

# Oil Properties and Their Impact on Spill Response Options

Literature Review

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Cover Illustration: Containment booms were used to contain oil spilled during the 2010 Deepwater Horizon oil spill in the Gulf of Mexico. Photo from: [https://en.wikipedia.org/wiki/File:Oil\\_containment\\_boom.jpg](https://en.wikipedia.org/wiki/File:Oil_containment_boom.jpg)

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May 2014

A handwritten signature in black ink that reads "Ronald Filadelfo". The signature is written in a cursive, flowing style.

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## Executive summary

In responding to an oil spill, the effectiveness of a response depends on the timely selection of appropriate remediation options. Several oil spill remediation technologies exist:

- In situ burning
- Dispersants
- Skimmers
- Sorbents
- Solidifying agents

The effectiveness of each technology depends on the timeframe in which it is used. This time-dependent effectiveness is called the “window of opportunity.” The window of opportunity is determined by the properties of the spilled oil, and by how these oil properties change over time after a spill. It is critical to understand both how oil properties change over time, and how the effectiveness of response options change as a function of oil properties.

CNA conducted a literature review on the performance of oil spill remediation technologies—specifically, how their performance varies with the properties of the oil spilled. This work was sponsored by the Department of the Interior’s Bureau of Safety and Environmental Enforcement (BSEE).

BSEE requested this study to compile oil spill remediation technology performance data from various sources into a single report. In particular, BSEE was interested in identifying work done on spill technologies in the peer-reviewed scientific literature. CNA identified and organized performance data from government, industry, and scientific literature, and formulated conclusions and recommendations about areas warranting further research and development in this field. CNA also organized system performance data from the various literature sources into a user-friendly database.

Summaries of the major conclusions for each technology follow.

## **In situ burning**

### **Key findings**

The most important factor governing the use of in situ burning in a response is the thickness of the oil slick, which should be at least 2–3 mm to support burning. Slick thickness can be maintained by using fire-resistant booms.

Most oil is suitable for in situ burning. One important exception is very light, refined oil products, for which burning poses a safety risk.

The ability to use in situ burning as a response option decreases with time and oil weathering. In situ burning might be suitable within 72 hours after a spill. For heavy or thick oils, burning may only be effective for 1 to 2 hours after a spill.

### **Recommendations for future research/development**

We recommend that future research be conducted on novel technologies that may improve the window of opportunity for in situ burning, including herding surfactants and emulsion breakers. Preliminary work on these technologies suggests that they might increase the window of opportunity for in situ burning by maintaining a favorable slick thickness, and by decreasing the water content of emulsified oil.

## **Dispersants**

### **Key findings**

We reviewed performance data on dispersants listed in the Environmental Protection Agency National Contingency Plan (EPA NCP) product schedule. Of the 18 dispersants listed, 9 were evaluated in independent tests. Only 3 of these (Corexit 9500, Corexit 9527, and Finasol OSR) performed as well in independent effectiveness tests as they did in tests conducted by the product manufacturers and reported to the EPA.

Corexit 9500 is the only dispersant among those tested in the field to demonstrate consistent dispersion of oil slicks in field tests. Corexit 9500 was also the only dispersant among those tested to effectively

disperse oil in three types of independent laboratory tests (swirling flask, baffle flask, and wave tank tests). This suggests that good performance in all types of laboratory testing might indicate that a dispersant will perform well in the field.

Finasol OSR was the only dispersant to demonstrate effectiveness equal to Corexit in independent laboratory tests.

#### **Recommendations for future research/development**

Since limited field trial data are available for Finasol OSR, it would be beneficial to conduct additional field tests on Finasol OSR to determine whether its performance in the field is consistent with its laboratory effectiveness.

## **Skimmers**

### **Key findings**

Unlike other remediation technologies, skimmers can be used to recover oils across a wide range of viscosities. Skimmers exist that can effectively recover oil across all of the ASTM viscosity categories (I through V).

Many “rules of thumb” about the selection of oil spill skimmers are based on performance tests conducted in the 1970s through the 1990s. Because skimming technology has not changed appreciably since that time, the standing rules of thumb are probably applicable to commercially available skimmers today.

Emerging skimmer technologies are being developed in academic settings to improve the oil recovery capabilities of oleophilic skimmers. Ongoing research includes the development of grooved patterns on drum skimmers, novel oleophilic surface coatings, and the application of nanotechnology to novel oleophilic surfaces.

Work by the Norwegian research organization, SINTEF, led to the development of highly effective skimmers for oil recovery in ice conditions.

### **Recommendations for future research/development**

We recommend that emerging skimmer technologies be incorporated into commercially available designs. As the most effective

skimmer test programs evaluated skimmers for a particular operational environment of interest (arctic conditions, for example), we recommend that targeted programs for the development of skimmers in operational environments of interest be developed and executed.

## **Sorbents**

### **Key findings**

Tests on commercially available sorbents demonstrated that synthetic sorbents yield better oil sorption capacity than natural materials. Polypropylene and aminoplast polymer sorbents exhibited the highest sorption capacity for light, medium, and heavy test oils. Inorganic materials exhibited poor oil sorption.

In the academic literature, several materials under development yielded higher oil sorption capacity than commercially available polypropylene sorbents

### **Recommendations for future research/development**

As synthetic sorbents yielded higher sorption capacities than natural materials in the academic literature, we recommend that promising adsorbent materials from the scientific literature—for example, electrospun polymers—be further developed into commercial oil spill sorbents. We also recommend that promising oil adsorbent materials be incorporated into other spill remediation technologies such as sorbent booms or oleophilic skimmers.

## **Solidifying agents**

### **Key findings**

The scientific literature on solidifying agents is sparse and limited in scope and scale. Most studies on solidifiers were done at the laboratory scale and have only assessed their effectiveness in light, refined petroleum products. The terminology used to define solidifiers is inconsistent, and standard metrics do not exist to describe or characterize solidifiers for oil spill cleanup.



New work in peer-reviewed journals suggests that gelating agents may be promising for the recovery and solidification of oil from water.

**Recommendations for future research/development**

We recommend that a standard definition be developed to define solidifiers and to distinguish solidifying agents from sorbents. Standard test methods and performance metrics should be developed to quantify the effectiveness of solidifiers.

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# Introduction

In oil spill remediation, it is critically important to understand the “window of opportunity” for various cleanup technologies. After an oil spill, timely decisions must be made about the most effective response to mitigate the environmental impacts of the spill. Multiple technologies are typically used in a spill response, including physical methods (skimmers, sorbents, or solidifying agents) and/or chemical methods (dispersants or in situ burning). Each technology has a different window of opportunity that strongly depends on the specific spill conditions and properties of the spilled oil.

The purpose of this study was to conduct a literature review on oil spill remediation technologies. This report compiles data relating the effectiveness of these technologies to the properties of the spilled oil. We included in situ burning, dispersants, skimmers, sorbents, and solidifying agents in our review. We focused on studies reporting the effectiveness of remediation technologies as a function of oil properties. From the performance studies encountered in the literature, we derived conclusions about their effectiveness for different types of oil, and we identified areas warranting further research and development.

In addition, we developed a searchable database to organize and cite performance data for skimmers, sorbents, and dispersants. All performance data were organized according to the test oil viscosity, allowing users to compare the performance of different technologies in similar oil types. In addition to viscosity, other oil properties are included for dispersants, where more fidelity (other than viscosity) is important to categorizing performance. The combination of this report with the performance database provides readers with the current state of the art in spill remediation research. Details on the

database development, structure, and contents are found in a separate report.<sup>1</sup>

## Methodology

In performing this review and in constructing the database, we accomplished the following:

1. Identified literature sources for in situ burning, dispersants, sorbents, skimmers, and solidifying agents
2. Identified performance metrics describing each technology
3. Identified a standard oil categorization method
4. Compiled and organized performance data and oil properties into project database
5. Developed database queries and searchable structure
6. Analyzed performance data

In the following sections, we describe the literature search methodology in detail.

## Literature search

We conducted an extensive literature search to identify sources of performance data on several remediation technologies. We searched for performance data on dispersants, skimmers, and sorbents. We also searched for studies on in situ burning and solidifying agents. Our search included academic journals and conference papers, government reports, and reports published by private industry. References are cited throughout this report, and a complete list of sources is also included in the project database.

In our search of academic publications, we gathered sources published since 2000 using both Google Scholar and EBSCO Discovery

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1. The accompanying report that documents the project database is: C. Federici and J. Mintz, *Oil Properties and Their Impact on Spill Response Options: Database Development and User Guide*, The CNA Corporation, IIM-2014-U-007467, 2014.

Service. EBSCO Discovery Service searches the following databases: Medline, PsycEXTRA, PsycINFO, Business Source Complete, Academic OneFile, Academic Search Complete, Military and Government Collection, GreenFILE, Agricola, Science Direct, and Elsevier.

Government reports and test programs were identified from the United States (Environmental Protection Agency (EPA)) and Environment Canada.

Our search of private industry reports led to the identification of significant oil spill test programs conducted both domestically and internationally. We drew on spill cleanup test programs conducted by BP, SINTEF (a Norwegian research organization), and SL Ross Environmental Research.

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# Oil characterization

The analysis and characterization of crude oil or refined petroleum products is a complicated endeavor. These oils are heterogeneous mixtures of hydrocarbons with physical properties that change depending on the exact oil composition, and on the environmental conditions.

## Oil properties

Both the chemical composition and the physical properties of oils have been carefully analyzed and documented for thousands of crude oils and refined oil products [1][2]. Physical properties influencing spill cleanup include viscosity, density, API gravity, pour point, flash point, and the chemical composition of the oil (i.e., wax content and SARA (saturated hydrocarbon, aromatic hydrocarbon, resin, asphaltene) content). Common oil properties used in spill remediation research are defined below, along with their common units of measure:

- **Viscosity:** The resistance to flow of a liquid (common units include pascal-seconds ( $\text{Pa}\cdot\text{s}$ ), centipoise (cP), or centistokes (cSt))
- **Density:** Mass per unit volume (usually reported in  $\text{g}/\text{cm}^3$  or  $\text{kg}/\text{m}^3$ )
- **API gravity:** A dimensionless form of density, describing a fluid's density relative to water (a dimensionless number, reported with a degree mark ( $^\circ$ ) as the unit. The API gravity of water is  $10^\circ$ ).
- **Flash point:** The lowest temperature at which a substance can vaporize to form an ignitable mixture ( $^\circ\text{F}$  or  $^\circ\text{C}$ )
- **Chemical composition:** The content of the following chemical groups is often reported for crude oil:
  - **SARA content:** The content of saturates, aromatics, resins, and asphaltenes in crude oil. The content of SARA components is correlated to the bulk physical properties of oil.

Saturate and aromatic contents are negatively correlated with viscosity (high saturate or aromatic contents correlate with low viscosity oils) [3]. Asphaltene content is positively correlated with oil viscosity. The high viscosity observed in heavy oil is related to its asphaltene content because asphaltene molecules tend to tangle, causing high oil viscosity [4]. In addition, oils with high asphaltene and resin contents tend to form stable emulsions [5].

- **Sulfur:** The content of sulfur-containing molecules in crude oil
- **Wax content:** Content of organic compounds that are malleable near ambient temperature. Waxes are typically insoluble in water, and soluble in organic solvents. Wax content is positively correlated with oil viscosity [6].

One comprehensive database of oil properties (including more than 1,000 crude oils and refined petroleum products) is included in the ADIOS (Automated Data Inquiry for Oil Spills) software package. ADIOS—an oil spill modeling software package developed by the National Oceanic and Atmospheric Administration (NOAA)—is available to download free of charge from NOAA’s website: <http://response.restoration.noaa.gov/oil-and-chemical-spills/oil-spills/response-tools/adios.html>.

## Oil weathering

In addition to understanding the physical and chemical properties of oil and petroleum compounds, it is critical to understand how these properties change over time during a spill incident. The process by which oil properties change during an oil spill is known as “weathering.” Oil weathering is a complex process, and detailed computational models exist to predict how oil properties change during a spill as a result of weathering [7][8]. During weathering, oil becomes more viscous through evaporative loss of volatile compounds and by collecting water (a process known as “emulsification”). The degree and rate at which oil properties change as a result of weathering depend on the type of oil and on the conditions surrounding the oil spill (weather, sea state, location of spill, etc.). A detailed discussion of oil weathering is beyond the scope of this study. We acknowledge that oil weathering is a critically important factor governing the selection of



remediation methods, and we mention the impact of oil weathering in our discussion of cleanup technologies where appropriate.

## ASTM standard categories

While many of the physical and chemical characteristics of oil influence remediation options, most studies evaluating cleanup technology describe oil using only a few key, descriptive properties. Often, viscosity, density, and API gravity are used to characterize test oils. ASTM developed many standard test protocols for the testing of spill cleanup technologies, including standard categories to describe test oils. Table 1 and table 2 show ASTM categories to describe oil in the testing of skimmers and sorbents, respectively. (The ASTM standard for in situ burning does not include viscosity categories for test oils. Instead, oil fire point and slick thickness are used to guide the selection of ignition devices.) In this paper, we described test oils according to these ASTM categories. For skimmers and dispersants, we used the categories described in table 1; for sorbents, we used the categories in table 2. In the project database, all studies are sorted according to the ASTM categories listed in table 1.

Table 1. Oil categories for skimmer testing (ASTM method F631-99)

Category	Viscosity (cSt)	Density (g/mL)
I	150 – 250	0.90 – 0.93
II	1,500 – 2,500	0.92 – 0.95
III	17,000 – 23,000	0.95 – 0.98
IV	50,000 – 70,000	0.96 – 0.99
V	130,000 – 170,000	0.96 – 0.99

Table 2. Oil categories for sorbent testing (ASTM method F726)

Oil description	Viscosity range (cP)	Density range (g/cm <sup>3</sup> )	Example oils
Light	1 – 10	0.820 – 0.870	Diesel fuel
Medium	200 – 400	0.860 – 0.970	Light Crude oil
Heavy	1,500 – 2,500	0.930 – 1.000	Bunker C oil
Weathered (added in 2012)	8,000 – 10,000	0.930 – 1.000	Emulsified crude oil

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## Literature review

In this section, we summarize the literature search for each technology separately (in situ burning, dispersants, skimmers, sorbents, and solidifiers).

### In situ burning

#### Description of in situ burning

In situ burning is the oldest technique used in oil spill cleanup and involves the controlled burning of oil slicks to eliminate spilled oil offshore before it reaches the coastline. This technique has been successfully used in many large spill responses, including the 2010 Deepwater Horizon spill, where an estimated 200,000–300,000 barrels of oil were burned at sea [9]. Benefits of in situ burning include extremely efficient and rapid oil removal (efficiencies often exceed 90 percent with removal rates on the order of 2000 m<sup>3</sup>/hr) [10]. In addition, when successful, no further downstream oil separation or removal processes are necessary following in situ burning. Once burned, the oil is eliminated. While typically effective, the choice to use in situ burning involves many factors, including environmental considerations (burning oil releases toxic fumes), operational constraints (the availability of fire-resistant containment booms and appropriate igniters at the site of the spill), and technical constraints (effectiveness of the technique for the particular oil spilled).

#### Measure of in situ burning effectiveness

Here, we consider the effectiveness of in situ burning as a function of oil properties. The operational challenges and environmental implications of in situ burning will not be discussed, nor will the factors involving equipment selection for in situ burning.

Three factors consistently emerged as the most important in determining the effectiveness of in situ burning in a spill: (1) oil slick thickness, (2) oil properties (flash point, volatility, and API gravity), and (3) oil emulsification. We will discuss each of these factors indi-

vidually and explain how these factors can help to identify a window of opportunity for using in situ burning in a spill.

The effectiveness of in situ burning is usually described according to its efficiency, defined as the percentage reduction in slick thickness as a result of burning. Slick thickness and oil properties (mainly API gravity) are thought to influence the effectiveness of in situ burning. These properties are discussed in the following subsections.

### **Influence of oil slick thickness**

Oil slick thickness is a significant consideration when conducting in situ burning. A slick thickness of at least 1 mm is required to achieve sustained burning (most slicks, however, are ignited when they are at least 2–3 mm thick). When slick thickness is reduced to less than 1 mm, burning is no longer sustainable [11][12].

Figure 1. In situ burning during Deepwater Horizon spill response



A containment boom is being carried between two boats to facilitate and control in situ burning [9].

Very dense or highly emulsified oils require thicker slicks (3–10 mm) to initiate burning [11]. This is because highly emulsified oils are difficult to ignite and burn (as discussed in more detail in the next subsection). Increasing slick thickness is one way to improve the applicability of in situ burning for highly weathered oils. Unemulsi-

fied oils can initiate and sustain burning with thinner oil slicks than emulsified oil, regardless of their properties. Unemulsified oil requires a slick thickness of 2–3 mm to initiate and sustain burning [12]. To maintain the slick thicknesses sufficient to support in situ burning, fire-resistant booms are deployed around the edge of the oil slick, as shown in figure 1.

### **Herding surfactants to maintain slick thickness**

Surfactant molecules (e.g., soaps or detergents) contain both hydrophilic (water-loving) and lipophilic (oil-loving) groups. Herding surfactants, which form layers on the water surface, can rapidly contract oil slicks, thereby increasing their thickness. A series of tests conducted by Buist and others demonstrated the effectiveness of herders to facilitate in situ burning in large-scale tank and field trials in icy conditions [13][14]. A literature review by SL Ross Environmental Research in 2010 highlighted the fact that herding surfactants are effective in both fresh and salt water to facilitate in situ burning [15].

## **Influence of oil properties on in situ burning**

To ignite oil, vaporization (the transition of some oil from the liquid to gas phase) is required to initiate a fire. Many oil properties—such as vapor pressure, volatiles content, flash point, API gravity, and degree of emulsification—are correlated to how well oil will vaporize and ignite. Oils that readily vaporize (oils with high vapor pressure) are easier to ignite than those that do not readily vaporize (oils with lower vapor pressure). For in situ burning, however, virtually any type of oil will burn on water if the oil slick is of sufficient thickness [12].

Highly emulsified and heavy oils are more difficult to burn than light oils because they do not readily vaporize. Emulsified oils typically have burning efficiencies of 30–60 percent, whereas very light oils, such as gasoline, burn at 95–99 percent efficiencies [12]. Several studies demonstrated that highly emulsified oils can be burned after adding a chemical emulsion breaker to deemulsify the oil [11][16]. The addition of an ignition primer, such as diesel fuel, can also be added to heavy or emulsified oils to enable their ignition [12].

Some refined products are not well suited for in situ burning for safety reasons. Certain highly flammable refined fuels present fire risks due to rapid evaporation and spreading. Oils with flash points below

37.8 °C and vapor pressures below 40 psi should not be considered for in situ burning due to the risk of an uncontrollable fire. Such flammable products include gasoline, propane, and butane [11].

While the physical properties of oil help predict its suitability for in situ burning, in a time-critical spill situation, having a simple set of selection criteria for cleanup methods allows for the most efficient, timely cleanup response. API gravity was identified by SL Ross Environmental Research as a single, good predictor of success for in situ burning. Based on testing of 17 crude oils, guidelines for in situ burning as a function of API gravity were developed. Light oils with API gravities higher than 35° burned easily, and heavy oils with API gravities less than 20° were difficult to ignite or unignitable. Oils with intermediate API gravities ranging from 20° to 35° had various degrees of ignitability, depending on their degree of emulsification [17]. Table 3 shows the in situ burning efficiency of various fuels as a function of API gravity. As a rule of thumb, oils with API gravity greater than 20° are suitable for in situ burning.

Decreased burning efficiency was reported over time with evaporative loss and oil weathering. The impact of weathering on burning efficiency is more pronounced for heavy oils than for light oils. In one case, the ability to burn light oils did not decrease dramatically with oil weathering, but the ability to burn heavy oils significantly decreased with increasing water content [18]. Additional work on the effect of weathering on in situ burning has been incorporated into the SINTEF oil weathering model. This software package predicts windows of opportunity for in situ burning for oils of various properties as they weather and accumulate water over time [19].

Table 3. In situ burning properties of various fuels

<b>Fuel type</b>	<b>Example</b>	<b>API gravity</b>	<b>Burning efficiency (percentage)</b>
Refined	Diesel fuel oil	37.2	90 – 98
Light crude	S. Louisiana crude	38	85 – 98
Medium crude	West Delta 143	30	80 – 95
Heavy crude	West Delta 30	23	75 – 90
	Santa Ynez	17	Unignitable
	Bitumen	< 10	13
Emulsion	Emulsified crude	NR	30 – 60

Burning efficiency data for various fuel types was reported in [12]. Examples of fuels and their API gravity values were reported in [17].

## Limitations of in situ burning

While most oils are suitable for removal by in situ burning, there is a limited timeframe after the initial spill in which in situ burning will be effective. As oil weathers over time, it becomes emulsified with water, and suffers evaporative losses of its volatile compounds. Both emulsification and evaporative loss increase with time and decrease the efficiency of in situ burning.

The window of opportunity for in situ burning is a function of oil weathering. In situ burning was estimated to be a viable response option for up to 72 hours after a spill, depending on the type of oil (heavy oils will have a shorter window of opportunity) [20]. For light and medium crude oils, in situ burning could be performed for 40–60 hours after a spill. For heavy crude oil, however, in situ burning became almost completely ineffective after just 1–2 hours because of the profound effect of oil weathering on burning efficiency [20].

The environmental conditions surrounding a spill may also influence oil weathering and the window of opportunity for in situ burning. For example, in arctic conditions, the window of opportunity for in situ burning may be extended for oils under a high degree (70–90 percent) of ice cover. Ice cover was found to reduce oil weathering, allowing a longer time window for in situ burning [21][22].

## Summary of in situ burning

We summarize in situ burning in three points:

- Oil slick thickness is the most important factor governing in situ burning. Slick thickness should be at least 2–3 mm to support burning. Slick thickness can be maintained by using fire-resistant booms.
- Most oil is suitable for in situ burning. Oils with API gravity of at least 20° will probably burn with high efficiency. One important exception is very light, refined oil products, for which burning poses a safety risk.
- The ability to use in situ burning as a response option decreases with time and oil weathering. In situ burning might be suitable within 72 hours after a spill. For heavy or thick oils, burning may only be effective for 1–2 hours after a spill.

## Research recommendation for in situ burning

We recommend that further research be pursued on herding surfactants and emulsion breakers in conjunction with in situ burning. Preliminary work on these technologies suggests that they might increase the window of opportunity for in situ burning by maintaining a favorable slick thickness and by decreasing the water content of emulsified oil.

## Dispersants

Dispersants are agents for treating chemical oil spills that are designed to “disperse” oil into water in very small droplets. Dispersants are surfactant molecules that are used in (1) preventing oil from reaching the shoreline in bulk and (2) promoting the biodegradation of oil at sea. Dispersants have been used in several large oil spill responses, including the 1989 Exxon Valdez and the 2010 BP Deepwater Horizon spills.

There is a large volume of scientific literature discussing the use of dispersants for oil spill response, including several excellent literature reviews. In 2005, the National Research Council released a comprehensive report on the use of dispersants in the United States [5]. In his 2011 textbook, Fingas published a review of over 450 studies on dispersants, from 1997 to 2011 [12]. These two reviews contain detailed information on dispersant chemistry, effectiveness tests, toxicity, and the operational implications of applying dispersants to oil spills. We refer the interested reader to these references for a detailed discussion of dispersants for oil spills. Here, we will briefly summarize dispersant chemistry and function, and we focus on literature about those dispersants listed on EPA’s National Contingency Plan (NCP) schedule.

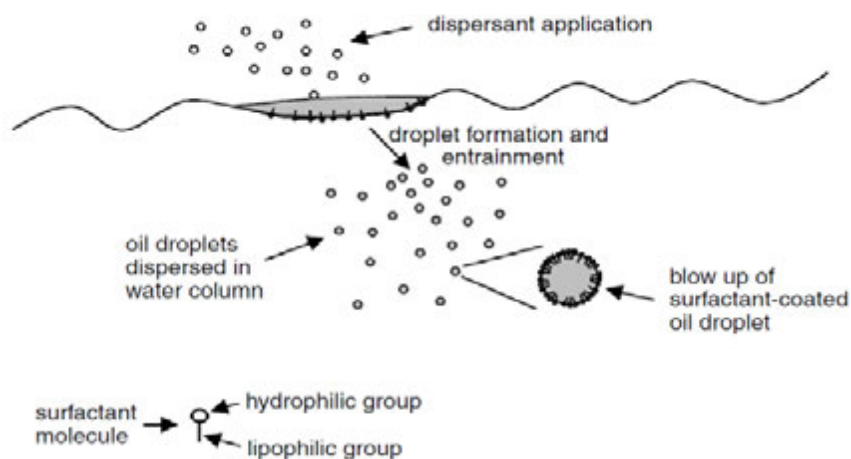
## Description of dispersant chemistry and function

Surfactants are most often characterized by a metric called the hydrophilic-lipophilic balance (HLB) which describes a dispersant’s affinity toward oil or water. The HLB can range from 0 (completely lipophilic or oil soluble) to 20 (completely hydrophilic or water soluble). Most dispersants designed for oil spill remediation have an HLB between 9 and 11, meaning that they are equally soluble in both oil and water.



Dispersants interact with an oil slick at the interface between the oil slick and the underlying water. Surfactant molecules align themselves along the oil-water interface (with the oil-soluble component in the oil, and the water-soluble component in the water), and will pull or “entrain” the oil into small droplets away from the slick, diluting the oil in the underlying water. Figure 2 depicts the chemical dispersion of an oil slick.

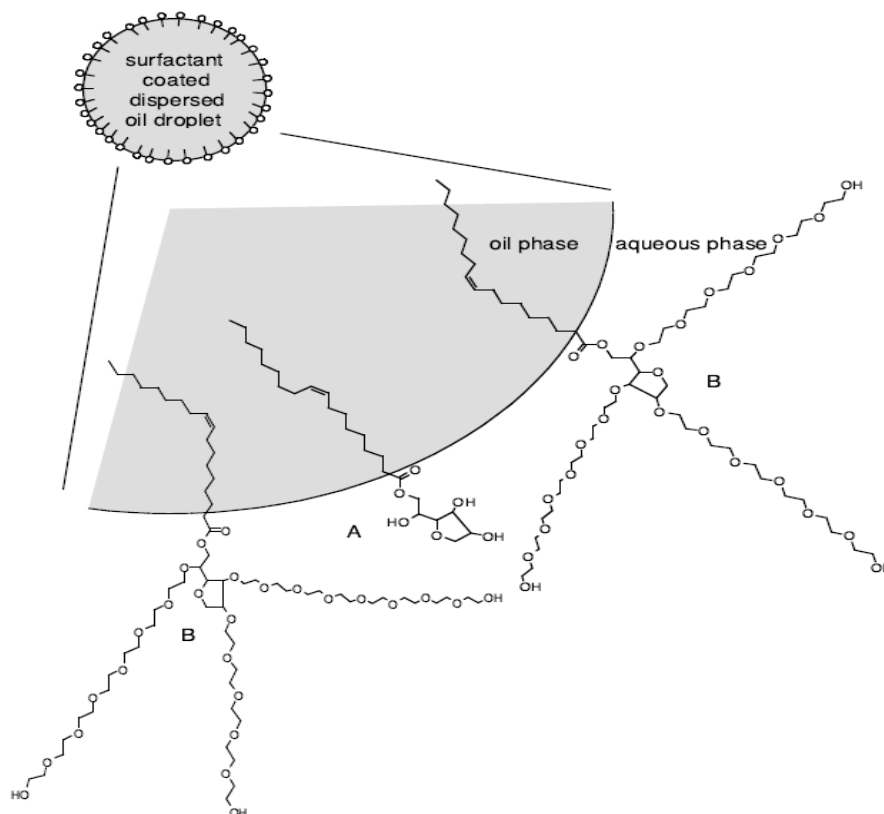
Figure 2. Dispersion of an oil slick using a chemical dispersant



Schematic from [5].

While the exact chemical composition of most commercially available dispersants is proprietary, the chemical properties of the surfactants used in such dispersants are known. Dispersants contain a mixture of nonionic (no chemical charge) or anionic (negatively charged) surfactant molecules [5]. Using a mixture of surfactants allows for close packing of surfactants around an oil droplet, allowing for stable droplet formation. The chemical composition of the Corexit dispersants, the only dispersants to have ever been used in a spill response in the United States, is known [23]. Figure 3 shows an example of surfactant packing along an oil droplet using two of the surfactants in Corexit.

Figure 3. Schematic of nonionic surfactant molecules aligned on the surface of an oil droplet in water



Surfactant "A" is sorbitan monooleate (a.k.a. Span 80) and surfactant "B" is ethoxylated sorbitan monooleate (a.k.a. Tween 80). Both surfactants are components in the Corexit dispersants [5].

After oil is dispersed as droplets through the water column, the hope is that it will be degraded by a process known as biodegradation. Biodegradation involves the degradation of oil by naturally occurring micro-organisms present in marine environments. Bioremediation refers to the addition of fertilizers or other agents to accelerate the rate of biodegradation. The environmental impacts from the Exxon Valdez and BP Deepwater Horizon spills were reduced as a result of bioremediation and subsequent biodegradation following dispersant application [24][25].

The use of dispersants in large-scale spill remediation, however, remains highly controversial. Some surfactants are toxic. A study in 2013 by Almeda and others found that dispersant-treated crude oil was more toxic to zooplankton than fresh oil [26]. Some argue that

the application of dispersants causes more environmental problems than it solves [27]. Despite this controversy, the development of dispersants for spill remediation is ongoing, and dispersants are used to clean up oil spills worldwide.

## Measure of dispersant effectiveness

Several tests, ranging from bench-scale flask tests to large-scale field trials, estimate the effectiveness of dispersants. Each test has its own measurement of “effectiveness.” In this report, we will define dispersant effectiveness as chemical effectiveness, the metric used in most tests. Chemical effectiveness is the amount of oil that the dispersant displaces into the water column (or aqueous phase of a lab-scale test) compared with the amount of oil remaining on the surface slick (see equation 1).

$$\text{Effectiveness (percent)} = \frac{\text{Amount of Oil in Water Column}}{\text{Initial Amount of Oil in Slick}} * 100 \quad (1)$$

Dispersant effectiveness depends on such factors as oil composition, oil properties, and the spill environment (temperature, wave turbulence, sea salinity, etc.). The type of experiment used also influences effectiveness data (different outcomes will be achieved in a swirling flask test and a large-scale wave tank, for example). The pros and cons of using different test protocols, and the discrepancies between different test protocols, have been reviewed elsewhere [5][12][28]. We focus this literature review on the dispersants listed on the EPA NCP product schedule. We make note of the test(s) used to determine effectiveness, with the understanding that lab-scale tests are not usually indicative of performance at sea.

## Influence of oil properties on dispersion

A few oil properties, including viscosity and chemical composition, usually determine the effectiveness of chemical dispersion. Dispersants are most effective immediately after a spill and become less effective as oil weathering alters the properties of the oil, decreasing its dispersibility [20]. Operational parameters (e.g., dispersant droplet size, dispersant concentration, and mixing energy) also factor into the effectiveness of chemical dispersion.

To predict the most effective time to apply dispersants in an oil spill, both oil weathering and dispersant effectiveness as a function of oil viscosity must be understood. The chemical composition of oil will predict both its initial dispersibility and its weathering behavior over time. The viscosity increase of oil over time depends on the spill conditions and elapsed time after the spill. Combining oil weathering dynamics with dispersant effectiveness studies enables the prediction of dispersant performance in a spill.

### Viscosity

Oil viscosity is possibly the most important factor influencing oil dispersibility. Many studies concluded that there exists an upper viscosity limit, above which oil becomes undispersible. This upper viscosity limit for dispersibility is oil dependent (some oils have a higher viscosity limit than others), but, for all oils, dispersibility decreases with increasing viscosity. One rule of thumb is that optimal dispersibility is achieved when viscosity is less than 2,000 cSt, and dispersion is impossible when viscosity becomes greater than 10,000 cSt [28]. Table 4 compares the viscosity limits with dispersion for two different types of crude oil, illustrating a typical relationship between oil viscosity and dispersibility.

Table 4. Crude oil dispersibility as a function of viscosity and oil type

	Viscosity range (cP)		
	Dispersible	Reduced dispersibility	Not dispersible
Alaska North Shore (ANS) Crude	< 1000	1000 – 10,000	> 10,000
Bonnie Light Crude	< 500	500 – 2,000	> 2,000

Dispersibility data as reported in [20]. Dispersibility was tested using the Mackay, Nadeau, Steelman (MNS) lab test method. The dispersants used in the test were not specified in the report. Dispersant effectiveness ranges follow: dispersible (>70 percent effective), reduced dispersibility (5 to 70 percent effective), and not dispersible (<5 percent effective).

### Oil composition

While viscosity is universally reported as a property that influences dispersion (higher viscosity is almost always correlated with low dispersibility), reports on oil composition are less concrete. Studies have

evaluated the impact of oil composition on dispersibility, but the results are highly dependent on the particular dispersant used and the oil type evaluated.

Crude oil components—including SARA—were studied for their influence on dispersibility. Some studies found that the inherent SARA contents of oil influenced its dispersibility (saturate contents increased dispersibility, and aromatic, polar, and asphaltene contents decreased dispersibility) [28].

Fingas and others conducted the most comprehensive work on the effects of oil composition on dispersibility in 2003 [29]. They developed a series of 13 mathematical models correlating dispersibility with Corexit 9500 with oil composition. The oil properties most strongly correlated with dispersibility were the content of C12 to C18 hydrocarbons, C26 hydrocarbons, and naphthalenes. In his textbook, Fingas suggests that the carbon number of hydrocarbons in crude oil (hydrocarbon chain length) is a good predictor of its dispersibility. Specifically, small hydrocarbons (up to C20) are dispersible, whereas large hydrocarbons (larger than C20) usually are not. He suggests that the composition of C12 and C14 hydrocarbons in crude is a very good predictor of its inherent dispersibility. We are not aware of any other work that has confirmed or further investigated these findings.

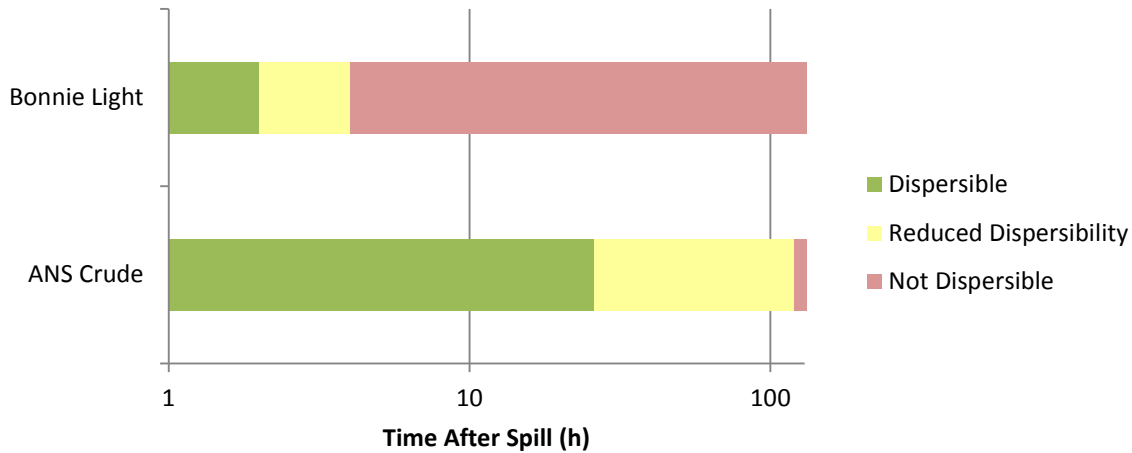
While the chemical composition of oil may be correlated to its dispersibility, this is probably due to the influence of chemicals on oil weathering rather than their direct involvement in the chemical dispersion process [12][28]. Since waxes promote oil emulsification, oils with high wax content probably have low dispersibility [28]. Rather than directly influencing chemical dispersibility, wax content influences oil weathering and emulsification. One study by SL Ross Environmental Research identified a set of three oil properties (sulfur, saturate, and wax content) that could be used in a modeling approach to predict oil dispersibility [30].

### **Oil weathering**

More important to dispersibility than oil composition is its degree of weathering and emulsification. As oil weathering occurs, viscosity increases, and dispersants become less effective over time. The effect of oil weathering on the dispersibility of two crude oils was estimated by Nordvik using an oil weathering model, demonstrating a decrease in

dispersibility over time after a spill, as shown in figure 4 [20]. While both types of crude in this study show decreased dispersibility over time, the rate at which they become undispersible is different. This result shows that the so-called window of opportunity for dispersant use depends on the unique weathering behavior of the spilled oil.

Figure 4. Dispersibility of crude oil as a function of weathering



Dispersibility data replotted from [20]. The dispersants used in the test were not specified in the report. Dispersant effectiveness ranges were defined as follows: dispersible (>70 percent effective), reduced dispersibility (5 to 70 percent effective), and not dispersible (<5 percent effective). Oil weathering for Bonnie Light and ANS crude was predicted using the IKU Oil Weathering Model assuming 5 m/s wind speed and seawater temperature of 15 °C.

The weathering behavior of oil depends on its chemical composition and on the spill conditions (wind speed, temperature, water salinity, etc.). Computational weathering models exist to predict the weathering behavior of specific oils over time and may be used to predict windows of opportunity for chemical dispersant use. One model, developed by SINTEF in Norway, accurately predicted the weathering behavior of crude oil in full-scale field trials. These modeling results were used to predict the dispersibility of several crude oils based on their weathering behavior and viscosity changes over time [7]. ADIOS software (developed by NOAA) is available free of charge on the internet and has utility in determining the window of opportunity for dispersant use in a spill environment [8]. The most recent version of ADIOS was developed using industry standard or peer-reviewed algorithms. Anecdotal evidence from modeling small spills suggests that

ADIOS provides reasonable agreement with oil behavior in a field setting [31].

The use of chemical agents, including dispersants, in a spill response requires approval from the federal government. In the United States, the EPA maintains a National Contingency Plan product schedule of commercially available chemical agents, including dispersants, which might be approved for use during a spill response. Inclusion on the EPA NCP schedule does not mean that a chemical is preapproved for use in a spill response. In a spill, appropriate government approval (state or federal) is required before dispersants may be used. Those products on the EPA NCP schedule are candidates for such approval.

There are 18 dispersants listed on the EPA NCP product schedule (published in May 2013) [32]. Table 5 lists the commercial name and manufacturer of the dispersants on the schedule.

Table 5. Dispersants on the EPA NCP product schedule (as of May 2013)

<b>EPA Bulletin number</b>	<b>Commercial name</b>	<b>Manufacturer</b>	<b>Documented use in spill response</b>
D-1	Corexit EC9527A	Nalco Environmental Solutions	YES (U.S., international, several uses)
D-2	Neos AB3000	NEOS Company Ltd	YES (Japan, 2006)
D-3	Mare Clean 200	Taiho Industries Co. Ltd.	-
D-4	Corexit EC9500A	Nalco Environmental Solutions	YES (U.S., international, several uses)
D-5	Dispersit SPC 1000	U.S. Polychemical Corp.	-
D-6	JD-109	GlobeMark Resources	-
D-7	JD-2000	GlobeMark Resources	-
D-8	Nokomis 3-F4	Mar-Len Supply	-
D-9	Biodispers	Petrotech America	-
D-10	Sea Brat #4	Alabaster Corp.	-
D-11	Finasol OSR 52	Total Fluides	YES (France, 1991)
D-12	Saf-Ron Gold	Sustainable Environmental Technologies	-
D-13	ZI-400	Z.I. Chemicals	-
D-14	Nokomis 3-AA	Mar-Len Supply	-
D-15	Supersperse WAO2500	Baker Petrolite Corporation	-
D-16	Accell Clean DWD	Advanced Biocatalytics Corporation	-
D-17	FFT Solution	Fog Free Technologies	-
D-18	Marine D-Blue Clean	AGS Solutions	-

The documented use of dispersants in spill response was from Fingas, taken from a list of spill responses from 1966 through 2009 [12].

The Corexit dispersants are the only ones on the schedule to have documented use in a spill response in the United States, having been used in many spills, including the Exxon Valdez oil spill (Corexit 9527) and the BP Deepwater Horizon spill (Corexit 9500). A few other dispersants on the schedule have documented use in spill responses internationally (as noted in table 5).

The active ingredients and formulation of most dispersants on the schedule are proprietary and not publicly available. For the Corexit dispersants (Corexit EC9527A and Corexit EC9500A), however, the compositions are published (see table 6). There are three nonionic active surfactants in Corexit (Span 80, Tween 80, and Tween 85), and the rest of the ingredients in the formulation either are solvents or additives. A schematic showing the interaction of Corexit surfactants with an oil droplet is shown in figure 2. While the active ingredients of the other dispersants on the EPA NCP schedule are not publicly known, it is believed that most dispersants use a similar mixture of anionic or nonionic surfactants that probably function as they do for Corexit. Cationic surfactants are not used as oil spill dispersants because they often contain quaternary ammonium salts that are inherently toxic to many organisms [5].

Table 6. Chemical components of Corexit 9527 and 9500 dispersants

CAS registry number	Chemical name	Alternate name	Notes
57-55-6	1,2-Propanediol	Propylene glycol	Solvent
111-76-2	Ethanol, 2-butoxy-	2-Butoxyethanol	Solvent, only in Corexit 9527
577-11-7	Butanedioic acid, 2-sulfo-, 1,4-bis(2-ethylhexyl) ester, sodium salt (1:1)	Aerosol OT	Additive
1338-43-8	Sorbitan, mono-(9Z)-9-octadecenoate	Span 80	Active nonionic surfactant
9005-65-6	Sorbitan, mono-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) derivs.	Tween 80	Active nonionic surfactant
9005-70-3	Sorbitan, tri-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) derivs.	Tween 85	Active nonionic surfactant
29911-28-2	2-Propanol, 1-(2-butoxy-1-methylethoxy)-	-	Solvent
64742-47-8	Distillates (petroleum), hydrotreated light	Exxol D80 Fluid	Solvent

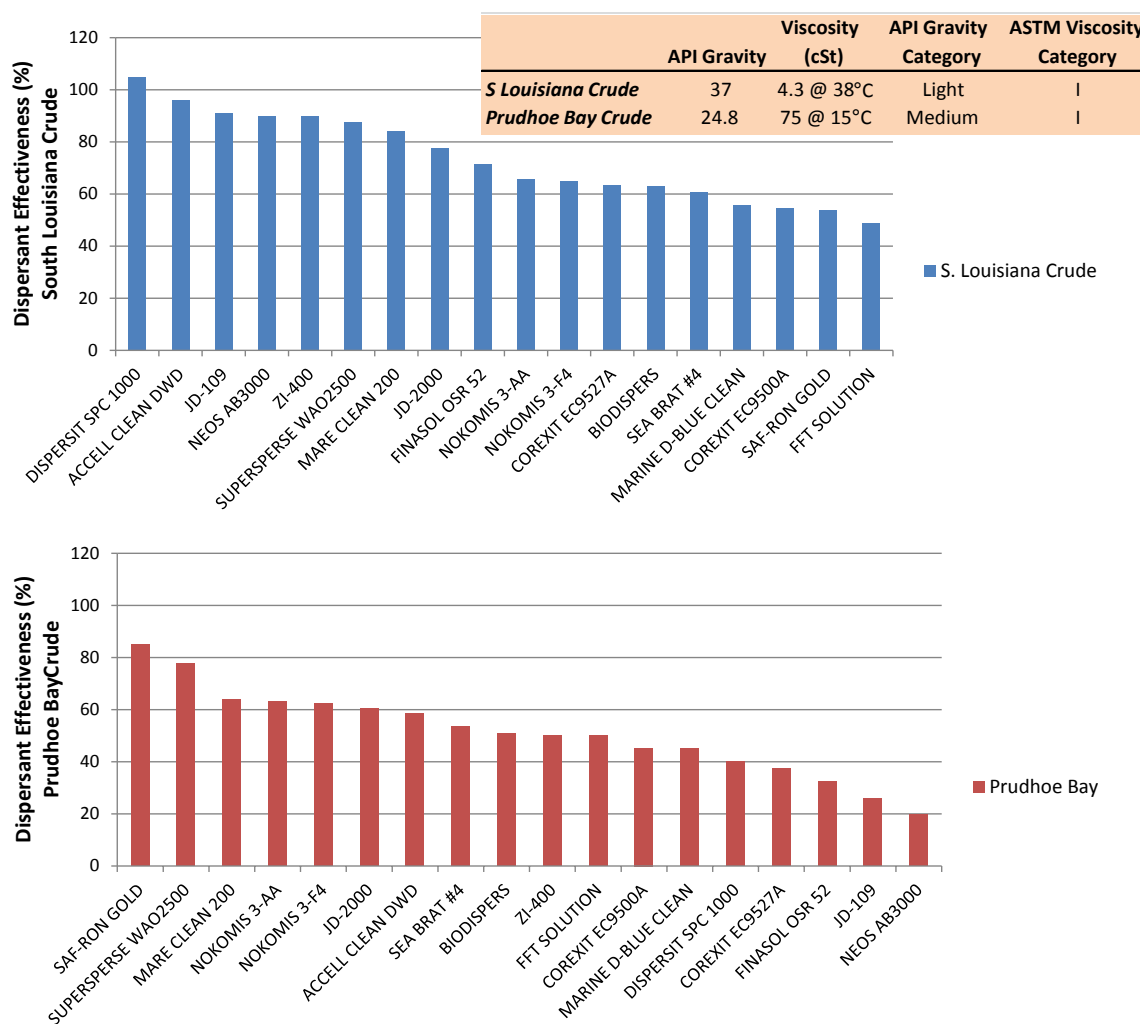
This list of the chemical components in Corexit is available on the EPA's website: [33].



### Manufacturer-reported dispersant effectiveness

To be included on the NCP list, the EPA requires manufacturers to submit effectiveness data for the dispersion of two types of oil (South Louisiana Crude and Prudhoe Bay Crude) using the swirling flask test, a standard laboratory-scale performance test [34]. For inclusion on the list, dispersants must have an average effectiveness of at least 45 percent for both test oils using the swirling flask laboratory test. The manufacturer-reported effectiveness data for the dispersants on the EPA NCP list are displayed in figure 5.

Figure 5. Manufacturer-reported effectiveness of EPA NCP dispersants using the swirling flask test



Data as reported to the EPA on the NCP product schedule technical specifications.

On average, the dispersants were more effective for the dispersion of South Louisiana Crude (74 percent average effectiveness) than for Prudhoe Bay Crude (51 percent average effectiveness) oil. Only one dispersant, Saf-Ron Gold, reported higher efficiency in Prudhoe Bay Crude. This result is consistent with most literature stating that chemical dispersion is most effective in oils with low viscosity (South Louisiana Crude is less viscous, 4.3 cSt @ 38 °C, than Prudhoe Bay Crude, 75 cSt @15 °C). Both crude oils used in this test are ASTM category “I” viscosity oils (the lowest viscosity category in ASTM standards as shown in table 1). If more viscous or emulsified crudes were used in the test, the dispersants would probably have decreased effectiveness.

Without knowing the formulations of the dispersants tested, it is impossible to make any conclusions about why certain formulations were more effective than others. Instead, in the subsequent sections, we will compare data reported to the EPA by the dispersant manufacturers to other independent effectiveness test reports on these dispersants.

#### **Independent dispersant effectiveness studies**

We identified independent studies that compared the relative effectiveness or toxicity of dispersants on the EPA NCP schedule side-by-side in bench-scale, wave-tank scale, and field tests. In 2010, following the Deepwater Horizon oil spill, BP conducted a series of three studies to evaluate the dispersants on the EPA NCP product schedule to comply with regulatory directives from the EPA in response to the spill [35][36][37]. These studies included effectiveness tests for the ability to disperse MC 252 crude oil. BP assessed effectiveness using bench-scale (swirling flask and Exxon dispersant effectiveness test (Exdet)), wave-tank, and field tests to compare dispersants. Another independent study was conducted by Venosa and Holder, in which eight dispersants on the EPA NCP product list were compared using the baffle flask bench-scale test [38]. Only those tests that compared more than one EPA NCP dispersant were included in this summary. (Note: Several independent studies have compared the environmental toxicity of the EPA NCP dispersants, but toxicity studies were not analyzed as part of this report.)

### **Analysis of EPA NCP dispersant studies**

Our analysis of the literature available on the EPA NCP dispersants resulted in two comparisons:

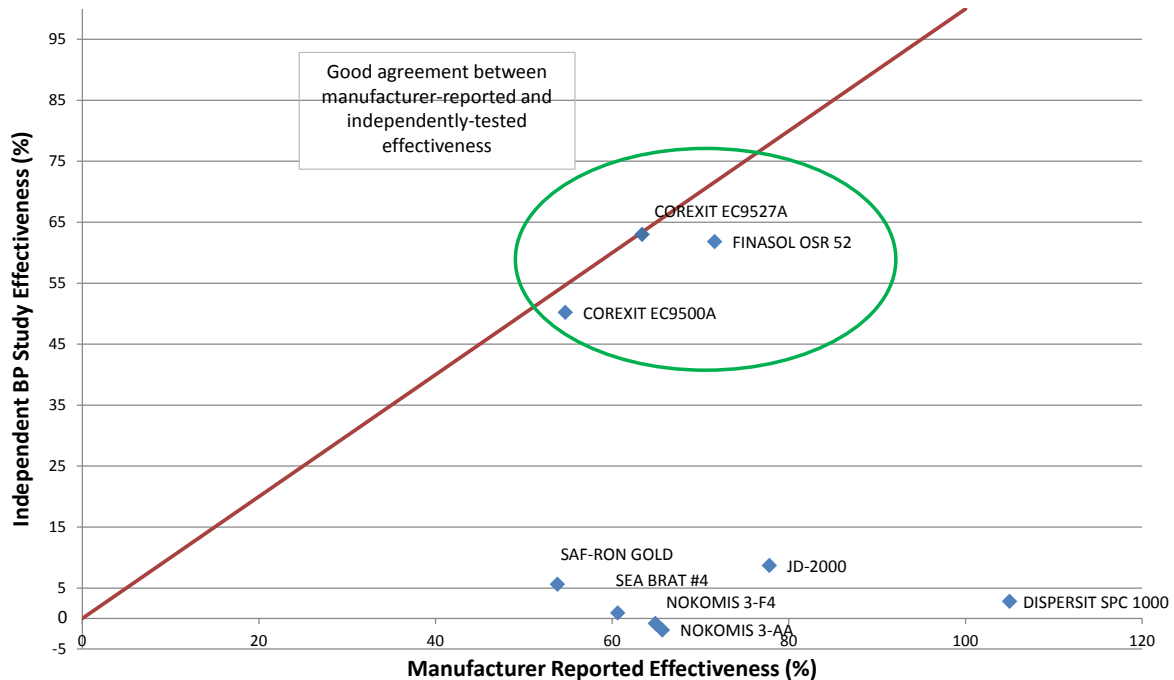
1. Comparison of manufacturer-reported and independently determined dispersant effectiveness
2. Comparison of dispersant performance in lab-scale tests (bench and wave tank) and performance in field trials

*Comparison 1: Manufacturer vs. independent effectiveness tests.* While inclusion on the EPA NCP product schedule requires that dispersant manufacturers report effectiveness data using a standard laboratory test, it is difficult (if not impossible) to compare data collected in different laboratories at different times. We wanted to determine whether the effectiveness data reported by dispersant manufacturers were consistent with data derived from independent studies. To this end, we compared the swirling flask effectiveness data reported to the EPA for the dispersion of South Louisiana Crude Oil (figure 5) with the swirling flask effectiveness data reported by BP in its testing of nine dispersants on the EPA NCP schedule [36]. BP used Mississippi Canyon Block 252 (MC252) crude oil in its study. While different test oils were used in the two data sets, they are both from the Gulf of Mexico region and have similar physical properties. South Louisiana Crude has an API gravity of 37°, and MC252 has an API gravity of 40°, both of which are considered “light” oils according to API standards [39]. We expect that the ability of dispersants to disperse South Louisiana Crude should be similar to their ability to disperse MC252.

A parity plot comparing the manufacturer-reported data with the BP-collected data is displayed in figure 6. Of the nine dispersants shown in both datasets, only three (Corexit 9527, Corexit 9500, and Finasol OSR) actually performed as well in BP’s testing as reported by the manufacturer to the EPA. The rest of the dispersants were less effective in BP’s testing than reported by the manufacturer. In addition, the performance threshold for inclusion on the EPA NCP product schedule is 45 percent effectiveness using the swirling flask test. According to the independent BP study comparing the dispersants side by side, only the Corexit products and Finasol OSR would meet the threshold for inclusion on the schedule. All other dispersants performed with effectiveness of less than 10 percent in the BP testing,

and many demonstrated no appreciable dispersion compared with the control (MC252 oil without dispersant, 0.5 percent dispersion).

Figure 6. Correlation between manufacturer-reported and independently tested dispersion using the swirling flask test



Manufacturer effectiveness as listed on the EPA NCP product schedule for the dispersion of South Louisiana Crude. The independent BP study (volume 2) is using the swirling flask test for the dispersion of MC252 oil, where all dispersants were compared side by side in a single experiment.

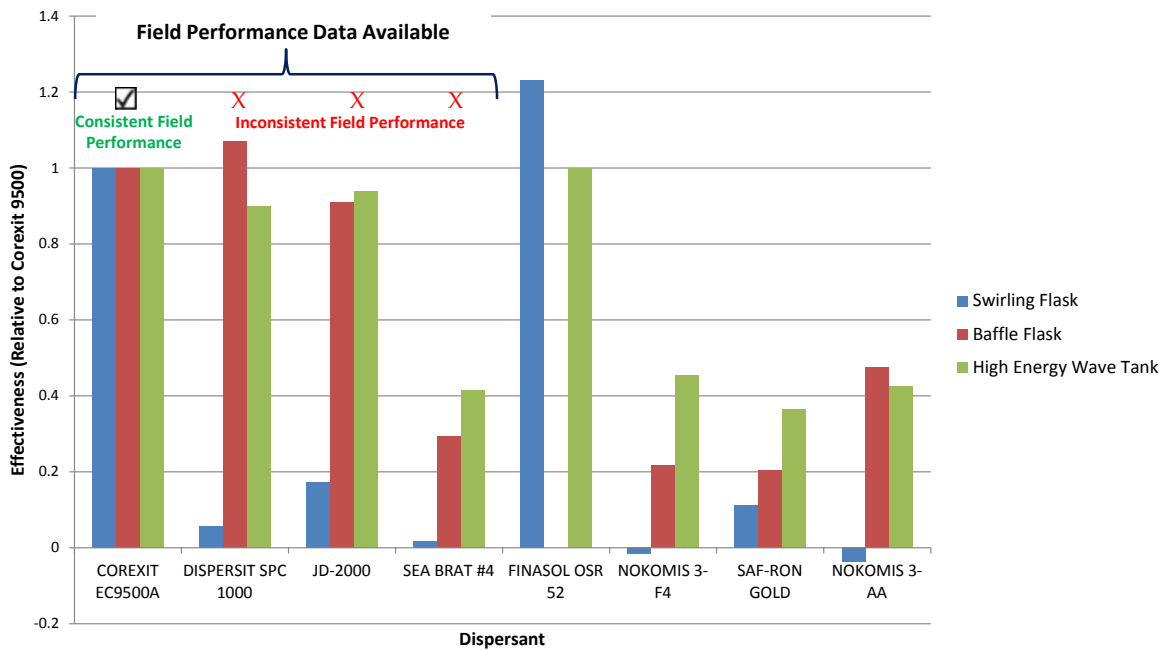
*Comparison 2: Correlation between lab-scale and field performance.* Lab-scale tests are useful for comparing the relative effectiveness of several dispersants side by side. The “percent effectiveness” derived from lab-scale tests does not translate to performance in the field. Lab tests are also useful in determining which dispersants might perform better in a spill response. Field trials are the best indicator of how well a dispersant will perform in a spill response; however, the unpredictable, uncontrollable field environment prohibits controlled experiments from being performed. In the field, results tend to be more qualitative than “percent effectiveness” by reporting “dispersion” or “no dispersion” of an oil slick using a particular dispersant.

We compared the performance of eight dispersants using the swirling flask test for MC252 crude (low-energy bench-scale test) [36], the baffle flask test for South Louisiana Crude (high-energy bench-scale test) [38], and a high-energy wave tank test (high-energy meso-scale test) for MC252 crude [35]. In our analysis, we reported performance on a normalized basis, comparing effectiveness with that of Corexit 9500. Quantitative effectiveness values cannot be directly compared from different tests, but relative effectiveness *can* be compared. In figure 7, we compare the performance of eight dispersants in three laboratory tests (swirling flask, baffle flask, and high-energy wave tank tests). For four of those dispersants (Corexit 9500, Dispersit SPC 1000, JD-2000, and Sea Brat #4), qualitative field test data were available. In the figure, we indicate whether field trials using those four dispersants were reported as “consistent” or “inconsistent.” Corexit 9500 was the only dispersant of the eight tested to demonstrate good performance in all three laboratory tests and to perform consistently well in field tests.

This analysis suggested that dispersants that performed well in the field will probably perform well in all of the laboratory tests. The only dispersant that had consistently good performance in the BP field test was Corexit 9500. Corexit was also the only dispersant to perform well in all three other independent tests (swirling flask, baffle flask, and wave tank). The other dispersants that were tested in the field (Dispersit, JD-2000, and Sea Brat) yielded inconsistent results in the (they demonstrated dispersion in some tests, and not in others). The dispersants with inconsistent field results had poor performance in the low-energy swirling flask test (Sea Brat did poorly in all three laboratory tests). This suggests that, if a dispersant is going to be effective in the field, it will probably be effective using other experimental tests, regardless of scale or mixing energy.

Finasol OSR performed as well as Corexit in the laboratory-scale tests. Finasol was the only dispersant to perform as well as Corexit in both the swirling flask and wave tank tests (Finasol was not tested using the baffle flask). We did not find recent reports of field effectiveness testing using Finasol OSR (a few field trials of “OSR 5” and of “Finasol” were recorded in the 1980s and 1990s [12], but we could not verify whether these were the same formulation as the “Finasol OSR” listed on the EPA NCP schedule). We recommend Finasol OSR as a candidate for additional field testing.

Figure 7. Dispersant performance across independent bench, wave tank, and field tests



Data derived from multiple sources. Swirling flask data from [36], the baffle flask data from [38], and the high energy wave tank data from [35]. All data are reported in a normalized fashion, showing the effectiveness of each dispersant relative to Corexit 9500.

## Summary of dispersants

We divide our summary points into two groups:

### 1. General dispersant performance

- Oil viscosity is a reasonable, single indicator of the effectiveness of chemical dispersion. Oils are most dispersible when their viscosity is less than 2,000 cSt, and they become undispersible when viscosity reaches ~10,000 cSt.
- The effectiveness of chemical dispersants decreases with time after a spill. As time progresses, oil becomes weathered, and its viscosity increases. Computational oil weathering software is a useful tool to predict the weathering behavior of various crude oils.
- Oil composition influences its dispersibility, primarily by influencing its weathering dynamics. Oil composition (such as the content of short and long-carbon chain hydrocar-

bons) may dictate the “starting dispersibility” of oil. Other factors, such as SARA and wax content, influence the weathering dynamics of oil, thus determining its viscosity changes (and decreased dispersibility) over time.

- An understanding of both oil weathering behavior and dispersant performance across a range of oil properties is essential to predicting dispersant performance in an oil spill.

## 2. EPA NCP dispersant literature

- Only three dispersants on the EPA NCP product schedule (Corexit 9500, Corexit 9527, and Finasol OSR) performed as well in independent effectiveness tests as they did in tests conducted by the product manufacturers and reported to the EPA. Of the eighteen dispersants listed on the EPA NCP product schedule, nine were evaluated in independent tests.
- Corexit 9500 is the only dispersant among those tested in the field to demonstrate consistent dispersion of oil slicks in field tests. Corexit 9500 was also the only dispersant among those tested to effectively disperse oil in three types of independent laboratory tests (swirling flask, baffle flask, and wave tank tests). This suggests that good performance in all types of laboratory testing might indicate that a dispersant will perform well in the field.
- Finasol OSR was the only dispersant to demonstrate effectiveness equal to that of Corexit in independent laboratory tests. Since limited field trial data are available for Finasol OSR, it would be beneficial to conduct additional field tests on Finasol OSR to determine whether its performance in the field is consistent with its laboratory effectiveness.

## Research recommendations for dispersants

First, we recommend that targeted testing on the impact of oil composition (C12-C14, SARA, wax content) on dispersion be conducted for commercially available dispersants of interest. Because dispersant effectiveness is highly dependent on dispersant chemistry, it is necessary to develop guidelines specific to particular dispersants. Most of the existing studies have only evaluated the effect of oil properties on dispersion using Corexit 9500. We believe that a library of dispersant

effectiveness data for critical oil properties will allow for the most effective selection of a dispersant in a time-dependent spill scenario.

Second, we recommend that additional large-scale field testing be conducted of Finasol OSR. Data from our literature search suggest that Finasol OSR may perform as well as Corexit in field trials. We believe that additional field testing on Finasol OSR is warranted and that its effectiveness should be compared to Corexit, a commercially available standard.

## Skimmers

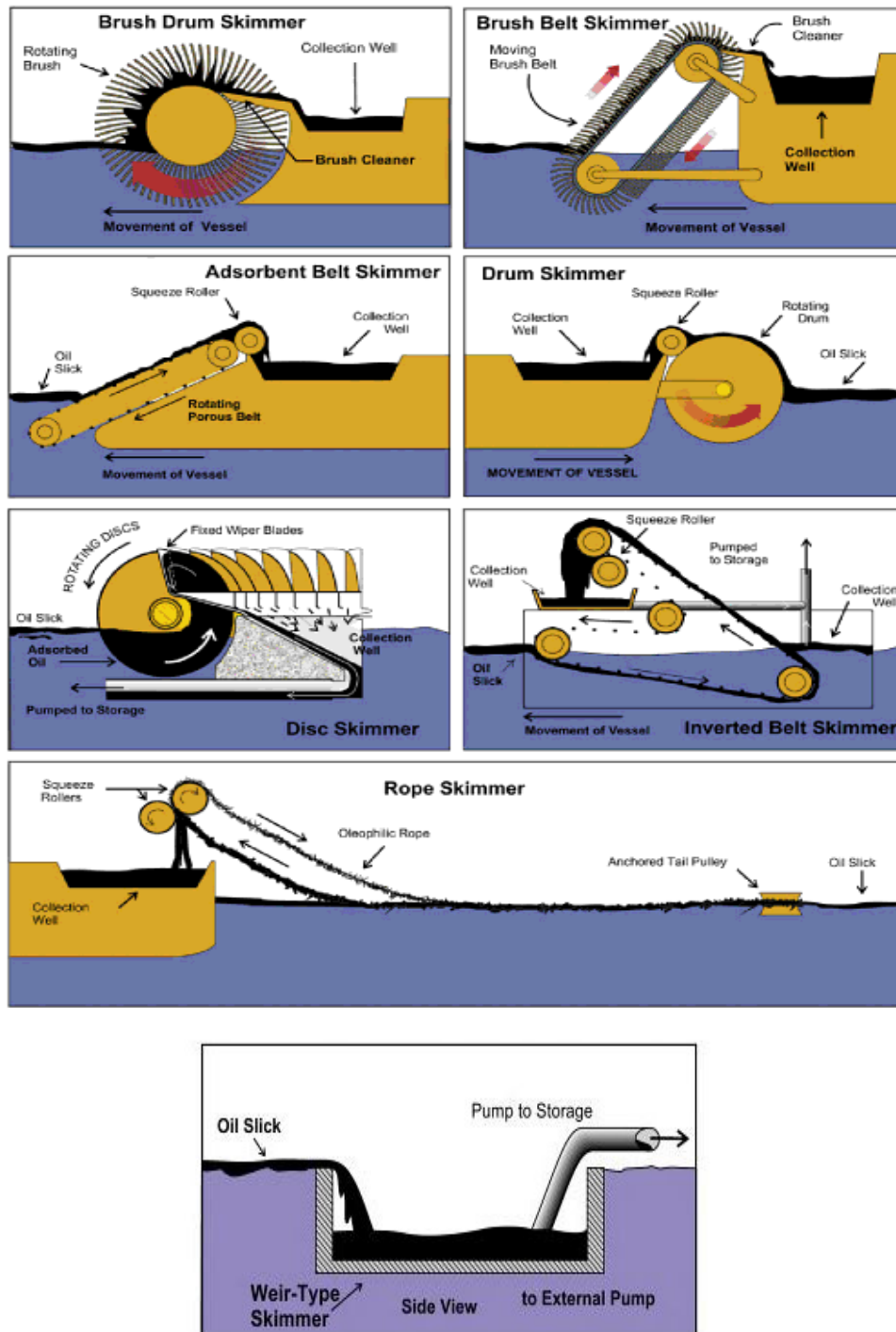
### Description of skimmers

Skimmers physically separate oil from water without the introduction of chemical agents. Due to the relative lack of environmental concerns with skimmers (compared with dispersants or in situ burning), skimmers are commonly used in oil spill cleanup. In the 2010 Deepwater Horizon oil spill, an estimated 3 percent (~147,000 bbl) of spilled oil was recovered by skimmers, when approximately 60 to 80 skimmers operated on a daily basis during cleanup operations [40].

Unlike dispersants, there is no chemical interaction between skimmers and oil. Skimmers separate oil from water using one of two principles. On one hand, “oleophilic skimmers” employ oil-attracting coatings on the surface of a drum, brush, or other shape to physically attract and separate oil from the underlying water. “Weir skimmers,” on the other hand, use gravity to separate oil from water. Figure 8 presents schematics illustrating the operating principles of oleophilic and weir skimmers.



Figure 8. Schematics of oleophilic and weir oil skimmers



Oleophilic skimmers (top seven panels) operate using an oil-attractive surface to attract and separate oil from water. Weir skimmers (bottom panel) use gravity to separate an oil slick from the underlying water. These figures were reprinted from [12] with permission from Elsevier.

Additional factors influencing the performance of skimmers are the volume of oil spilled, the spill environment (open or protected water), the sea state, presence of debris or ice, and the properties of the spilled oil. Hundreds of different skimmers by many different manufacturers are available to address the wide variety of potential spill conditions. In a spill, however, the selection of a suitable skimmer depends not only on the spill conditions, but also on the availability of skimmer equipment at the time and location of the spill. In the subsections that follow, we will summarize available performance tests of oil spill skimmers and will make recommendations about selection of skimmers based on technical performance tests. We will exclude equipment availability at the site of the spill in our analysis of skimmer performance.

## Measure of skimmer performance

Standard measures of effectiveness to characterize skimmer performance were developed by ASTM and were most recently reapproved in 2008 [41][42]. The most commonly reported performance metrics are defined below:

- Oil recovery rate (ORR). The volume of oil recovered by the device per unit time ( $\text{m}^3/\text{hr}$ ).
- Recovery efficiency (RE). The ratio, expressed as a percentage, of the volume of oil recovered to the volume of total fluids recovered (percent).
- Throughput efficiency (TE). The ratio, expressed as a percentage, of the volume of oil recovered to the volume of oil encountered (percent).

While ASTM published standards for the collection and description of skimmer performance, very few standardized test reports for oil spill skimmers are published or publicly available. Government and privately owned facilities are equipped to conduct skimmer performance tests. These include the National Oil Spill Response Research & Renewable Energy Test Facility (OHMSETT) in Leonardo, New Jersey;<sup>2</sup> SINTEF Materials and Chemistry Ice Basin in Trondheim,

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2. This study was sponsored by the Department of the Interior's BSEE, which oversees the OHMSETT testing facility.

Norway; and the SL Ross Test Tank in Ottawa, Ontario, Canada. While skimmers are tested at these facilities, few efforts have been made to compile and publish skimmer test results from various facilities. The single, most comprehensive report summarizing independent skimmer test reports from many facilities was published in 1998 by Robert Schulze [43]. In this report, Schulze provided a detailed summary of independent skimmer performance tests, most of which were conducted in the 1970s. The comprehensive analysis performed by Schulze resulted in many skimmer selection guidelines and rules of thumb that are widely cited in spill literature and used to develop spill cleanup plans. Here, we will first summarize the conclusions from Schulze's report and then will report on skimmer performance test reports that have become available since the publication of his report.

## **Skimmer performance**

### **ASTM performance tests**

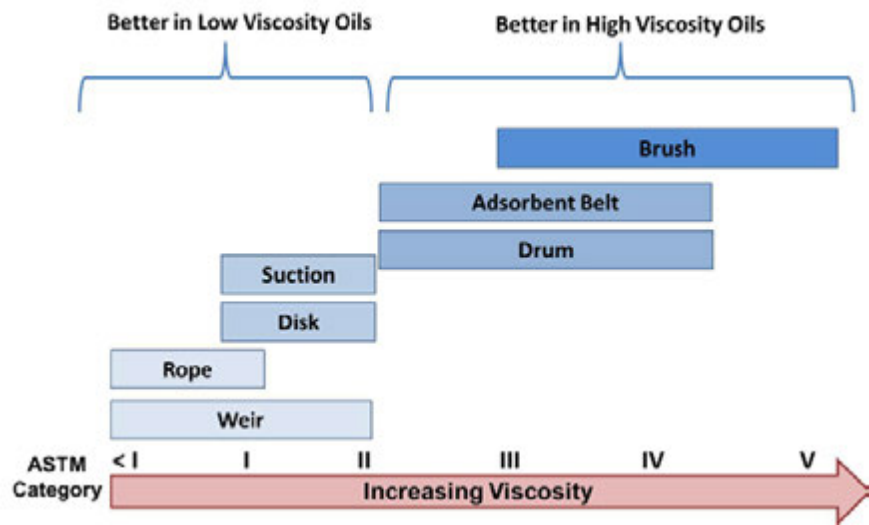
Schulze's report provides detailed skimmer test data from numerous, independent tests over more than 20 years. The inherent variability in available test data (tests performed on different skimmers, at different facilities, at different times) makes it difficult, if not impossible, to draw quantitative conclusions about skimmer performance. We summarize the test data available in Schulze's report in table 7. While quantitative values from this report (percent efficiency and ORR) are probably not predictive of skimmer performance in a spill, the relative performance of skimmers in various oil types is valuable to identifying an appropriate type of skimmer to use in a spill.

In figure 9, we display the most effective type of skimmers as a function of ASTM viscosity. This represents our own interpretation of the data presented in Schulze and is generally consistent with other reports summarizing skimmer effectiveness [12][44][45].

Table 7. Summary of skimmer performance testing reported in Schulze, 1998

Skimmer type	Manufacturers tested	Oil types tested (ASTM viscosity category)	Performance notes
<b>Oleophilic</b>			
Disk	Prototype, manufacturer not reported	- Refined (< I), I, I-II - Emulsified refined products	- High efficiency (>90 percent) reported in refined and light products - Decreased efficiency with oil emulsification
Drum	OSR Systems, Elastec	- I, I-II, II-III	- High efficiency (>90 percent) reported in all oils tested - Better performance with increasing viscosity (best performance in category II-III oils) - Improved recovery with thick oil slicks (slicks up to 40 mm tested)
Adsorbent belt	MARCO	- I, I-II, II-III - Emulsion (70 percent emulsion of category II-III oil)	- High efficiency (>90 percent) in more viscous oils (best performance in category II-III) - Efficiency maintained (>90 percent) in highly emulsified (70 percent) oil
Brush	Lori (fine and coarse brush models)	- Refined (< I), I-II, III, IV, V	- Not effective in refined products (category < I) - Shows high efficiency and recovery rates in viscous oils (up to category V)
Rope	Crowley, Oil Mop	- Refined (<I), II	- Effective in light, refined products (category <I) (efficiencies 80-99 percent reported) - Decreased effectiveness reported in heavier, emulsified oil (category II)
<b>Weir</b>	Acme, SlimPak, Lamor, Hydrovac, Desmi, Bohus (stationary and advancing models tested)	- Refined (<I), I-II, II, II-III, V	- Best efficiency reported in light oils (up to category II). Tests in heavier oils (category II-III and V) generally showed decreased efficiency. - Performance affected by waves (calm water is best)
<b>Suction</b>	Slickbar	- I-II, II	- Best performance in lightest oils tested (category I-II) - Variable performance across tests. Devices prone to clogging and air intake.
<b>Submersion plane</b>	U.S. Navy devices (fixed and moving plane models)	- Refined (<I)	- Only light, refined products tested for U.S. Navy spills - Requires calm water

Figure 9. Most effective skimmer types to clean oil of varying viscosity



The oil type (by ASTM viscosity category) in which each type of skimmer is most effective. According to our interpretation of data reported in Schulze [43].

### SINTEF tests

SINTEF conducted a series of experiments to evaluate several skimmers from 2008 to 2010 [46] [47] [48] [49] [50]. The objective of SINTEF's testing was to document the capability and potential of commercially available skimmers for recovering oil on ice. SINTEF evaluated skimmers (drum, brush, rope, mop, and weir) from different manufacturers (Desmi, Lamor, and Framo). All tests were conducted using IF-30 bunker oil (ranging from 5,000 to 8,000 cP, ASTM category II–III). Tests were conducted in an ice basin tank owned by SINTEF; some field tests in the Barents Sea were also executed for the most promising skimmers. In addition to evaluating existing commercial skimmers, SINTEF worked with the manufacturers of the most promising models to develop customized skimmers optimized for oil recovery from ice.

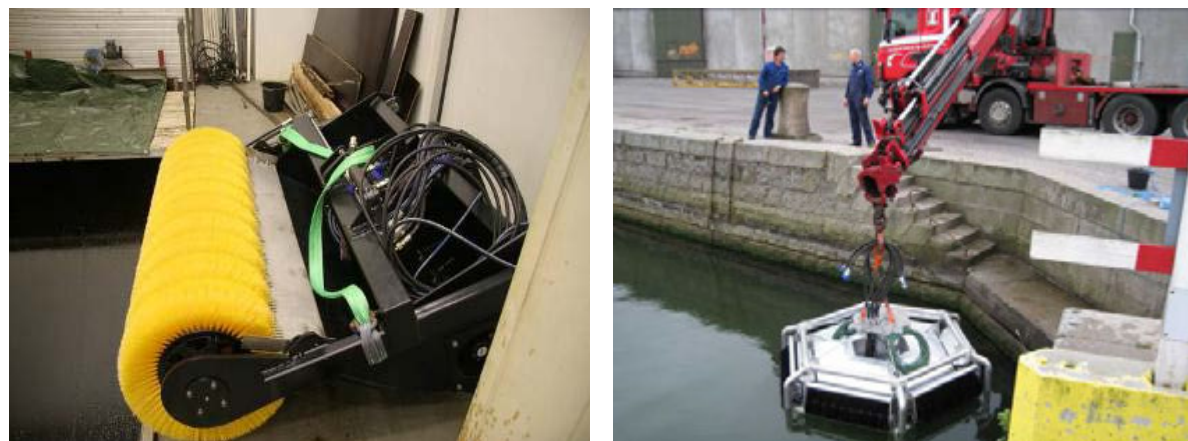
The skimmer tests conducted by SINTEF are summarized in table 8. These targeted experiments identified highly effective skimmers for the spill environment (arctic conditions) of interest. The two most effective skimmers (Desmi Polar Bear and Lamor LRB 150) for oil recovery on ice are pictured in figure 10.

Table 8. Summary of skimmer performance tests conducted by SINTEF for oil recovery on ice

Skimmer	Skimming mechanism	Tank test conditions	Field test conditions (% ice cover)	Results
Desmi Ice Skimmer	Weir with a drum brush adapter	No ice Broken ice Slush	N/A	No further testing warranted. Ice blocks prevented oil flow to the drums, and there was a high amount of undesirable water up-take in this model.
Desmi Sea Mop 4090	Oleophilic rope mop	N/A	Broken ice, 60%	Proof-of-concept test. Rope mop skimmers are subject to freezing in ice conditions.
Desmi Helix 1000	Weir with a drum brush adapter	Broken ice Slush	Broken ice, 10% Broken ice, 30% Broken ice, 60%	Further development of design is warranted for recovery on ice. Worked with manufacturer to improve model.
*Desmi Polar Bear (improved Helix 1000)	Custom weir with drum brush	No ice Slush	Broken ice, 30% Broken ice, 50% Broken ice, 70%	Effective for oil recovery up to 70% ice cover
Lamor GT 185	Oleophilic brush conveyor	No ice	N/A	Ineffective in ice conditions
*Lamor LRB 150	Oleophilic drum brush	No ice Broken ice Slush	Broken ice, 70% Broken ice, 90%	State-of-the-art technology for oil recovery on ice
Framo Prototype	Drum brush	N/A	Broken ice, 50%	Skimmer not optimized for ice conditions

Asterisks identify the most promising designs identified for oil recovery on ice, the custom Desmi Polar Bear and the Lamor LRB150 skimmers.

Figure 10. Most effective skimmers for oil recovery on ice in SINTEF testing



The Lamor LRB 150 drum brush skimmer (left) and the Desmi Polar Bear weir skimmer with a customized drum brush adapter (right) were the most effective skimmers for oil recovery on ice in SINTEF testing.

The Desmi Polar Bear was a custom design, produced specifically as a result of SINTEF's testing. Both skimmers recovered oil emulsion with 100-percent efficiency in field tests with high levels (70–90 percent) of ice cover. Both effective skimmer models include an oleophilic drum brush, suggesting that drum brush skimmers are effective for the recovery of oil in arctic environments.

The successful outcome of these skimmer tests demonstrates the importance of conducting targeted evaluations of skimmers for a particular spill environment. SINTEF identified two highly effective skimmers for arctic environments through its series of testing.

### ***World Catalog***

The *World Catalog of Oil Spill Response Products* contains qualitative, manufacturer-reported skimmer effectiveness information [51]. Published annually by SL Ross Environmental, the *World Catalog* includes information about hundreds of models of commercially available spill cleanup equipment, including skimmers, sorbents, booms, and dispersant distribution systems. For skimmers, some effectiveness data (recovery efficiency and recovery capacity) are reported when available from the skimmer manufacturer. In addition, most skimmers are described by a category called “Best in Oil Type,” in which the manufacturer reports the ASTM categories in which their skimmer has the best performance. The *World Catalog* provides a reliable, updated list of commercially available skimmers. Because the performance data reported there are often qualitative and provided by the manufacturers, it would be worthwhile to conduct independent tests to verify skimmer performance for a particular application.

### **OHMSETT tests**

The OHMSETT test tank facility was actively involved in the development of new ASTM methods for skimmer testing. Before 2008, a standard test protocol to determine the capacity and effectiveness of skimmers did not exist. Without a standard testing procedure, it was impossible to compare the data provided by different manufacturers since testing conditions greatly influence skimmer performance. Therefore, the OHMSETT facility conducted tests of many skimmers to develop the standardized ASTM test methods. In 2008, the standard methods were finalized and published by ASTM [41][42].

Two reports discuss the skimmer testing conducted at OHMSETT supporting the ASTM test development [52][53]. A third report summarizes the testing of prototype oleophilic skimmers using the ASTM test methods [54].

In the tests conducted at OHMSETT, the manufacturer and model of skimmers tested is proprietary and not publicly available. However, performance data are available for the skimmers according to their type (oleophilic drum, weir, etc.). We compared the results from these tests of oleophilic skimmers (drum, disk, and brush) in different types of test oil. Oleophilic skimmers (several drum and brush types) were evaluated in two standard test oils, one “light” (ASTM category I) and one “heavy” (ASTM category III), during method development [52].

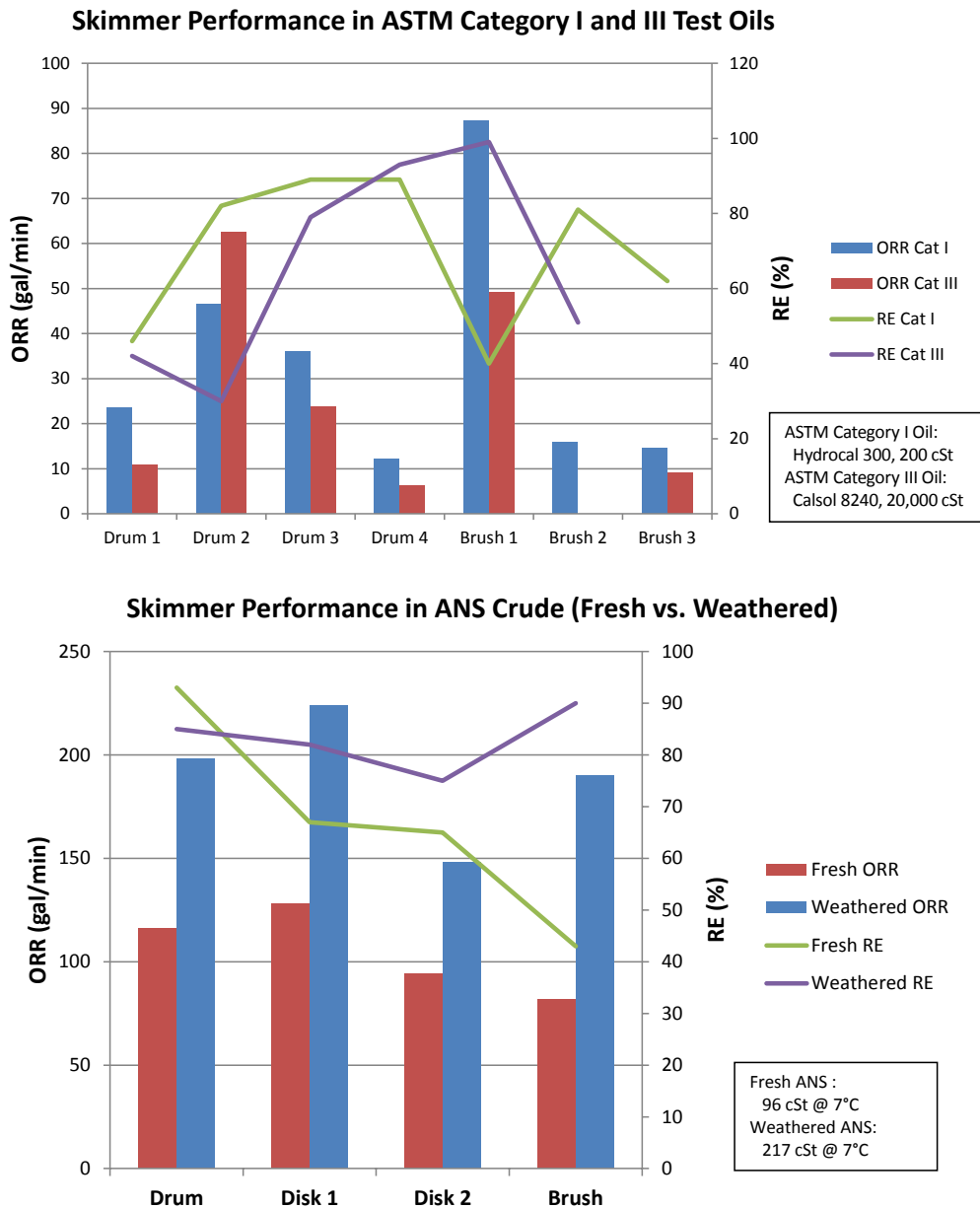
After the ASTM method was developed, other tests on prototype oleophilic skimmers (drum, disk, and brush) were conducted using fresh and weathered Alaska North Slope (ANS) crude oil (ASTM category I). Figure 11 presents a summary of skimmer performance from these tests. We make the following observations about the data:

- The drum and brush oleophilic skimmers tested tend to have higher oil recovery rates (ORRs) in ASTM category I oil than in ASTM category III oil.
- There is no noticeable trend in recovery efficiency (RE) between ASTM category I or III oils for the oleophilic skimmers tested.
- The oleophilic skimmers tested showed better performance (both ORR and RE) in weathered ANS crude than in fresh ANS crude oil.
- The oleophilic skimmer systems tested at OHMSETT would probably be best suited for the collection of weathered light crude oil (such as ANS crude).

These tests highlighted the importance of conducting tests of skimmers side-by-side using a standard methodology. Even without knowing the manufacturer and model of the skimmers tested, the standard methodology allowed for useful comparisons between skimmer types in oil of various properties.



Figure 11. Performance of oleophilic skimmers in various test oils at OHMSETT



Top: Guarino [52]. Bottom: Meyer [54].

Additional performance studies, sponsored by skimmer manufacturers, were conducted at OHMSETT in recent years. The performance data are proprietary, but we have provided a summary of the tests conducted in table 9 according to publicly available reports. We have only included those studies conducted using the ASTM F2709-08 test method in this summary table [55] [56].

Table 9. Skimmer tests conducted at OHMSETT using the ASTM F2709-08 method, 2010–2012

Year	Manufacturer	Model	Type	Test oils
2010	Crucial	Prototype	Oleophilic, Disk	Fresh ANS Crude (category I)
	Ro-Clean Desmi	Giant Octopus, prototype	Oleophilic, Belt brush	Fresh ANS Crude (category I) Calsol 8240 (category III)
	Ro-Clean Desmi	Polar Bear	Weir with drum brush	Fresh ANS Crude (category I) Calsol 8240 (category III)
2012	Elastec/American Marine	Magnum 600	Oleophilic, Grooved drum	Category II Oil, 2000 cP
	Elastec/American Marine	TDS 136	Oleophilic, Grooved drum	Category II Oil, 2000 cP
	Elastec/American Marine	X150	Oleophilic, Disk	Category I Oil, 200 cP Category II Oil, 2000 cP
	Lamor	Minimax	Oleophilic, Brush	Category I Oil, 200 cP
	Lamor	LNXG 100, prototype	Oleophilic, Brush	Category I Oil, 200 cP
	Lamor	LNXG 1000, prototype	Oleophilic, Brush	Category I Oil, 200 cP

## Emerging skimmer technologies

Novel technologies are under development to improve skimmer effectiveness; most are being studied in academia. Most of these initiatives involve novel oleophilic skimmer surfaces, designed to increase the amount of oil that oleophilic skimmers can attract and separate.

One study by Broje and Keller added a groove pattern to the surface of oleophilic drum skimmers [57]. The addition of grooves increased the oil recovery capacity and efficiency of drum skimmers. This technique was particularly useful for the recovery of light, refined products, such as diesel fuel. Performance tests were conducted at the OHMSETT facility for this work.

Additional work on novel oleophilic skimmer surfaces was conducted at the University of California, Santa Barbara [58]. This work utilized the groove patterning developed by Broje and Keller and evaluated different surface coatings to improve oil recovery in cold weather conditions. The authors identified neoprene and low-density polyethylene as promising coatings for oil recovery in ice conditions. The grooved surface of a drum skimmer is pictured in figure 12.

Early-stage research used nanotechnology to create oil-adsorbent paper as oleophilic material for skimmers. To our knowledge, the tech-

nology, developed at MIT, has not been commercialized. However, the researchers have developed prototype oil skimmers, called Seaswarm, using the nanotechnology-based paper (the prototypes are pictured in figure 12), and have applied for a patent on the robotic skimmer design [59]. More information about the ongoing research effort can be found at the Seaswarm project website: <http://senseable.mit.edu/seaswarm/index.html>.

Figure 12. Emerging oil skimming technologies



Oil skimming technologies under development include grooved patterning on an oleophilic drum skimmer (left), and a prototype oil skimmer utilizing nanotechnology-based oleophilic paper (right).

## Summary of skimmers

Five summary points follow:

- Many rules of thumb about the selection of oil spill skimmers are based on performance tests conducted from the 1970s through the 1990s. Because skimming technology has not changed appreciably since that time, the standing rules of thumb are probably applicable to commercially available skimmers today.
- In 2008, standard protocols for evaluating skimmer performance were developed at OHMSETT and were published by ASTM. The development of these protocols was an important step in standardizing the testing and evaluation of skimmers. Since these protocols have been published and adopted, the testing and evaluation of skimmers should be more consistent

between manufacturers, and the results more useful to those who need to select a skimmer.

- Unlike other remediation technologies, skimmers can be used to recover oil with a wide range of viscosity. Skimmers exist that can effectively recover oil across the ASTM viscosity categories (I, II, III, IV, and V).
- Recent work by SINTEF led to the targeted development of highly effective skimmers for recovery of oil in ice conditions.
- Emerging skimmer technologies are being developed in academic settings to improve the oil recovery of oleophilic skimmers. Research includes development of grooved patterns on drum skimmers, use of novel oleophilic surface coatings, and application of nanotechnology to novel oleophilic surfaces.

## **Research recommendations for skimmers**

We offer the following research recommendations:

1. We recommend that targeted programs for the development of skimmers in operational environments of interest (i.e., arctic versus warm environments) be developed and executed. The recent work done by SINTEF to develop skimmers for arctic conditions is a good example of such a successful test program. Since the performance of skimmers is highly dependent on their operational environment, we believe that skimmer design should be optimized for particular spill environments.
2. Second, we recommend that emerging skimmer technologies be incorporated into commercially available designs. The literature suggests that skimmer technology has remained relatively unchanged in the last 40 years. Some promising ideas are being pursued in the academic literature that may vastly improve the performance of skimmer technology. Some, such as the development of novel coatings for oleophilic skimmers, may be incorporated into existing commercial skimmer technology, eliminating the need to develop completely new systems.

## Sorbents

Sorbents, or oil-absorbing materials, are commonly used in oil spill remediation, most often for final shoreline cleanup. Sorbents may also be used to clean up the final traces of oil on water, or as a backup to other recovery methods. Sorbent materials may be incorporated into other cleanup technologies; for example, sorbent booms contain oil-absorbing materials to improve the boom's ability to contain oil. A wide variety of materials, both natural and synthetic, have been studied as oil spill sorbents, but most commercially available oil spill sorbents are made from synthetic polymers [60]. First, we will summarize sorbent materials, and the performance metrics used to evaluate their effectiveness. Then, we will review the literature on sorbent performance and will draw conclusions about sorbent effectiveness for oil of various properties.

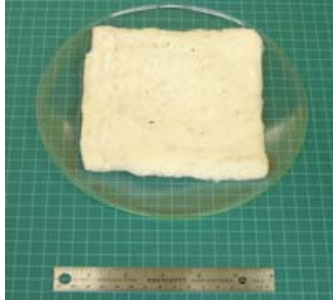
### Description and characterization of sorbent materials

Sorbents used in oil spill remediation can be made using either natural (moss, wood products, clay, etc.) or synthetic (polyester or polypropylene) materials. Sorbent materials are further characterized as organic (carbon-containing materials, including synthetic polymers and natural materials, such as cotton) or inorganic (non-carbon-containing materials, including such minerals as calcium carbonate or fly ash). In addition to their material, sorbents are classified by the form or shape in which the material is fashioned. In its standard test method for evaluating the performance of sorbents, ASTM has defined sorbent “types” to describe the common shapes of spill sorbents, pictured in figure 13 [61]:

- Type I: Roll, film, sheet, blanket, or pad
- Type II: Loose adsorbent (powder form)
- Type III: Enclosed sorbent (pillows, adsorbent booms)
- Type IV: Agglomeration unit (“pompoms”—for highly viscous oils)

Figure 13. Examples of sorbents according to ASTM shape classification

Type I: Pad (Instasorb)



Type II: Loose (Sansorb)



Type III: Enclosed Sorbent (Markleen)



Type IV: Agglomeration Unit (Crucial Inc.)



Photos of type I and type II sorbents are from the Environment Canada sorbent database (<http://www.etc-cte.ec.gc.ca/databases/sorbent/>). Type III and type IV sorbent photos are from the manufacturers' websites: Markleen (<http://www.markleen.com/products/ecosorb-sorbent-booms-with-skirts/>) and Crucial Inc. ([www.crucialinc.com](http://www.crucialinc.com)).

## Measure of sorbent performance

Sorbent performance is measured according to the quantity of oil it can absorb per unit weight of sorbent material, which is defined as the sorption capacity (equation 2).

$$\text{Sorption Capacity (g oil / g sorbent)} = \frac{\text{Mass Oil Recovered}}{\text{Original Mass of Sorbent}} \quad (2)$$

It is important to ensure that sorbent performance reports account for the undesirable water absorption of a sorbent material. In some tests, it may appear that a sorbent is highly effective; however, the sorbent may actually be collecting a high mass of unwanted water in-

stead of oil. Some test methods, including the ASTM standard method, describe testing techniques and calculations that subtract the amount of recovered water from the sorbent performance, allowing for a more accurate representation of sorbent effectiveness for the recovery of oil [61]. Sorbent performance tests conducted by Environment Canada also account for the unwanted collection of water.

Sorbents are typically evaluated in a variety of test oils representing a range of viscosities. Oil viscosity is almost exclusively the single variable evaluated in sorbent performance tests. Since sorbents are typically used in shoreline cleanup or in a contained open-water spill, environmental variables, such as wave turbulence, do not significantly affect sorbent performance. This is unlike skimmers or dispersants where environmental factors are critically important to their performance. One notable exception would be absorbent booms because environmental conditions influence the ability of booms to contain oil.

While standard viscosity ranges are defined for sorbent performance tests, they have not been commonly adopted in the literature on sorbent performance. Particularly in academic literature, researchers tend to report sorbent performance in test oils of interest to their study or application rather than using any standard guidelines. ASTM has adopted standard viscosity ranges to describe test oils in sorbent performance, which are reported in table 2. In its 2012 revision of the test method for sorbents, ASTM added an additional oil category, “weathered,” to describe the heaviest test oils used in the evaluation of sorbents.

## **Sorbent performance**

The most comprehensive set of sorbent performance data is from a sorbent test program by Environment Canada conducted from 1999 to 2004 [62]. Additional sorbent performance data are available in the 2013 *World Catalog*, where performance data were provided by sorbent manufacturers [51]. In both datasets (Environment Canada and the *World Catalog*), sorbent performance tests were conducted using ASTM standard test method F726. Therefore, it is possible to aggregate and compare the results of these datasets since they were derived using the same standard methodology. Both Environment

Canada and the *World Catalog* report data on the performance of commercially available sorbents.

There are also studies on sorbent performance in the academic literature. The academic studies seldom employ the ASTM F726 test method, and they report on novel prototype sorbent materials that are not yet commercially available. However, the academic literature provides important scientific insights on sorbent function. It also describes innovative materials that may warrant commercialization for use in oil spill remediation.

Here, we will first evaluate the performance data for commercially available sorbents (Environment Canada and *World Catalog* data). Then, we will review data in the academic literature and will provide conclusions and recommendations about sorbent materials for oil spill remediation.

### **Commercially available sorbents**

Environment Canada conducted a sorbent test program from 1999 to 2004, the results of which are available on its website [62]. Their test program was conducted using three test oils in accordance with the ASTM F276 standards (“light,” “medium,” and, “heavy” oils were used).

Performance data on commercially available sorbents are also reported in the *World Catalog* [51]. These data were reported by the sorbent manufacturers and were not collected by an independent laboratory.

We aggregated these datasets (Environment Canada and *World Catalog*) to draw conclusions about the results of these collective studies. We analyzed sorbent performance both as a function of sorbent material (natural or synthetic) and as a function of oil type (light, medium, or heavy, as defined in table 2). We did not analyze the effect of sorbent shape type (roll, powder, pad, etc.) because sufficient data were not available to perform this analysis. We only included materials for which quantitative performance data values (sorption capacity) were available for all three categories of test oil.

We assigned a material category of either “natural” or “synthetic” to each sorbent tested. The material assignments are shown in table 10.



In some cases, the sorbent material was not explicitly listed, but a descriptive name (such as “synthetic” or “treated organic”) was used to describe the sorbent. Those category assignments are also included in table 10. A total of 155 materials were included in this analysis. Of the materials, 67 were characterized as natural (43 percent), and 88 were characterized as synthetic (57 percent). Fifty-five of the sorbents tested (35 percent of all sorbents) were made from polypropylene. Commercially available sorbents were almost exclusively made from organic (carbon-containing) materials. Vermiculite was the only inorganic material reported in the dataset of commercially available sorbents.

Table 10. Sorbent materials included in analysis of commercial performance tests

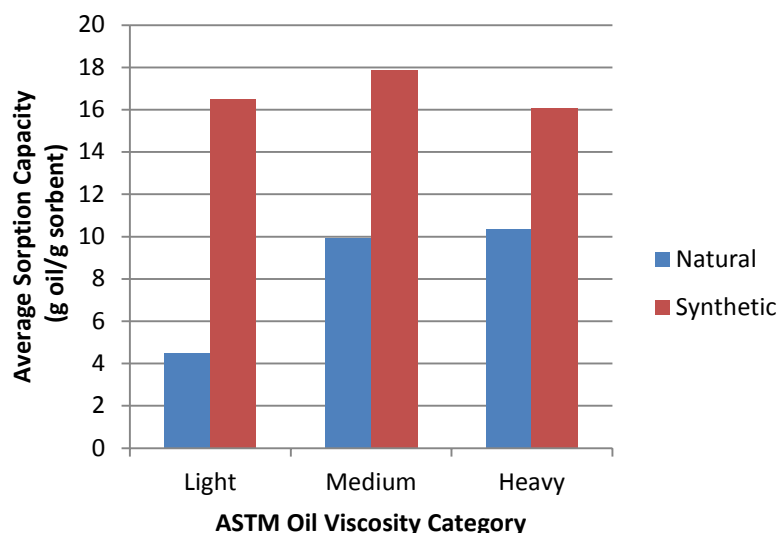
<b>Natural materials</b> <i>(43 percent of sorbents tested)</i>	<b>Synthetic materials</b> <i>(57 percent of sorbents tested)</i>
Clay	Polyurethane
Cork	Polypropylene
Cotton	Aminoplast polymer
Hair	“Synthetic”
Cellulose	“Biodegradable polymer foam”
Peat moss	“Hydrocarbon”
Rubber	
Vermiculite*	
Wood	
Wool	
“Treated organic”	
“Woven fibers”	

\* Indicates inorganic sorbent material.

The sorption capacities reported for the two material types (natural and synthetic) and the three oil types (light, medium, and heavy) were averaged and are plotted in figure 14. From these aggregated data, we made the following observations:

- Synthetic sorbents have higher sorption capacities than natural sorbents for all oils tested.
- Synthetic sorbents have similar sorption capacities for light, medium, and heavy oils.
- Natural sorbents have similar sorption capacities for medium and heavy oils, and have a lower sorption capacity for light oil.

Figure 14. Average sorbent performance by sorbent type and oil viscosity (commercially available sorbents)



Average data from sorbent performance tests conducted by Environment Canada and reported in the *World Catalog*. All performance tests were conducted using ASTM standard test method F726.

We organized the performance data to display more information about the sorbent materials in table 11. Here, sorption capacity was grouped into categories (poor (<5 g/g), fair (5–10 g/g), or good (>10 g/g)), and materials that had performance data in each of those categories were listed. Materials were listed multiple times when the same sorbent material from a different manufacturer displayed different performance. Organization of the data in this manner allowed us to make the following observations:

- Polypropylene and aminoplast polymer synthetic sorbents consistently displayed “good” sorption capacities for all oil types tested.
- Cotton was the only natural material to exhibit “good” sorption capacity for all oil types.

- The only materials to exhibit “poor” sorption of any oil type were natural. Synthetic materials always exhibited either “fair” or “good” oil sorption.
- Vermiculite, the only inorganic material tested, exhibited “poor” sorption of light, medium, and heavy test oil.

Table 11. Sorption capacities of commercially available sorbent materials

Oil viscosity category	Poor sorption (< 5 g/g)	Fair sorption (5–10 g/g)	Good sorption (>10 g/g)
Light	Cellulose	Cellulose	Cotton
	Clay	Cotton	<b><u>Aminoplast polymer</u></b>
	Cork	Wood	<b><u>Polypropylene</u></b>
	Cotton	Wool	
	Hair	<b><u>Polypropylene</u></b>	
	Peat moss	<b><u>Polyurethane</u></b>	
	Rubber		
	<i>Vermiculite*</i>		
Medium	Cellulose	Cellulose	Wool
	Clay	Cork	<b><u>Aminoplast polymer</u></b>
	Cotton	Hair	<b><u>Polypropylene</u></b>
	Peat moss	Wood	
	Rubber	<b><u>Polyurethane</u></b>	
	<i>Vermiculite*</i>		
Heavy	Clay		
	Cotton		
	Peat moss		
	Rubber		
		<b><u>Polypropylene</u></b>	<b><u>Polypropylene</u></b>
	<i>Vermiculite*</i>		

**Synthetic materials** are highlighted in bold text and underlined. *Inorganic materials\** are denoted with an asterisk and italics. Performance data are according to *World Catalog* and Environment Canada sources. Materials appear multiple times when the same sorbent material from a different manufacturer displayed different performance.

In general, the results of these performance tests illustrate that synthetic materials display better oil sorption than naturally derived materials. These results are consistent with other reports and reviews stating that synthetic materials tend to have higher sorption capacities than natural materials [12][60].

Despite their poorer performance, there are many benefits to using natural materials instead of synthetic materials in oil spill response. Natural sorbent materials might be more readily available at the site of an oil spill, are biodegradable, and are usually less costly than synthetic alternatives. Therefore, there is significant research ongoing in the academic literature for the identification and development of natural materials as oil spill sorbents, and also in the design of novel synthetic materials as low-cost, effective alternatives.

Next, we will review the research published in scientific journals on the development and performance of oil spill sorbents. We focus our review on studies that compare novel sorbent materials with the commercially available standards, polypropylene and polystyrene.

### **Academic literature**

*Sorbents in basic research.* There is a significant body of academic literature on oil spill sorbents. Unlike the tests previously described for commercially available materials, the studies conducted in academic literature generally do not use a standard test method to conduct sorbent performance tests. However, most academic studies report sorbent performance according to sorption capacity (g oil/g sorbent). We compiled and compared the sorption capacity values reported across many papers.

We identified publications in peer-reviewed journals since 2000 that reported performance data on sorbent materials, and we compiled performance data from these articles. We selected articles for inclusion that reported properties of the oil tested, and that provided quantitative sorption performance data. A total of 22 articles were included in our analysis, as table 12 shows. From these articles, sorbent performance values (g oil/g sorbent) were extracted. To enable comparison of academic results with those obtained for commercially available sorbents, we described the test oils used in each paper according to ASTM categories (shown in table 2). Oils were described as light, medium, or heavy. We did not use the “weathered” category because it was not used in the available tests of commercially available sorbents. Oils falling into this category were classified as heavy.

Table 12. Alphabetical list of sorbent tests in academic literature

Reference	Material(s) evaluated
[63] Abdullah, M.A., et al.	Kapok
[64] Annunciado, T. R., et al.	Sawdust, sisal, coir fiber, sponge gourd, leaves
[65] Arbatan, T., et al.	Calcium carbonate powder
[66] Banerjee, S., et al.	Sawdust, amino-acid grafted sawdust
[67] Bayat, A., et al.	Polypropylene, bagasse, rice,
[68] Ceylan, D., et al.	Butyl rubber, commercial polypropylene,
[69] Choi, H.	Milkweed, cotton fiber, polypropylene fiber
[70] Inagaki, M., et al.	Exfoliated graphite, carbon fiber felt
[71] Karakasi, O.	High-calcium fly ash
[72] Lim, T., and Huang, X.	Kapok, polypropylene
[73] Lin, J., et al.	Polystyrene (electrospun), polypropylene mats
[74] Medeiros, M., et al.	Vermiculite
[75] Moriwaki, H., et al.	Silkworm cocoon waste
[76] Radetic, M., et al.	Recycled wool material
[77] Rajakovic, V., et al.	Wool fiber, sepiolite, zeolite, bentonite
[78] Ribiero, T., et al.	PeatSorb (commercial), salvinia biomass
[79] Srinivasan, A., et al.	Walnut shells
[80] Suni, S., et al.	Cotton grass, polypropylene
[81] Tanobe, V., et al.	Polyurethane foams
[82] Teas, C., et al.	Cellulose, polypropylene, perlite
[83] Toyoda, M., and Inagaki, M.	Exfoliated graphite
[84] Zhu, H., et al.	Polypropylene, PVC/PS electrospun fibers

In the same manner as done for commercial test data, we assigned a material category of either “natural” or “synthetic” to each sorbent tested. The material assignments are described in table 13. Most sorbent materials tested in the academic literature were made from organic materials (88 percent of test materials). Those sorbents made from inorganic materials are denoted by an asterisk in table 13.

In a similar manner as in the analysis of commercial sorbent data, we organized the performance data in table 14. Here, sorption capacity was grouped into four categories: poor (<5 g/g), fair (5-10 g/g), good (10-50 g/g), or excellent (>50 g/g). Materials were listed multiple times when the same sorbent material from a different study displayed different performance.

Table 13. Sorbent materials included in performance test analysis (academic journal articles)

Natural materials	Synthetic materials
Bagasse	Butyl rubber
Bentonite*	Carbon fiber felt
Cellulose	Electrospun PVC/PS fiber
Coir Fiber	Electrospun PS fibers
Cotton	Exfoliated graphite
Fly ash*	PeatSorb (commercial hydrocarbon)
Kapok	Polypropylene
Leaves	Polyurethane
Milkweed	Sawdust- modified
Perlite*	Vermiculite- modified*
Rice	
Salvinia biomass	
Sawdust	
Sepiolite*	
Silk cocoon	
Sisal	
Sponge	
Walnut shell	
Wool	
Zeolite*	

\* Denotes inorganic sorbent materials.

In table 14, **synthetic materials** are highlighted in bold and underlined. *Inorganic materials\** are shown in italics and are followed by an asterisk. Performance data are according to 22 independent academic publications. Materials appear multiple times when the same sorbent material from a different manufacturer displayed different performance.

From these aggregated data, we observed that synthetic materials tended to have higher oil sorption capacities than natural materials for light, medium, and heavy test oils. Only naturally derived sorbents (with the exception of chemically modified Vermiculite, a natural material that was chemically treated) exhibited “poor” oil sorption. Most of the materials exhibiting “excellent” oil sorption were synthetic; the exceptions are kapok and silk cocoon, both natural materials. Further, all inorganic sorbent materials evaluated in the academic literature yielded “poor” sorption of light oil. No inorganic materials were evaluated in medium or heavy oils.

Table 14. Sorption capacities of sorbent materials in academic literature

Oil viscosity category	Poor sorption (< 5 g/g)	Fair sorption (5-10 g/g)	Good sorption (>10 g/g)	Excellent sorption (≥ 50 g/g)
Light	Bagasse <i>Bentonite</i> * Cellulose Fly ash Leaves <i>Perlite</i> * Rice Sawdust <i>Sepiolite</i> * Sponge Walnut shell <i>Zeolite</i> * <u><i>Vermiculite-modified</i>*</u>	Bagasse Cellulose Coir fiber Rice Salvinia biomass Sisal Sawdust Wool <u>Polypropylene</u> <u>Sawdust-modified</u>	Cotton Kapok Milkweed Wool <u>Butyl rubber</u> <u>Carbon fiber felt</u> <u>Electrospun PVC/PS fiber</u> <u>PeatSorb (hydrocarbon)</u> <u>Polypropylene</u>	<u>Electrospun PVC/PS fiber</u> <u>Exfoliated graphite</u>
Medium	Walnut shell	<u>Polypropylene</u>	Cotton Kapok Salvinia biomass Wool <u>Butyl rubber</u> <u>Polypropylene</u>	Kapok Silk cocoon <u>PeatSorb (hydrocarbon)</u> <u>Electrospun PVC/PS fiber</u> <u>Electrospun PS fiber</u> <u>Exfoliated graphite</u> <u>Polyurethane foam</u> <u>Exfoliated graphite</u>
Heavy		Cotton <u>Polypropylene</u>	Cotton Milkweed <u>Polypropylene</u>	<u>Exfoliated graphite</u>

Novel sorbent materials that exhibited “excellent” oil sorption of at least 50 g/g were identified in these scientific publications. These outstanding sorbents included synthetic materials (electrospun polymers or exfoliated graphite) and natural materials (kapok fiber and silk cocoon). To our knowledge, these materials do not exist as commercially available sorbents for oil spill remediation.

Below, we summarize our observations on comparison of the data from commercially available sorbents (table 11) with the data from sorbents in academic literature (table 14):

- Novel sorbents in the academic literature achieved higher sorption capacities (>50 g/g) than sorbents that are commercially available.

- In both the commercially available and academic datasets, synthetic sorbents had higher sorption capacities than naturally derived sorbents. Inorganic sorbents performed poorly in both datasets.
- In both datasets, highly effective sorbents (in the “good” or “excellent” categories) tended to work well in light, medium, and heavy test oils.

Next, we discuss in detail the most promising sorbent materials identified in the academic literature.

*Promising sorbent materials from academic journal articles.* Some novel sorbent materials were identified that may warrant further research and development as commercial sorbents for oil spills. These sorbents exhibited excellent (>50 g/g) sorption of oil in the published studies and are listed in Table 15.

Table 15. High-sorption-capacity materials from academic literature

Material	Sample sorption capacity	Reference
Electrospun polyvinylchloride (PVC)/polystyrene (PS) fiber	150 g/g in motor oil (medium)	[84] Zhu, H., et al.
Electrospun polystyrene (PS) fiber	111 g/g in motor oil (medium)	[73] Lin, J., et al.
Exfoliated graphite	75 g/g in crude oil (medium), 70 g/g in C-grade test oil (heavy)	[83] Toyoda, M., and Inagaki, M.
Silkworm cocoon waste	50 g/g in motor oil (medium)	[75] Moriwaki, H., et al.
Malaysian kapok	50.8 g/g in new engine oil (medium)	[63] Abdullah, M. A., et al.

Of these promising sorbent materials, two are naturally derived: silkworm cocoon waste [75] and Malaysian kapok [63]. While both of these natural materials exhibited excellent sorption of medium oil (~50 g/g), they have limited availability (each is available primarily in localized regions in Asia). Thus, they probably will not be used as spill sorbents worldwide.

The other high-performing sorbents were synthetic. First, exfoliated graphite exhibited high oil sorption, up to 75 g/g in medium crude



oil, or 70 g/g in heavy oil [83]. While effective, exfoliated graphite does pose limitations that may have inhibited its development into a commercial sorbent. The production of exfoliated graphite requires significant processing (heating graphite to extremely high temperatures), and it is expensive [85]. The fine, delicate, powder texture of exfoliated graphite may be difficult to handle and apply to oil spill applications. However, because of its excellent potential oil sorption capacity, exfoliated graphite may warrant further development as an oil spill sorbent.

The second set of promising synthetic materials is electrospun polymer fibers. Two recent studies demonstrated very high sorption of medium motor oil by electrospun polystyrene (PS) fibers or polyvinylchloride/polystyrene (PVC/PS) fiber mixtures [73][84]. Electrospinning is a polymer processing technique that allows for the production of very thin (~1–5  $\mu\text{m}$  in diameter) fibers of polymers. Commercially available polypropylene sorbents have diameters on the order of tens to hundreds of microns. Electrospun polymer fibers have a very high surface area and low bulk density, providing them with a high capacity to absorb oil between the fibers. Electrospinning is simply a different manufacturing technique of existing polymer materials, rather than a new material. Thus, it may be easily applied to the manufacturing of commercial oil spill sorbents.

## Summary of sorbents

The following bullets summarize the literature on sorbent performance and present our recommendations:

- Environment Canada and the *World Catalog* contain performance data on many commercially available sorbents. These tests demonstrated that synthetic sorbent materials yield better oil sorption capacity than natural materials. Polypropylene and aminoplast polymer sorbents exhibited the highest sorption capacity for light, medium, and heavy test oils. Inorganic materials exhibited poor oil sorption in both commercial and academic datasets.
- There are numerous studies in the scientific literature to evaluate novel sorbent materials. Several materials under development in academic literature yielded higher oil sorption capacity than commercially available polypropylene sorbents.

In particular, electrospun polymers may warrant further investigation as oil spill sorbents.

## **Research recommendations for sorbents**

Two research recommendations follow:

1. We recommend that promising adsorbent materials from the scientific literature be further developed into commercial oil spill sorbents. Existing materials and methods may be applied to significantly improve the sorption capacity of commercially available oil spill sorbents.
2. We believe that some of the effective sorbent materials may have utility as oleophilic coatings in oil spill skimmers. We recommend combining the advances in sorbent materials with skimmer technology.

## **Solidifying agents**

### **Description of solidifiers**

Solidifying agents, or solidifiers, are classified by the EPA as chemical agents that form a strong physical bond with oil, causing the oil's viscosity to increase to that of a rubberlike solid [86]. Solidifiers are distinct from sorbent materials in the nature of their interaction with oil, but the terminology used to distinguish them is often inconsistent. In some definitions, solidifiers are strictly reagents causing a chemical cross-linking reaction with oil. In other definitions, solidifiers can be agents that form strong bonds with oil (such as hydrogen bonds), but not a true chemical reaction [87]. Solidifiers are listed on the EPA NCP schedule as "miscellaneous agents," and may be approved for use in conjunction with sorbent materials to clean up small quantities of oil. The solidifiers listed on the EPA NCP schedule are composed of dry, high-molecular-weight polymers with a porous matrix and a large surface area. These solidifiers form strong physical interactions with oil but do not chemically react with oil. If solidifiers are to see widespread use in oil spill remediation, the definition of solidifying agents, and their distinction from sorbents, must be established.

While they are listed on the EPA NCP schedule, solidifiers have not found widespread use in spill cleanup both for practical reasons and

because of environmental concerns with their use. Practically, it is difficult to determine ideal conditions in which to apply solidifiers since their effectiveness varies significantly depending on the oil type and spill conditions. Environmentally, solidifiers are a concern because solidified oil may sink below the water surface, rendering it difficult or impossible to recover. In addition, solidifiers that chemically react with oil may be nonspecific—also causing undesirable chemical reactions with other organic substances in the spill area (wood, containment booms, etc.).

Further, there are not standard test methods or metrics to describe the effectiveness of solidifying agents, making it difficult to compare and contrast agents from different manufacturers. Unlike dispersants or other chemical agents on the EPA NCP schedule, manufacturers of solidifying agents are not required to report effectiveness data to be included on the EPA NCP schedule in the “miscellaneous” category. There are a few studies in the scientific literature that report information about the mechanism of action and effectiveness of solidifying agents.

### **Solidifier performance**

In 2008, Fingas published a literature review of solidifier studies published from 1990 to 2008 [88]. In that review, only 10 peer-reviewed articles were published on solidifying agents in the 18-year window. All other reports of solidifiers were available only in the “gray literature,” published privately by manufacturers. Conclusions from this review were largely that the literature on solidifiers is inconsistent and not comprehensive, and the development of standard testing procedures and metrics for solidifiers was recommended. Here, we discuss the peer-reviewed literature published since 2008.

A 2010 study by Rosales and others evaluated the effectiveness and mechanism of action of five commercially available solidifiers for the removal of Prudhoe Bay crude oil from seawater [89]. The objective of this study was to learn about the chemical mechanisms involved in oil solidification by solidifying agents (commercial solidifiers were not identified in the study). The authors identified an ideal application ratio (1:4 solidifier:oil) that worked well for all solidifiers tested. In addition, using chemical analysis, the authors concluded that the solidification process is not specific to a particular chemical compo-

ment in oil. All components within the oil were equally involved in the solidification reaction. This sort of mechanistic study is important to understanding the solidification process and may help to develop standardized metrics and tests that can be used to evaluate solidifiers for oil spill applications.

A new class of oil solidifiers, gelators, was reported and evaluated in several peer-reviewed journals since 2008. Gelators are amphiphilic chemical molecules that self-assemble into matrices or other structures and entrap oil within their porous structure. Gelators have strong molecular interactions (via hydrogen bonding) with oil, resulting in an increase in the oil's viscosity into a gel-like, solidified state. These solidifiers have only been evaluated in the academic literature in a laboratory setting and have no large-scale tank or field trial data.

A 2010 study by Jadhav and colleagues reported sugar-derived gelator molecules for the solidification of various light and refined oils [90]. The authors conducted a proof-of-concept study demonstrating that sugar-based gelators could be used to solidify and recover diesel fuel from water in a laboratory-scale experiment. A similar study was conducted in 2012 by Basak and others who developed amino-acid-based organogels for the recovery of light oils (including diesel fuel and kerosene) from water [91]. In 2013, Lee and Rogers reported sorbent xerogels as agents for the recovery of diesel fuel and gasoline from water [92]. Other amphiphilic gelators for oil spill remediation were reported in a patent application in 2012 [93].

The concept of using molecular gelators as oil spill solidifying agents is in its infancy. All work on these agents has been conducted in the laboratory (no large-scale or field testing is available), testing has been limited to few oil types (primarily light, refined petroleum products), and the environmental impacts of these compounds are unknown. Therefore, significant research would be required to move gelators from the laboratory into practical use in spill remediation.

## Summary of solidifiers

The following list presents a summary of the literature on solidifiers:

- The terminology used to define solidifiers is inconsistent, and standard metrics do not exist to describe or characterize solidifiers for oil spill cleanup.

- The scientific literature on solidifying agents is sparse and limited in scope and scale. Most studies on solidifiers were done at the laboratory scale and have only assessed their effectiveness for light, refined petroleum products.
- New work in peer-reviewed journals suggests that gelating agents may be promising for the recovery and solidification of oil from water.

### **Research recommendations for solidifiers**

First, we recommend that a standard definition be developed to define solidifiers and to distinguish solidifying agents from sorbents.

Second, we recommend that standard test methods and performance metrics be developed to quantify the effectiveness of solidifiers.

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## Conclusions

Our conclusions for each technology follow.

### In situ burning

Oil slick thickness is the most important factor governing in situ burning, where oil slicks of at least 2-3 mm can support in situ burning. Most oils are suitable for in situ burning, as long as their API gravity is at least 20°. In situ burning is most effective when employed shortly after a spill (within 72 hours for most oil types, or within 1-2 hours for heavy or thick oils). In situ burning is well understood, and reliable guidelines exist regarding slick thickness, oil properties, and appropriate windows of opportunity.

We recommend that future research be conducted on novel technologies that may improve the window of opportunity for in situ burning, including herding surfactants and emulsion breakers. Preliminary work on these technologies suggests that they might increase the window of opportunity for in situ burning by maintaining a favorable slick thickness, and by decreasing the water content of emulsified oil.

### Dispersants

Oil viscosity is a reasonable indicator of the effectiveness of chemical dispersion. Oils are most dispersible when their viscosity is low (less than 2,000 cSt), and they become undispersible when their viscosity is high (greater than ~10,000 cSt). Dispersants are the most effective when used immediately after a spill, and their effectiveness decreases over time after a spill due to oil weathering and emulsification. The window of opportunity for dispersant use is highly dependent on the oil chemistry, spill conditions, and the dispersant used.

Oil composition influences dispersibility, primarily by influencing the oil's other physical properties (such as viscosity) and the oil's tendency to form emulsions after weathering. The exact influence of oil

composition on dispersibility is complicated and highly dependent on the dispersant used. Most of the work done evaluating this has used the Corexit 9500 dispersant. We recommend evaluating the influence of oil chemistry on dispersion using other dispersants of interest.

Following analysis of the literature containing performance data on the dispersants listed on the EPA NCP product schedule, we observed that only three dispersants on the EPA NCP product schedule (Corexit 9500, Corexit 9527, and Finasol OSR) performed as well in independent effectiveness tests as they did in tests conducted by the product manufacturers and reported to the EPA. Of the eighteen dispersants listed on the EPA NCP product schedule, nine were evaluated in independent tests.

Corexit 9500 is the only dispersant among those tested in the field to demonstrate consistent dispersion of oil slicks in field tests. Corexit 9500 was also the only dispersant among those tested to effectively disperse oil in three types of independent laboratory tests (swirling flask, baffle flask, and wave tank tests). This suggests that good performance in all types of laboratory testing might indicate that a dispersant will perform well in the field. Finasol OSR displayed a performance profile suggesting that it will perform well in large-scale field trials. We recommend that further large-scale tests of Finasol OSR be conducted.

## Skimmers

Rules of thumb about the selection of oil spill skimmers are based on performance tests conducted from the 1970s through the 1990s. Since skimming technology has not changed appreciably since that time, the standing rules of thumb are probably applicable to commercially available skimmers today. Unlike other remediation technologies, skimmers can be used to recover oil with a wide range of viscosity. Skimmers exist that can effectively recover oil across the ASTM viscosity categories (I, II, III, IV, and V).

The most effective recent skimmer test programs have evaluated skimmers for a particular operational environment of interest (arctic conditions, for example). We recommend that targeted programs for



the development of skimmers in operational environments of interest be developed and executed.

Emerging skimmer technologies are being developed in academic settings to improve the oil recovery of oleophilic skimmers. Ongoing research includes the development of grooved patterns on drum skimmers, novel oleophilic surface coatings, and the application of nanotechnology to novel oleophilic surfaces. We recommend that such emerging skimmer technologies be incorporated into commercially available designs.

## **Sorbents**

Our analysis of commercially available sorbent performance data demonstrated that synthetic sorbent materials yield better oil sorption capacity than natural materials. Polypropylene and aminoplast polymer sorbents exhibited the highest sorption capacity for light, medium, and heavy test oils.

There is a wealth of academic literature evaluating oil adsorbent materials that are not commercially available. Our analysis of the academic literature illustrated that materials under development in academic literature yielded higher oil sorption capacity than commercially available polypropylene sorbents. In general, synthetic sorbents yielded higher sorption capacities than natural materials in the academic literature. We recommend that promising adsorbent materials from the scientific literature be further developed into commercial oil spill sorbents.

## **Solidifiers**

The scientific literature on solidifying agents is sparse, and limited in scope and scale. Most studies on solidifiers were done at the laboratory scale and have only assessed their effectiveness for light, refined petroleum products. The terminology used to define solidifiers is inconsistent, and standard metrics do not exist to describe or characterize solidifiers for oil spill cleanup.

We recommend that a standard definition be developed to define solidifiers and to distinguish solidifying agents from sorbents, and that standard test methods and performance metrics be developed to quantify the effectiveness of solidifiers.

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# Glossary

ADIOS	Automated Data Inquiry for Oil Spills
ANS	Alaska North Shore or Alaska North Slope Crude Oil
API	American Petroleum Institute
ASTM	American Society for Testing and Materials (ASTM International)
BSEE	Bureau of Safety and Environmental Enforcement
cP	Centipoise
cSt	Centistokes
DOI	Department of the Interior
EPA	Environmental Protection Agency
HLB	Hydrophilic-Lipophilic Balance
OHMSETT	Oil and Hazardous Materials Simulated Environmental Test Tank
mm	Millimeter
MNS	Mackay, Nadeau, Steelman Laboratory Test Method
NCP	National Contingency Plan
NOAA	National Oceanic and Atmospheric Administration
ORR	Oil Recovery Rate
PS	Polystyrene
PVC	Polyvinylchloride
RE	Recovery Efficiency
SARA	Saturated Hydrocarbon, Aromatic Hydrocarbon, Resin, Asphaltene
SINTEF	Foundation for Scientific and Industrial Research at the Norwegian Institute of Technology
TE	Throughput Efficiency

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