Comparative Testing of Corexit EC9500A, Finasol OSR52, Accell Clean DWD, and ZI 400 at Ohmsett in a Simulated Arctic Environment

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Abstract

The Bureau of Safety and Environmental Enforcement (BSEE) recently conducted independent dispersant effectiveness testing. Several products were tested under simulated arctic conditions at Ohmsett. The test program was conducted to better understand the effectiveness of various dispersants under the test conditions and compare the products. The results will assist BSEE and its federal partners in their decision making in regards to the various dispersants being considered by the oil spill response organizations (OSROs) for use on the U.S. Outer Continental Shelf.

Four dispersants were selected from the Environmental Protection Agency's (EPA) National Contingency Plan (NCP) Product Schedule and were tested on an Alaskan crude oil. They include Corexit® EC9500A, Finasol® OSR 52, Accell® Clean DWD, and ZI 400. To capture operational effectiveness issues, the dispersants were applied to a surface slick using Ohmsett's spray bar, which simulated a system similar to a boat spraying system.

Data collected included dispersant effectiveness (DE) based on the volume of the surface slick which remained after the test as compared to the volume dispersed into the water column and particle size distribution of the oil droplets dispersed at 1 meter and 2 meters below the water surface. Particle size distribution was captured using two LISST-100x instruments from Sequoia Scientific. The instruments allowed researchers to quantify the performance of each dispersant. Oil concentration, paired with particle size distribution, showed how much oil was dispersed into the water column and the size of the water droplets that were created. For this test program, droplets sizes of 70 microns (μm) or smaller were considered to be fully dispersed because they are assumed to stay suspended in the water column whereas the larger droplets may resurface and coalesce into a new slick.

The performance of the products was quantified and compared to each other based on DE and the droplet size of dispersed oil. Corexit EC9500A performed very well in this study as compared to the other dispersants, producing the highest average DE, the most improvement in dispersion compared to the tests with untreated oil, and the smallest median droplet size. Finasol OSR 52 demonstrated a performance close to that of Corexit, producing the second highest average DE, and a median droplet size only slightly larger than Corexit. The average DE for Accell fell between that of Finasol and ZI 400, as did the median droplet size. ZI 400 performed poorly relative to the other products tested.

In addition to providing performance data of the products in pseudo-field conditions, operational performance was captured as a general discussion about the ease of use, limitations, and concerns about the products in the environment simulated by the test conditions. BSEE intends to use the results of these tests to provide both OSROs and BSEE with information for their decision making processes.

Introduction

There has been over 30 years of previous dispersant effectiveness data collected in arctic conditions through laboratory, wave basin, and field studies. The majority of these studies involved the use of one or more of the Corexit™ family of dispersant formulations. Recently, dispersant formulations, such as Finasol OSR 52 produced by Total Fluides of France, have seen increased domestic interest and are included in the Environmental Protection Agency's (EPA) National Contingency Plan (NCP) Product Schedule of approved technologies for oil spill response and mitigation. Accordingly, a need was identified to conduct comparative studies in dispersant effectiveness in cold water using Corexit EC9500A. Except for Corexit, all of the products were purchased new, either direct from the manufactures or through a distributer. Because of difficulty in purchasing Corexit from Nalco, an existing supply at Ohmsett was used.

In February of 2014, the U.S. Department of Interior's Bureau of Safety and Environmental Enforcement (BSEE) conducted independent dispersant effectiveness testing to compare available formulations. Four dispersants were selected from the EPA's NCP Product Schedule and tested on an Alaskan crude oil under mesoscale simulated arctic conditions at the Ohmsett facility. The study was conducted to better understand and compare the effectiveness of various dispersants under simulated arctic test conditions

Methods

The oil selected for this testing was an arctic crude oil blend of two crude oils, which were readily available at Ohmsett, to create a large enough volume to complete the 15 planned tests. A sample of the test oil was sent to Petroleum Laboratories Inc. for composition analysis (Table 1). Additionally, the viscosity of the oil was 158.8±12 centipoise (cP) @ 20°C and could be calculated from 10°C to -1.5°C using the equation Viscosity (cP) = $855.02e^{-0.113\text{temperature(deg. C)}}$. This was used to determine the viscosity of the oil once applied to the water's surface.

All testing was conducted in the Ohmsett testing facility in Leonardo, NJ. Ohmsett's above ground concrete test tank is one of the largest of its kind, measuring 203 meters long by 20 meters wide by 3.4 meters deep. The tank is filled with 2.6 million gallons of saltwater. The tank's water was not changed between testing. Previous studies have shown that dispersant concentrations maintained below 400 parts per billion (ppb) do not affect the outcome of tests at this site (SL Ross Environmental Research, 2000). To capture operational effectiveness, the dispersants were applied to a surface slick using Ohmsett's spray bar. Data collected included droplet size distribution of the dispersed oil using two LISST-100x instruments from Sequoia Scientific and dispersant effectiveness (DE), which was measured using the volume of the oil which remained on the surface after the test as compared to the total volume dispensed onto the surface for the test.

Parameters	Method	Results
API Gravity @ 15.56°C	ASTM D287	22.7°
Flash Point, Closed Cup	ASTM D93	30°C (86°F)
Paraffin – wt%	---	2.77
Pour Point	ASTM D97	10°C (50°F)
Sulfur – wt%	ASTM D4294	1.66
Saturates – wt%	ASTM D2007	25.94
Aromatics – wt%	ASTM D2007	52.58
Asphaltenes – wt%	ASTM D2007	1.16
Resins – wt%	ASTM D2007	20.31

Table 1 - Test Oil Properties

For the purposes of this program, the test procedure was adapted from the Ohmsett dispersant effectiveness test protocol developed between 2000 and 2003 by MAR Inc. and SL Ross and documented in "Dispersant Effectiveness Testing on Alaskan Oils in Cold Water" (SL Ross Environmental Research & MAR Incorporated, 2003). An established test area was cleared of surface oil prior to beginning each test and the waves were generated so that every fourth to sixth wave was a breaking wave. Once dispersants were applied, tests would continue for 20 minutes to allow for mixing and dispersion to take place. Once a test ended, the remaining surface oil was collected and the tank was allowed to settle for three hours before preparing for the next test.

One of the main limitations of Ohmsett is that it is an outdoor facility exposed to the elements. In this particular sequence of tests, air temperature varied from -4.9°C to 8.7°C, with an average of 1.2°C over the course of the study, falling within temperatures that are typically observed in the Arctic from June through September (National Research Council, 2014). The tank's water temperature ranged from -1.2°C to 1.3°C and water surface temperature for each test ranged from -3.3°C to 0.0°C. The tank's water salinity ranged from 26.7 parts per thousand (ppt) to 28.4ppt.

Each dispersant was tested on the oil in three separate replicates, and three controls of untreated oil were distributed throughout the test schedule. The replications were intended to avoid confounding effects of weather changes, human error, operational variations, and property changes of the tank water. These items were controlled for in the analysis if significant. Control runs were used for calculating the volume of oil lost to natural dispersion and the operation of the test itself. The same instrumentation used during the control runs was also used for the dispersant runs to establish a baseline oil concentration and droplet size distribution at the instrument depths.

For this test program, dispersant effectiveness (DE) was described as the percentage of oil which no longer remained on the surface as compared to the original volume of oil spilled once the volume of oil spilled and the emulsion collected were adjusted for water content. The dispersant to oil ratio (DOR) was also calculated for each test as the volume of dispersant applied to volume of oil dispersed. DOR was not a variable for this test program and a DOR of 1:20 was the goal. This DOR is a generally rule of thumb used for dispersant operations. The true DOR for each test was calculated by using the known dose of the system (liters of dispersant per square meter) and the surface area of the slick (estimated based on physical measurement of the slick). This gave a percentage of sprayed dispersant which was applied to the slick. DOR was then calculated using the volume of dispersant applied to the oil and the volume of oil distributed for each test.

For the purposes of this test, 70µm was used as a cutoff point for considering droplets to be dispersed. This is based on measurements of dispersed oil droplets measured at sea by Tim Lunel and presented at the Arctic and Marine Oil Spill Program (AMOP) in 1993. In his findings, Lunel reports that 99% of the oil droplets contained within a good dispersion are <70µm (Lunel, 1993). Additionally, this benchmark has been used rather consistently for numerous BSEE sponsored studies performed by SL Ross Environmental Research Ltd (SL Ross Environmental Research & MAR Incorporated, 2007) (SL Ross Environmental Research & MAR Incorporated, 2009) (SL Ross Environmental Research & MAR Incorporated, 2010) (SL Ross Environmental Research & MAR Incorporated, 2011).

Results

Dispersant performance was captured by calculating the Dispersant Effectiveness (DE) and by volumetric droplet size distribution and median droplet size which are given by the LISST devices. Table 2 shows a summary of the DOR and DE for each product. As shown in Table 2, Corexit dispersed the highest percentage (DE=72.7%) of the oil based on the average of three tests. As compared to the untreated control (DE=49.8%), the oil treated with Corexit demonstrated a 46% improvement for dispersing the surface slick into the water column. Based on DE calculations, Finasol performed almost identically to Corexit with a DE=72.2% and a 45% improvement over the untreated oil with a mean DOR slightly lower than Corexit (1:20 for Corexit, 1:33 for Finasol). The average DE for Accell is 62.6%, a 25.7% improvement over the untreated control. The mean DOR for the Accell tests was the same as the Finasol (1:33). ZI 400 performed poorly, and was observed to reduce dispersion compared to the untreated oil (-8% improvement and a DE=45.7% with a mean DOR of 1:25) in this study. A summary is provided in Table 3.

	Dispersant to Oil Ratio			Dispersant Effectiveness		
	Lowest	Mean	Highest	Lowest	Mean	Highest
Corexit	1:50	1:20	1:11	66.0	72.7	76.4
Finasol	1:33	1:33	1:33	68.1	72.2	78.9
Accell	1:50	1:33	1:25	28.7	51.3	64.3
ZI400	1:33	1:25	1:20	36.3	45.7	51.6
Control	-	-	-	43.0	49.8	59.7

Table 2 - DOR and DE summary for each product

	DE	% Improvement Over Control	Performance Compared to Corexit ($DE_{product}/DE_{Corexit}$)
Corexit	72.7	46%	---
Finasol	72.2	45%	99%
Accell	62.6	26%	86%
ZI 400	45.7	-8%	63%
Control	49.8	---	---

Table 3 - Summary of DE performance. Table 3 provides a summary of the products tested and their performance as compared to the control runs and Corexit.

Droplet size distribution data was collected during each test. This data allowed for the calculation of median droplets sizes as well as the determination of what percentage of measured droplets fell below ≤ 70µm. Figure 1 illustrates the cumulative curves for the droplet size distributions for each product tested and the control based on the mean values for the three tests. The LISST captures a data range from 2.5-500µm and is presented on a logarithmic scale.

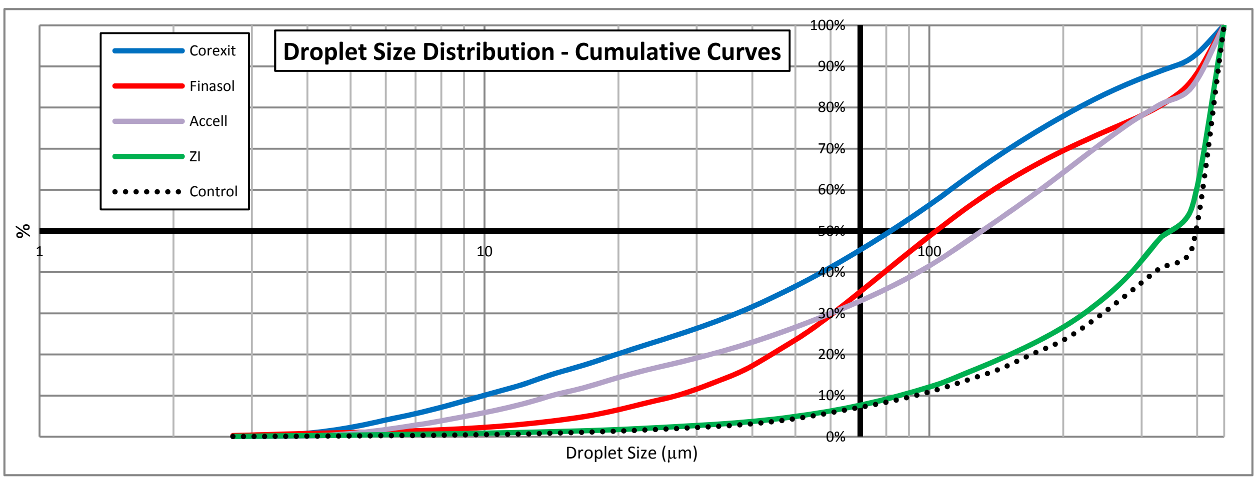

Figure 1- Droplet size distribution - Cumulative curves based on product mean

Corexit EC9500A had a higher distribution of small droplet sizes (<70µm) over the other products (Figure 2). Corexit produced a significantly higher percentage of droplets below 70µm than the control, and ZI400. The Finasol OSR 52, which had an effectiveness almost identical to that of Corexit, also had a greater portion of the dispersed droplets within the 50-100µm range. Finasol produced a significantly higher percent of droplets below 70 um than the control, and ZI400. Accell Clean DWD was not as effective as Corexit or Finasol, but the droplet size distribution reveals that the oil that was dispersed consisted of a larger percentage of very small droplets (10-50µm) over the dispersed oil from Finasol. Accell produced significantly higher percentage of droplets below 70 um than ZI400, and the control. However, both Accell and Finasol had roughly 30% of all measured droplets below 60µm with Finasol having only slightly more at the 70µm cutoff. ZI 400, which demonstrated no improvement over natural dispersion as measured by DE, also did not improve the droplet size distribution of the dispersed oil.

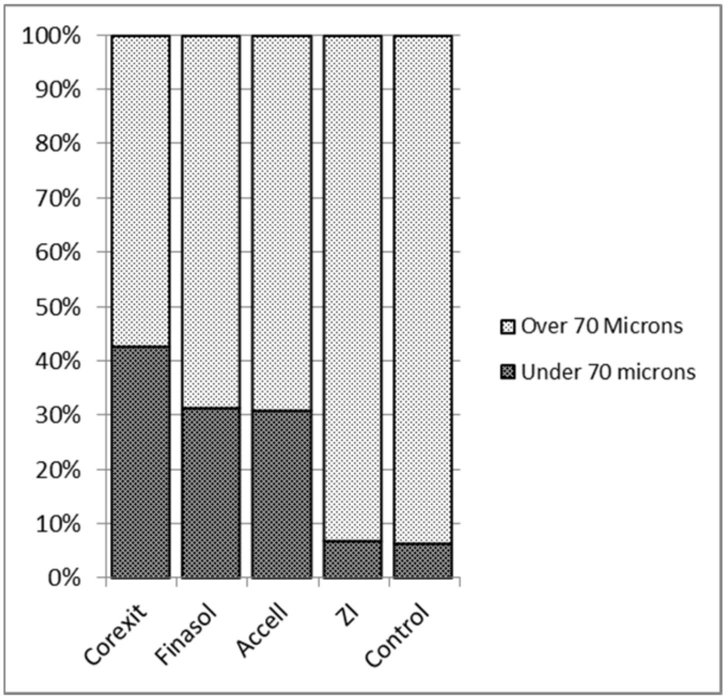

Figure 2 - Figure 2 reflects the information as Figure 1, but simplifies the distribution into two particle size ranges, 2.5-70µm and 70-500µm.

From the droplet size distributions, the median droplet size of the plume (based of the range of droplet measured by the LISST) can be calculated. The average median droplet size for the control tests is 457.26µm. ZI 400 was only marginally better with a median droplet size of 382.98µm. Corexit and Finasol showed significant reduction in median droplet size with 83.85µm and 95.28µm, respectively. Accell did not demonstrate as large of a reduction, but still reduced the median droplet size to 138.37µm.

	Median Droplet Size (µm)
Corexit	83.85
Finasol	95.28
Accell	138.37
ZI 400	382.98
Control	457.26

Table 4 - Median Droplet Sizes

General Observations about Each Product

Corexit served as the benchmark for this test program. It is considered to be the most heavily used and tested dispersant available. While circulating through the Ohmsett pumping system, it produced no foam and had no issue freezing in the system. Visually, the resulting oil droplets dispersed deep into the tank and the deepest instrument recorded a fair amount of data. The amount of oil that resurfaced after the waves were stopped was minimal compared to the other products.

Finasol is slightly more viscous than the Corexit and required about 5% more pressure to spray through the same nozzles, otherwise this product behaved similar to Corexit. There was very good dispersion and little resurfacing oil.

Accell produced a small amount of surface foaming in the reservoir, but this quickly dissipated and did not affect the product. Based on visual observation the product produced a good dispersion, but the instrument readings indicated that the droplets appeared to remain closer to the water's surface than the plumes created by Corexit or Finasol. During collection of the surface oil there was a large amount of café-latte colored froth floating on the water surface as shown in Figure 3. This froth continued to resurface throughout the test program and seemed to increase after each test conducted with Accell. A sample of the froth showed that it contained very little oil by volume. This was not further investigated so it cannot be definitively associated with Accell; however it is recommended that any future work with this product at Ohmsett is observed mindfully for surface froth after dispersion in an effort to determine if the product causes it or if it was a combination of other impinging factors present during the test series.

Figure 3 - An example of the foam that appeared after the introduction of Accell to the Ohmsett tank.

ZI 400 created a large amount of foam on the surface of the liquid in the reservoir. This foam was very stable and continued to grow without intervention. This foam did not affect the liquid product in the reservoir or the performance of the product. Figure 4 shows the difference in behavior of ZI 400 and Finasol while recirculating in the reservoir and pumping system. The dispersion created by ZI 400 appeared to be much more superficial. The oil would break up and spread along the surface but did not appear to disperse deep into to the water. Also, the lower LISST recorded a significant reduction in concentration data indicating the oil droplets did not mix into the water column to the level of that LISST. There was also much more oil resurfacing after the test was completed as compared to the other products. Additionally, although tests were conducted above the manufacturer's stated freezing point of the product, the product in the nozzles became frozen. Twice, this resulted in the nozzles being clogged and the system having to be thawed to remove the product.

Figure 4 - Comparison of ZI 400 and Finasol while recirculating through the pump and reservoir

Conclusions

The goal of this test program was to conduct comparative dispersant effectiveness testing at the Ohmsett facility in an effort to capture both qualitative and quantitative data for multiple commercially available dispersant products. Based on the metrics captured, the following conclusions can be made:

Corexit EC9500A demonstrated the best performance of the group of dispersants. It was among the easiest to work with (along with Finasol OSR 52) and produced relatively consistent data. It also produced the highest average DE and best improvement over the control (72.7%DE, 46% improvement) as well as the largest distribution of droplets under 70µm and the smallest median droplet size (45%, 83.85µm). Corexit did not entrain any air while being pumped and maintained its consistency throughout the tests. Although a direct comparison has not been made to its performance on the same oil in warm weather conditions, Corexit did not seem to be negatively affected by the range of temperatures experienced during this testing series.

Finasol OSR 52 demonstrated a performance close to that of Corexit. It was easy to work with, but between the three tests with this product, it produced data with higher variability than Corexit. Calculated DE results for the three Finasol tests were 78.9%, 68.1% and 69.8% with 78.9% being the highest DE of any product. Finasol had the second highest average DE and second largest improvement over the control (72.2%DE, 45% improvement). The LISST data showed that Finasol produced the second largest distribution of droplets under 70µm (35%) and median droplet size slightly larger than Corexit (95.28µm). Like Corexit, Finasol did not entrain any air while being pumped and maintained its consistency throughout the tests. Similar to Corexit, Finasol did not seem to be negatively affected by the cold environment.

Accell Clean DWD performed well based on the LISST data, but less successfully based on the average effectiveness. The average DE for Accell was 62.6%, a 26% improvement over the untreated control. The droplet size distribution data for Accell remained relatively consistent between all three test runs. Based on the average of this data, the median droplet size of the dispersed oil was 138.37µm and 32% of all droplets were under 70µm. With the parameters used for these tests, Accell demonstrated a good ability to aid in the formation of droplets smaller than 70µm, but did not disperse a large volume of the oil slick. A higher DOR would most likely result in a higher DE (a DOR of 1:10 is recommended by the manufacturer for Accell as compared to 1:20 or less for other products). In general, Accell Clean DWD was easy to work with, but while being pumped through the system, the liquid in the reservoir would generate a thin foamy head that would quickly dissipate. The product below the foam appeared to be unaffected in any way. And, like Corexit and Finasol, Accell did not seem to be negatively affected by the cold environment.

ZI 400 performed poorly relative to the other products and the untreated control tests. The average calculated DE for ZI 400 was 45.7%, which represents a deterioration of 8% from the average DE for the control runs. The data for ZI 400 remained relatively consistent and fell within the same range of variability as the control runs. The droplet size distribution was a very close match to the control data. The median droplet size for the dispersion was 382.98µm, with only 8% of all droplets being below 70µm. The control runs had a median droplet size of 457.26µm with about 7% below 70µm. Visually, the dispersion caused by ZI 400 appeared to be very shallow. Although the oil slick would disperse, it would remain along the surface with most of the oil resurfacing very quickly. ZI 400 also was the most difficult to work with. Twice, the hoses for the pumping system had to be either flushed with warm water or brought inside to thaw. Also, while circulating the product through the pump the product would create a large foamy head, which would continue to grow, making it difficult to obtain accurate measurements. Overall ZI 400 was observed to be negatively impacted by the cold weather environment.

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