Dispersant Efficacy and Effectiveness

Thomas Coolbaugh, Ph.D.
ExxonMobil
Amy McElroy, LT
U.S. Coast Guard

Introduction

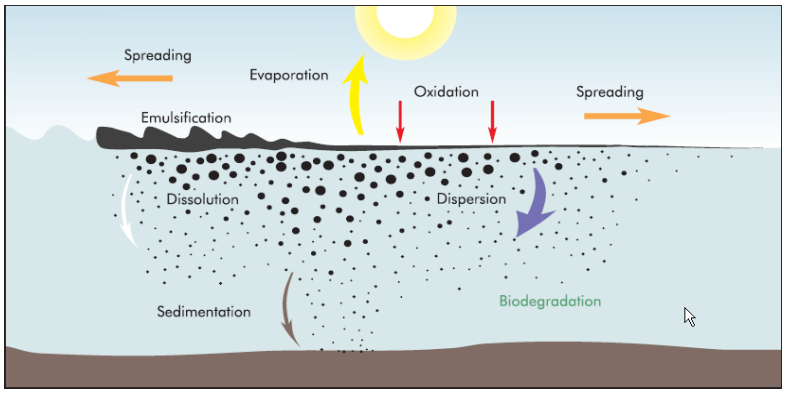
Dispersants have been researched extensively and used for oil spill mitigation for more than 40 years, yet there are opportunities to enhance our understanding, including with respect to their long term fate and effects and how to optimize dispersant use. For example, the 2005 National Academy of Sciences report, *Understanding Oil Spill Dispersants: Efficacy and Effects*, suggested a number of areas where increased understanding would help support the use of dispersants. Throughout the summer of 2010 dispersants were used in unprecedented quantities and, in the case of sub-sea application, with novel application methods following the Deepwater Horizon incident. The focus of this paper is to provide a brief overview of spilled oil behavior, chemical dispersants efficacy and effectiveness, and a discussion of the state of knowledge pre-, during, and post- Deepwater Horizon.

Oil Behavior

After oil is spilled, it typically undergoes eight main fate and weathering processes (Figure 1), which may all occur simultaneously in different degrees:[1]

1. Spreading and advection
2. Evaporation
3. Dissolution
4. Dispersion
5. Emulsification
6. Photo-oxidation
7. Sedimentation and shoreline stranding
8. Biodegradation

Figure 1 – Processes Acting on Spilled Oil (ITOPF)[2]



Dispersant Overview

Natural dispersion of oil into water can be enhanced through the application of dispersants, either at the water surface by aerial or vessel spray application or by using subsea injection at the source of a subsea spill. The primary objectives of dispersant use are to reduce environmental impacts associated with surface slicks (e.g., impacts to marine mammals, seabirds, marshes, etc.), enhance removal of oil from the environment through biodegradation, and rapidly reduce toxicity through dilution.

The overall effectiveness of oil dispersion has three components:[3]

1. Operational effectiveness, which describes how well dispersant is applied and incorporated into the released oil
2. Chemical effectiveness, which describes the fraction of treated oil that is entrained as small droplets in the water column
3. Hydrodynamic effectiveness, which describes the transport of the chemically dispersed oil plume and its dilution by turbulent diffusion through horizontal and vertical mixing processes

One of the primary benefits of using dispersants is that they are not nearly as limited by natural conditions/processes as mechanical recovery and *in situ* burning. While booms begin to lose effectiveness in wave heights greater than 1 m (3 feet), dispersants are in fact more effective as mixing energy (e.g., wave energy) increases. The upper wave-height limit for dispersant application is typically defined by personnel safety concerns caused by high winds and rough seas. However, for low-viscosity oils that have not weathered and emulsified, natural dispersion (i.e., dispersion without using dispersants) will quickly remove oil from the surface when waves exceed 3 m (10 feet)[4].

Further, dispersants can be applied from airplanes and helicopters in addition to vessel application, allowing for rapid deployment over long distances and rapid treatment of large areas. Both mechanical recovery and *in situ* burning are limited to boat-based operations, which means relatively slow transit times and even slower operational speeds because of their reliance on boom-based systems, which leads to lower encounter rates with the oil. In the case of vessel-mounted dispersant spray systems both large and small vessels may be used, offering a level of flexibility with respect range of operation (see Figure 2, for example). When one considers that, from a risk perspective, small and medium spills happen more frequently, the use of vessels may offer an effective dispersant response. For example, in Norway, contingency plans that include the use of dispersants are based on the analysis of various scenarios, including those from spills of less than 100 m^3 (625 bbl, 26,250 gal).

Figure 2 - Example of Large Scale Vessel-Mounted Dispersant Spray System

Photo courtesy of Sintef

As a result, the use of dispersants during an oil spill, both surface and, more recently, subsurface, is a critical element in reducing the size and duration of surface slicks and in preventing significant oiling of sensitive shoreline habitats. During the Deepwater Horizon incident, subsurface dispersants were also used to keep oil from surfacing near the well site. This eliminated potential health and safety risks to well-control personnel from volatile hydrocarbon vapors.

While dispersant use has many advantages, it has raised concerns in the media for example, long-term effects on human health, seafood, wildlife, and ecosystems. Key advantages of dispersants are summarized as follows:

- Dispersants can be used over a wider range of environmental / meteorological / oceanographic conditions than other response options. They can be applied in rough seas (up to 3 m) and on thinner oil slicks (<<1 mm). Furthermore, subsea injection of dispersants may have even fewer restrictions since it can proceed 24 hours per day and is less susceptible to weather conditions at the surface. Modern sensing technologies (e.g., aircraft fitted with real time down link transfer of forward looking infra-red video (FLIR- video) offer the possibility of night time operation of spray vessels as well.[5]

- Dispersants can treat much more oil over time than other response options. They can be applied at high speeds by aircraft. In addition, aircraft allow for rapid transit to a spill location and relocation to slicks separated by significant distances. Modern vessel-based application could potentially be a primary strategy, especially in those areas supply/response vessels are fitted with spray systems, large capacity storage, and state of the art high and low dosage spray systems for added response flexibility, especially as windrows and other less homogeneous slicks form. In addition to these well established methods of dispersant use, , the use of subsea dispersant injection can continuously treat all oil at the source before it spreads over a large area at the surface.

- Dispersants reverse, stop, or eliminate water-in-oil emulsion formation particularly when applied to low-viscosity oils. Emulsions can become very stable and a challenge to treat with any response option. If emulsions form, the potential for oils to reach shorelines increases.

- Dispersants accelerate the biodegradation of oil by decreasing droplet size and thereby increasing the amount of oil surface area available to bacteria. In addition, rapid dilution of dispersed oil ensures that biological activity does not exhaust available nitrogen, phosphorous, and oxygen needed for biodegradation.

- Subsea injection of dispersant reduces the amount of oil coming to the surface and this in turn (a) reduces the potential for exposure of surface vessels and personnel to volatile components of the oil and (b) reduces the need for surface recovery, *in situ* burn, and surface dispersant operations, thereby reducing a variety of safety risks for response personnel potentially involved with these operations. Surface application of dispersants in the vicinity of well containment operations can also reduce the potential for personnel exposure to volatile oil components.

Dispersant use often transfers oil into the water column increasing its probability for reaching subsurface marine organisms that might not otherwise be exposed to oil. Other concerns with dispersant use include:

- Dispersants in oil may reduce the performance of oleophilic skimmers, which rely on the adhesive properties of oil. There have been a few suggestions that the effect of residual surfactants on oil adhesion may reduce the efficiency of this type of skimmer although there is little supporting evidence for this, in fact, experience in Norway indicates that an increase in efficiency may be obtained in some instances. [6]

- Dispersants are not universally effective on all types of oil. Higher viscosity oils, oils that have weathered and become more viscous, oils that have cooled significantly below their pour point, and oils that have emulsified are less dispersible than light, low-viscosity oils. Empirical studies have shown that oils with pour points up to 10-15° C higher than the sea temperature may still be chemically dispersed.[7] However, current research has focused on dispersants that are formulated to work on heavy and weathered oils.

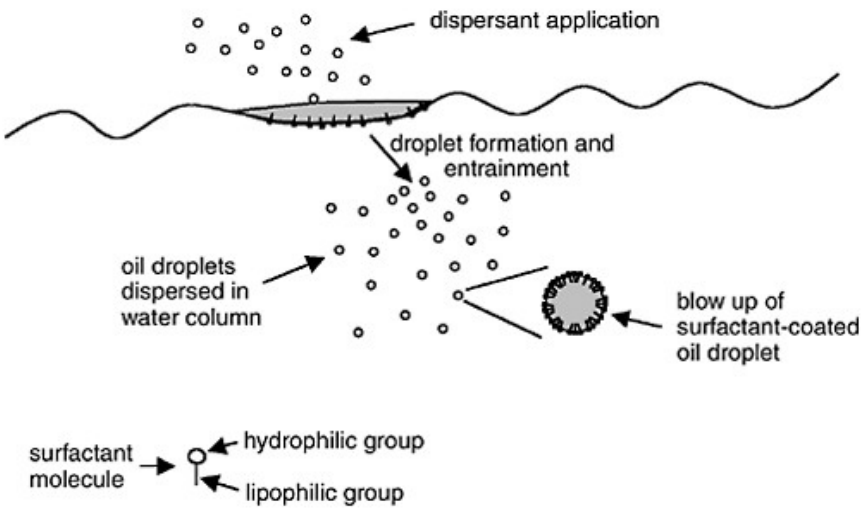
- Dispersant use on patchy slicks can be inefficient when applied by large fixed wing aircraft. For example, a large C-130 plane may have a swath width significantly greater than the width of slicks after they line up in relatively narrow windrows over time. This inefficiency can be addressed by applying dispersants to these slicks by boat to avoid spray drift or smaller aircraft with more appropriate swath width.

Mechanism of Chemical Dispersion

Modern dispersant formulations facilitate natural processes that remove oil from the environment through biodegradation. They are mainly composed of surfactants that reduce interfacial tension between oil and water to allow the formation of micron-sized droplets of oil that are entrained into the water column by wave energy (Figure 3). For

comparison, without dispersants, thick oil slicks generate millimeter-sized droplets when impacted by waves. These larger droplets tend to rapidly rise back to the surface where they coalesce and reform the slick. The smaller droplets (e.g., 70 microns) formed after applying dispersants remain in the water column and become a concentrated energy source for oil-degrading bacteria. Marine environments around the world contain oil degrading bacteria that have evolved to consume oil released by natural seeps.[8,9]

Figure 3 – Mechanism of Chemical Dispersion (National Research Council)[4]



A misperception about dispersants is that they cause oil droplets to rapidly sink to the seabed. This is not the case since dispersants are less dense than sea water and dispersed oil droplets remain positively buoyant *unless* they encounter and associate with heavier marine sediments or lose significant amounts of their lighter components via dissolution, evaporation or degradation. In marine waters far from shore, encountering enough sediment to rapidly sink large quantities of dispersed oil is unlikely. The droplets generated after applying dispersants range in size from a few microns up to 100 microns in diameter. The rise velocities of these droplets are insignificant compared to the turbulence found in the open ocean. If these droplets become negatively buoyant through degradation or dissolution, they would be even smaller with very low fall velocities. The end result is that once dispersed oil enters the water column, it tends to remain entrained without resurfacing or falling to the seabed until it is removed from the environment through biodegradation.

Efficacy

A significant amount of research shows that low-viscosity oils, disperse even after significant weathering and at cold temperatures.[10,11,12,13,14,15] Other research has shown nearly complete dispersion during wave-basin tests of several low viscosity Alaska North Slope crude oils.[16] However, dispersant effectiveness tests provide conflicting evidence

of the benefits of using dispersants under low-energy conditions and for water-in-oil emulsions because lab and basin tests can result in highly understated estimates of field effectiveness, i.e., lab test efficacy results may not be completely representative of real world dispersant effectiveness. Even in the case of the largest outdoor test tanks, oil spreading is constrained and dispersant effectiveness may be underestimated as a result (Figure 4).

Figure 4 – Large Wave Basins Constrain Slick Spreading

Photo of the BOEMRE OHMSETT (Leonardo, NJ) Test tank courtesy of TS Coolbaugh

Effectiveness tests are performed to determine if a dispersant can disperse a specific type of oil. These tests are conducted in closed systems, e.g., lab beakers or large wave basins, and for short durations, i.e., from a couple of minutes for some lab tests to 30 minutes for some wave-basin tests. Although it takes time, oil can spread to an extremely thin layer at sea, whereas beakers and basins keep oil artificially thick by limiting its natural tendency to spread. Constraining both time and surface area in dispersant efficacy tests can lead to underestimation of effectiveness because a) more viscous oils such as weathered crudes or water-in-oil emulsions take more than a few minutes to disperse and, b) thin oils disperse more easily than thick oils. In low-energy conditions, the dispersion process can take longer as well because oils must spread thinner before they disperse.

Currently six basic laboratory efficacy tests are routinely employed to evaluate the performance of dispersants. [17] Each test method has its own distinct characteristics and care should be taken to when comparing results between them. While the numerical results of these tests are useful for comparing dispersants on a relative basis, they may not be representative of actual performance expected at sea; clearly there is room for harmonizing testing methodologies.

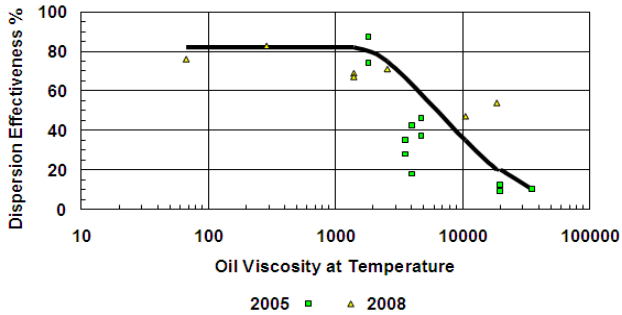
Viscosity Effects

Unfortunately, recent literature on dispersant effectiveness can be misleading. The goal of a large percentage of recent research on dispersants has been to determine the operational limits for viscous crude oils and emulsions. But, as indicated above, many

viscous crudes and emulsions may not rapidly disperse in wave basins and beakers. In contrast, a light crude oil, like the ~35°API gravity* crude spilled during the Deepwater Horizon incident, can be easily dispersed. The fact that recent literature has focused on oils that are difficult to disperse leads to the erroneous conclusion that dispersants sometimes work and sometimes do not. This conclusion may be true for certain viscous oils and water-in-oil emulsions but the scientific literature supports the conclusion that light oils readily and rapidly disperse.

It has been known for many years that it is more difficult to disperse a high viscosity oil than an oil of low or medium viscosity. Some laboratory testing has shown that the effectiveness of dispersants may be related to oil viscosity, being most effective when the oil viscosity is about 1,000 or 2,000 mPa.s and then declining to a lower level of effectiveness as the oil viscosity approaches 10,000 mPa.s. It was therefore considered that some generally applicable viscosity limit, such as 2,000 or 5,000 mPa.s could be applied to all oils. However, recent work has shown that this is not necessarily the case and modern oil spill dispersants are generally effective up to an oil viscosity of 5,000 mPa.s or more. Some research has shown that their performance does gradually decrease with increasing oil viscosity and that oil with a viscosity of more than 10,000 – 20,000 mPa.s may not be effectively dispersed (see Figure 5).[18]

Figure 5 – Wave Basin Dispersant Effectiveness vs. Oil Viscosity



The data in Figure 5 indicate that oil viscosity alone does not control dispersant effectiveness. Oil composition appears to be as important as viscosity and that these are only two of several factors that affect dispersant performance. Other important factors include the amount of energy being transmitted to the slick from waves, the degree of oil weathering (i.e., the extent to which lighter hydrocarbon components have evaporated), emulsification (i.e., the extent to which water has been entrained in the continuous oil phase), the dispersant type and the dispersant treatment rate (also known as the dispersant-to-oil ratio, or DOR).[19]

Additionally, recent work has shown that dispersant may be applied to oil in ice-infested water using a novel vessel-based maneuverable spray arm system followed by artificial turbulence from propeller wash / jet water to increase mixing energy.[20] This may serve to

* API Gravity is defined as: 141.5/SG – 131.5, where SG is the specific gravity of the fluid being evaluated. In the case of water, SG = 1.0 and API Gravity = 10. The lower the SG, the higher the resulting API Gravity

enhance response effectiveness as oil viscosity increases, as well as showing good potential for smaller spills in ice in general.

Dispersant to Oil Ratio Discussion

Surface vs. Sub-Sea Dispersant Use

Over 4,000 m^3 (25,000 bbls, 1 million gallons) of dispersant were applied to the surface waters of the Gulf of Mexico during the Deepwater Horizon incident.[21] The standard application ratio to achieve effective dispersion, as a baseline application, has been defined as 1 part dispersant to 20 parts oil for surface application (a DOR of 1:20), although the Macondo oil released during the Deepwater Horizon incident has readily dispersed at a DOR as low as 1:250. [22,23]

Figure 6 - Aerial Dispersant Application

Image from Oilspillcommission.gov[24]

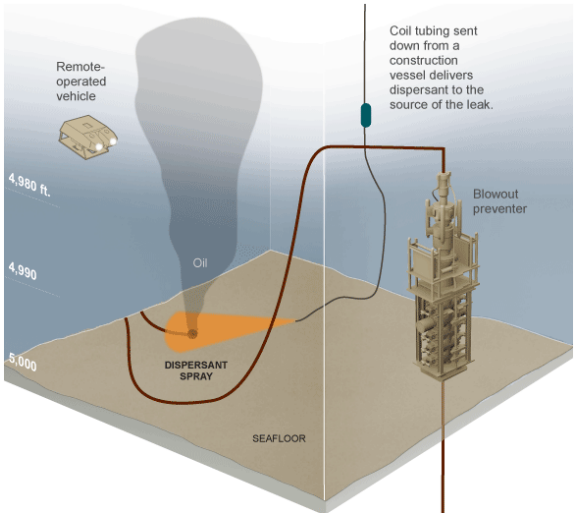
Almost 3,000 m3 (over 18,000 barrels or 700,000 gallons) of dispersant were applied via sub-sea injection directly at the wellhead during the Deepwater Horizon incident.[17]

Considering the oil was very low in viscosity, fresh, concentrated, and discharging into very turbulent conditions, application of dispersants at the wellhead was likely highly efficient, perhaps approaching the effective dispersion ratio of 1 part dispersant to 250 parts oil found for the Macondo oil as discussed above.

As opposed to the primarily aerial application of the surface use of dispersants, the sub-sea introduction of dispersants allowed for the possibility of treating the concentrated release on the sea floor in an extremely effective manner. As the schematic diagram shows in Figure 7 (a), the dispersant was fed into the oil release by means of coiled tubing extended from a surface vessel. Photography of a wand used to deliver the dispersant at an early stage of the spill, Figure 7 (b), indicates that even though it was not always directly inserted into the cloud of oil, it appears that delivery was effective as evidenced by the dispersant moving into the oil.

Figure 7 - Sub-Sea Dispersant Application

(a) **(b)**

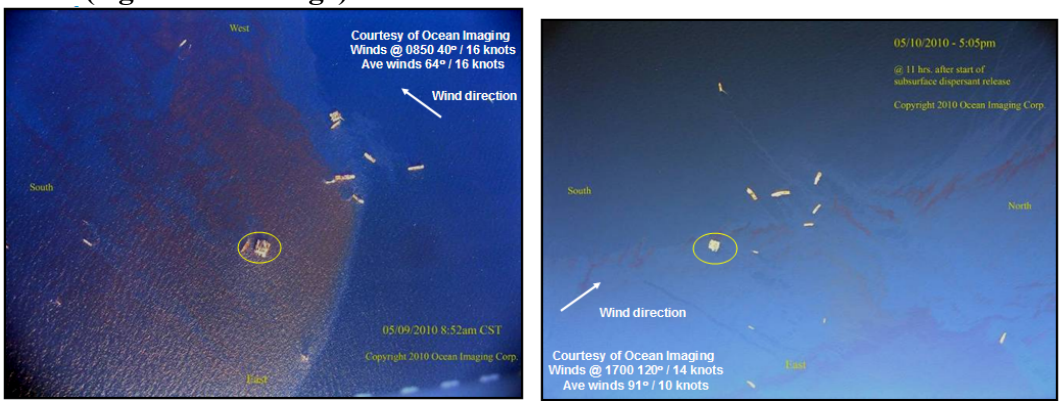


(a) http://www.oilspillcommission.gov/media/response/response-actions-dispersants.html
(b) Used with permission. © BP p.l.c.

The turbulence associated with the oil and gas plume is quite evident. The volumetric gas-to-oil ratio (GOR) at standard conditions was about 3000:1. At the temperatures and pressures experienced 1,500 meters below the sea surface (4°C and 2,200 psi), the volumetric ratio is closer to 1:1[25].

As is apparent in the following aerial photographs (Figure 8) taken during the DWH incident, the use of sub-sea dispersant delivery may have significantly reduced the surface expression of released oil. Before sub-sea injection, a large surface slick was present. After 11 hours of injection, the surface slick near the well site appears to be much reduced.

Figure 8 – Before (left aerial image) and after 11 Hours of Sub Sea Dispersant Injection (right aerial image).



Images courtesy of Ocean Imaging

Dispersants – the Future State

Following the Deepwater Horizon incident, a number of questions were raised regarding dispersant effectiveness and additional research will provide valuable insight into addressing these questions.

For example, with respect to dispersant effectiveness:

Questions that Remain Unresolved During the DWH Incident

- Do dispersants work effectively in low energy (quiescent sea surface states) mixing regimes?
- Is there a dependable performance measurement extrapolation that may be used to translate from lab and basin studies to the real world?
- Can known characteristics of the oil be used to estimate dispersant effectiveness as the oil weathers and emulsifies?

New Questions that Resulted from the DWH Incident

- Can dispersant effectiveness in high pressure (and low temperature) environments be accurately modeled and the results used to optimize dispersant use?
- Can dispersant effectiveness in high energy, high encounter rate (turbulent sub-sea release) regimes be accurately modeled and the results used to optimize dispersant use?
- Can the interactions of dispersant constituents with oil/gas mixture be modeled and the results used to understand dispersant effectiveness?
- Are there new, more effective formulations that work for a variety of oil spills at much lower DORs (e.g., <1:250)?
- Are there "green" materials or processes that can be used in the production of dispersants?
- How can the general public become educated about dispersants, their use and value as a response tool?

R&D Needed to Resolve Outstanding Questions

The large scale use of dispersants during the Deepwater Horizon incident has helped identify the need for a thorough review of the understanding of this response option. This is especially true with respect to its efficacy in minimizing environmental impacts, identification of the products that may be most effective, the environmental conditions under which dispersants are most effective, and the factors that most influence their performance.[26] Information that results from such a technical review will allow for the identification and description of key areas that will be most amenable to new or continuing research.

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