carried out between January 30 and February 1, 2008, in estuarine waters of the St. Lawrence River off the coast of Matane, Quebec). During each experiment, the ice-breaker, CCGS Martha L. Black, was positioned with its stern directly against a section of undisturbed ice while 200 L of Heidrun crude oil was released by gravity feed from a ship’s hose onto the sea surface dominated by ice. Prior to initiation of the experiment, the ship’s twin propellers were used at alternating speeds to break up and mix the broken ice while maintaining its approximate relative position to create a field of broken-ice for the experimental study. During Tests 1 and 2 (January 30 and 31), a slurry (to enhance OMA formation) of 133 g/L calcite mineral fines in seawater (an excess based on previous mesocosm tank feasibility studies by the CCG) was sprayed onto the oil using pressurized fire-hoses, while the ship used its propellers to generate sufficient mixing energy to facilitate OMA formation. Visual observations showed remarkable differences between OMA treatment in Test 1 and the control run (Test 3). With the addition of mineral fines (Tests 1 and 2), the oil was quickly dispersed by physical mixing using the icebreaker’s propeller wash; the OMA was dispersed into the water column, and the re-coalescence and resurfacing of the dispersed oil was insignificant. In the control (Test 3), without the addition of mineral fines during the first stage, dispersion was ineffective.

This field study represents the sole case where the effectiveness of mineral fines on oil in ice has been assessed at sea. The test oil was fresh Heidrun crude oil, the mineral fines were calcite, there was very high ice coverage and additional mixing was provided by prop-wash from the ice-breaker. The addition of mineral fines caused effective dispersion of the oil under these conditions.

3.3 References about mineral fines

Bassin, N. J., and T. Ichiye. 1977. Flocculation behavior of suspended sediments and oil emulsions. Journal of Sedimentary Petrology. 47:671-677.

Boehm, P.D. 1987. Transport and transformation processes regarding hydrocarbon and metal pollutants in offshore sedimentary environments. Long-term environmental effects of offshore oil and gas development., D.F. Boesch and N.N. Rabalais (eds.), Elsevier Applied Science, London and New York, 233-287.

Karickhoff, S.W. 1981. Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. Chemosphere. 10:833-846.

Payne, J.R., J.R. Clayton Jr., G.D. McNabb, B.E. Kirstein, C.L. Clary, R.T. Redding, J.S. Evans, E. Reimnitz, and E.W. Kempema. 1989. Oil-ice-sediment interactions during freezeup and breakup. U.S. Department of Commerce, NOAA, OCSEAP. Final Report 64, 382 pp.

Lee, K., S.E. Cobanli, J. Gauthier, S. St-Pierre, G.H. Tremblay, and G.D. Wohlgeschaffen. 1999. Evaluating the addition of fine particles to enhance oil degradation. In Proceedings of the 1999 International Oil Spill Conference. American Petroleum Insitute. Washington D.C. pp.433-438.

Owens, E.H. 1999. The interaction of fine particles with stranded oil. Pure and Applied Chemistry. 71(1):83-93.

Lee, K., Z. Li, B. Robinson, P. E. Kepkay, X. Ma, S. Cobanli, T. King, M. Blouin and B. Doyon. 2009. *In-situ* remediation of oil spills in ice-packed waters: Enhanced dispersion and biodegradation of petroleum hydrocarbons. *In Proceedings of the 10th International In Situ and On-Site Bioremediation Symposium*.

Lee, K., T. Lunel, P. Wood, R. Swannel, and P. Stoffyn-Egli. 1997. Shoreline cleanup by acceleration of clay-oil flocculation process. In: The 1997 International Oil Spill Conference, pp. 235-240.

Lee, K., P. Stoffyn-Egli, G.H. Tremblay, E.H. Owens, G.A. Sergy, C.C. Guenette, and R. Prince. 2003. Oil-mineral aggregate formation on oiled beaches: Natural attenuation and sediment relocation. Spill Science & Technology Bulletin. 8(3):285-296.

Blouin, M. 2001. Dispersion of oil spills stranded in ice and its environmental effects. Canadian Coast Guard Research and Development Plan 2001-2002 . pp. 49-50. http://dsp-psd.pwgsc.gc.ca/Collection/T31-83-2002E.pdf. Canadian Coast Guard. 2002. Research and Development Plan/2001-2002. Available online: http://dsp-psd.pwgsc.gc.ca/Collection/T31-83-2002E.pdf, accessed 1 March 2011.

Kenneth Lee, Zhengkai Li, Brian Robinson, Paul E. Kepkay. Field Trials of in-situ Oil Spill Countermeasures in Ice-Infested Waters. International Oil Spill Conference 2011

CHAPTER 4. RESEARCH DESCRIBING ARCTIC CAPABLE DISPERSANT DELIVERY SYSTEMS

4.1 Existing dispersant spray systems

Most existing dispersant delivery systems are designed to spray dispersant, most often at a rate of 5 US gallons/acre, over as wide an area possible and as evenly as possible (Lindblom and Cashion, 1983 and Lindblom, 1987).

The assumptions that have been made are (i) that the oil to be sprayed with dispersant will be in a layer than has an average thickness of 0.1mm and (ii) that a DOR (Dispersant to Oil Ratio) required is 1:20. Both of these assumptions are known to be only averages of very wide ranges.

1. Spilled oil on the sea surface exists as layers of thicknesses ranging from less than 1 micron up to several millimetres thick or more. It is widely understood that ‘sheen’ should not be sprayed with dispersant because:

    a) It would be very wasteful to spray dispersant at 5 US gallons/acre onto thin oil as there would be very significant over-treatment, and;

    b) Thin oil layers will eventually be naturally dispersed by wave action.

    Thicker oil layers are most often of emulsified oil, although Heavy Fuel Oils (HFO) spilled in cold water form layers that can be several centimetres, or more, thick. The problem of very large variations in oil layer thickness over short, localized distances is compounded by the current inability of any remote-sensing system to quantify oil layer thickness.

2. The recommended dispersant treatment rate of a DOR of 1:20 is an average. Freshly spilled crude oils can often be dispersed with a DOR of 1:100 while DORs of 1:10 or less can be ineffective on highly weathered oils.

These uncertainties are well known, but cannot be resolved to provide a better solution than that already used with assumed average values for oil thickness and DOR. Dispersant spraying is therefore an inherently inaccurate process.

Spraying dispersant from aircraft, rather than from ships, is often preferred for operational reasons; much larger areas of oil can be treated more rapidly.

4.2 The behaviour of spilled oil in ice

Oil spilled amongst ice pieces on the sea surface will congregate on the water surface in between the ice pieces. The oil will be partially corralled by the ice into thicker layers than would occur in open water and this slows down the weathering processes compared to the rate on the open sea.

The assumption that the spilled oil will be present as a layer with an average thickness of 0.1mm would be even more incorrect in these circumstances. Spraying the entire area of ice and spilled oil with dispersant at a DOR of 1:20 has been done during wave tank tests (see section 2.2) and produced high dispersant effectiveness in some cases. However, a more targeted approach will be to spray dispersant only onto the oil between the ice pieces. The dispersant spray would need to be directed onto the oil and not onto the ice. This would not be feasible by spraying dispersant from fixed-wing aircraft, although could be feasible from a helicopter, but most operational concerns would be addressed by spraying dispersant from ships.

4.3 Development of dispersant spraying system for use in the Arctic

Lewis and Daling, 2007 considered that the most critical parameters for the operational use of dispersants under Arctic conditions are:

1. Dispersant performance and properties under relevant conditions (salinity, temperature, oil type).
2. Dispersibility and weathering properties at low temperatures.
3. Good access and contact between dispersant and oil.
4. Sufficient energy for the dispersion process.

Following considerations of what was required for dispersant spraying in the Arctic it was concluded that any system should:

- Be based on manoeuvrable hydraulic spraying arms instead of traditional “static” spray arms to allow for flexible application of dispersant onto spilled oil on the water between ice floes.
- Should be easily transportable.
- Should be protected from icing (containerized) and be operational for use under extreme cold conditions.
- Should be capable of being operated from a wide range of vessels and to be operated by a remote control unit.

After design and laboratory testing of components such as nozzles with different dispersants a prototype system was constructed. The system is based on a 10-foot standard freight container that can be easily lifted on board the deck of a boat. Inside the container, a 12.5 m long hydraulically operated crane arm is stored. The arm is divided into three jointed 2.5 m long sections that can be individually articulated by means of hydraulic cylinders. In addition, the arm can be horizontally rotated through circa 300 degrees. At the outer end of the crane arm, there is a hydraulic motor-driven swivel that allows the nozzle section to be rotated through 360 degrees. The nozzle section with three nozzles (on a 4 m spray boom/manifold, delivering a total of 30 l/min) can easily be replaced by quick coupling and changing to a mouthpiece section with a single nozzle (delivering a total of 10 l/min).

The crane arm is a constructed framework of extruded aluminum with joints and hinges made from stainless steel. This gives it a high strength and low weight which makes it possible for the unit to be hand carried and assembled/disassembled by two persons. The crane arm base is attached with hinges to the inside wall of a container that is reinforced with a steel beam. The foundation can then be swung out and supported using two hinged arms with a solid screw and a foot pad against the deck of the vessel. An insulated and temperature controlled dispersant day tank with a capacity of 1000 litres, an electric motor driven by a centrifugal pump dispersant, plus a hydraulic power unit (HPU) are integrated in the container. The dispersant in the hoses between the nozzles and the dispersant in the tank is continuously recirculated in order avoid cooling in, e.g. “stop” periods during application under cold conditions. The technical specifications of the system are given in detail in a scientific report, see Daling et al., 2010B.

The final step in the development of the new dispersant spray arm was to test the spray system under real Arctic field conditions during the large-scale FEX 2009 field experiment, which took place in the marginal ice zone in the Barents Sea in the period from May 9 to 25, 2009 (Sørstrøm et al., 2010). The prototype performed well and is shown in Figure 1. Weathered Troll crude oil was sprayed with Corexit 9500 and prop-wash or water-jet washing from the MOB boat caused dispersion of the dispersant-treated oil in ice (Daling et al, 2010 AMOP).

Figure 1. Prototype manoeuvrable spray system being used to spray dispersant onto oil in ice

4.4 References about Arctic capable dispersant delivery systems

Daling, P.S., A. Holumsnes, C. Rasmussen, P.J. Brandvik, and F. Leirvik, Development and Testing of a Containerized Dispersant Spray System for Use in Cold and Ice-covered Areas. Oil-in-Ice JIP report no 13. SINTEF report, STF80MK 2010B.

Lewis, A. and P.S. Daling,. “Evaluation of dispersant spray systems and platforms for use on spilled oil in sea with ice present”. Oil in Ice JIP Report no. 12, SINTEF report: STF80MK F07094, 20 p., 2007B

Per S. Daling, Arne Holumsnes, Claus Rasmussen, Per Johan Brandvik and Frode Leirvik. Development and Field Testing of a Flexible System for Application of Dispersants on Oil Spills in Ice. AMOP 2010.

Lindblom, G.P. and B.S. Cashion, “Operational Consideration for Optimal Deposition Efficiency in Aerial Application of Dispersants”. In Proceedings of the 1983 International Oil Spill Conference, pp. 53 – 60, 1983.

Lindblom, G.P. . "Measurement and Prediction of Depositional Accuracy in Dispersant Spraying from Large Airplanes", In Proceedings of the 1987 International Oil Spill Conference, pp. 325 – 333, 1987.

Sørstrøm, S.E., P.J. Brandvik, I. Buist, P.S. Daling, D. Dickins, L-G. Faksness, S. Potter, J.F. Rasmussen and I. Singsaas, “Joint Industry Program. Oil Spill Response for Arctic and Ice-covered Waters”. Summary Report – Oil in Ice JIP, SINTEF report A14181, ISBN no. 978-82-14-04759-2. 2010.

CHAPTER 5. EXPERIMENTAL DISPERSANT TECHNOLOGY

The term 'green dispersant technology' has come to mean many different things to different people. In general, it refers to 'environmentally friendly', or sustainable, products that are designed to cause minimum harm to the environment and/or human health. There is a commonly-held presumption that 'natural' products or chemicals are less harmful than 'man-made' chemicals and should therefore be used in preference to man-made chemicals where possible. The foundation of this presumption can easily be questioned as some natural products can be extremely harmful to human health, but the view that 'natural' products are inherently better than 'man-made' products is held by many people.

5.1 'Green' chemistry

One origin of the term is rooted in the concept of 'green chemistry'. 'Green chemistry' is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances. Green chemistry relies on a set of 12 principles as described in *Green Chemistry: Theory and Practice,* authored by P. T. Anastas (former head of R&D at the US EPA) and J. C. Warner, (Oxford University Press: New York, 1998). The US EPA (http://www.epa.gov/greenchemistry/) states that: "*Green chemistry consists of chemicals and chemical processes designed to reduce or eliminate negative environmental impacts. The use and production of these chemicals may involve reduced waste products, non-toxic components, and improved efficiency. Green chemistry is a highly effective approach to pollution prevention because it applies innovative scientific solutions to real-world environmental situations."* The US EPA further expands the definition:

"*Chemical products and processes should be designed to the highest level of this hierarchy and be cost-competitive in the market.*

1. *Green Chemistry: Source Reduction/Prevention of Chemical Hazards*
    - *Design chemical products to be less hazardous to human health and the environment**
    - *Use feedstock's and reagents that are less hazardous to human health and the environment**
    - *Design syntheses and other processes to be less energy and materials intensive (high atom economy, low E-factor)*
    - *Use feedstock's derived from annually renewable resources or from abundant waste*
    - *Design chemical products for increased, more facile reuse or recycling*
    - *Reuse or Recycle Chemicals*
2. *Treat Chemicals to Render Them Less Hazardous*
3. *Dispose of Chemicals Properly*

*******chemicals that are less hazardous to human health and the environment are:*

- Less toxic to organisms and ecosystems
- Not persistent or bioaccumulative in organisms or the environment
- Inherently safer with respect to handling and use"

5.2 Green chemistry and dispersant technology

The relevance of applying green chemistry to users or formulators of dispersants is difficult to judge.

Potential impacts on marine organisms from the use of dispersants are a result of the potentially toxic chemical components in the dispersed oil, not from the chemical compounds used in the dispersant. Currently available dispersants are generally less toxic than the crude oils they are used to disperse.

Reducing the inherent toxicity of dispersants to even lower levels will not influence any potential outcomes caused by exposure to dispersed oil in the water column. The dispersion of oil can make the oil components more available to marine organisms, but the exposure regime (concentration of oil components in water column and duration of exposure to these concentrations) experienced by marine organisms when oil is dispersed in relatively deep water is unlikely to cause anything other than very localized and short-term effects.

Commercially-available dispersants are produced by blending commercially-available surfactants and solvents to a formulation that produces the required effect. No synthesis of specific chemical compounds for use only in dispersants is involved.

The principles of green chemistry that might have some influence on dispersant technology are that the ingredients should be; (i) of low toxicity to humans, organisms and ecosystems, (ii) be manufactured from annually renewable raw material or feedstock, (iii) should not be persistent in the environment and (iv) should be safe with respect to handling and use.

In many respects, the surfactants and solvents used in many dispersants already conform to these green chemistry principles. The Span™ and Tween™ surfactants used in many dispersants are sorbitan esters and ethoxylated sorbitan esters. Sorbitan is dehydrated sorbitol, a sugar, and produced from a renewable resource. Similarly, the fatty acid in the ester is derived from vegetable oils. The ethylene oxide used to produce the ethoxylated surfactant is from a non-renewable petrochemical source, but ethoxylated surfactants are currently used in a very wide range of consumer products. The surfactants used in the Corexit 9527 and Corexit 9500 dispersants are food-grade, so inherent toxicity to humans is low. During and after the *Deepwater Horizon* incident some people raised concerns over the sodium di-isooctylsulphosuccinate (DOSS) anionic surfactant because of its apparent persistence and the possibility of harm to human health. Follow-up studies on these aspects are in progress, but DOSS is present in many household products and has been detected at very low concentrations very far away from where dispersants were used. It is therefore most likely that some detections of DOSS taken as indications of dispersant residue are incorrect.

5.3 Bio-surfactants in dispersants

One aspect of ‘green’ dispersant technology that is periodically proposed is the use of bio-surfactants (Juwarkar et al., 1993, Josefsen et al. 1995, Lepoly et al., 1997 and Crescenzi et al., 1999). No commercial bio-surfactant based dispersants seemed to have appeared on the markets and effectiveness testing at SINTEF on the bio-surfactants developed by Eni several years ago did not indicate that the effectiveness of such materials would rival that of conventional surfactant based dispersants.

Interest in bio-surfactant based dispersants, and in other dispersant formulation approaches, has been resurrected by the GoMRI (Gulf of Mexico Research Initiative) funded by BP. The

Consortium for the Molecular Engineering of Dispersant Systems (C-MEDS) is a research collaboration involving 43 investigators from 22 universities in the US. The Consortium is based on the premise that dispersants are an essential aspect in the effective management and mitigation of large oil releases from deep ocean environments.

No 'green' dispersants of proven high effectiveness in the tests currently used for dispersant approval around the world have been commercialised.

5.4 References for green dispersant technology

Pradeep Venkataraman, Jingjian Tang, Etham Frenkel, Gary L. McPherson, Jibao He, Srinivasa R. Raghavan, Vladimir L Kolesnichenko, Arijit Bose, and Vijay T. John. 2003. Attachment of a Hydrophobically Modified Biopolymer at the Oil-Water Interface in the Treatment of Oil Spills ACS Appl. Mater. Interfaces, Just Accepted Manuscript • DOI: 10.1021/am303000v • Publication Date (Web): 25 Mar 2013 Downloaded from http://pubs.acs.org on April 3, 2013

Asha Juwarkar, P. Sudhakar Babu, Kirti Mishra, Megha Deshpande. 1993. Application of Bio-surfactant in Oil Spill Management. In Proceedings of the 1993 International Oil Spill Conference. pp 503-504

Joe Eugene Lepoly M. Patricia Hancock, Candy L. Zuleger, and Katharine Roupp-Edwards, Tim Reilly and David E. Fritz. 1997. Effectiveness and Safety of Bio-surfactants as agents of Oil Spill Response. In Proceedings of the 1997 International Oil Spill Conference. pp 689 - 696

Francesco Crescenzi, Marcello Camilli, Eugenio Fascetti, Filippo Porcelli, Giulio Prosperi, and Pasquale Sacceddu. 1999. Microbial Degradation of Bio-surfactant Dispersed Oil. In Proceedings of the 1999 International Oil Spill Conference. pp 1039-1042

Josefsen, K,.,P. Sveum, S. Ramstad, S. Markusen, K. Folkvord, S. Krigsvoll, R. Aune, I. Storrø, 1995: In-Situ Production of Bio-Surfactants: An Alternative Method for Dispersing and Bioremediating Marine Oil Spills. In Proc. AMOP (Arctic Marine Oilspill Program) , 1995, vol.2 pp. 1243-1262.