NRT SCIENCE & TECHNOLOGY COMMITTEE
Fact Sheet: EMULSION BREAKERS AND INHIBITORS FOR TREATING OIL SPILLS

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SUMMARY
Emulsions are a suspension of droplets, greater than 0.1 micron in diameter, consisting of two completely immiscible liquids, one of which is dispersed throughout the other. Emulsification of oil is caused by the uptake of water by the oil which results in a substance with increased viscosity. This oil/water substance can severely hamper recovery capabilities of skimmers; reduce pumping volumes; and increase handling, oily waste disposal, segregation, and storage problems. In addition, non-mechanical response techniques, such as the use of dispersants and in situ burning, are rendered less effective or ineffective by formation of high-viscosity emulsions. Since the 1980's, when the oil spill response community's demand for emulsion breakers as a potential operational decision-making tool increased, there has been considerable research into ways to prevent or break emulsions and lower viscosities to allow response technologies to function more effectively over a longer period of time. This paper provides the oil spill response community with an up-to-date summary of emulsion breaker research and identifies key areas where further research is needed.

Emulsions are frequently quite persistent in the environment and resist decomposing into their original constituents of oil and water. Research into chemical agents to break or inhibit the formation of water-in-oil emulsions has been limited. Even a basic understanding of the characteristics of emulsions, the important factors affecting their formation, and the important measurements to classify them is rudimentary. The 'stability' of emulsions has recently been studied and a correlation between stability and viscosity has been observed. Recent test results show that laboratory tests have the potential to evaluate the effectiveness of emulsion breakers and inhibitors; however, the similarity of emulsions generated in the laboratory to those in the field has not been verified. Standardized testing protocols to evaluate emulsion breaker effectiveness have not been validated so that different oils can be tested against different emulsion breakers or inhibitors. It is concluded that the field is immature and requires more research and development before broad application is possible.

WHAT ARE EMULSIONS?

Oils spilled at sea can form water-in-oil emulsions, consisting of water droplets suspended in an oil matrix. Once oil enters the sea it moves on the water's surface by advection and spreading. This movement increases the exposure area of the oil to subsequent "weathering processes," one of which is emulsification (National Research Council, 1985). Although the process of emulsification is not well understood, it is known that some type of mixing energy, such as breaking waves, is needed to form an emulsion. In addition, it is speculated that the rate of emulsification is correlated with wind speed, a major source of mixing energy. Some emulsions have high water content and are relatively stable, maintaining their chemical attributes for several days; these are sometimes referred to as "chocolate mousse." With the uptake of water, the properties of the oil can change dramatically. The viscosity can increase by orders of magnitude and the density can increase to nearly that of water. For these reasons and because approximately 3/4 of the emulsion can be water, the emulsification of an oil spill significantly complicates spill cleanup. In fact, many skimmers or other control equipment are ineffective once oil becomes emulsified.

'Stability' is widely used to refer to the persistence of an emulsion in the environment, and has been identified as an important characteristic of water-in-oil emulsions. Some emulsions quickly decompose into separate oil and water phases once removed from the sea surface, while more stable emulsions can persist for days to years. Recent work indicates that the viscosity of an emulsion is correlated with its stability.

One classification scheme separates emulsions according to stability and includes specific operational definitions for stable, unstable, and meso-stable emulsions:

- Unstable emulsions usually persist for only a few hours after mixing stops. These emulsions readily separate into oil and water due to insufficient water particle to water particle interactions. However, small amounts of water may be retained by the oil, especially if the oil is viscous.

- Stable emulsions will persist for days, weeks and longer. They show viscoelastic properties and their viscosities are at least three orders-of-magnitude greater than that of the starting oil. In addition, some, if not most, stable emulsions increase in viscosity over time. It has been postulated that the stability derives from the strong visco-elastic interface caused by asphaltenes, perhaps along with resins. Increasing viscosity may be caused by increasing alignment of asphaltenes at the oil-water interface.

- Meso-stable emulsions are probably the most commonly-formed emulsions in the field. These emulsions can be red or black in appearance. Meso-stable emulsions have properties between stable and unstable emulsions. It is suspected that these emulsions either lack sufficient asphaltenes to render them completely stable or contain too many destabilizing materials such as smaller aromatics. The viscosity of the oil may be high enough to stabilize some water droplets for a period of time. Meso-stable emulsions may also degrade to form layers of oil and stable emulsions.

CHARACTERISTICS OF EMULSION BREAKERS

De-emulsifiers are products used to 1) break or prevent the formation of emulsions on the open seas, and 2) break recovered emulsions in skimmers or tanks. To date, most de-emulsifier products are hydrophilic surfactants, that is surfactants with a strong tendency to make oil-in-water emulsions from waterÐinÐoil emulsions. These surfactants are more soluble in water than in oil, and therefore have the ability to revert the water-in-oil emulsion into two separate phases. Consequently, such de-emulsifier products are most effective when used in a confined environment; they are likely ineffective on open water. Meso-stable emulsions, the most frequent emulsion produced at sea, are relatively easy to break and may be broken with as little as 1/100 of the same de-emulsifier product required to break a stable emulsion. A stable emulsion is difficult to break and some de-emulsifier products are not capable of breaking these emulsions.

PAST RESEARCH EFFORTS

The class and characteristics of the emulsion broken or dealt with is of utmost importance in evaluating the benefits of a particular emulsion-breaking product. The validity of many past studies is questionable because the state of the emulsion was not specified nor were, in most cases, adequate analytical techniques applied. Prior to the 1980's, several sets of experiments were conducted with emulsion-breaking agents on a variety of oils under a variety of conditions. It was noted that laboratory effectiveness did not appear to correlate with effectiveness in real situations.   The test results, however, have limited applicability because of differences in test procedures and measurements. The U.S. Minerals Management Service and Environment Canada have collaborated since 1987 to evaluate emulsion breakers and inhibitors, both in test tanks and in field trials. In 1990, they began to develop a series of laboratory tests to evaluate both emulsion breaking and inhibition tendencies of products. Twelve test concepts were evaluated from which four tests were further developed to be the final procedures for evaluating test products. A standard crude oil (Alberta Sweet Mixed Blend) and a heavy oil (California 10), were used for most tests. The tests mimicked open and closed systems and focused on emulsion breaking or inhibition of formation. Two treating agents, Vytac DM and 60% Alcopol 0, were tested in these systems and found to be effective at ratios varying from 1:7,000 to 1:250, depending on product and test.

A Marine Spill Response Corporation study on emulsion breaking examined the role of heat in aiding emulsion breaker activity. It was noted that temperatures up to 70oF increased the effectiveness of the agent. A field trial using LA 1842 showed good effectiveness on a North Sea crude emulsion. Tests were done at sea with demulsifier sprayed from aircraft at a nominal ratio of 1:600. One slick was subsequently sprayed with dispersant. The apparent effectiveness of the dispersant indicated to the experimenters that both treatments could be applied in tandem to a given oil spill. Other combinations of demulsifiers and dispersants have been tried, giving varying results, dependent in great part, on the type of oil and the characteristics of the emulsions.

To date, studies have shown that the important factors for testing emulsions and emulsion breakers/inhibitors (or for interpreting product test results) are as follows:

1. Stability of the emulsion - emulsions must be stable to yield consistent test results. This is readily achieved using a known stable-emulsion-producing oil in a high energy device.

2. Energy in the test vessel - breaking of an emulsion requires some energy. The energy requirement is variable with different types of agents, some agents may not break an emulsion without energy. The form of energy induction, be it rotation or shaking, does not appear to have an effect.

3. End-point test - a variety of test measures have been tried, but have primarily focused on water content and viscosity. It has been found that a loss of water as low as 10% can result in the breaking of an emulsion. The presence of large water droplets in a “broken” emulsion makes water-content methodology “noisy.” Measuring the viscosity of the emulsion is a more consistent method. This is best done with a rheometer or a plate-plate viscometer.

4. Oil-to-water ratio - Many agents are water-soluble and when the oil-to-water ratio is large, these agents are much less effective than those that are not water-soluble. A minimum ratio of 1:300 is required to differentiate these products.

5. Mixing time - Adequate mixing time is necessary to yield a consistent result; this time is variable with the type of agent. A minimum of one hour has been found necessary to reduce noise. Most tests show no additional increase in agent effectiveness after three hours.

6. Treatment ratio - Most agents are operative from 1:100 down to about 1:2,000, agent to oil ratio.

FUTURE NEEDS IN R&D

Future research should focus on the following topics which include research needs outlined in a 1993 Marine Spill Response Corporation workshop on Formation of Water-in-Oil Emulsions (Hayward Walker et al., 1993):

1. Establishing standard procedures for generating emulsions that are internationally acceptable for laboratory testing of emulsion breakers and that have been validated as realistic.

2. Testing and evaluating products in real spill situations to evaluate protocols under different field conditions.

3. Testing a large variety of agents with the new tests using standardized procedures to create a database of products’ performance.

4. Developing appropriate toxicity protocols.

5. Developing a database of toxicity results using different products.

6. Continuing emulsion formation and stability studies to enable a broader range of oils to be treated.

7. Conducting studies to measure relevant characteristics of emulsions including: rheology, water content, density, water droplet size, etc. using a set of standard emulsions, some prepared in the lab and some obtained during actual spills.

8. Measuring the rate of emulsion formation at sea under a variety of conditions.

9. Conducting a series of tests at sea to develop parameters for numerical model input.

10. Developing a reference set of data on emulsions, their characteristics and properties through a series of experiments at sea.

11. Establishing protocols for the collection, handling and storage of water-in-oil emulsions.

CONCLUSION

The field of emulsion breakers and inhibitors is very immature at this time and extensive research and development is needed in all phases. This research cannot build on many of the findings from past studies since it has only recently been shown that, to a great extent, the stability of the emulsion changes the ratio of material needed. Since past studies did not adequately evaluate the stability of the emulsion, subsequent findings are difficult to evaluate. Older studies did not apply analytical procedures that would yield usable results.

Currently, a product must be listed on the National Contingency Plan's Product Schedule before federal On-Scene Coordinators can use it. In order to fulfill this requirement, the product manufacturer must conduct the applicable aquatic toxicity test and other requirements, as defined in the NCP. In addition to information regarding a products' toxicity, it is expected that federal On-Scene Coordinators will want information regarding product effectiveness. At this time, effectiveness data are not required for listing because an effectiveness test for emulsion breakers has not been developed. Further research on the development of effectiveness protocols is required to ensure that consistent data is available for the federal On-Scene Coordinators to evaluate product efficacy.

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