Assessing the Dispersibility of Heavy and Viscous Oils

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Introduction

This paper reviews research addressing dispersion of heavy and viscous oils and documents the complexity involved in understanding and explaining results from tests conducted in laboratory systems, wave basins, and field trials. Thirty years of research by governments, industry, and independent organizations into dispersant effectiveness has resulted in the development of improved dispersants that possess lower toxicity and increased effectiveness across a broader range of oil types. In recent years, dispersant formulations have been enhanced to be effective in dispersing weathered crude oils and heavy fuel oils that are highly viscous as well as viscous emulsified oils which were previously believed to be un-dispersible. Oils with viscosities ranging from 2000 to 8000 cP have been effectively dispersed in simple laboratory and wave basin tests, and some field trials have shown that oils with viscosities greater than 12,000 cP may be dispersible as well (Lewis et al 1998; Lessard and DeMarco 2000; Trudel et al 2005; Clark et al 2005)

Although a wide range of research has been carried out in this area, it has not been conclusive in providing a simple answer regarding a viscosity limit for successful dispersion. For example, some heavy oils have been shown to be readily dispersible while others with similar characteristics have not. It is clear that it is not simply the viscosity of the oil that determines its dispersibility, but an array of factors that include mixing energy, sea temperature, oil weathering and chemical composition, dispersant formulation, the method of dispersant application and its dosage. Many of these factors are accommodated differently in various standard and experimental performance evaluation procedures. These may lead to reported test results that have been influenced in ways that may not be clear. In any event, the differences between test procedures and among oil samples may make it difficult to isolate the distinct role that viscosity has in determining an oil’s dispersibility.

Because cooler temperatures increase the viscosity of oils, there is a high level of interest in the effectiveness of dispersants in very cold environments (Belore et al 2009). Also, there is increased interest in the dispersion of heavy oils due to several heavy fuel oil spills which resulted in environmental impacts to sensitive coastal environments. For example, consider the environmental issues and spill clean up activities associated with the *Erika* spill in 2000, the *Prestige* spill in 2002 and the Cosco Busan spill in 2007. Concerns over potential large fuel spills from shipping vessels supplied with huge volumes of heavy fuel oils has increased awareness of the need to understand the utility of dispersing heavy fuel oils.

Dispersing heavy crude oils or fuel oils offshore to avoid a coastal impact could reduce the potential for short-term, direct and longer-term, indirect impacts associated with shoreline stranding, as well as offering a less intrusive, more efficient and lower overall cost response and clean-up method (IPIECA 2000; 2001). However, this would be a preferred option only if it generates a net environmental benefit, e.g., trading off longer-term shoreline impacts for shorter-term ecological impacts at sea (IPIECA 2000). Recovery rates for populations of bird species and higher mammals are very much slower than water column organisms; it can take years for affected wildlife populations to return to pre-spill levels. In general, offshore, water column impacts are much shorter lived due to rapid dilution of the dispersed oil, ability of fish communities to move out of the affected areas and the high fecundity of offshore communities (NRC 1989; IPIECA 2000; IPIECA 2001).

Challenge of dispersing heavy crudes and emulsions

A number of research programs have been carried out on heavy crudes and heavy fuel oils (often named HFOs) to evaluate whether they would be amenable to dispersion. While it was previously believed that emulsions formed from heavy oils cannot be dispersed, newer dispersant formulations may be able to break the emulsion and then facilitate dispersion (Lewis et al 1998; Fiocco et al 1999). The process is illustrated in Figure 1, taken from the North Sea Field Trials using crude and heavy oils weathered at sea (Lewis et al 1998; Lessard and DeMarco 2000). This can be a slow process and may require multiple dispersant applications–initially with a very low dosage to break the emulsion then at a higher dosage to induce the actual dispersion. Alternatively, a demulsifier can be applied followed by a dispersant, although compatibility between the two substances must be ensured (Guyomarch and Merlin 1999). Most crude oils purchased for transit to a refinery undergo chemical profiling prior to loading to document the petroleum composition of the oil. If the type of crude and its specific chemical characteristics are known early on in a spill, better predictions of dispersibility may be deduced.

HFOs present a more difficult problem when assessing dispersibility. Recent research has been at times very encouraging (Lewis et al 1998; Trudel et al 2005), and at other times using many of the same variables and apparently the same grade of HFO, the results have been very different (Fiocco et al 1999; Canevari et al 2001). It is possible that this is a result of the chemical composition of the individual HFOs tested. These products generally are the remnants of the refining process after removal of the more economically valuable lighter molecules and are categorized and sold by their viscosity properties alone. For example, an IFO 380's predominant characteristic is that the viscosity be no more than 380 cSt at 50°C. Refineries use a variety of different crude oils and product lines as feedstock; thus, the chemical composition of a specific

Figure 1. Alaska North Slope Crude Oil Emulsion Dispersing After Dispersant Application in the 1997 North Sea Trials.

grade of HFO will vary significantly from batch to batch and from refinery to refinery. Thus, it cannot be said that all IFO 380s are, or are not, dispersible. Viscosity can, in fact, be a misleading parameter on which to solely base any dispersion decision.

Research on dispersing heavy and viscous oils in North America has been carried out on a very wide range of crude oils including Alaska North Slope (ANS), California Outer Continental Shelf (OCS) and Hibernia Crude oil. European and North American researchers have also evaluated heavy fuel oils including IFO 180, IFO 380 and Bunker C to assess amenability to dispersants. The results and success rates vary greatly due to a wide variety of testing protocols, oil composition, dispersant application ratio and dispersant composition, to name but a few (NRC 1989; Clayton et al 1993; Canevari et al 2001; Trudel et al 2005; Clark et al 2005).

One of the important differences between laboratory tests for dispersant efficacy is the level of energy employed to induce dispersion (Clayton et al 1993; Clark et al 2005). Dispersants are formulated to reduce the interfacial tension between oil and water since it is the resistance to mingling oil and water that has to be overcome in order to disperse the oil. Heavy and viscous oils rank among products with the greatest interfacial tension, making them the most difficult for oil spill scenarios. As dispersants reduce the interfacial tension, the amount of mixing energy needed to disperse the oil droplets into the water column is reduced. Therefore, various dispersant test methods, most of which differ quite significantly in mixing energy, will give differing results as to the dispersibility of a specific test oil and results compared across different sources can become quite confusing.

Viscosity, density and dispersibility.

In many cases, oil spill responders use a crude oil's density (commonly reported as API gravity), rather than its specific measure of viscosity, as an indication of whether it will be dispersible or not, assuming a general link between crude oil dispersibility and the oil's density. Considering the full range of crudes from heavier oils (API gravity <12) to lighter oils (API gravity >32), a basic generality has been demonstrated showing that light crudes are much more dispersible than heavy crudes. However, the use of density can be very misleading when focusing only on groups of heavy crudes and fuel oils with a more limited range in density, as can be seen from Figure 2. This shows test results compiled from 16 different dispersant studies in Norway, the US, Canada, and the UK. Further, these tests were conducted using use a variety of laboratory and wave basin test methods, each with its own unique test protocol and level of mixing energy. This plot shows a wide range of results in dispersibility of crude oil and fuel oils in the heavy end of the spectrum, without obvious positive correlation among either crude or fuel oils.

From following broad reports in the dispersant literature, it would be expected that oils with greater density (lower API gravity) would show lower dispersant effectiveness. This, however, is not the case for all data. In ExxonMobil tests using the EXDET apparatus, some oils with API gravity of just over 10 have shown dispersant effectiveness of over 90%. Other points in Figure 2 show lighter oils with API gravity around 16 having a dispersant effectiveness of less than 10%. Out of the 345 tests plotted on the graph, over a third of the heavy oils tested had dispersant effectiveness percentages of over 60%, irrespective of the API gravity. This illustrates the poor suitability of using API gravity (i.e., oil density) as a basis to assess a heavy oil's amenability to dispersion. Indeed, specific test variables or environmental factors need to be taken into consideration when attempting to predict dispersant effectiveness for heavy oils.

A better link between oil viscosity and dispersibility is illustrated in Figure 3. As expected, more viscous oils are generally less dispersible than lighter oils. The information illustrated in Figure 3 also benefits from being obtained from a single set of research data. Since the data came from the same testing protocol (EXDET) under the same conditions, as opposed to the multiple data sets represented in Figure 2, the results are more internally consistent and amenable to direct comparison.

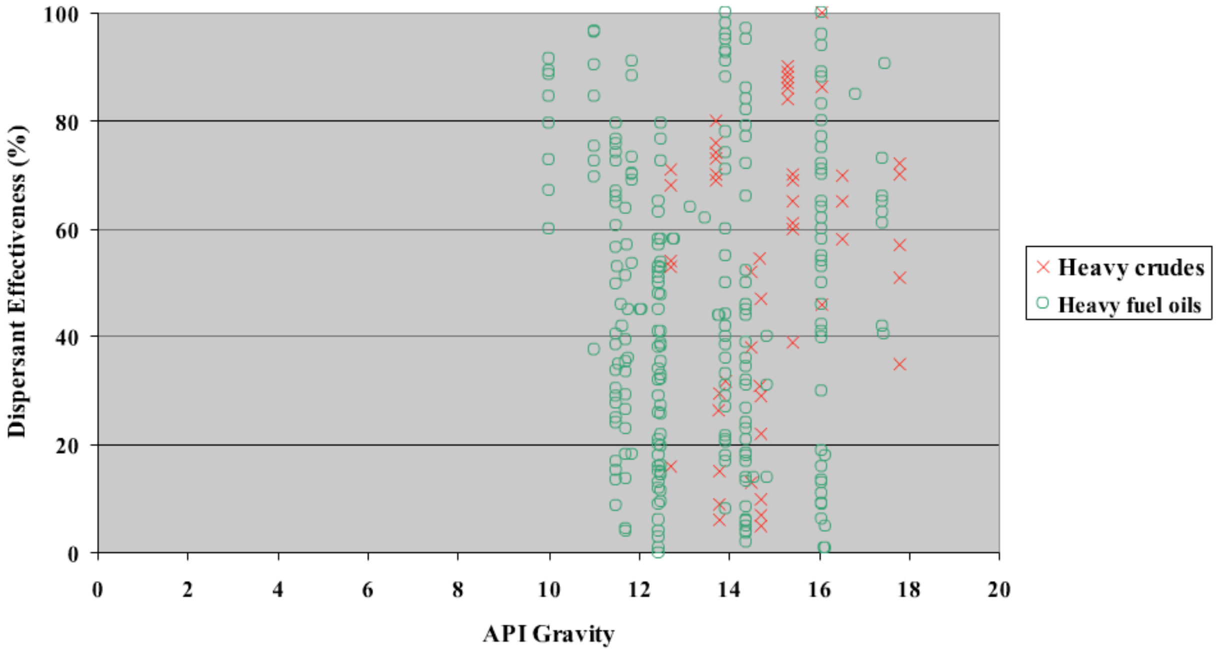

Figure 2. Plot of Data Taken from Multiple Sources Comparing Percent Dispersant Effectiveness for Heavy Crude Oils and Heavy Fuel Oils of Various API Gravities Using Different Test Methods.

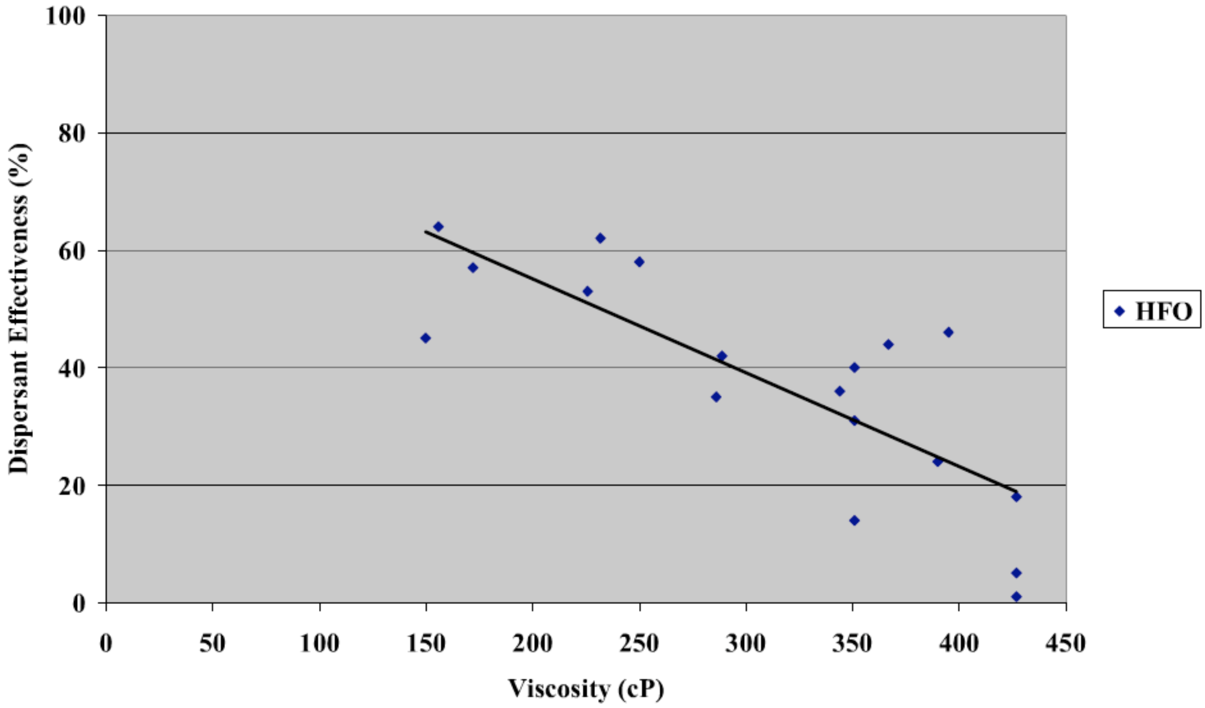

Figure 3 Plot Comparing Percentage Dispersant Effectiveness for Heavy Fuel Oils of Various Viscosities Measured at 50°C Using the EXDET test (from Fiocco et al 1999)

Figure 4 again shows a correlation between dispersant effectiveness and oil viscosity. As in Figure 3, this relationship is clearer when data from tests using a consistent experimental method are included. In this instance the research was carried out in a large outdoor test tank, the US Minerals Management Service OHMSETT test facility in Leonardo, New Jersey (SL Ross and Mar 2006). This wave tank allows the use of more realistic wave conditions, ambient air and water temperature, wind effects, dilution extent, etc. This shows that dispersants can be effective on heavy oils in wave basin conditions.

Building on data from Figure 4, additional tests were conducted at OHMSETT with crude oils selected to fill data gaps in a defined viscosity range, producing an insightful trend for setting expectations for viscosity limits for dispersing heavy crude oils. Figure 5 is a plot of results for a range of crude oil viscosities successfully dispersed and results for viscous crudes with very low dispersion effectiveness under the experimental wave conditions at OHMSETT.

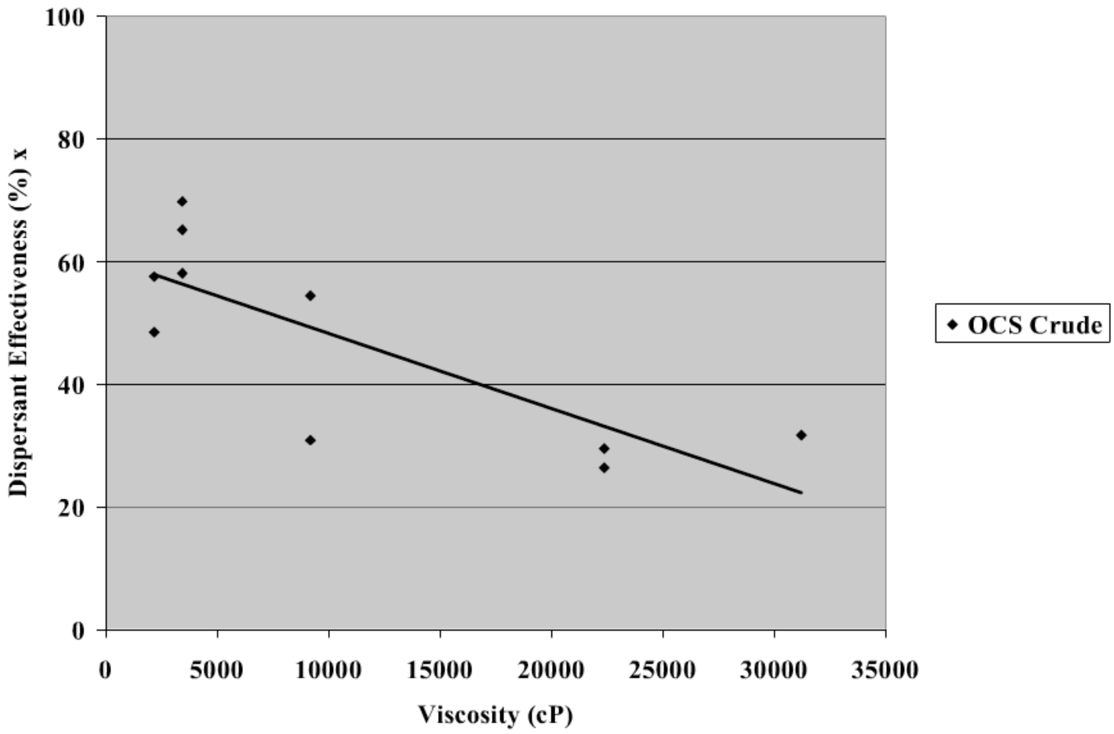

Figure 4. Plot Comparing Percentage Dispersant Effectiveness for Outer Continental Shelf (OCS) Crude of Various Viscosities Measured at 15°C (from SL Ross and MAR, 2006)

Results from Field Trials with Viscous Oils

To test the effects of weathering under real world conditions and assess potential viscosity limits for oil dispersibility, a number of field trials were conducted in the UK in 1997 (Lewis et al 1998). Four large slicks of oil were laid down in the North Sea: two of Forties blend crude (50 tonnes each), one of Alaska North

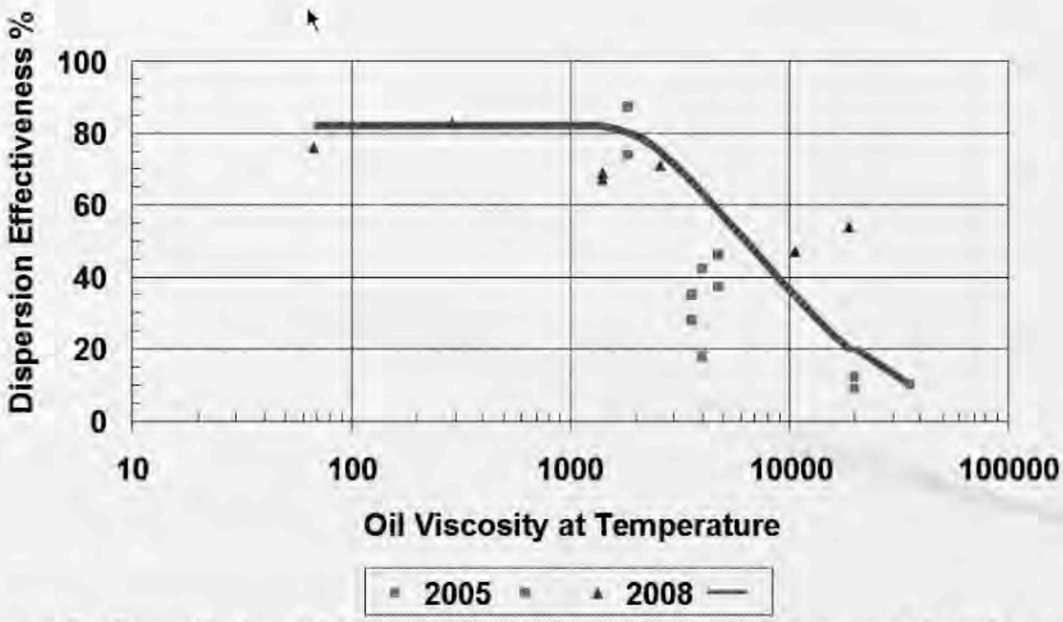

Figure 5. Compilation of viscosity and dispersant effectiveness data from tests conducted in 2005 and 2008 for a broader range of heavy crude oils at the OHMSETT wave tank (data from SL Ross and MAR 2006, 2008).

Slope (ANS) crude (30 tonnes) and one of IFO 180 (20 tonnes). The crude oils were left to weather and emulsify under ambient conditions for two days and then sprayed with dispersant from an aircraft. As it weathered, the Forties crude exhibited only minor changes in viscosity and stayed readily dispersible using two different dispersant products. The ANS weathered at sea for 55 hours, attaining viscosities ranging from 15,000 to 20,000 cP (measured at 15°C and 10 sec^{-1}). Upon application of Corexit 9500 dispersant, the surface emulsion broke immediately (Figure 1). Following subsequent application of Corexit 9500, monitoring equipment indicated elevated dispersed oil concentrations over a large volume of the subsurface sea (Lewis et al 1998; Lessard and DeMarco 2000). This demonstrated that, for weathered and emulsified crude oils, dispersants can be a feasible response option even after a 55 hour delay for an emulsifiable crude oil when dispersants designed for heavy oil treatments are used (Lessard and DeMarco 2000).

Corexit 9500 was then applied on IFO-180 that had weathered for 4.5 hours at sea. The viscosity of the IFO-180 was approximately 6,000 to 8,000 cP. The average dispersant-to-oil ratio (DOR) was 1:44, less than the intended 1:20 dosage rate. Only partial dispersion of the emulsified IFO-180 was achieved at the low DOR, probably due to under-dosing. Logistical problems delayed timely additional dispersant application and the IFO-180 remaining on the sea surface continued to emulsify and increase in viscosity. Corexit 9500 was applied again at approximately 23 hours. Some dispersion of the IFO-180 occurred, but subsurface concentrations of oil remained low. It was concluded that emulsion with a viscosity less than approximately 20,000 to 30,000 cP had been dispersed, but not emulsion with the higher viscosities (Lewis et al 1998; Lessard and DeMarco 2000).

The field trials showed that dispersants can in some instances be effective on highly viscous crude oil and IFO-180 emulsions. Prior to these North Sea trials, IFO-180 had been considered not dispersible. The trials also showed that the time window for Corexit 9500 can extend for two or more days following a crude oil spill. Lessard and DeMarco (2000) also report successful dispersant use during response to actual spills of heavy fuels at sea. Research and field data show that the conservative viscosity limit predictions of around 10,000 cSt or approximately 10,500 cP (ITOPF, 2005) deserve reconsideration, and broader inputs such as sea state and type of dispersant available should be factored in to deciding if a dispersant response should be considered. These data do reinforce the need to be cautious in making dispersant use decisions, as weathering and emulsification do have a major influence in reducing dispersant effectiveness and need to be considered as part of the overall decision-making making process.

Conclusions Regarding Heavy Oil Dispersion

The wide range of research that has been carried out so far in this area is fairly inconclusive with respect to a simple answer regarding a viscosity limit for successful dispersion. Some heavy oils have been shown to readily disperse where others with similar gravity or compositional characteristics have not. It is not simply the viscosity of the oil that determines dispersibility but an array of factors including mixing energy, sea temperature, weathering, chemical composition, dispersant formulation, and dispersant dosage. Further, a new dispersant formulation in development shows even more promise in working on heavy and viscous oils, delivering active ingredients in concentrated form to heavy oil slicks (Nedwed et al 2008).

Studies attempting to relate the mixing energy of laboratory test system and wave basins to mixing energy found in open waters are only beginning to show how we might best use data from controlled experiments to assess the potential for dispersant effectiveness in the field. Current understanding of the effects of wave energy is best captured in text from a report by SL Ross and Mar (2005):

> "While the at-sea tests suggest that an oil with a viscosity of 7000 cP may limit the dispersibility under some conditions, both at-sea and OHMSETT tests suggest that this limitation may be overcome by increasing the mixing energy. Indeed the OHMSETT results suggest that in the 33.3 cpm waves the limiting viscosity may lie between 7,100 and 19,000 cP. Operationally, this means that despite the evidence for oil viscosity limiting dispersion of IFO 380 at sea in winds of 7 to 10 knots, oils of 7000 cP or greater may indeed be dispersible if the level of mixing energy is high enough."

Because cooler temperatures increase the viscosity of oils, there is a high level of interest in whether oils can be dispersed in very cold and arctic environments.

Based on available test data, dispersants can be effective in even the coldest waters (even below 0°C) depending on the oil viscosity at these temperatures (Belore et al 2009). Dispersants should not be ruled out based on low temperature considerations alone.

The overall conclusion that is reached after reviewing previous and ongoing research is that many heavy and viscous oils may be amenable to dispersion under a certain suite of conditions. As a result, in the event of a heavy oil spill under the appropriate set of conditions, and with the consent of statutory bodies, it would be prudent to carry out a test application of dispersants immediately to show whether they might be effective. A positive test result could help preclude premature decisions being made that would exclude dispersants from consideration based solely on laboratory or field studies that may not have accurately reflected the real world situation. Additionally, the cost of such a real world performance test would be trivial if dispersants were shown to be effective when compared to the potentially enormous cost of shoreline cleanup and remediation in the event that they are not applied.

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