# Dispersant Effectiveness Experiments Conducted on Alaskan and Canadian Crude Oils in Very Cold Water

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Abstract: Dispersant effectiveness (DE) experiments were conducted to determine the effectiveness of using two chemical dispersants, Corexit 9500 and Corexit 9527, applied to fresh and weathered Alaskan and Canadian crude oils in very cold water. The primary goal of the experiments was to demonstrate that dispersants could be a viable countermeasure on these crude oils in cold weather conditions. Two series of experiments were conducted, the first in February-March 2002 and the second in February 2003. The experiments were conducted at Ohmsett – The National Oil Spill Response Test Facility, located in Leonardo, New Jersey. Ohms ett is a large outdoor above ground test tank which measures 203m long by 20m wide by 3.4m deep and is filled with 9.84 million liters of crystal clear salt water. The tank has wave generator capable of generating waves up to 1m in height, a moveable beach to reduce wave reflection and is spanned by moveable bridges that is used to tow full scale oil spill response equipment over the waters surface. During the 2002 experiments, a refrigeration unit was installed to maintain the tank water at a constant near-freezing temperature. The unit was not required in 2003 due to very cold outside air temperatures. A total of twenty-six full-scale DE experiments were successfully conducted (twelve in 2002 and fourteen in 2003) with various combinations of oil type, weathering and dispersant-to-oil (DOR) ratios. The effectiveness of the dispersant in each experiment was documented through visual observations and using the following three measurements. First a numerical estimate of the DE was made for all experiments by recovering and measuring the surface oil remaining within the containment boom at the end of each test. Second, in-water oil concentrations were made using two flow-through fluorometers and analysis of grab water samples using IR spectrophotomery. Third, oil drop size distributions were recorded using a laser particle size analyzer suspended in the tank. Results from these limited experiments indicate that both dispersants were effective in dispersing the crude oils tested in very cold water. Further research is recommended on both evaporated and emulsified crude oil samples to determine the "time window" for dispersant use.

# Background

In North America, crude oil is produced and transported in a number of areas that have cold water, especially during the winter months. In Canada, crude oil is being produced on the Newfoundland Grand Banks where the water temperatures average

about 10°C in summer and 1°C in winter. In the Alaskan Beaufort Sea, crude oil is produced on the Outer Continental Shelf and in Alaskan State waters which are always cold. From Valdez, Alaska, crude oil is loaded and transported to the lower 48 states by tanker through the cold waters of Prince William Sound, Gulf of Alaska and the Pacific Ocean. Crude oils are also imported into ports on the East Coast of North America and the St. Lawrence River during months when the water is cold. Oil spill response planners, decision-makers and responders in these areas need to know whether the crude oils that are being transported can be chemically dispersed in the event of an oil spill and the "time window" where they are effective.

There are concerns that chemical dispersants may not be effective on spills of Alaskan and Canadian crude oil in cold water, especially those that could take place in the colder months and that dispersants should not be or cannot be used in these conditions. This concern is generally based on a lack of information, especially with regards to dispersant effectiveness data. One main concern is that in very cold water, the spilled oil may become too viscous to successfully disperse. Dispersants also have different effectiveness on different oil types (e.g. waxy or naphthenic crudes, asphaltene rich crudes and bunker fuels) (Brandvik et al 1992). Preliminary laboratory dispersant testing indicated that unemulsified crude oils should be dispersible and that semiemulsified crude oils should also be dispersible (SL Ross 2001). Results from the laboratory scale experiments were promising, however small-scale testing does not incorporate sufficient environmental realism (variables and scale) to permit confident predictions about real-world situations. It was believed that larger-scale testing was required. Controlled field studies, while valuable for realism are expensive, uncontrollable in many instances, and are very hard to implement due to regulatory barriers. Large tank experiments conducted at Ohmsett provide a critical link between small-scale laboratory and open-water experiments because they can simulate real-world conditions without the cost of a field release.

Research data collected over a 4-year period has demonstrated that full scale DE testing feasible in the Ohmsett tank and a preliminary test protocol was developed (SL Ross 2000a, SL Ross 2000b). DE test results show that dispersant concentrations in the tank water can reach at least 400 parts per million (ppm) before having a noticeable effect on the dispersion of floating oil. In the Ohmsett test tank, dispersant concentrations of 400 ppm equate to about 4,160 liters of dispersant. This means that researchers can perform a number of consecutive DE in the tank without concern that the dispersant concentration might reach a level that could skew DE results (SL Ross 2001). It also means that the entire 10 million liters of the Ohmsett test tank does not have to be drained and refilled between each DE experiment. In the 2002 and 2003 experiments approximately 70 liters of dispersant were used in each test series. MMS has developed, tested and built a simple, inexpensive system for expediently removing dissolved dispersant from the Ohmsett tank water using Powdered Activated Charcoal (PAC) (SL Ross 2003). Combining the three to five days required to operate the filter to reduce dispersed oil concentrations below 10ppm (SL Ross 2000b) and a two to three day period of treatment with PAC, it is possible to return the Ohmsett tank water to a quality that meets the standard

## **Test Facility**

Ohmsett (an acronym for Oil and Hazardous Materials Simulated Test Tank) is the world's largest tow/wave tank designed to evaluate the performance of equipment that detects, monitors and cleans up oil spills under environmentally safe conditions (www.ohmsett.com). Ohmsett is the largest tow/wave facility where oil spill response testing, research and training can be conducted with a variety of crude oils and refined petroleum products. Following the Exxon Valdez oil spill in Prince William Sound, Alaska, Title VII of the Oil Pollution Act of 1990 (OPA-90) mandated the reactivation of Ohmsett. The facility is maintained and operated by the U.S. Department of the Interior, Minerals Management Service (MMS) and is open year-round for used by industry, academia and federal agencies (US and foreign) to conduct full-scale oil spill research and development programs. Unlike field-testing which is very expensive, requires permits, and impossible to reproduce conditions, Ohmsett provides a safe, controlled, reproducible testing environment. The MMS has recently upgraded the testing capabilities of Ohmsett to provide a controlled environment for cold water training and testing including the ability to simulate realistic broken ice conditions. Funds to operate Ohmsett are appropriated from the Oil Spill Liability Trust Fund (OSLTF) which was established under OPA-90. The OSLTF receives funds from a \$0.05 tax on each barrel of oil produced or imported into the U.S. By making payments into the fund as required by OPA-90, the potential polluters pay for the operation and maintenance of the facility. Thus Ohmsett's operational costs are fully funded by industry. As intended by OPA-90, companies that produce and transport oil are supporting research to improve oil spill response capabilities.

#### **Description of Facilities**

Ohmsett is located on the waterfront at Naval Weapons Station Earle, in Leonardo, New Jersey, about one hour drive south of New York City. The heart of the facility is the large outdoor, above ground concrete test tank which measures 203 meters long (the approximate length of two football fields) by 20 meters wide, by 3.3 m deep. It is filled led with 9.84 million liters of crystal clear natural sea water, and is maintained at oceanic salinity (35ppt.), through the addition of salt. Water clarity is maintained by the filtration and chlorinating systems to enhance underwater video of equipment being tested (Fig. 1)

Spanning the tank are three bridges that move back and forth along the length of the tank on rails. The main bridge moves along the tank towing full-size spill response equipment through the water to simulate actual towing at sea or deployment in current. The towing bridge is capable of exerting a force of 151 kilonewtons while towing equipment at speeds up to 3.3 meters/sec. The bridge includes an oil distribution system that allows a variety of test oils to be deposited on the water in front of equipment being tested, to simulate a spill at sea. In this way, reproducible thicknesses and volumes of oil can be achieved for multiple test runs. Equipment tests are conducted in accordance with the American Society of Testing and Materials (ASTM) Standards.

Conditions simulating ocean wave conditions are created with a wave generating system and a wave dampening artificial beach. Waves up to one meter (3 feet) in height as well as a simulated harbor chop can be generated. Tests can be viewed from traveling

bridges, the control tower, or underwater viewing windows on the side of the tank. The data collection and video systems record test results both above and below the water's surface. Ohmsett also has a Chemistry Laboratory and a Machine Shop.

The towing, oil distribution and wave generation systems at Ohmsett combine to provide the capability for testing oil spill control equipment and systems under a wide range of repeatable conditions and settings. This allows researchers and manufactures to obtain specific performance data to support development, refinement and efficient operation of spill control systems and equipment.



Figure 1. Aerial view of Ohmsett - The National Oil Spill Response Test Facility

### **Dispersant Experiment Test Equipment**

The major equipment used in the DE experiments were the Ohmsett test tank, wave generating system, equipment bridges, oil distribution and, dispersant spray systems, and the oil containment boom. Photos of the Ohmsett facility each of these components are contained on Fig. 2-8.



Figure 2. Ohmsett Test Tank with Oil Containment Boom



Figure 3. Ohmsett Wave Generator



Figure 4. Oil Distribution System



Figure 5. Main Bridge with Dispersant Spray Bar in Foreground, Oil Distribution Behind



Figure 6. Oil Delivery Pump and Supply Drum



Figure 7. Dispersant Supply Tank and Pump



Figure 8. Dispersant Spray Bar in Operation During Testing

### **Ohmsett DE Test Procedure**

The following steps were completed for each experiment.

- 1. Set up boom / oil distribution system / dispersant spray bar and pump.
- 2. Clear entire tank and inner boom area of oil. Remove tramp oil slicks from the tank or isolate them from the test area using the auxiliary bridge boom.
- 3. Set up fluorometer and particle size instrumentation. Deploy fluorometer pumps shortly before start of test to prevent freezing of water lines. Pumps were left running in a tank of water on deck (with flow re-cycling into the on-deck tank) to ensure proper flow at test time.
- 4. Transfer oil to open top drum on main bridge. Fill the oil discharge manifold with oil. Measure and record the depth of oil in the drum.
- 5. Fill dispersant supply tank and keep warm with immersion heater to ensure proper spray pattern.

- 6. Test spray bar operation to ensure even spray from all nozzles (visual confirmation). Measure and record the depth of dispersant in the supply tank. Leave dispersant spray pump running and re-circulate the dispersant through the supply return line to keep supply line contents warm.
- 7. Position main bridge north of the center of the boomed area.
- 8. Start data collection for fluorometers and particle size analyzer just prior to starting the discharge and spraying of the oil to provide background readings.
- 9. Move bridge to the south at 1 knot (0.5 m/s).
- 10. Start oil pumping when the bridge is a few meters south of the center of the boomed area and continue pumping for 35 to 40 seconds at 40 gpm. Time the duration of the oil discharge and measure and record the depth of oil in the drum at the end of the discharge.
- 11. Start wave paddle at 35 cycles per minute (cpm) with 3-inch stroke at same time that oil discharge is started.
- 12. Start dispersant spray at start of oil pumping and continue spraying until 1 m past last surface oil (spray pressure 45 to 55 psi). Time the duration of the dispersant spraying and measure and record the depth of dispersant in the supply tank at the end of the spraying operation.
- 13. Rotate the oil distribution bars up away from the water surface to prevent contact with waves or the end containment booms.
- 14. Videotape and photograph the test with emphasis on providing a good overview of the development (or lack thereof) of any dispersed oil cloud that forms.
- 15. Ten minutes after the formation of the first breaking waves, move the bridge over the main dispersed oil cloud (or surface slick if no cloud is evident) at a speed of 0.25 knots and collect oil concentration data (fluorometer readings and water grab samples) and particle size data. Move the instrument chain so the fluorometer pumps pass through the center of any dispersed oil cloud. The duration of the sampling run should be about 8 minutes.
- 16. Repeat in-water sampling passes 30 and 50 minutes after the start of waves.
- 17. Stop the wave paddle 60 minutes after the start of breaking waves.

- 18. Flush the oil remaining within the boom to the down-wind end of the boom and collect either using a ladle or a suction tube.
- 19. Decant free water from the collected oil and measure the quantity of oil (or emulsion) collected.
- 20. Completely mix the collected material and take a 500 ml sample of the product oil for water content and density determination. This data is used to determine total quantity of oil collected.
- 21. Clean and prepare the tank for the next test.

## **Full Scale Dispersant Effectiveness Testing**

### February - March 2002 Test Series

In February-March 2002, a total of twelve full-scale experiments were successfully completed (SL Ross 2002). The experiments were funded by the US Minerals Management Service (MMS) and ExxonMobil Research and Engineering Co. Corexit 9500 and 9527 were applied to fresh and weathered Alaskan and Canadian crude oils, in dispersant-to-oil ratios (DORs) ranging from 1:14 to 1:81. The water temperature was maintained between -0.5 and +2.4°C throughout all of the testing. Between 60 and 80 liters of oil were used in each test and the oil was spread on the waters surface to form slicks between 1.1 and 1.8 mm thick. The total quantity of oil used in the test program was approximately 900 liters. Between 6 and 8 liters of dispersant were used in each test. The total quantity of dispersant used in the testing program was approximately 70 liters. The concentration of dispersant in the Ohmsett tank water at the end of testing was less than 10 ppm. This is based on the 10 million liter volume of the tank and the 70 liters of dispersant. Waves were generated using a wave paddle stroke of 7.6 cm and a frequency of 35 cycles per minute. The average wave amplitude for the experiments ranged between 16.5 and 22.5 cm and the average wave period was between 1.7 and 1.9 seconds.

The physical properties of the Alaskan crude oil used in the experiments are summarized in Table 1. The physical properties of the Canadian crude oil used in the used in the experiments are summarized in Table 2. The percentage values shown in Tables 1 and Tables 2. are expressed as volume percent evaporated. The evaporated oils were generated by bubbling air through heated drums of the oil. The weight of the oil was measured during the air sparging using a weight scale and a drum lift (Fig.9). The weathering approach used is common in North America and elsewhere, and the degree of weathering is reported as percent (%) of volume lost. This percent (%) loss can then be related to spill modeling results (volume percent loss) for "time window" estimations for dispersant use. It is a valid and useful indicator of degree of weathering. Boiling Point (BP) data was not collected for the crude oils used in these experiments. However, the information below is from BP curves derived from similar (not exact) crude oils used in the experiments. For Hibernia crude 10% evaporated by volume corresponds to a 134 °C (vapor T). For ANS crude 10% loss by volume corresponds to 65 °C (vapor T), 20% corresponds to 84.5 °C (vapor T).

Table 1. P	Physical	Properties	of Fresh an	nd Evaporated	Alaska No	rth Slope (	Crude Oil
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Alaska North Slope Crude	Density (kg/m³)	Viscosity Pa.s (cP) @1.3 °C & 10 s <sup>-1</sup>	Pour Point <sup>o</sup> C	
Fresh	873	0.025 (25)	<-13	
10% Evaporated	903	0.16 (160)	-	
20% Evaporated	923	1.94 (1940)	-13	

 Table 2. Physical Properties of Fresh and Evaporated Hibernia Crude Oil

Hibernia Crude	Density (kg/m <sup>3</sup> )	Viscosity Pa.s (cP) @1.3 °C & 10 s <sup>-1</sup>	Pour Point <sup>o</sup> C	
Fresh	854	0.43 (430)	-6	
7.9% Evaporated	867	0.66 (660)	-	
10.3% Evaporated	876	1.87 (1870)	13	



Figure 9. Oil Evaporation Setup

#### February 2003 Test Series

In 2003, the MMS funded another series of experiments to evaluate the DE of Corexit 9527 on Alaskan crude oils with a variety of physical properties. Results from preliminary testing in small wave tank in Ottawa, Canada (completed as part of the 2003 MMS experiments) showed that Corexit 9500 and Corexit 9527 gave similar DE on all of the Alaskan crude oils tested. These results led to the use of only Corexit 9527 for the 2003 Ohmsett DE experiments. MMS selected Corexit 9527 because this is the primary dispersant currently stockpiled in Alaska. The small-scale experiments also provided an indication of the DORs needed to effect dispersion for each of the oil types at the test temperature ( $\sim$ 0°C).

In February 2003, a total of fourteen large-scale tests were successfully completed at the Ohmsett facility (SL Ross and MAR, Inc.2003). Corexit 9527 was applied to fresh and weathered Alaskan crude oils, in DORs ranging from 1:18 to 1:29. Five Alaskan crude oils selected for testing Alaska North Slope (ANS), Northstar, Endicott and Pt. McIntyre (all from the Prudhoe Bay, AK area), and Middle Ground Shoals (MGS) from the Cook Inlet, AK area.. The water temperature during each test was constant and the average water temperatures for the 14 experiments ranged between -0.4 to -1.8 °C. The air temperature during the test period ranged from 2.8 to -7.4 °C. Between 90 and 110 liters of oil were used in each test. With the exception of one test, the estimated average oil thicknesses for the oil slicks were very close to the 1 mm design thickness. Only test No. 2, which used light Northstar crude, had a significantly different thickness of about 0.75 mm. Waves were generated using a wave paddle stroke of 7.6 cm and a frequency of 35 cycles per minute. The average wave amplitude for the experiments ranged between 16.7 and 21.8 cm and the average wave period was between 1.8 and 2.2 seconds. The physical properties of the Alaskan crude oils used in the experiments are summarized in Table 3. The crude oils were again evaporated by bubbling air through heated drums and the weight of the oil was measured during the air sparging using a weight scale and a drum lift (Fig.9).

Oil Type (% evaporated)	Density (kg/m <sup>3</sup> at 25 °C)	Viscosity (cP at 0 °C)	Oil-Water Interfacial Tension (dynes/cm)	Pour Point <sup>1</sup> (°C)
ANS (fresh)	873	98	20.5	< -12
ANS (17%)	912	496	20.9	-12
Endicott (fresh)	878	1630	26.0	-3
Endicott (11%)	914	2525	25.3	3
NorthStar (fresh)	812	101	14.4	< -9
Northstar (29%)	864	522	14.8	12
Pt. McIntyre (fresh)	890	740	22.4	-3
Pt. McIntyre (9%)	902	-	-	3
MGS (fresh)	856	36	26.9	< -18
MGS (20%)	914	3180	25.4	0

Table 3. Physical Properties of Fresh and Evaporated Alaskan Crude Oils

<sup>1</sup> Pour Points reported are from historical records for these oils with the exception of MGS. Pour point shown for MGS is from recent analysis of oil used in the current test program.

### Results

#### February-March 2002 Test Series

A total of twelve tests were successfully completed with various combinations of oil type, dispersant type, and DORs. Table 4. summarizes the tests that were conducted, ordered by oil type. It was clear from visual observations which tests resulted in significant dispersion and which did not. With the exception of the control tests (Test No. 1 and Test No. 6) and Test No. 11, all of the tests resulted in high percentages of oil dispersing into the water column. The significant dispersion was observed by those who attended the tests and is extensively documented in the video clips provided for each of the tests. Fluorometry measurements were not taken in the 2002 DE experiments.

In the control case (Test No. 1 with no dispersant applied), all of the oil remained on the surface and was wind herded to the end containment barrier where occasional cresting waves would splash the oil over the end boom. Entrainment or leakage under the boom was not observed. A significant amount of oil was seen to exit the containment area by this process, thus making for a poor control test. The oil from this control test was observed to remain on the surface after the splash over. End boom "splash over" was not as prominent in the tests where dispersant was applied because most of the oil dispersed into the upper water layer prior to being herded to the downwind end containment barrier. In some of the tests where dispersant was applied, oil-and-water mixtures (coffee colored mixtures) were observed splashing over the end containment boom. However, this oil quickly dispersed into the water column after the splash over. This is seen in the video records of the tests. The one exception to this behavior occurred in Test No. 11, where low dispersant dosage was used. In this test "black" oil observed splashing over the end boom remained on the surface as sheen and did not appear to disperse.

Oil Type	% Evap. By Volume	Air Temp °C am pm	Water Temp °C am pm	Oil Volume (liters)	Oil Thickness (mm)	Dispersant Type	DOR	Max DE (%)	Test #
Hibernia	0.0	5.6 6.1	1.6 2.4	86	1.17	none	0	84*	1
	0.0	5.6 6.1	1.6 2.4	82	1.21	Corexit 9500	1:33	>90	2
	7.9	0.6 6.7	0.3 0.8	88	1.47	Corexit 9500	1:38	82	3
	10.3	0.6 10.0	-0.5 0.4	68	1.76	Corexit 9500	1:14	95	5
Hot Hibernia	0.0	0.6 10.0	-0.5 0.4	69	1.80	Corexit 9500	1:14	98	7
ANS Crude	0.0	0.6 10.0	-0.5 0.4	20	n/a	none	0	n/a	6
	0.0	-5.0 2.8	-0.4 0.0	71	1.15	Corexit 9527	1:32	98	9
	10	1.7 3.9	0.2 2.0	79	1.28	Corexit 9527	1:48	99	8
	20	-5.0 2.8	-0.4 0.0	77	1.25	Corexit 9527	1:44	99	10
	0.0	0.6	0.3	71	1.14	Corexit 9500	1:34	97	4

 Table 4. 2002 Cold Water Dispersant Effectiveness Test Results Summary

	6.7	0.8						
0.0	3.3 16.7	-0.3 0.9	74	1.20	Corexit 9500	1:81	93*	11
20	3.3 16.7	-0.3 0.9	76	1.23	Corexit 9500	1:38	96	12

\* A considerable quantity of black, non-dispersing oil escaped the containment area in these tests

After each test the oil remaining in the containment area was collected and its volume determined. The collected volume was compared to the quantity of oil discharged in the test to determine the maximum possible DE of the test. Oil loss over the end containment barrier has not been accounted for in these calculations. The DE values reported for Test No. 1 and Test No. 11 are known to be too high due to the observed loss of non-dispersing oil over the end containment barrier. Loss of oil through evaporation has not been accounted for when determining the maximum DE values. In the chemically treated tests the oil dispersed within 10 to 15 minutes after the application of dispersants and wave energy. Only a small amount of oil would evaporate during this short time frame, especially for the oils that were pre-evaporated prior to the test. The use of inwater oil concentrations determined by UVF or other methods to attempt to determine the quantity of oil dispersed into the water or to estimate DE is not viable due to the non-uniform dispersed oil plume and the need for a very large number of measurements to be made simultaneously to characterize the plume at any given time. It was not feasible on this scale of experiment and this fact has been recognized by many researchers.

Between 60 and 80 liters of oil were used in each test and the oil was spread on the waters surface to form slicks between 1.1 and 1.8 mm thick. The total quantity of oil used in the test program was approximately 900 liters. Between 6 and 8 liters of dispersant were used in each test. The total quantity of dispersant used in the 2002 test series was approximately 70 liters. The concentration of dispersant in the Ohmsett tank water at the end of testing was less than 10 ppm.

#### February 2003 Test Series

A total of fourteen experiments were completed with various combinations of oil type and DORs. Table 5. summarizes the tests that were completed, ordered by oil type and the maximum DE values reported.

It was clear from visual observations alone which experiments resulted in a significant dispersion of oil and which did not.



Figure 10. Good Dispersion. No oil on water's surface.



Figure 11. Poor Dispersion. Oil remaining on water's surface.

The visual observations were supported in three separate ways. First of all, a numerical estimate of the dispersant effectiveness (DE) was made for all tests by recovering and measuring the surface oil remaining at the end of the test period. Secondly, in-water oil concentration measurements were made using two flow-through fluorometers (Turner Designs 10-AU fluorometers) and analysis of water grab samples using IR spectrophotometry. Finally, oil drop size distributions were recorded using a laser particle size analyzer (Sequoia LISST-100, 2.5 to 500  $\mu$ m particle size range) suspended in the tank.

Oil	% Evap. By Weight	Average Air Temp °C	Average Water Temp °C	Oil Volume Spilled (liters)	Approx. Oil Thickness (mm)	DOR	% Oil Recovered from Surface	Max. Dispersant Effectiveness (%)	Test #
ANS	17	-3.1	-0.6	107	0.92	1:24	15	85	1
ANS	17	-1.7	-0.4	101	0.97	1:25	14	86	9
Endicott	0	-2.1	-0.4	113	1.1	1:31	26	74	8
Endicott	11	-1.9	-0.6	94	0.91	1:22	97	3	14
Northstar	0	-4.4	-0.4	78	0.75	1:18	0	~100	2
Northstar	29	-7.4	-0.7	105	1.1	1:19	92	8	10
MGS	0	-6.1	-0.5	98	0.95	1:24	18	82	11
MGS	20	-5.3	-1.1	105	0.90	1:27	20	80	3
Pt. McIntyre	0	-5.6	-0.5	103	1.0	1:29	23	77	12
Control Tests									
ANS	0	-4.3	-1.0	96	0.93	0	69 <sup>a</sup>	-	4
ANS	0	-1.4	-0.9	108	1.1	0	97	-	7
Endicott	0	2.8	-1.0	103	1.0	0	84	-	6
Northstar	0	-3.6	-1.8	103	1.0	0	93	-	5
Pt. McIntyre	0	-3.7	-0.8	104	1.0	0	58	-	13

Table 5. Cold Water Dispersant Effectiveness Test Results Summary

<sup>a</sup> This control test was completed with only a single end containment barrier. All other control tests had a double boom in place at the north end of the tank to improve oil containment.

After each test the oil remaining in the containment area was collected and its volume determined. The collected volume was compared to the quantity of oil discharged in the test to determine the maximum possible DE of the experiment.

The DE values measured in the test program ranged from 3 to 100%, as reported in Table 5. The chemically dispersed runs resulted in high percentages (75 to ~100%) of oil dispersing into the water column, with the exception of tests No. 10 (evaporated Northstar) and No. 14 (evaporated Endicott). The DE trends identified in the smaller scale testing were mirrored in the large-scale test results. The heavily evaporated Northstar and evaporated Endicott crude oils were resistant to chemical dispersion in both the small-scale and Ohmsett experiments. A higher percentage of the fresh Endicott crude oil was dispersed in the Ohmsett experiments when compared to the small-scale results (74% vs. 20 to 30%). This may be due to additional mixing energy present in the Ohmsett tests, in the form of breaking waves that do not develop in the preliminary small tank tests that were completed as part of this project.

The oil concentration measurements taken at the 1-meter depth were the largest measured and the most variable in all of the experiments, especially on the first pass of

the fluorometers through the dispersed oil cloud. The concentrations at 1-meter depth tended to decline and stabilize on subsequent passes, presumably due to the diffusion of the dispersed oil cloud and/or the rise of larger oil drops to the surface. The concentrations measured at the 2-meter depth were generally lowest on the initial pass and often increased on subsequent passes. These results suggest an initial dispersion of oil in the upper water layer with a gradual diffusion of the cloud to depth. It was found that the oil concentration estimates made using the flow-through fluorometers were in general 4 to 5 times lower than the concentration estimates made using IR spectrophotometry.

The UV-fluorometers are generally very sensitive to both oil type and oil droplet size. The best (most reliable) method is to "calibrate" the response to the UVF-instrument for each test against water samples taken simultaneously, and where the oil/THC concentration has been quantitatively determined. This is how the 4 to 5 times estimate quoted above was established. The oil concentration measured in grab samples was compared to UVF values and the 4 to 5x's trend identified from this data. However, the relative concentrations measured with the fluorometers provide a valid picture of the change in oil concentration over time and space.

There was no possibility of obtaining a "mass balance" based on the UVF measurements. The spatial and temporal measurement requirements needed to accurately account for the quantity of dispersed oil in the tank would be enormous. The UVF concentrations are captured only to provide evidence of the presence of dispersed oil.

Particulate matter in the water column was measured at the 2-meter depth using a laser particle size analyzer. The data was adjusted to account for the presence of background particles prior to each experiment. The measured drop size distributions suggest that a high percentage (average of all experiments was 78%) of the oil mixed into the tank, in the cases where dispersant was applied, would remain dispersed under typical ocean mixing conditions (all oil drops less than 100  $\mu$ m in diameter assumed permanently dispersed) (Lunel 1993). Only about 30% (average of all experiments) of the oil present in the water column in the control experiments was in the form of drops that could be considered permanently dispersed. The concentrations of oil in the water column during the control experiments were also generally much lower than for the chemically dispersed cases.

The percentage of oil recovered from the surface was measured for each control experiment (no dispersant applied). The oil remaining in the containment boom at the end of each experiment was collected and the total volume, water content and density (of parent oil not oil and water mixture) of the collected emulsions were measured. The parent oil density data were used to estimate the amount of oil that evaporated over the duration of each control experiment. Between 80 to 120% of the spilled oil was accounted for in the control experiments indicating that the test protocol achieved a mass balance accuracy of about  $\pm 20\%$ . (For cases where a high percentage or virtually all of the oil dispersed prior to reaching the boom barriers it can be assumed that the mass balance accuracy would be higher than this  $\pm 20\%$ ).

A small, undetermined amount of oil splashed over the north-end containment boom in the first control experiment (test No. 4). No oil loss over the end containment was seen in the first three experiments (tests No. 1, No. 2 and No. 3) as most of the oil dispersed within minutes of the application of dispersant. After test No. 4, a second end barrier was installed approximately ten feet south and parallel to the original barrier to improve the oil containment. Loss of oil outside of the second containment barrier was not observed in any of the subsequent experiments. Between 80 to 120% of the oil discharged in the control experiments was recovered or accounted for through evaporation losses at the end of the test periods. The in- water oil concentration measurements from the fluorometers did not show any significant quantities of oil in the water column for any of the control experiments. There were very low concentrations or amounts of oil dispersed in the control runs as determined by the UVF measurements. What little oil was present had a specific droplet size distribution which suggested approximately how much oil would remain dispersed.

The Ohmsett tank water temperature stayed between -0.4 to -1.8 °C throughout all of the experiments without the need to use artificial chilling. This was due to the unusually cold weather experienced during the test period. The total quantity of oil used in the 2003 test series was approximately 1500 liters. Between 7 and 9 liters of dispersant were used in each test. The total quantity of dispersant used in the 2003 test series was approximately 90 liters. The concentration of dispersant in the Ohmsett tank water at the end of testing was less than 10 ppm. The dispersant added to the Ohmsett tank water during the test program did not affect the results of experiments; dispersant in the water begins to affect DE test results.

### Conclusions

A total of twenty-six full-scale DE experiments (twelve in 2003 and fourteen in 2003) were successfully conducted with various combinations of oil type, weat hering and dispersant-to-oil (DOR) ratios to help answer the question "Would dispersants (Corexit 9500 and Corexit 9527) be effective in dispersing the fresh and slightly weathered Alaskan and Canadian crude oils in very cold water." Results from these experiments demonstrate that both dispersants (Corexit 9500 and Corexit 9527) were effective in dispersing the crude oils tested, in very cold water. The experiments reveal that high levels of effectiveness were achieved in a number of tests, but effectiveness varied with crude oil type and its degree of weathering. For example, slicks of fresh Endicott and Northstar crude oil were dispersible while slicks of weathered Endicott and Northstar crude oil were dispersible while slicks of weathered Endicott and Northstar crude oil type and the could only speculate as to why they did not disperse. We do not have the detailed chemical property data on the oils used in the experiments or the knowledge in the dispersant community at large to use this data to definitively determine why certain oil's do or do not chemically disperse.

The success of a dispersant operation to clean up an oil spill in cold water will depend on the oil type, degree of weathering and the prevailing meteorological and oceanographic conditions. MMS anticipates that results from these experiments will assist U.S. Regional Response Teams to make science based decisions on the potential use of dispersants as a response tool for oil spills in cold water.

The experiments demonstrate that Ohmsett test tank provides a realistic facility and reliable test procedures to measure dispersant effectiveness. MMS will continue to pursue a long-term program to use Ohmsett for chemical dispersant research and effectiveness testing.

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