FINAL REPORT

Chemical Dispersibility of U.S. Outer Continental Shelf Crude Oils in Non-Breaking Waves

For

U.S. Department of the Interior Minerals Management Service Herndon, VA

By

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Executive Summary

Effectiveness of dispersants has been documented in breaking wave environments at sea (Lewis 2004, Colcomb at al. 2005) and in a wave tank (SL Ross et al. 2005). The importance of mixing energy in controlling dispersion performance is well known (NRC 2005) and has been demonstrated repeatedly in laboratory tests. As a consequence, the question of potential dispersant performance at sea at low sea states in non-breaking waves is frequently raised in workshops and training sessions. Laboratory-based studies have been of limited use in addressing this question, but recent wave-tank tests have offered some insights. In work with viscous oils (viscosities 2075 cP and 7100 cP at 15° C and 10s⁻¹), dispersant-treated slicks were readily dispersed by breaking waves, but were not dispersed in non-breaking waves (SL Ross et al. 2005). A less viscous oil (viscosity = 1145 cP) was similarly dispersed in breaking waves, but appeared to show some dispersion, though limited, even in non-breaking waves. Many crude oils produced in offshore areas of the United States have fresh oil viscosities lower than 1145 cP at ambient temperatures. The objectives of this study were to determine if these lowviscosity oils could be chemically dispersed in non-breaking waves and, if so, to determine the oil viscosity limit to chemical dispersion in non-breaking waves. To meet these objectives, tests were completed to determine the chemical dispersibility, in nonbreaking waves, of a number of oils with viscosities in the range of 2 to 2000 cP. Preliminary tests were completed in the SL Ross wave tank. Full-scale tests were conducted in the Minerals Management Service's National Oil Spill Response Test Facility (Ohmsett) located in Leonardo, New Jersey.

In the preliminary tests in the SL Ross wave tank, using oils with viscosities ranging from 7 to 600 cP at 21^{0} C, most of the oils showed little chemical dispersion in non-breaking waves. Only the lightest and least viscous of the crude oils (Alaska North Slope crude oil (ANS) (viscosity 7 cP at 21^{0} C) consistently showed high levels of dispersion in non-breaking waves.

In tests in non-breaking waves at Ohmsett, using OCS crude oils, effectiveness was assessed using three methods: visual observations, direct measurements of effectiveness

and measurements of in-water oil concentrations and droplet-size distributions. The oils ranged in viscosity from 14 cP to 1825 cP at 15^{0} C and 1 s⁻¹) (Table ES1). The nonbreaking wave environment selected for testing was the highest energy, non-breaking wave environment available at the Ohmsett facility, as characterized earlier by Asher (2005, <u>Table ES2</u>). The principal observation in the study was that there did not appear to be any dispersion caused by non-breaking waves in any experimental test with any oil, regardless of oil viscosity. A summary of the test results is presented in <u>Table ES3</u>. Even the least viscous oil, Galveston 209, with a viscosity of 14 cP, did not disperse in non-breaking waves.

Oil Type ^a	Water	Dens (kg/i	sity m ³)	Viscosity Pa.s (cP)				
		Density	Temp.		@ 15 °C			
	/0	(kg/m^3)	°C	$@ 1 s^{-1}$	@ 10 s ⁻¹	@ 100 s ⁻¹		
Galveston 209	0	0.852	24.7	14	-	-		
	0	0 0.937		336	316	-		
IFO 30	0	0.934	21.4	-	252	-		
	0	0.931	25.0	-	180	229		
Ewing Bank 873	2.5	0.943	25.0	-	683	773		
West Delta 30	4	0.943	24.5	1026	1067	-		
Harmony	50	na ^a	na	1825	_	-		
a. na – not availab	le							

Table ES1 Physical Properties of Oil Tested at Ohmsett in Non-Breaking Waves

Table ES2 Characteristics of Waves Used for Dispersant Testing at Ohmsett in This and Other Recent Studies (based on Asher 2005)

Paddle Frequency, Cpm	Breaking/non- breaking	Significant Wave Height, H _{1/3} , m	Wave Length, m	Wave Frequency
				min
29	Non-breaking	.33	7.1	27.8
33	Breaking	.406	5.4	32.1
35	Breaking	.403	5.1	33.3
a. Stroke length $= 3$.	0 inches			
b. Based on Asher 2	005			

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Test #	Oil Type	Viscosity cP @ 15° /10s ⁻¹	Dispersant Type	Measured DOR _M	Oil Volume Spilled, liters	Vol. Emulsion Rec'd litres	Water Content Rec'd Emulsion %	Volume Oil Rec'd litres	Volume Oil Rec'd %	Volume Oil Disp'd %	DE %	Visual, ^a 0-3 minutes	Visual, 4-10 minutes	Visual, 11-20 minutes	Link to Video Clips
3	GA 209	14	Control	0	74.90	66.4	2	65.1	86.9	13.1	13.1	1	1	1	458 LSS 3.mpg
4	GA 209	14	Control	0	80.24	72.0	1	71.2	88.8	11.2	11.2	1	1	1	<u>458 LSS 4.mpg</u>
5	GA 209	14	Corexit 9500	1:10	71.33	283.1	83.9	45.5	63.8	36.2	36.2	1	1	1	<u>458 LSS 5.mpg</u>
14	GA 209	14	Corexit 9500	1:9.1	66.2	226.2	66.1	76.6	115.7	-15.7	-15.7	1	1	1	458 LSS 14.mpg
1	IFO 30	252	Control	0	72.84	75.9	11	67.6	92.8	7.2	7.2	1	1	1	<u>458 LSS 1.mpg</u>
2	IFO 30	252	Control	0	76.82	76.7	4	73.6	95.9	4.1	4.1	1	1	1	458 LSS 2.mpg
9	IFO 30	252	Corexit 9500	1:13.3	76.41	253.1	66.5	84.8	111.0	-11.0	-11.0	1	1	1	<u>458 LSS 9.mpg</u>
10	IFO 30	252	Corexit 9500	1:30.5	77.09	227.8	66.0	77.4	100.5	-0.5	-0.5	1	1	1	458 LSS 10.mpg
11	EB 873	683	Control	0	72.98	60.9	2.5	59.4	81.4	18.6	18.6	1	1	1	458 LSS 11.mpg
12	EB 873	683	Corexit 9500	1:11.6	70.65	268.9	68.4	85.0	120.3	-20.3	-20.3	1	1	1	<u>458 LSS 12.mpg</u>
13	EB 873	683	Corexit 9500	1:13.8	73.11	268.9	65.4	93.0	127.2	-27.2	-27.2	1	1	1	458 LSS 13.mpg
6	WD 30	1067	Control	0	70.78	74.3	24	56.5	79.8	20.2	20.2	1	1	1	458 LSS 6.mpg
7	WD 30	1067	Corexit 9500	1:20	75.31	Nd ^b	-	-	-	-	-	1	1	1	<u>458 LSS 7.mpg</u>
8	WD 30	1067	Corexit 9500	1:19.9	76.54	183.5	51	89.9	117.5	-17.5	-17.5	1	1	1	<u>458 LSS 8.mpg</u>
15	Harmony	1825	Control	0	71.47	121.8	55.0	54.8	76.7	23.3	23.3	1	1	1	458 LSS 15.mpg
16	Harmony	1825	Corexit 9500	1:14.6	73.66	189.8	56.1	83.3	113.0	-13.0	-13.0	1	1	1	458 LSS 16.mpg
17	Harmony	1825	Corexit 9500	1:14.5	71.88	Nd ^c	-	-	-	-		1	1		458 LSS 17.mpg

Table ES3 – Summary of Direct Measurements and Visual Observations of Dispersant performance in All Ohmsett Tests in Non-Breaking Waves

a. Visual assessment based on four-point scale of Lewis 2004: 1= no visible dispersion; 2= slow and partial dispersion; 3=moderately rapid dispersion; 4= very rapid and total dispersion.

b. No dispersion observed visually during test, but heavy rain following test appeared to cause rapid and total dispersion of the test slick leaving no oil to collect.

c. No dispersion observed visually in this test, but at the end of the test an error in the shut-down sequence creating a single breaking wave which caused near-complete dispersion of the test oil.

There was good agreement between data from the SL Ross wave tank and the Ohmsett tank. In short, there was no dispersion in non-breaking waves at Ohmsett and there was no dispersion with almost all oils in the SL Ross wave tank. The exception was that the least viscous oil tested in the SL Ross tank showed some dispersion, while an oil of similar viscosity did not at Ohmsett. Based on visual observations of the underside of slicks during the SL Ross tank experiments, it is believed that the energy added to the system by the bubble-barrier used to contain slicks in the SL Ross tank was the reason for the dispersion of the light oil in that environment.

Despite the fact that treated slicks did not disperse in non-breaking waves, there was evidence that the dispersant-treated slicks might have disperse if sufficient mixing energy were added. In a separate Ohmsett project, samples of fresh Galveston 209, Ewing Bank 873 and IFO 30 oils dispersed when treated with Corexit 9500 were tested in breaking waves. There was evidence of potential dispersion in the present project too. In the present project, small patches of dispersing oil were observed in the wakes of cables of sampling instruments that were drawn through treated slicks. Following each experimental test, as the undispersed oil was being collected, small light brown clouds of dispersed oil droplets formed at the edges of the slicks if they were manipulated too vigorously with the collection tools. This tendency for the oil remaining on the surface after each test to disperse during collection was common in this study, though it had generally not been observed in other studies involving breaking waves. There are several potential explanations for this behavior. One hypothesis is that, in non-breaking wave tests dispersant may persist in the treated slicks even after a 30-minute test, while in breaking wave tests it might not.

An in-situ laser particle-size analyzer (LISST) was used to monitor in-water oil concentrations and particle size distributions at a depth of 1.5 meters under treated and untreated slicks during these tests. The LISST output showed no detectible change in particle concentration or in particle size distribution while the slicks were agitated using non-breaking waves. This confirmed that no detectible amounts of dispersed oil droplets were generated when non-breaking waves passed through treated or untreated slicks in this study.

Introduction

Effectiveness of dispersants has been documented in breaking wave environments at sea (e.g., Lewis 2004) and in a wave tank (SL Ross et al. 2005, Trudel et al. 2005). The importance of mixing energy in controlling dispersion performance is well known (NRC 2005) and has been demonstrated repeatedly in laboratory tests (e.g., Delvigne and Sweeney 1988, Fingas et al, 1996). As a consequence, the question of potential dispersant performance at sea in lower energy environments and non-breaking waves has been frequently raised in workshops and training sessions. This study addresses the question of dispersant performance in non-breaking waves.

Based on the wind speed-wave-condition relationship described in the Standard Beaufort Scale, non-breaking wave conditions occur at wind speeds of 6 knots or less. The frequency of occurrence of wind speeds of 6 knots or less varies widely with location and season in US coastal and offshore waters, but monthly means range from 8 to 30% (Gilhousen et al. 1990). Hence this concern over potential dispersant performance in non-breaking wave conditions is a significant one for decision-makers in US coastal areas.

Laboratory-based studies have been of limited use in addressing this question, but wavetank tests have offered some insights. In recent Ohmsett dispersant tests with viscous oils (viscosities 2075 cP and 7100 cP), dispersant-treated slicks were readily dispersed by breaking waves, but were not dispersed in non-breaking waves (SL Ross et al. 2005). In the same project a less viscous oil (viscosity = 1145 cP) was also dispersed in breaking waves, but unlike the more viscous oils showed some evidence of limited dispersion even in non-breaking waves, suggesting that less viscous oils might be dispersible in nonbreaking waves. Because many if not most of the crude oils produced in offshore areas of the US have viscosities lower than 1145 cP at ambient temperatures, the questions arose, "Will low-viscosity oils disperse readily in non-breaking waves?" and, if so, "Is there an oil viscosity limit to chemical dispersion in non-breaking waves as there appears to be in breaking waves?" This project addressed these questions by testing the chemical dispersibilities in non-breaking waves of a number of oils with viscosities in the range of 10 to 2000 cP at ambient temperature.

The project objectives were:

- 1. To determine whether chemically-treated low-viscosity OCS crude oils disperse in a non-breaking wave environment; and
- 2. If so, to determine whether there is a limiting oil viscosity for chemical dispersion for crude oils in non-breaking waves, as there appears to be in breaking waves.

The approach was to conduct dispersibility tests on a number of petroleum oils in nonbreaking waves in near-at-sea conditions at in the large Ohmsett wave tank. The role of oil viscosity in influencing dispersibility in non-breaking waves was considered by testing a number of oils that spanned the viscosity range from 10 cP to 2000 cP. Tests were conducted on oils produced in the OCS region to ensure that results could be directly applied to these oils. The highest energy, non-breaking waves that had been characterized in the Ohmsett tank (Asher 2005) were used in these tests.

Prior to testing at Ohmsett, a preliminary series of smaller-scale tests were completed in the SL Ross wave tank in order to: a) gather preliminary information to aid in selecting oils for use in Ohmsett testing; and b) to gather additional information about scaling up dispersion processes from tests in small wave tanks to large wave-tank tests to predict oil behaviour at sea.

Methods

The dispersibility of samples of US Outer Continental Shelf crude oils and one marine fuel oil were determined in the SL Ross wave tank and at Ohmsett. Standard dispersant effectiveness testing protocols were used in all tests with the exception that the breaking waves used routinely in the protocols were replaced with non-breaking waves. Corexit 9500 dispersant was used in all tests. Properties of the oils used in the testing, test methods and the characteristics of waves used in testing are described briefly below.

Oil Acquisition and Analysis

OCS crude oils with the viscosities needed for testing were identified by analysing information on properties of crude oils produced in the Outer Continental Shelf area of the US. The following sources were consulted to identify potential oils for the study: 1) US Minerals Management Service monthly reports on oil production; 2) Environment Canada, Environmental Technology Centre Oil Properties Database (http://www.etc-cte.ec.gc.ca); and 3) corporate emergency response plans. With the exception of the Environment Canada database, none of the sources provided oil viscosity measurements. Because of this, an approximate relationship between API gravity and viscosity at 15° was developed and used to select the oils. The most up-to-date values of API gravity were then obtained for all OCS crude oils and candidate oils were selected. The OCS oils shown in Table 1 were selected for use in this study and three-drum samples of each were requested from the producing companies for testing. A marine fuel oil, IFO 30, blended on site from commercially available IFO 380 and marine gas oil was included in this list of oils because no crude oil in the viscosity range 50 to 500 cP was available for testing.

Oil Name	Identifier	Approximate Viscosity, cP @ 15 deg C	Supplier	Geographic Sector
Galveston 209	GA 209	10	ExxonMobil	GOM
Ewing Bank 873	EB 873	100	Marathon	GOM
Marine Fuel Oil 30	IFO 30	300	Blended at	Blended at
			Ohmsett	Ohmsett
West Delta 30	WD 30	1000	ExxonMobil	GOM
Hondo	Hondo	2000	ExxonMobil	PAC
Harmony	Harmony	2000	ExxonMobil	PAC

 Table 1 Outer Continental Shelf Crude Oils and Marine Fuel Oils Considered for

 Testing in This Project

SL Ross Wave Tank

Preliminary dispersion tests in non-breaking waves were conducted in the SL Ross wave tank. Five oils spanning a range of viscosities from 7 to 600 cP were tested. Samples of the oils selected for testing at Ohmsett did not arrive in time for preliminary testing in the wave tank. Five surrogate oils spanning the viscosity range to be tested Ohmsett were

selected from among those available at the lab. Corexit 9500 was the dispersant used in all tests. The oils tested and their viscosities when fresh are shown in <u>Table 2</u>.

Oil	Fresh Oil Viscosity CP @21 °C and 10 sec ⁻¹
Alaska North Slope crude oil	7
Endicott crude oil	75
Bunker C Diesel Fuel Blend (A)	200
Harmony crude oil	500
Bunker C Diesel Fuel Blend (B)	620

 Table 2 Oils Used in Non-Breaking Wave Tests in SL Ross Wave Tank

The standard dispersant effectiveness testing protocol (Belore 2003) developed for the SL Ross wave tank was used in this testing with a few modifications. The wave energy used in the testing was reduced to simulate the low-energy, non-breaking wave conditions at Ohmsett. The wave paddle was operated at approximately 31 rpm to achieve this. The wave energy was applied for 30 minutes rather than the usual 20 minutes to provide additional time for slower, long-term dispersion.

The test procedure included the following steps.

- 1. For each test a seven hundred and fifty millilitre sample of oil was weighed and then placed on the tank surface and was contained and maintained in the center of the tank using a air-bubble curtain barrier.
- 2. Dispersant was sprayed onto the slick at the required dosage using an overhead spray nozzle (the target dosage was a 1:20 dispersant-to-oil ratio for all tests).
- 3. The wave paddle was started and operated at 31 rpm for 30 minutes.
- 4. The oil remaining on the surface at the end of the 30-minute test was collected, weighed and compared with that initially spilled for an estimate of the amount of oil lost through dispersion.

Ohmsett Wave Tank

The Ohmsett facility has become a world leader in realistic dispersant effectiveness testing by first developing a standardized, calibrated, realistic dispersant effectiveness testing protocol and then using this protocol in an extensive program of research and testing aimed at a) resolving controversial questions hindering effective dispersant planning and b) understanding dispersant processes at sea. The protocol used at Ohmsett to test dispersant effectiveness has been documented fully in a variety of technical reports and publications (Belore 2003, SL Ross 2000; 2002, 2003, 2005, SL Ross and Mar 2000). Abbreviated descriptions of the equipment and test methods used in this study are provided in the following sections. The standard protocol was used in all tests except that only non-breaking waves were used instead of the usual breaking waves. These non-breaking waves were created by operating the wave maker at a frequency of 29 cpm with a 3.0-inch stroke. This differs from earlier tests that used mostly breaking waves produced by operating the wave maker at frequencies of 35 or 33 cpm, also with a 3.0-inch stroke. Characteristics of waves produced under all of these conditions were reported in Asher (2005).

Major Test Equipment Components

The main equipment components of the dispersant effectiveness (DE) test procedure include: a) Ohmsett tank, b) wave-making system, c) main equipment bridge, d) oil distribution system, e) oil containment boom, and f) dispersant spray system. Descriptions and photos of most components have been reported in SL Ross and MAR (2006) and are not described here. One component, the containment boom system, was improved for the present tests. In previous tests oil was contained within a 50-m x 10 m rectangle of containment boom, with a second pocket boom located at the north end of the rectangle (the down-wave) end to capture any undispersed oil that is driven over or under the end boom by the waves. In earlier tests it appeared that the booms on the sides of the containment area were causing two potential problems: a) interactions between the waves and booms caused turbulence that contributed to dispersion of the dispersanttreated oils; and b) the booms provided a large surface area which absorbed oil and may have contributed to artifactual oil losses in the tests. These problems were remedied by eliminating the side booms completely and extending the end-booms and pocket-boom to the sidewalls of the tank. End- and pocket-booms were attached directly to the sidewalls with brackets that provided a leak-proof seal of the boom against the sidewall. This allows the boom ends to travel vertically to ride the waves, thus preventing the oil from being pushed over or under the boom. In addition, the test area was lengthened from 50 to 100 yards in length. In all tests, the oil moves slowly from south to north in the tank under the influence of the waves and wave driven current and collects at the north end against the end-boom. With the 50-m long test area used in earlier tests, the oil commonly reached the end boom before the end of a 30-minute test. The oils were then mixed by the waves against the end boom for several minutes before the end of the test period. By lengthening the test area to 100 yards, the test is completed before the oil arrives at the end boom, thereby eliminating this potential source of error.

Test Procedure

The Ohmsett dispersant testing protocol was developed several years ago and has been refined through experience gained over the past three years. For each test:

- 1. The oil distribution system on the Main Bridge is charged with the required quantity of the test oil.
- 2. The dispersant supply tank is filled, the spray bar is tested briefly outside of the boomed area, and control solenoid is closed so dispersant re-circulates back to the supply tank until the spray operation commences.
- 3. The main bridge is positioned at the southern quarter point within the boomed area.
- 4. Waves are initiated at the required setting and time is allowed for the waves to fully develop.
- 5. Data acquisition and video recording of the test is started.
- 6. LISST Laser particle-size analyzer and Sontek Acoustic Doppler Current Velocimeter instruments are initialized and tested.
- 7. The bridge is accelerated to the required speed.
- 8. When the Main Bridge oil distribution system is in the appropriate position, the test slick discharge is initiated and oil is discharged over a 20-meter travel distance. The duration of the oil discharge is timed.

- 9. When the dispersant spray bar is 1 meter from the beginning of the test slick, spraying is initiated and continued until the spray bar is 1 meter past the end of the test slick.
- 10. The LISST instrument is suspended from the bridge rail on the Main Bridge in the appropriate cross-tank positioned to pass under the test slick and/or through the dispersed oil cloud during the pass along the tank. The LISST sensor positioned at a depth of 1.5 metres. Transects are made with the LISST along the tank to monitor oil concentrations and dispersed oil droplet size distributions at the required locations in the tank by moving the Main Bridge slowly (0.25 knots) along the tank at approximately 1-3 minutes, 4-9 minutes and 10-19 minutes after beginning of the test. At the end of each pass, in-water current velocity measurements are recorded using the Sontek ADV.
- 11. The quantities of dispersant and oil discharged in the test are measured.
- 12. Visual assessments of effectiveness are made.
- 13. The wave maker is stopped 30 minutes after the discharge of oil and five minutes are allowed for the waves to subside.
- 14. Water spray from Main Bridge fire monitors is used to gently sweep any oil remaining on the water surface to a common collection area.
- 15. The collected oil is then removed from the water surface using a doublediaphragm pump and suction wand and placed in a collection drum. (Note that if very small quantities of oil remain it is collected using a long-handled ladle and placed in a five-gallon bucket.)
- 16. A small quantity of emulsion breaker is thoroughly mixed into the collected oil and the mixture is allowed to stand overnight so entrained water drops can separate from the oil. The free-water phase on the bottom of the barrel is decanted. (Note, for small samples water is decanted from the five-gallon buckets by drilling a small diameter hole in the bottom of the bucket and allowing any free water to drain away from the floating oil.)
- 17. The remaining oil, which may still contain small amounts of water, is well mixed and a sample is taken for analysis of the water content and for physical property determination.

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- 18. The volume of liquid in the drum is measured. This volume measurement is then adjusted for the volume of water present (as determined by a water content analysis) to obtain an estimate of the quantity of oil recovered at the end of the test.
- 19. The effectiveness of the dispersant is reported as the volume of oil discharged minus the amount collected from the surface all divided by the amount discharged.

Wave Characterization

Asher (2005) characterized the Ohmsett breaking and non-breaking wave environments to facilitate comparisons between Ohmsett conditions and conditions in OCS offshore environments where Ohmsett test results would be applied. Working with combinations of wave paddle frequency (15 to 45 cpm) and stroke length (1.5, 3.0 and 4.5 inches) Asher described wave characteristics (wave height, length, frequency, period and presence/absence of breaking waves) and studied the variability of these as a function of location in the 200-m by 20-m tank and time in 30-minute runs for both "regular wave" and "harbour chop" conditions. Earlier dispersant effectiveness tests had considered dispersant performance on oils of intermediate viscosity (1125 to 7500 cP viscosity at 15 deg C) in Ohmsett waves of frequencies 29, 33 and 35 cpm with a 3-inch stroke. In those tests, wave frequency setting of 33 and 35 cpm produced breaking waves, while only those at 29 cpm produced non-breaking waves. Photographs of non-breaking and breaking waves are provided in Figures 1 and 2. As discussed above, all tests in the present study were conducted at a wave frequency of 29 cpm with a 3-inch stroke. These wave maker conditions produced glassy, smooth, regular waves throughout the tank for the full 30-minute duration of each test. The characteristics of the 29-cpm waves are compared to those of the 33- and 35-cpm waves in Table 3, based on the work of Asher.

Paddle Frequency, Cpm	Breaking/non- breaking	Significant Wave Height, H _{1/3} , m	Wave Length, m	Wave Frequency min ⁻¹								
29	Non-breaking	.330	7.1	27.8								
33	Breaking	.406	5.4	32.1								
35	Breaking	.403	5.1	33.3								
a. Stroke length $= 3$.	a. Stroke length = 3.0 inches											
b. Based on Asher 20	005											

Table 3 Characteristics of Ohmsett Waves Used in Dispersant Testing^{a, b}



Figure 1 Oil Slick on Non-Breaking Waves



Figure 2 Oil Slick on Non-Breaking Waves (see center of photo).

Oil Concentrations and Oil Droplet Size Distributions in the Water Column

In-water oil concentrations and particle size distributions were estimated at a 1.5 metre depth under slicks using a LISST particle size analyzer. This was done by suspending the instrument from the Main Bridge rail in the across-tank position to pass beneath the main body of the surface slick. In-water oil measurements were made repeatedly on transects along the long axis of the tank passing under the main part of the oil slick. The LISST device uses laser light scattering technology to measure the numbers of particles present in a number of size categories in the range from 2 to 500 microns. Results are output on a time-averaged basis (few seconds) in terms of a) abundance of particles in each size class; and b) cumulative concentration (v/v) of particles in the 2 to 500 micron diameter size range. The latter is an indicator of the oil concentration in the water column at the point of measurement. Comparisons of estimates of oil concentration made using the LISST and with other methods (e.g., Turner Fluorometer, extraction and measurement of grab samples) were performed in other studies (SL Ross, in press). Technical details of the operation of this instrument can be found at www.sequoiasci.com.

Results

SL Ross Wave Tank

The test results are summarized in <u>Table 4</u> and Figures 3 and 4. It is clear from the results of SL Ross wave tank tests that only the least viscous of the crude oils (Alaska North Slope crude oil (ANS) (viscosity 7 cP at 25^{0} C) showed high levels of dispersion in the absence of breaking waves. The more viscous oils showed little or no dispersion.

Oil	Water Temperature ° C	Viscosity ^a cP	Percent Dispersed	DOR	Test #
ANS	21	7	100	1:15	3
ANS	22	7	78.5	1:15	6
Endicott	22	75	25.5	1:23	5
Fuel Blend	21	200	35.6	1:17	4
Harmony	21	500	23.5	1:38	2
Fuel Blend 21		620	27	1:49	1
a. Viscosity m	neasurements ma	ade at test ten	perature and at	shear rates of 1	0 sec^{-1}

Table 4 Results Summary Non-breaking Wave Tests in SL Ross Wave Tank

Dispersant was applied using identical spray nozzles and pressures in all tests. This resulted in a variation in the dispersant-to-oil ratios (DOR) due to the different spreading characteristics of the oils tested. These modest differences in DOR did not have a significant impact on dispersibility as shown in Figure 4 where effectiveness is plotted against DOR.

All oils tested had been tested in this facility in the past using high-energy wave conditions and all had dispersed completely in these conditions. Based on this experience, it is clear that the low dispersant effectiveness values in the current study were due to lack of mixing energy and not under-dosing with dispersant. The single data points on Figure 4 show the effectiveness of Corexit 9500 in high-energy mixing tests, on the same oils (ANS and Harmony) and a fuel oil (1500 cP diesel-bunker mix) heavier than those used in the low energy tests. The oils dispersed much more in the high-energy tests at

similar or lower dispersant doses than in the low energy tests indicating that the difference in effectiveness was primarily due to mixing energy and not dispersant dosage.



Figure 3 Percent of Oil Dispersed in Low Energy Waves vs Fresh Oil Viscosity



Figure 4 Percent of Oil Dispersed in Low Energy Waves vs DOR

Testing at Ohmsett

Properties of Test Oils

The physical properties and water content of the oils tested at Ohmsett reported in <u>Table 5</u> show that the oils used in these experiments ranged in viscosity, at test temperature, from approximately 14 cP to 1825 cP (@ $1s^{-1}$).

Oil Type ^a	Water	Dens (kg/1	sity n ³)	Viscosity Pa.s (cP)				
	Content	Density	Temp.		@ 15 °C			
	%	(kg/m^3)	°C	$@ 1 s^{-1}$	$@ 10 s^{-1}$	@ 100 s^{-1}		
Galveston 209	0	0.852	24.7	14	-	-		
	0	0.937	23.9	336	316	-		
IFO 30	0	0 0.934		-	252	-		
	0	0.931	25.0	-	180	229		
Ewing Bank 873	2.5	0.943	25.0	-	683	773		
West Delta 30	4	0.943	24.5	1026	1067	-		
Harmony	50	0.949	20.0	1825	1530	-		

Table 5 Properties of Oils Tested at Ohmsett

Dispersant Effectiveness Tests

Visual assessments and direct measurements of effectiveness observed in the tests completed at Ohmsett are summarized in <u>Table 6</u> below. Results of in-water particle measurements made during each test using the Sequoia laser particle-size analyzer (LISST) are presented in detail in <u>Appendix 1</u>, and are summarized below.

Direct Measurements and Visual Assessments

Visual assessments and direct measurements of effectiveness are reported in <u>Table 6</u> below. Columns 1 through 5 describe the experimental conditions in the tests; 6 through 12 provide data used to compute the direct measurement of dispersion effectiveness; 13 through 15 show the results of visual assessments (using four-point visual scale employed

in earlier tests Lewis 2004, SL Ross et al. 2005); and column 16 contains links to video clips from the experiments.

In the control tests for the different oils (no-dispersant), visual observations showed that no detectible dispersion occurred. Direct measurements showed 77 to 96% of the oil that had been discharged at the beginning of the control tests was ultimately recovered following each 30-minute test. These levels of oil recovery in control tests were consistent with control test in other recent studies involving breaking waves. These levels of oil recovery serve as estimates of the "background" level of oil recovery against which oil recoveries in experimental tests are compared.

In the experimental spills, slicks were dosed with Corexit 9500 at nominal DORs of 1:20 and measured DOR values ranged from 1:9.3 to 1:30.5. The principal observation in this study was that, based on visual observations, there did not appear to be any dispersion whatsoever caused by waves in any experimental test with any oil, regardless of oil viscosity. Not even the least viscous oil, Galveston 209, with a viscosity of 14 cP, dispersed in non-breaking waves. Very small amounts of dispersion appeared to occur in some tests in local areas of turbulence where the cables of sampling devices passed through the treated slicks. In these cases, tiny, localized light-brown clouds formed in the wake of the cables. The clouds were assumed to be of fine droplets of dispersed oil.

In the dispersant-treated tests, the amounts of oil recovered at the end of each test were uniformly high, showing that little oil was lost through chemical dispersion during the tests. This is consistent with the visual observations and leads to the conclusion that none of the dispersant-treated oils were dispersed by non-breaking waves at Ohmsett. The possible exception was test #5 involving the Galveston 209 oil, the oil with the lowest viscosity (14 cP at 25⁰ C). In this test, the DE value was 36% suggesting that some dispersion had actually occurred even though no dispersion had been observed visually during the test. This single observation appeared to suggest that very low-viscosity oils might indeed disperse to a degree in non-breaking waves. However, when the test with the Galveston 209 oil was repeated (Test #15), no dispersion was observed by either

visual, direct measurement or LISST method, suggesting that the test #5 result was an artifact.

In seven out of eight dispersant-treated tests in this study, the estimates of the amount of oil recovered at the end of each test appeared to exceed the measured amounts of oil discharged at the beginning by from 0.5% to 27%. One possible explanation for this apparent inaccuracy is that the analytical method used in measuring water-content of the collected water-in-oil emulsion may systematically underestimate water content in the recovered emulsion. The net result of this would be an overestimate of the volume of oil recovered and underestimate dispersant effectiveness. In most other Ohmsett dispersant studies, where levels of effectiveness are high, the amounts of emulsified oil collected at the end of a test run are small (in one recent study the amounts of emulsified oil recovered was 42% of the amount of oil discharged) and the water content was low (22%), so that errors in estimating water content of as much as 0.3 of the latter amount would not significantly impact estimates of amounts of oil recovered or the conclusions of the study. However, in the present study the amounts of emulsion recovered were 3.4 times the volume of the test oil discharged and contained an average of 65% water. Under these conditions an error of 0.3 of the estimate of water content would account for the overestimates of recovered oil that were observed. Fortunately in this study, both the visual assessments of dispersion effectiveness and the in-water measurements of dispersed oil showed clearly that little dispersion took place in any of the tests.

Table 6 Summary of Test Results at Ohmsett

1	2	3	4	5	6	7	8	9	10	11	12		13	14	15	16
	Oil						Water						Visual ^a	Visual	Visual	
Test	Туре				Oil	Volume	Content	Vol.Oil	Volume	Vol.ume			at	at	at	
#		Viscosity,	Dispersant	Measured	Volume	Emulsion	Rec'd	Rec'd	Oil	Oil			0-3	4-10	11-20	
		CP @	Туре	DOR _M	Spilled,	Recovered,	Emulsion	litres	Rec'd	Dispersed	DE'	DE	minutes	minutes	minutes	Links to Video Clips
		15°C /10s ⁻¹			liters	Litres	%		%	%	%	%				
3	GA 209	14	Control	0	74.90	66.4	2	65.1	86.9	13.1	13.1	12.1	1	1	1	458 LSS 3.mpg
4	GA 209	14	Control	0	80.24	72.0	1	71.2	88.8	11.2	11.2	12.1	1	1	1	<u>458 LSS 4.mpg</u>
5	GA 209	14	Corexit 9500	1:10	71.33	283.1	83.9	45.5	63.8	36.2	36.2	24.0	1	1	1	458 LSS 5.mpg
14	GA 209	14	Corexit 9500	1:9.1	66.2	226.2	66.1	76.6	115.7	-15.7	-15.7	-27.9	1	1	1	458 LSS 14.mpg
1	IFO 30	252	Control	0	72.84	75.9	11	67.6	92.8	7.2	7.2	5.7	1	1	1	458 LSS 1.mpg
2	IFO 30	252	Control	0	76.82	76.7	4	73.6	95.9	4.1	4.1		1	1	1	458 LSS 2.mpg
9	IFO 30	252	Corexit 9500	1:13.3	76.41	253.1	66.5	84.8	111.0	-11.0	-11.0	-16.7	1	1	1	458 LSS 9.mpg
10	IFO 30	252	Corexit 9500	1:30.5	77.09	227.8	66.0	77.4	100.5	-0.5	-0.5	-6.3	1	1	1	458 LSS 10.mpg
11	EB 873	683	Control	0	72.98	60.9	2.5	59.4	81.4	18.6	18.6	18.6	1	1	1	458 LSS 11.mpg
12	EB 873	683	Corexit 9500	1:11.6	70.65	268.9	68.4	85.0	120.3	-20.3	-20.3		1	1	1	458 LSS 12.mpg
13	EB 873	683	Corexit 9500	1:13.8	73.11	268.9	65.4	93.0	127.2	-27.2	-27.2		1	1	1	458 LSS 13.mpg
6	WD 30	1067	Control	0	70.78	74.3	24	56.5	79.8	20.2	20.2	20.2	1	1	1	458 LSS 6.mpg
7	WD 30	1067	Corexit 9500	1:20	75.31	Nd ^b	-	-	-	-	-		1	1	1	458 LSS 7.mpg
8	WD 30	1067	Corexit 9500	1:19.9	76.54	183.5	51	89.9	117.5	-17.5	-17.5		1	1	1	<u>458 LSS 8.mpg</u>
15	Harmony	1825	Control	0	71.47	121.8	55.0	54.8	76.7	23.3	23.3	23.3	1	1	1	458 LSS 15.mpg
16	Harmony	1825	Corexit 9500	1:14.6	73.66	189.8	56.1	83.3	113.0	-13.0	-13.0		1	1	1	458 LSS 16.mpg
17	Harmony	1825	Corexit 9500	1:14.5	71.88	Nd ^c	-	-	-	-			1	1		458 LSS 17.mpg

a. Visual assessment based on four-point scale of Lewis 2004: 1= no visible dispersion; 2= slow or partial dispersion; 3= moderately rapid dispersion; 4= rapid and total dispersion.

b. No dispersion was observed visually during this test, but heavy rain occurred during post-test collection, appeared to cause rapid and complete dispersion of the test slick laving no oil on the surface for collection following the rain

c. .No dispersion was observed visually in this test, but at the end of the test an error in the shut-down sequence created a single breaking wave which caused near-complete dispersion of the test oil.

Despite the evidence that the treated slicks did not disperse in non-breaking waves, there was clear evidence that the slicks might readily disperse if sufficient mixing energy were added. In other tests involving these oils, fresh Galveston 208 and IFO 30 premixed with 9500 at a DOR of 1:20 dispersed readily in breaking waves, even after the premixed oil had sat undisturbed on the tank for up to 149 hours. In the present project, as mentioned above, small patches of dispersing oil were observed in small areas of turbulence caused where the cables of sampling instruments were drawn through treated slicks. Also in the present project, "recovered oil" results were not reported for Tests #7 and #17. In Test #17, involving the Harmony crude oil, there was no visible evidence of dispersion during the test and considerable oil remained on the surface of the tank at the end of the test. However, a single, large breaking wave was accidentally generated in the tank after the end of the test, resulting in considerable dispersion of the remaining test oil, so oil collection was abandoned. Similarly, in Test #7, involving the West Delta 30 oil, there had been no visible evidence of dispersion during the test and considerable oil remained on the surface at the end of testing. However, a brief period of heavy rain (accompanied by lightening) occurred after the end of the test, but prior to oil collection, forcing a brief suspension of tank operations for safety reasons. When researchers returned to the tank moments after the storm, the rain had dispersed the all of the oil. All of these observations suggest that the treated oils would have dispersed readily if sufficient mixing energy were added.

Following each experimental test, large amounts of emulsified oil remained on the surface of the tank for collection. Small light brown clouds, presumably of dispersed oil droplets, formed at the edges of the slicks if they were manipulated too vigorously during collection. As a consequence, great care was exercised when collecting the oil to avoid dispersing it during collection. This tendency to disperse during collection was common among experimental tests in this non-breaking wave study, but has generally not been observed in tests involving breaking waves, even in tests where there has been considerable dispersion. This suggests that in tests where oils are dosed with a DOR of 1:20, in non-breaking waves enough surfactants persist in the treated slick even after a 30-minute test to permit some dispersion. On the other hand, if tests involve breaking

waves, the oil remaining on the surface at the end of each test shows little tendency to disperse. The latter suggests that either the oil remaining at the end of a 30 minute test in breaking waves has had the dispersant washed out of it or that the remaining oil did not receive dispersant when sprayed at the beginning of the test.

In-Situ Oil Measurements

An in-situ laser particle-size analyzer or LISST was used to monitor in-water oil concentrations and particle size distributions during tests. Measurements were made on along-tank transects at a depth of 1.5 m in the water column, with the detector passing beneath the center of the oil slick. In other studies where effective dispersion is clearly occurring, the instrument was positioned to pass through the centre of any visible cloud of dispersed oil. In the present test, where virtually no dispersion was observed during tests the instrument was passed through the area most likely to contain dispersed oil droplets, namely, the area recently traversed by the slick. One or more passes with the LISST were completed during each 30-minute test. The LISST output from all tests, showing concentrations of particles and 50% volume diameter (VD50) and 90% volume diameter (VD90) are shown in figures in <u>Appendix 1</u>. In other projects where dispersant application clearly resulted in rapid or moderately rapid dispersion, the LISST output has followed a clear and reproducible pattern during transects through dispersed oil clouds. At the beginning of the transect, while the LISST traversed "clean water" outside of the cloud, the output commonly showed background concentrations of particles (=few ppm or less) and VD50 and VD90 values are highly variable. As the LISST passed through clouds of dispersed oil droplets, the particle concentration increased gradually to peak at several tens to 100 ppm or greater depending on level of effectiveness and degree of spreading of cloud, and then declined to background levels as the list passed out of the cloud. While the LISST was in the cloud, the VD50 and VD 90 values became less variable and show pronounced shift generally downward compared to background conditions. In the present study, LISST output showed no detectible change in particle concentration or in particle size distribution as it passed beneath control or treated slicks. This suggests that no detectible amounts of dispersed oil droplets were generated by treated slicks in non-breaking waves in this study and is further confirmation that no significant dispersion occurred during these tests.

Summary, Conclusions and Recommendations

Wave tank tests were conducted in the Minerals Management Service outdoor wave tank facility, Ohmsett, to determine if chemically-treated low-viscosity crude oils would disperse in a non-breaking wave environment; and, if so, whether there is a limiting oil viscosity for chemical dispersion in non-breaking waves. Ohmsett tests were completed using fresh Outer Continental Shelf (OCS) crude oils spanning a viscosity range of 2 to 2000 cP at ambient temperature. Tests were conducted using the standard Ohmsett dispersant effectiveness testing protocol, with the exception that non-breaking waves were used instead of breaking waves. Before conducting the tests at Ohmsett, preliminary tests were completed in non-breaking waves in the smaller SL Ross wave tank.

Tests in non-breaking waves in the SL Ross wave tank showed that the more viscous oils showed little tendency to disperse in non-breaking waves when treated with Corexit 9500 at a DOR of 1:20. Only the least viscous of the crude oils, Alaska North Slope crude oil (ANS) (viscosity 7 cP at 21° C) showed high levels of dispersion in non-breaking waves.

In tests in non-breaking waves at Ohmsett, the principal observation was that, based on visual observations, direct measurements of effectiveness and measurements of in-water oil concentrations there did not appear to be any dispersion caused by waves in any experimental test with any oil, regardless of oil viscosity. Not even the least viscous oil, the Galveston 209, with a viscosity of 14 cP, dispersed in non-breaking waves.

All data showed good agreement between results from the SL Ross wave tank and the Ohmsett tank. In short, there was no dispersion in non-breaking waves at Ohmsett and there was no dispersion with almost all oils in the SL Ross wave tank. The exception was that the least viscous oil tested in the SL Ross tank (viscosity = 7 cP at 23 °C) showed some dispersion, while an oil of similar viscosity (viscosity = 14 cP at 23 °C) did not disperse at Ohmsett. Visual observations made in the SL Ross wave tank suggest that the dispersion of the very light oil was caused by mixing energy imparted by the bubble barrier that was used to contain the slicks in these tests.

Despite the fact that treated slicks did not disperse in non-breaking waves, there was considerable evidence that the slicks would have dispersed if sufficient mixing energy were added. In a separate Ohmsett project, samples of fresh Galveston 208, Ewing Bank 873 and IFO 30 dispersed when treated with Corexit 9500 in breaking waves. This confirmed that these oils do disperse readily in breaking waves at Ohmsett after being treated with Corexit 9500 at a DOR of 1:20. In the present project, small patches of dispersing oil were observed during the tests in the wakes of cables of sampling instruments that were drawn through treated slicks. In addition, following each experimental test, as the undispersed oil was being collected, small light brown clouds of dispersed oil droplets formed at the edges of the slicks if they were manipulated too vigorously with the collection tools. This tendency to disperse during collection was common among experimental tests in this study, but had generally not been observed in tests involving breaking waves. This suggests that in non-breaking waves some dispersants persist in the treated slick even after a 30-minute while in tests in breaking waves they do not.

An in-situ laser particle-size analyzer or LISST was used to monitor in-water oil concentrations and particle size distributions under treated and untreated slicks during tests. The LISST output showed no detectible changes in particle concentration or in particle size distribution as it passed beneath control or treated slicks, confirming that no detectible amounts of dispersed oil droplets were generated when non-breaking waves passed through treated or untreated slicks in this study. In future tests involving the LISST the background particle environment should be thoroughly quantified and its variability along the long axis monitored with "waves up" prior to each test so that background particle concentrations and VD50 and VD90 values and their variability are known.

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Appendix 1. Results of Laser Particle Size Analyses in Test Runs

Below are results of laser particle size analyses on long-axis transects at a depth of 1.5 m, with the sensor passing below control and treated slicks. Most traces include measurements of tank background as well as one or more transects made during the 30-minute test.



LISST Data Run 1 IFO30 Control





LISST Data Run 2 IFO30 Control



LISST Data Run 3 GA209 Control



LISST Data Run 4 GA-209 Control



LISST Data Run 5 GA-209 Corexit 9500



LISST Data Run 6 West Delta 30 Crude Oil Control



LISST Data Run 7 West Delta 30 Corexit



LISST Data Run 8 West Delta 30 Corexit



LISST Data Run 9 IF0 30 Corexit



LISST Data Run 10 IFO 30 Corexit 10



LISST Data Run 11 Ewing Bank 873 Oil Control



LISST Data Run 12 Ewing Bank 873 Oil Corexit 9500



LISST Data Run 13 Ewing Bank 873 Oil Corexit 9500



LISST Data Run 14 Galveston 209 Oil Corexit 9500



LISST Data Run 15 Harmony Oil x Control



LISST Data Run 16 Harmony Oil x Corexit 9500



LISST Data Run 17 Harmony Oil x Corexit 9500