# Assessment of Demulsification and Separation Technologies for Use in Offshore Oil Recovery Operations

Report to

Bureau of Safety and Environmental Enforcement

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*Photo: On-water fishing vessel training in Prince William Sound, Alaska (Roy Robertson, PWSRCAC)*


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## Abstract

Nuka Research and Planning Group, LLC was contracted by the Bureau of Safety and Environmental Enforcement (BSEE) to determine the current state of demulsification and oil-water separation technology (Contract E17PS00129). This study assessed both technologies used in the field by Oil Spill Response Organizations (OSROs) and technologies that are being developed or evaluated in laboratories and testing facilities to enhance demulsification and oil water separation techniques.

The research team categorized technologies identified through a literature search and subject matter expert interviews and characterized them based on the technological approach and industry of origin, past use in oil spill operations, maturity, efficiency, cost, and potential for use in-line with oil recovery systems during offshore spill response. Key findings include:

- Gravity separation remains the preferred approach to separating oil, water and emulsions during spill response.
- Several new and emerging technologies show promise for enhancing separation and demulsification during on-water recovery. These include coalescent surfaces, hydrocyclones and vortexes, membrane and particle nanotechnologies, and electro-coalescence.
- Multi-step or multi-method technologies that separate and demulsify in stages is a common approach to wastewater treatment, and may show promise for oil recovery operations if systems can be developed to accommodate the throughput rates of on-water skimming systems.

To encourage the adoption of new, more efficient demulsification and separation technologies by the U.S. oil spill response industry, BSEE and other regulators should examine the policy framework that drives innovation and consider opportunities to encourage new technologies and novel approaches.

# 1 Introduction

Nuka Research and Planning Group, LLC (Nuka Research) developed this report for the U.S. Department of the Interior's Bureau of Safety and Environmental Enforcement (BSEE) under contract #E17PS00129.

## 1.1 Purpose

This report presents research and analysis to support BSEE in optimizing oil demulsification and separation during offshore oil recovery operations. The report describes the state-of-technology for demulsification of oil and separation of oil from free water recovered during offshore mechanical recovery operations.

## 1.2 Scope

This report describes and evaluates both existing and emerging technologies that may be used to demulsify oil-in-water and water-in-oil mixtures and to separate free water from recovered oil. It draws on published information from the academic and technical literature, patents, news articles, and manufacturer specifications. The information reviewed for this report is not limited to oil spill recovery technologies, but includes oil production and refining, shipping, food, and wastewater treatment.

Published studies dating back to the 1970s were reviewed, with a strong focus on more recently published studies and new or ongoing research. Subject matter experts, including researchers, spill responders, and regulators, were interviewed to provide firsthand knowledge and expertise. Our review focused on North American and European sources.

## 1.3 Background

On-water oil recovery with mechanical systems removes oil from the sea surface; however, along with the oil, mechanical systems also pick up water and emulsions. High-capacity skimmers commonly used for offshore recovery may pick up 70% water and only 30% oil. The management, storage and disposal of these fluids can quickly overwhelm temporary storage, compromising response effectiveness, and the time required to offload fluids or decant free water may disrupt skimming, reducing overall recovery (IPIECA, 2013).

Emulsions are defined as a suspension of droplets, greater than 0.1 micron in diameter, in which one immiscible liquid is dispersed throughout the other (NRT, 1997). During on-water oil recovery operations, emulsification of oil is caused by the uptake of water by the oil, typically at the skimmer head. Emulsions also form at sea as an oil slick weathers. Regardless of how oil emulsifies, the resulting substance will have a higher viscosity than oil alone, which can severely hamper skimmer operations and impact pumping rates (NRT, 1997). Depending upon the type of oil, emulsification may increase the total volume of the slick by two to five times (Nordvik, 1996). Free water, which is not emulsified but enters the skimmer head along with recovered oil, adds to the total amount of water recovered during on-water skimming operations.

### 1.3.1 Separation and Demulsification to Support Offshore Oil Spill Recovery

Demulsification and oil-water separation are critically important to the overall efficiency of offshore oil recovery using mechanical systems, because on-water recovered oil storage is often a limiting factor to the pace and efficiency of mechanical recovery operations. By reducing the volume of water that must be stored along with recovered oil, demulsification and free water separation technologies may enhance the capacity for a given on-water recovery system and increase the volume of oil recovered.

There has been research into technologies to demulsify or separate oil-water mixtures (sometimes referred to as “emulsion breaking”) dating back to the 1970s. While oil spill researchers and response professionals general recognize the importance of demulsification and separation to enhancing on-water oil recovery, this is a field where few major advances have occurred over the past 40 years (Nordvik, 1996; IPIECA, 2013).

During the 2010 Macondo well blowout in the Gulf of Mexico, the duration and scale of on-water recovery operations provided a reminder of how on-water storage of recovered oil, water, and emulsions can limit the overall effectiveness of on-water recovery. There were significant efforts to identify, test, and use novel technologies to enhance the cleanup, including a prominent experiment with a large-scale centrifuge system designed to separate oil from water (Butler, 2012). Despite challenges with that particular system, one outcome of the 2010 spill was an enhanced focus on the need to improve demulsification technologies to support spill response (Fitzpatrick and Fields, 2013).

### 1.3.2 Technology Transfer from Other Industries

Oil and water mixtures and emulsions occur in many processes globally, including wastewater generation, petroleum production, and food production. The shipping industry has dealt with similar challenges to oil spill recovery operations – the need to clean oily bilges so that bilge water can be legally discharged overboard – for many years. This report scans technologies from all of these industries and examines them through the lens of on-water oil recovery to identify technologies or research areas that may be applied to the challenge of optimizing demulsification and oil-water separation during offshore spill response.

## 2 Research Methods

A research team from Nuka Research and DNV-GL conducted an interdisciplinary literature review and expert interview process to answer the following research questions:

- What is the state of demulsification and separation technology and the research associated with that technology?
- What technologies are currently being used during oil spills?
- What types of technology can or should be developed to increase oil spill response capacity?

## 2.1 Literature Review

### 2.1.1 Initial Search

Figure 2-1 characterizes the source of the literature reviewed for this study.

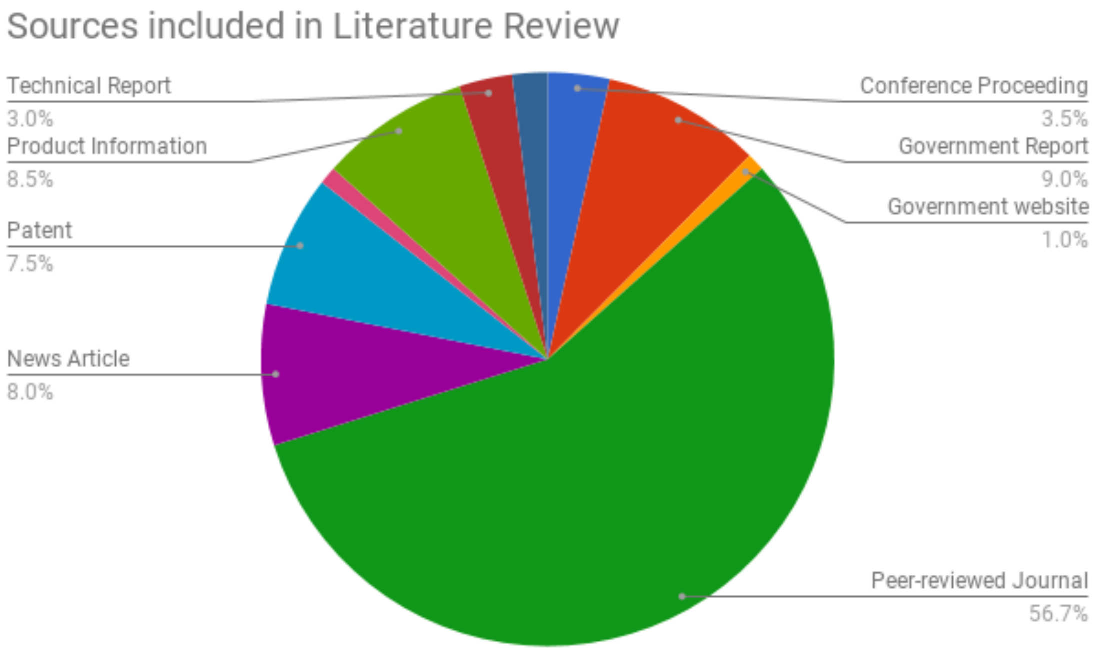


*Figure 2-1. Literature Review Sources*

The research team conducted a literature search for both currently approved and available technologies, technologies under development, and new techniques for demulsification and oil-water separation reported in the scientific and technical literature. Search methods included internet search platforms (e.g. Google Scholar), as well as online journal databases (e.g. Elsevier), and conference proceedings databases (e.g. International Oil Spill Conference). The Department of Interior assisted with procurement of restricted articles through their inter-library loan (ILL) program. Literature sources included: scientific journals; government reports; conference proceedings; patents; manufacturer product specifications; technical reports; news articles; and thesis/dissertations. A total of 222 unique references were compiled and underwent initial review. Of these, 201 were retained as relevant to this study.

### 2.1.2 Categorization of Technologies

The research team reviewed all sources retained after the initial literature search, and systematically categorized each article based on a series of criteria. The literature was sorted initially to distinguish background articles, which provided overviews of demulsification and oil-water separation but did not assess specific technologies, from technical articles that considered specific technologies (or, in some cases, compared specific technologies). Background articles (25 total, 12% of literature reviewed) provided general information that was referenced or consulted in developing this paper. The remainder of the articles (176 total, 87% of literature reviewed) described testing or application of specific demulsification or separation technologies.

The technology literature was categorized based on the primary mechanism for separating oil and water, with five broad categories: (1) physical; (2) nanotechnology; (3) chemical; (4) multi method approaches; and (5) other. Figure 2-2 shows the proportionate breakdown among these five categories.

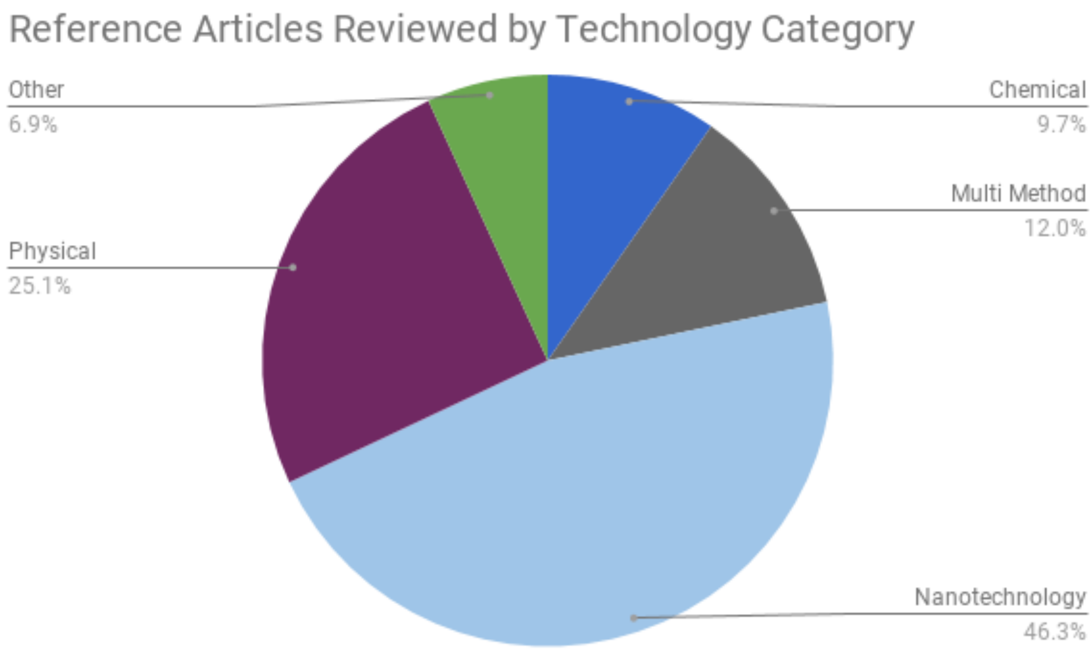


*Figure 2-2. Technology Categories Used to Sort and Review Literature*

The literature describing technologies was further sub-categorized within each of these five broad areas, and this categorization scheme provided a basis for comparing different approaches. The number of articles reviewed in each technology category has no direct relationship to the maturity, effectiveness, or appropriateness for any particular technology for offshore oil spill recovery. Section 4 describes the state of research in each category and sub-category, and includes a table of references reviewed.

### 2.1.3 Industrial Applications

All articles describing demulsification or separation technologies were also categorized based on the industrial application for which the technology was either currently in use or, in the case of experimental technologies, in which the article indicated that the researchers were pursuing the technology for a specific application. The literature describes technologies from oil production and refining; the food industry; wastewater treatment; shipping (bilge treatment); and oil spill recovery. A few technologies were described in the context of multiple industries, and a few experimental studies did not identify the intended industrial application. Figure 2-3 summarizes this information.

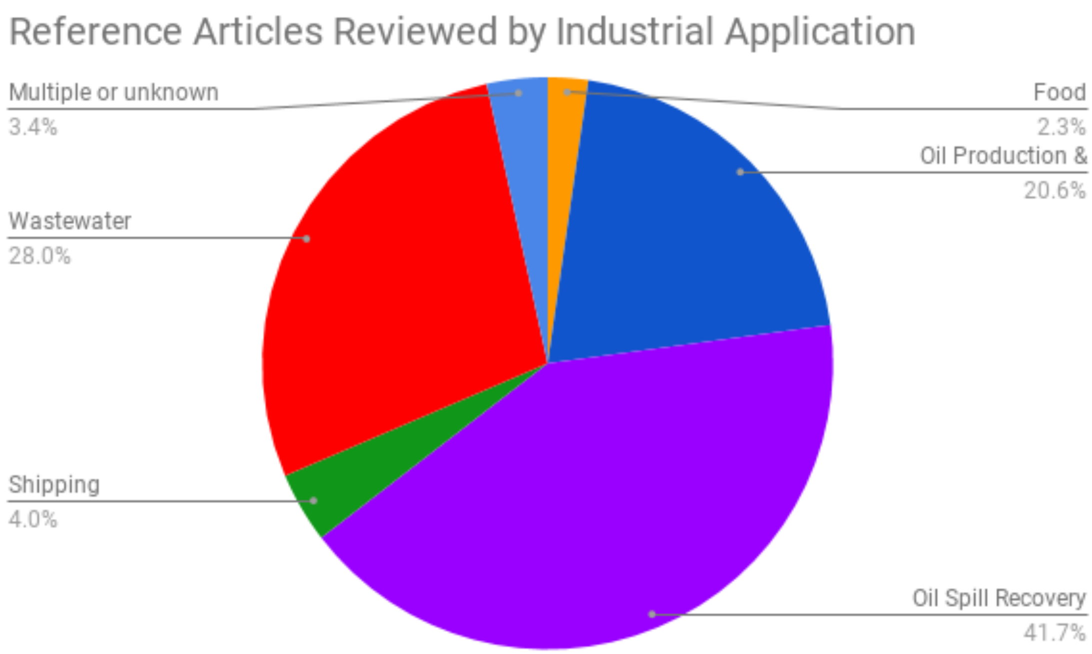


*Figure 2-3. Industrial Applications Identified for Technologies in Literature Review*

## 2.2 Subject Matter Expert Interviews

The research team conducted individual interviews with 14 subject matter experts, including oil spill responders, inventors of oil recovery technology, researchers, and regulators. Several of the experts had experience with demulsification technologies in the oil and gas and shipping industries, and all had expertise in how separation technologies are used in oil spill recovery.

Table 2-1 summarizes the interviews conducted to support this study and identifies general discussion topics that were covered. Interview questions were tailored based on individual expertise. Interviews were conducted concurrent with literature review, and in many cases their outcome influenced the literature search.

Information provided through expert interviews is summarized throughout this report, but direct attribution of statements to individuals is not provided based on requests by several of the experts interviewed.

*Table 2-1. Expert Interviews Conducted and Topics Covered*

| Area of Expertise | Organization | Individual | Examples of Discussion Topics |
|---|---|---|---|
| **Research and Regulation** | SINTEF | Ivan Singsaas | • Firsthand involvement in or knowledge about research and development of technologies<br>• Regulatory drivers of or barriers to innovation |
| | US Coast Guard | Kurt Hansen | |
| | | Scott Knutson | |
| | Norwegian Coastal Administration | Rune Bergstrøm | |
| | | Steinar Gyltnes | |
| **Oil Spill Removal Organizations (OSROs)** | NOFO | Hans Walter Jensen | • Technologies currently in use, their efficiencies and limitations<br>• New technologies that may enhance demulsification<br>• Operational considerations for incorporating technologies into on-water recovery systems |
| | MSRC | John Swift | |
| | NRC | John Heilschler | |
| | Clean Gulf Associates | Frank Paskewich | |
| **Technology Companies and Vendors** | T&T Water Solutions | Joshua Allsworth | • How specific technology or system works and its maturity, cost, efficiency, scalability, previous use in responses or full scale trials, and its overall response potential<br>• Drivers of or barriers to research, development, and innovation for demulsification technologies |
| | Qualitech | Mark Ploen | |
| | PPR Alaska | Kevin Kennedy | |
| | Extreme Spill Technology | David Prior | |
| | T&T Marine Salvage | Jim Elliott | |

## 2.3 Technology Assessment

The literature review and categorization of technology-focused references provided a foundation for assessing technologies based upon a range of factors that may impact their fitness for application to offshore mechanical recovery. Within each technology category and sub-category, technologies were assessed for the following: (1) maturity; (2) cost; (3) efficiency; (4) previous use in oil recovery; and (5) potential use as part of an in-line mechanical oil recovery system. Subject matter expert interview input was factored into this process. Section 5 presents this assessment and identifies the assessment criteria.

## 2.4 Limitations and Assumptions

The information and analysis in this report represents the best professional judgment of the authors based on the information we reviewed. Our analysis assumes that statements made in literature or during interviews are accurate. Over half of the literature reviewed was derived from peer-reviewed scientific journals (See Figure 2-1), contributing to our confidence in the quality of the information.

The research team included European and North American investigators, and while we attempted to scan the worldwide literature, our research excluded studies that were not available in English or Norwegian.

Demulsification and separation technologies continue to evolve, and the analysis in this report reflects research published before April 2018.

# 3 Current State of Demulsification and Separation Technology

A number of existing technologies are used to separate oil and water during oil spill recovery operations. There are also technologies used in oil and gas production and refining, food production, shipping, and waste water management that could be applied or adapted for use in offshore oil recovery. This section summarizes how these technologies are currently used in order to provide context for the analysis of emerging and experimental technologies in subsequent sections of this report.

## 3.1 Offshore Oil Spill Recovery

Offshore oil spill recovery skims oil from the sea surface, transferring the recovered oil and any water that has mixed in through a series of pumps, hoses, and storage chambers. The additional water that is recovered with oil, either as an emulsion or as free water, increases the total volume of recovered fluids. This requires additional time to handle, separate, and dispose of the water and oil.

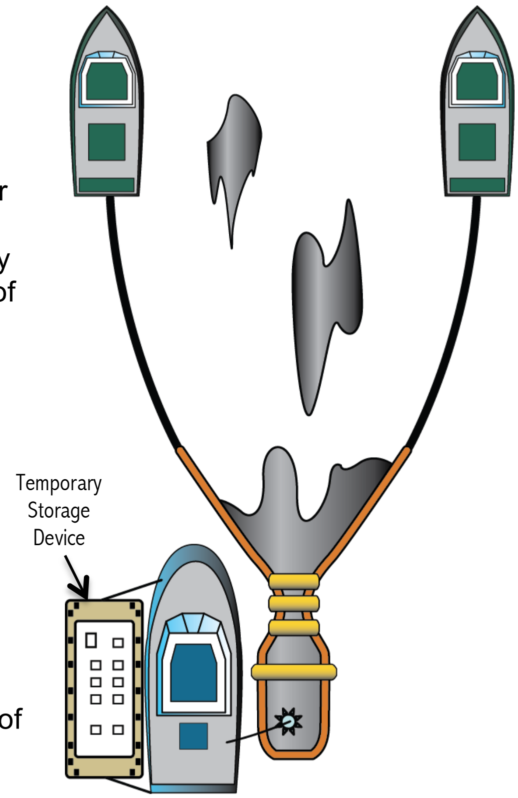


*Figure 1-1. On-water recovery configuration showing recovered oil being pumped from the containment area to a mini barge alongside the vessel*

### 3.1.1 Emulsion and Oil-water Mixtures in Oil Recovery Operations

Recovered emulsions, oil, and free water are initially stored together, either within the skimming system or into a primary storage device (sometimes referred to as temporary storage device, or TSD). Once the primary storage is filled, it must be emptied or recovery will be disrupted. A full TSD would typically be emptied into a larger secondary storage container (floating barge or shoreside recovery tank). Figure 1-1 shows a conceptual diagram of a typical on-water recovery task force.

Oil and water separation may occur at various points during the recovery process. It is most common to separate recovered oil from water before recovered fluids are transferred from primary to secondary storage. Some amount of separation will occur as a simple factor of time and gravity, allowing for the floating oil to be pumped off and the water that has settled out to be disposed of. Recovered water that contains more than 15 ppm of hydrocarbons must be treated as contaminated. Water that falls below the 15 ppm standard, which is established in international law (MARPOL 73/78) and federal regulation (33 CFR 151, 155 and 157), may be decanted overboard during offshore oil recovery operations (beyond the 24 nautical mile contiguous zone of U.S. waters).

Additional water quality standards established through state regulations may apply to oil recovery operations closer to shore, although these are typically waived during spill response, with the 15 ppm standard as a default. Therefore, any technology or system that can separate oil from water at a pace that matches on-water recovery rates, and ensure that the water falls below the contamination threshold, would significantly reduce the storage volume and save time transferring recovered fluids. The closer this occurs to the skimming operations, the less time spent transiting between primary and secondary storage locations.

### 3.1.2 Demulsification and Separation Technologies

The simplest method for separating oil from water is through retention of the oil-water mixture within the TSD until gravity separates out some or all of the fluids. There has been some work to evaluate optimal retention times, which tend to range from 30 to 60 minutes depending upon a number of variables, such as oil type and slick thickness (S.L. Ross, 2005). In the 1980s, the use of demulsifiers (chemical emulsion breakers), either alone or in combination with retention/gravity separation, also became a common practice for marine oil recovery. While these chemicals can speed up the separation process, they also introduce another chemical into the waste stream (IPIECA, 2013).

### 3.1.3 Technologies in Use by U.S. and European Response Organizations and Agencies

Interviews with subject matter experts from U.S. oil spill removal organizations (OSROs) and the U.S. Coast Guard confirmed that gravity separation within the TSD is still the most common practice for separating oil and water during recovery operations. Baffled separation tanks are sometimes incorporated into the recovered oil-water separation, incorporating a combination of over/underflow baffles to enhance gravity separation as the oil-water mixture moves through a series of compartments. A final step uses sorbent materials to remove remaining oil before decanting water back into recovery areas. U.S. OSROs note that these systems have been built *ad hoc* at a spill site using modified roll-off containers, such that they can be deconstructed after the spill response concludes.

Interviews with European response experts (government and industry response organizations) indicated that it is common practice to decant free water back into the recovery area, thereby reducing the constraint on temporary storage.

Chemical demulsifiers are not favored for use during on-water recovery operations, though they are sometimes used during the recovered oil treatment and disposal process that occurs away from the on-water recovery area. Demulsifiers may be used to separate oil and oily water waste streams when they are transported to shore-based disposal facilities.

Expert opinions differed regarding the need for enhanced demulsification and oil-water separation technologies to support spill response. Representatives of some U.S. OSROS indicated an interest in new or emerging technologies to enhance demulsification and separation, but noted that existing approaches satisfy planning standards. This makes it more difficult to justify investing in new technologies.

While the literature discussed in Section 4 includes a number of “polishing” techniques that are intended to reduce oil-in-water concentrations to below applicable standards, these are not used by U.S. OSROs during on-water recovery. The oil spill response organizations and experts interviewed indicated that common practice does not include testing decanted water for hydrocarbon concentration prior to discharging to recovery areas.

## 3.2 Other Industrial Applications

The literature reviewed described several industrial applications where demulsification and oil-water separation technologies have been researched and developed. Some of this research may be transferable to oil spill recovery. This section describes the industrial applications where oil-water separation and demulsification technologies are typically used, and the current state of practice and research as reflected in the literature reviewed. Potential transferability of technologies to offshore oil spill response is explored in Sections 5.2 and 6.1.

### 3.2.1 Oil Production and Refining

Produced water is a significant waste stream generated by oil and gas production, and oily water is also produced during the refining process. Separation of oil and water is a component of both the production and refining processes.

In oil and gas production operations, offshore operators face limits to the permissible oil content in produced water before it can be discharged back into the ocean. Limits are typically set by national authorities and include both instantaneous and average discharge limits. In the U.S., federal regulations set the daily maximum limit at 42 mg/L average and 50 mg/L instantaneous for waters inside the territorial sea, which extends 12 nautical miles (nm) offshore (40 CFR 122). For offshore oil and gas operations (beyond the territorial sea), the daily maximum limit is 48 mg/L average and 72 mg/L for an instantaneous discharge (40 CFR 435). To meet these regulations, oil and gas operators must treat produced water to remove enough oil to meet these thresholds before it can be released.

For oil production and refining operations in offshore waters (beyond the 24 nm contiguous zone), discharge standards must adhere to the International Convention for the protection of Pollution from Ships (MARPOL 73/78) standards, which require contaminant concentrations below 15ppm. There are technologies – many similar to the types of wastewater treatment used for other industries – designed to meet MARPOL standards (Ahmadun, 2009).

Oil-water separation also comes into play for oil and gas production operations during the production process. Drilling operators inject fluids into well formations to assist with upward flow, and in addition to those injected fluids, there may also be formation water that comes up with the oil or gas. Separating these three phases – oil, gas, and water – is an integral part of the production process, and there are technologies in use that may have applicability for oil spill recovery, although many are highly complex (Badr et al., 2014; Peachey, 1995; McMillan, 1984).

### 3.2.2 Shipping

The shipping industry produces oily waste streams in the form of bilge water, oily residues (sludge), and tank washings (slops). Depending upon the operator, any or all of these waste streams may require treatment onboard so as not to disrupt vessel operations. The shipping industry has adjusted to increasingly stringent regimes over time regarding discharge of contaminated water, and there are a number of technologies that have evolved to support the cleaning of oily wastes from ships (CE Delft, 2016).

Gravity separation has traditionally been the preferred method of separating oil and water onboard ships, but there have been new technologies that have emerged to address a second phase of "polishing" oily water before it is discharged (EPA, 2011). Oily sludges generated by a number of ship systems, including the oily water separators, are often incinerated onboard (CE Delft, 2016).

Oily water separation systems developed for shipping may have transferability to spill response because they are designed for operation on a moving vessel. However, the volume of oily water generated by a single ship is only a small fraction of what would be involved in a major offshore oil spill response. For example, a typical separation rate for bilge oil-water separation systems is 1 $m^3$/hr (EPA, 2011). A high capacity skimming system could recover oil and water at 30 times that rate. Scalability is a key factor for examining the application of bilge systems to on-water oil recovery.

Of the technologies evaluated in Section 4, only a handful came from the shipping industry. Most of these combine methods, and some include the use of chemical emulsion breakers (WVT Industries, 2018; EPA, 2011; Little and Patterson, 1977).

### 3.2.3 Food

The food production industry faces the need to separate different food oils, such as olive oil, essential oils, and palm oil, which may emulsify during the production process (Chen et al., 2017). Often times, these demulsification systems are designed within the food production system and not as a secondary treatment. One exception is olive oil production, where the emulsion is formed during the pressing and processing phases and then is demulsified before the oil is bottled and distributed. The primary method of demulsification and separation of oil in the food industry tends to be microwave technology (Kuo et al., 2010 and Chen et al., 2017), which has not been evaluated for use in oil recovery applications.

### 3.2.4 Wastewater Treatment

Municipal and industrial wastewater systems must deal with large volumes of water contaminated with oil, among other substances. There are a number of oily water separation and treatment technologies on the market, and many others in the experimental literature, that address wastewater. After oil spill recovery, which was a target of the literature search for this study, articles related to wastewater treatment technologies were the most prevalent. There has been a significant volume of research into nanotechnologies to enhance wastewater treatment. Some of this research may benefit oil spill recovery, although wastewater treatment processes typically do not deal with the same time constraints faced during oil spill recovery.

# 4 Technology Review

Technologies assessed for this study were grouped into five categories: (1) physical separation; (2) nanotechnology; (3) chemical; (4) multi method; and (5) other.

This section summarizes the information collected for each of these categories, with a focus on studies that identified oil spill recovery as a potential application for the technology. Section 5 compares technologies based on this categorization scheme, including both information from the literature review and input from subject matter experts.

## 4.1 Physical Separation

### 4.1.1 Overview and Trends

Physical separation technologies use physical processes to separate oil from water. Within the literature reviewed, we identified four sub-categories that captured most of the technologies described: agitation; centrifuge; coalescing surfaces; and gravity. A fifth category was created for technologies that did not fit into any of these categories. Figure 4-1 summarizes the literature reviewed and the manner in which it was sub-categorized and attributed to various industrial applications by the research team. Table 4-1 at the end of this section shows how each reference was categorized.

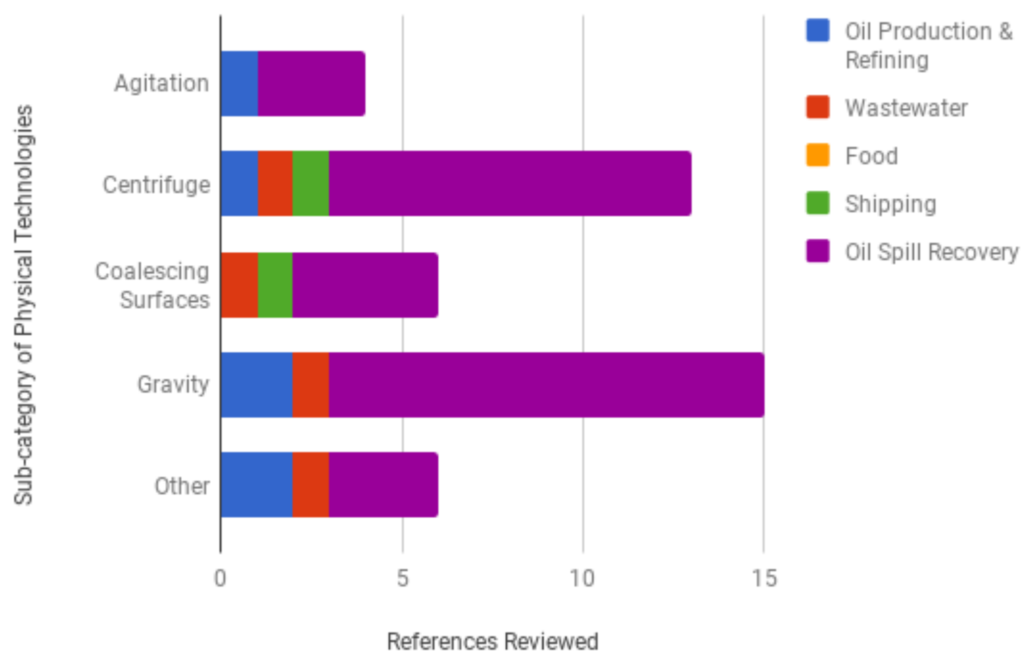


*Figure 4-1. Summary of Physical Separation Technology Literature Reviewed by Sub-Category and Industrial Application*

Physical separation technology references accounted for about 22% of the technology-focused literature reviewed for this study. Research in this area was predominantly focused on oil spill recovery applications, which is consistent with the fact that this has been the preferred and customary approach for offshore response. Physical separation technologies are also derived from oil production and refining, wastewater treatment, and shipping.

### 4.1.2 Gravity

The use of gravity to separate oil and water is not a technology so much as a technique, but it is a commonly applied technique and the current standard for offshore oil recovery. The gravity separation literature reviewed dates back to a 1983 study by the U.S. Coast Guard describing a prototype oil recovery system that integrated oil-water separation into the recovery unit. The report notes that during performance trials, the retention time required for separation became a limiting factor on overall system performance (Cohen and Dalton, 1983).

More recent research and trials that looked at gravity separation for oil spill response applications considered modifications within the TSD (or equivalent component) to speed up the separation process. One patent application describes a two-chamber system, enhanced by a heating system in the first chamber. The heat is intended to reduce oil viscosity in cold conditions (Jauncey, 2014). Other technologies manipulate the shape or configuration within a TSD (or equivalent component) to promote gravity separation (Zhang and Zhang, 2014; Restco, 2015; Tristar, 2014).

Research into submersed oil recovery has evaluated similar approaches, with a slightly different focus derived from the need to re-float heavy oil as an interim recovery step (Hansen et al., 2011; Hansen et al., 2012). This initial research has yielded one new product to the market, which uses voraxial separation (hydro-cyclone) to enhance skimming capacity. A hydrocyclone is a device that applies centrifugal force to a flowing liquid mixture to promote separation of components based on their weight. They are similar to centrifuges, but hydrocyclones are more passive and apply less force. Manufacturer specifications note that this in-line system can result in a 10-times increase in on-water recovery capacity by reducing recovered oil storage by 90% (Voraxial, 2018). System testing during the 2011 Wendy Schmidt Oil Cleanup X Challenge yielded an average recovery efficiency of 49.2%, which reflected a relatively high proportion of recovered water compared to other technologies tested (Meyer et al., 2016). Cyclonic separation was incorporated into several other technologies described in the literature (Li, X., et al., 2016; Murdoch et al., 1995; Peachey, 1995; Tolmie and Stone, 2006; Young et al., 1994).

There are skimming systems that attempt to enhance oil-water separation by reducing the velocity of oil as it encounters the skimmer head, reducing the amount of emulsification that occurs during the recovery process (Meyer et al., 2016). Another system integrates a dual-chambered vacuum system into the skimming system, separating the recovered oil and water using a vacuum, which forces the oil and water to separate based on specific gravity (PPR Alaska, 2016). Tank tests of a skimming system using this gravity separation system demonstrated oil recovery efficiency of over 99% (ASRC, 2017). Because oil/water separation and demulsification occurs within the vacuum chamber, water is discharged directly from the skimming unit. Effluent testing from this system during a creosote remediation project on Lake Superior showed that the water discharged from the skimming unit was compliant with Great Lakes water quality standards.

Gravity separation is also used in the oil production industry, to separate oil and gas from produced water used in the drilling process. In some cases, these processes are conducted within a fixed facility, allowing for more space and more sophisticated technology, such as using a series of vortexes to enhance gravity separation in a large cylindrical tank (Badr and Ahmed, 2014). There are also “downhole” technologies that attempt to separate fluids at production wells, using similar principles (Peachey, 1995).

The wastewater industry has also generated some gravity-based separation technologies. The principles are similar to those used in other applications, including vortexes and hydrocyclones (Tolmie and Stone, 2006).

### 4.1.3 Coalescing Surfaces

Coalescing surfaces enhance gravity separation by introducing a series of surfaces of various shapes that encourage oil droplets to coalesce as they move through a tank or series of tanks.

The first reference to this technology came from the U.S. Navy, where coalescent plates were used to treat oily bilge water from ships during the late 1970s in response to emerging environmental regulations. The technology was not integrated into the ship's hull; it was housed in a shoreside facility (Hura and Mittleman, 1977).

The use of coalescent surface technology for oil spill recovery operations has been contemplated for some time (Peigne, 1993), and there are currently several technologies on the market (Freylit, no date; Filter Technology, 2016; Technomar, 2018), in addition to the *ad hoc* techniques used by U.S. OSROS (See Section 3.1.3). Figure 4-2 shows an illustration from a manufacturer's website of a technology that uses cone-shaped plates to coalesce oil as it is pumped through the system.

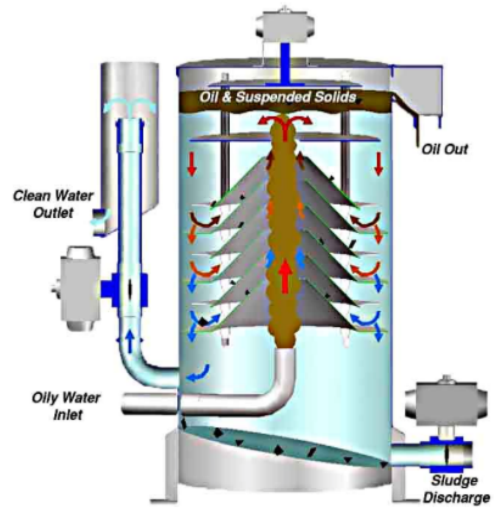


*Figure 4-2. Coalescing Surface Separator Technology (Filter Technology, 2016)*

According to media reports, a mobile system with coalescent plate technology was successfully used to separate oil and water during a spill response near Athens, Greece in 2017. The Freylit system, developed in conjunction with the U.S. Defense Logistics Agency, produced effluent water that was clean enough to discharge back into the sea (Braesch, 2017). The technology is not new; these separators have been in use in water treatment for decades. Recent media reports and manufacturer information indicate a push toward adapting this technology for spill response. The company's website indicates that this technology was used during the Deepwater Horizon spill response, and that it can achieve 5 ppm oil concentration in treated oil. Conceptual diagrams for marine systems show a large catamaran-based system with a capacity of 37,800 liters/minute and shallow water systems ranging from 18-60 liters/minute (Freylit, no date). There is no indication that prototype vessel-based systems have been developed.

More recent studies have investigated novel shapes and configurations for coalescing oil droplets. One experimental technology mimics the spikes of a cactus skin to separate microscopic oil droplets from the water column, mimicking the mechanism that cactuses use to collect water in the desert (Yirka, 2013).

### 4.1.4 Centrifuges

Centrifuges have a long history of use in oil-water separation, but despite research dating back to the 1970s (Mensing and Stoeffler, 1971; Miller, 1973; Sammons and Fox, 1979), there has been limited success in using them as part of an offshore oil recovery system. A study in the 1990s evaluated the use of a centrifugal system in line with a skimmer as a dual "skimmer/separator" model, but the system performance was uneven (Fickel and Bretz, 1996).

Centrifuge technology gained popular attention during the 2010 Macondo well blowout, during which a prototype unit produced by Ocean Therapy Solutions was deployed in the Gulf of Mexico. However, the system performed unevenly. The introduction of debris into the system reduced flow rates and destabilized the centrifuge, and wave action reduced efficiency by disrupting the system's orientation. Pumping mechanisms did not work well on viscous emulsions (Bluebird Electric, 2010; Sahagun, 2010).

European researchers have developed a prototype for a hovercraft-mounted rotating oil-water separator that uses centrifugal motion to achieve separation in-line with skimming operations (Maj et al., 2014; Ylec Consultants, no date). The light-weight system was created specifically to work on the Hoverspill™ platform, which provides a relatively stable base, but the separator can also be used as a standalone system. In meso-scale testing, the separated water held a minimum of 30 ppm hydrocarbons (Maj et al., 2014). The manufacturer's website (Multipurpose Air Cushion Platform/MACP) indicates that the Hoverspill™ system is commercially available.

### 4.1.5 Agitation

Physical agitation technologies enhance gravity separation by adding energy to the system and allow it to separate faster. In most technologies, air bubbles are fed into the bottom of a tube or tank and then are allowed to float up through the mixture. Oil particles are adsorbed on to the air bubbles and float through the mixture with the air bubble to refloat the oil.

One researcher concluded that smaller bubbles had more surface area onto which oil could adsorb and had higher effectiveness in removing oil (Etchepare et al., 2017). Two recent research projects assessed the effectiveness of air bubble agitation systems. One focused on removing oil from within a waterbody by positioning the system below the surface of the water to float oil to the surface for collection. This technology proved highly effective in a lab setting, but at test-tank scale, removal rates were significantly lower (Balsley and Fitzpatrick, 2017). The second project focused on the potential use of air bubbles for oil spill recovery in arctic marine environments. This experiment proved to be highly effective in a lab setting, removing oil to 13.3 ppm, but the oil mixture that was separated had significantly high residual water content, requiring more processing before the oil can be disposed of or used (Shi et al., 2017).

### 4.1.6 Other Technologies

While gravity, centrifuge, and agitation technologies tended to dominate the category of physical separation technologies, additional research has been conducted on novel physical separation techniques such as suction, freezing, and combustion.

One government patent reported on the use of heating the oil-water mixture to enhance gravity separation during oil recovery, and then pumping the oil into an in-situ combustion chamber to be burned. After burning, the air emissions were scrubbed of heavy particles before releasing to the atmosphere (Wehrle et al., 1995). There is no indication that this technology was ever brought to market.

Freezing and thawing has been used, sometimes in conjunction with other methods, to enhance separation during oil production (Chen and He, 2003). A variation on agitation that feeds an emulsion through a bed of resin beads was also reported as an experimental technology for use in wastewater treatment (Kundu and Mishra, 2013).

### 4.1.7 Table of References

Table 4-1 shows how each physical separation technology reference was categorized. A complete reference list is included in Section 7.

*Table 4-1. Categorization of Physical Separation Technology References*

| Lead Author & Date | Type of Reference | Sub-Category | Market Readiness | Industrial Application |
|---|---|---|---|---|
| ASRC, 2017 | Technical Report | Gravity | Market Ready | Oil Spill Recovery |
| Awasthi and Srivastava, 2017 | Journal | Centrifuge | Market Ready | Oil Spill Recovery |
| Badr and Ahmed, 2014 | Patent | Gravity | Unknown | Oil Production & Refining |
| Balsley and Fitzpatrick, 2017 | Govt. Report | Agitation | Development | Oil Spill Recovery |
| Bluebird Electric, 2010 | News Article | Centrifuge | Market Ready | Oil Spill Recovery |
| Braesch, 2017 | News Article | Other | Market Ready | Oil Spill Recovery |
| Chen and He, 2003 | Journal | Other | Market Ready | Oil Production & Refining |
| Cohen and Dalton, 1983 | Conf. Proceeding | Gravity | Market Ready | Oil Spill Recovery |
| Etchepare et al., 2017 | Journal | Agitation | Experimental | Oil Spill Recovery |
| Fickel and Bretz, 1996 | Govt. Report | Centrifuge | Market Ready | Oil Spill Recovery |
| Filter Technology, 2016 | Product Info | Coalescing | Market Ready | Oil Spill Recovery |
| Freylit, no date | Product Info | Coalescing | Market Ready | Oil Spill Recovery |
| Hansen et al., 2011 | Conf. Proceeding | Gravity | Development | Oil Spill Recovery |
| Hansen et al., 2012 | Govt. Report | Gravity | Market Ready | Oil Spill Recovery |
| Hura and Mittleman, 1977 | Journal | Coalescing | Market Ready | Shipping |
| Jauncey, 2014 | Patent | Gravity | Market Ready | Oil Spill Recovery |
| Kundu and Mishra, 2013 | Journal | Other | Experimental | Wastewater |
| Li, X. et al., 2016 | Journal | Agitation | Experimental | Oil Production & Refining |
| Maj et al., 2014 | Conf. Proceeding | Centrifuge | Market Ready | Oil Spill Recovery |
| McMillan, 1984 | Patent | Other | Unknown | Oil Production & Refining |
| Meikrantz et al., 2002 | Journal | Centrifuge | Unknown | Oil Spill Recovery |
| Mensing and Stoeffler, 1971 | Journal | Centrifuge | Experimental | Oil Spill Recovery |
| Meyer et al., 2016 | Govt. Report | Gravity | Market Ready | Oil Spill Recovery |
| Miller, 1973 | Patent | Centrifuge | Market Ready | Shipping |
| Murdoch et al., 1995 | Govt. Report | Centrifuge | Development | Oil Spill Recovery |
| Navalprogetti, 2018 | Product Info | Gravity | Experimental | Oil Spill Recovery |
| Oil Spill Products, 2017 | Product Info | Coalescing | Market Ready | Wastewater |
| Peachey, 1995 | Patent | Gravity | Market Ready | Oil Production & Refining |
| Peigne, 1993 | Conf. Proceeding | Coalescing | Market Ready | Oil Spill Recovery |
| PPR Alaska, 2016 | Patent | Gravity | Market Ready | Oil Spill Recovery |
| Restco, 2015 | Govt. Report | Gravity | Experimental | Oil Spill Recovery |
| Sahagun, 2010 | News Article | Centrifuge | Market Ready | Oil Spill Recovery |
| Sammons and Fox, 1979 | Patent | Centrifuge | Market Ready | Wastewater |
| Shi et al., 2017 | Govt. Report | Agitation | Development | Oil Spill Recovery |
| Technomar, 2018 | Product Info | Other | Market Ready | Oil spill Recovery |
| Tolmie and Stone, 2006 | Patent | Gravity | Unknown | Wastewater |
| Tristar, 2014 | Product Info | Gravity | Market Ready | Oil Spill Recovery |
| Ultraspin, 2017 | Product Info | Centrifuge | Market Ready | Oil Spill Recovery |
| Voraxial., 2018 | Product Info | Gravity | Market Ready | Oil Spill Recovery |
| Wehrle et al., 1995 | Patent | Other | Unknown | Oil Spill Recovery |
| Yirka, 2013 | News Article | Coalescing | Experimental | Oil Spill Recovery |
| YLEC Consultants 2018 | Product Info | Centrifuge | Development | Oil Spill Recovery |
| Young et al., 1994 | Journal | Centrifuge | Market Ready | Oil Production & Refining |
| Zhang and Zhang, 2014 | Journal | Gravity | Experimental | Oil Spill Recovery |

## 4.2 Nanotechnology

### 4.2.1 Overview and Trends

Nanotechnology describes a range of techniques and applications that use nano-scale particles to enhance oil and water separation. Nanotechnologies generally use one of two approaches. The first filters out oil from water based using selectively permeable membranes treated with films or compounds that make them oleophilic or oleophobic. Some technologies are considered "switchable" and can selectively be oleophilic or oleophobic depending on their required use (Lee et al., 2017).

Particles are a second type of nanotechnology that selectively absorb one substance and repel the other. The addition of particles to an oil/water mixture creates the need for an interim step to remove them or include them in waste streams. A popular approach is to magnetize the particles so that the oil-particle aggregates can be removed using magnets (Mirshaghassemi et al., 2017; Xu et al., 2018; Jassby, 2016).

In this section, technologies are categorized as membrane, particle, or other. Figure 4-3 summarizes the literature reviewed and the manner in which it was sub-categorized and attributed to various industrial applications by the research team. Table 4-2 at the end of this section shows how each reference was categorized.

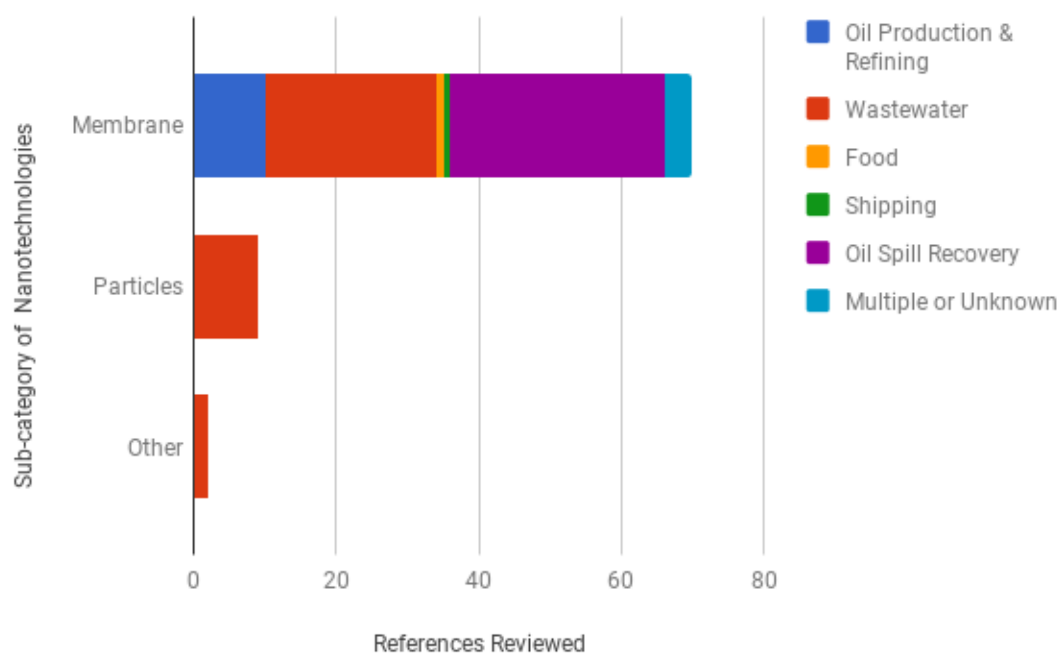


*Figure 4-3. Summary of Nanotechnology Literature Reviewed by Sub-Category and Industrial Application*

Nanotechnology references accounted for nearly half of the technology-focused literature reviewed for this study. Most of the research reviewed considered the use of nanotechnology for either wastewater treatment or oil spill recovery. There is a wide body of research on nanotechnology for water purification generally, and the application of this technology to oil recovery draws from wastewater and water purification studies.

Of nanotechnology literature reviewed that focused on oil production and refining, nearly all were experimental technologies. Most of the mature technologies come from wastewater treatment, and the references reviewed for this study focused on the use of nanotechnology to remove oily substances from wastewater effluent. There is relatively little research on nanotechnology within the food and shipping sectors. Several of the multi method studies reviewed include nanotechnologies blended with physical or chemical methods.

### 4.2.2 Membranes

Membrane technology is an area of active research, with a range of technologies reported, including: brushes, ceramics, fabrics, fibers, foam, graphene, mats, mesh, micro porous, poly coating, sheets, wires, and sponges. The membrane technology literature reviewed was all relatively recent, with the earliest description of research from a 1999 study considering the use of poly-coated membranes for wastewater treatment (Kong and Li, 1999). Most of the references dated from 2010 forward.

#### 4.2.2.1 Fibers, Fabrics, and Mesh

A significant body of research evaluates membrane nanotechnologies to support oil spill recovery. Many of these use coated fabrics, fibers, or mesh to separate the substances, and laboratory scale experiments report high efficiencies (University of Pittsburg, 2010; Zhang and Seeger, 2011; Wang et al., 2017.) Several researchers evaluated coated mesh substances, and there is literature that considered the impact of different coatings and pore sizes (Gondal et al., 2017; Qian et al., 2018; You et al., 2018; Jiang et al., 2017; Pi et al., 2016). Figure 4-4 shows an example of a coated mesh substance and its effectiveness at separating oil droplets from water.

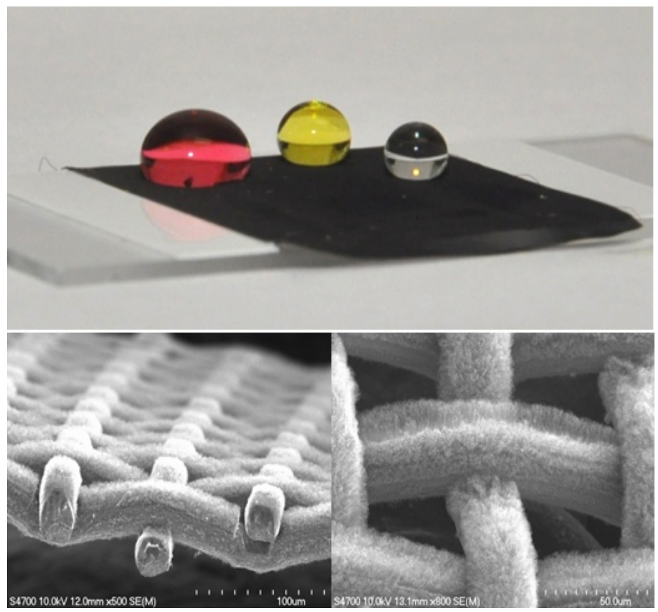


*Figure 4-4. Stainless steel mesh coated with carbon nanotubes (Lee et al., 2017)*

Most of these experiments relied on gravity to initiate separation, often pouring the oil-water mixture through a funnel or basket, or over a sheet of mesh (Zhu et al., 2017; Lo et al., 2017; Khosravi and Azizian, 2017). Researchers evaluating mesh for use in oil production have experimented by adding pressure to speed up the separation process (Chen and Xu, 2013). Some membranes are developed to be switchable, allowing them to be hydrophilic or hydrophobic, depending upon the substance with which they are pre-wetted. Experimental data for these switchable membranes show high efficiency rates (in the 99-100% range), though some of the studies focused on wastewater treatment rather than oil recovery (Tao et al., 2014; Li, J. et al., 2017; Cao et al., 2017).

One series of studies focused on layering composite-coated stainless steel meshes to optimize separation; this “layer cake” technology has been proposed for application to spill response, though initial experiments have been laboratory scale (Brown and Bhusan, 2015; Shaffer, 2015). A similar concept, depicted in Figure 4-5, used a layered, hierarchical pore size structure to tailor the technology to the droplet size in the emulsion (Solomon et al., 2014). Multi-layered membranes have also been evaluated for use in ships' bilges (Tomaszewska et al., 2005).

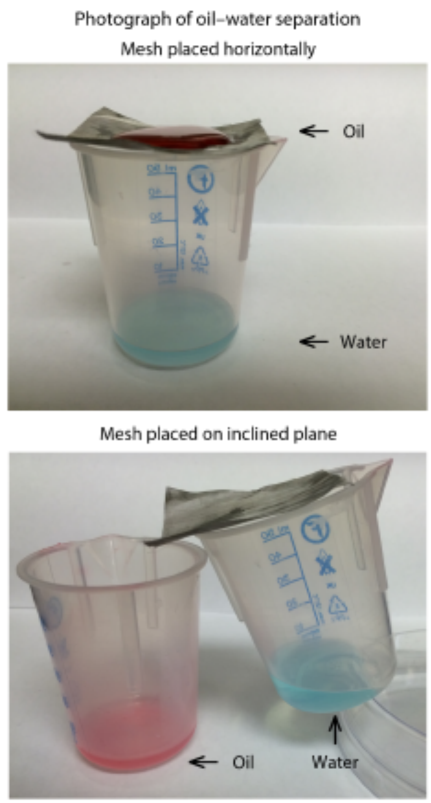


*Figure 4-5. Laboratory experiments confirm that multi-layered coated mesh is effective in separating oil and water both in a pour-through configuration and on an inclined plane (Solomon et al., 2014)*

Researchers have experimented with novel shapes and substances to attempt to maximize separation; a recent study uses a fern—shaped brush structure to enhance separation by trapping oil and repelling water (Furness, 2018). Technologies have been assessed for heavy oils, using a poly-coated foam membrane that works at the high heat needed for heavy oils to flow (Zhang et al., 2015). Research from the wastewater treatment field reports the use of electrical current to create an "on-demand" filtration system (Kwon, et al., 2012). Researchers have also considered re-usability of membranes, for a variety of uses, and it has been reported that some technologies can be reused up to 50 times with minimal loss of efficiency (Li, J. et al., 2017).

The Canadian government has invested in an ongoing research study to evaluate the use of nano-composite membrane technology to support on-water oil recovery operations; this study is still underway at the University of Alberta (Natural Resources Canada, 2017).

#### 4.2.2.2 Foams and Sponges

Foam and sponge nanotechnologies work a bit differently than filtration membranes; most absorb oil to separate it from water. One technology uses carbon-coated sponges to repel water and absorb oil, similar to traditional sorbents. Sponges can be squeezed and reused up to 10 times without significant reduction to efficiency, as reported from laboratory experiments (Sultanov et al., 2017).

Another researcher used a similar sponge technology in conjunction with a laboratory-scale vacuum suction device. By mounting the oleophilic-hydrophobic sponge at the interface of the vacuum suction and the floating oil slick, the sponge enhanced separation of the oil (in this study, gasoline) from the water at a very high efficiency (Wu et al., 2014).

There has also been work to evaluate the use of nano-coated sponges at high temperatures (Wang and Zheng, 2017), and with different combinations of coating (Wang, J. et al., 2018), focused on oil spill recovery applications.

### 4.2.3 Particles

There is considerably less focus in the literature on particle-based nanotechnology, compared to membranes.

Adding particles to oil-water mixtures has been tested as a means to promote separation using oleophilic particles that attract oil droplets and then cause them to either float or sink. One study focused on the potential for this technology to recover oil spills used magnetized particles that floated the oil to the surface of a test tank where a magnet was used to remove the oil attached to the magnetic particles (Hardesty, 2012). The research was conducted in a small-scale laboratory setting and has not been field-tested. There has been subsequent research along the same lines (Lu et al., 2018; Mirshahghassemi et al., 2017). One additional study combined membrane technology with particle technology to reduce fouling of the membranes. These particles were also magnetized, which allow for rapid removal of the particles using a magnetic drum separator and their eventual re-use. The small-scale study contemplated scaling up the technology for use in skimming, either to further concentrate recovered oil or to remove the emulsified oil fraction from free water prior to decanting, as the technology could clean water to 7 ppm. The high cost of replacing the nanoparticles lost during the separation process is a barrier to operationalization (Jassby, 2016).

Similar studies have focused on the use of particles for wastewater treatment, both with and without magnetics (Xu et al., 2018; Li, Y. et al., 2017). There is a technology on the market that uses peat to separate oil and water as part of a mobile water treatment system (BATTA Technologies, 2016). According to product marketing, BATTA's AFX Absorber can be used for oil spill response and applied on bodies of water or on soil. The literature reviewed did not indicate effectiveness of the peat in removing oil from the water. Another market-ready technology uses clay-based flocculants combined with magnetic particles for oil-water separation in wastewater treatment (CETCO, 2018).

### 4.2.4 Table of References

Table 4-2 shows how each nanotechnology reference was categorized. A complete reference list is included in Section 7.

*Table 4-2. Categorization of Nanotechnology References*

| Lead Author & Date | Type of Reference | Sub-Category | Market Readiness | Industrial Application |
|---|---|---|---|---|
| Adhithya et al., 2017 | Journal | Membrane | Unknown | Wastewater |
| Alzahrani and Mohammad, 2014 | Journal | Membrane | Experimental | Oil Production & Refining |
| Balsley and Fitzpatrick, 2017 | Govt. Report | Membrane | Development | Oil Spill Recovery |
| BATTA Filters, 2016 | Product Info | Particles | Market Ready | Wastewater |
| Bong et al., 2015 | Journal | Membrane | Experimental | Oil Production & Refining |
| Brown and Bhushan, 2015 | Journal | Membrane | Experimental | Oil Production & Refining |
| Cao et al., 2013 | Journal | Membrane | Experimental | Wastewater |
| Cao et al., 2017 | Journal | Membrane | Experimental | Wastewater |
| Carnevale et al., 2016 | Journal | Membrane | Market Ready | Food |
| CETCO, 2018 | Product Info | Particles | Market Ready | Wastewater |
| Chang et al., 2014 | Journal | Membrane | Experimental | Wastewater |
| Chen and Xu, 2013 | Journal | Membrane | Experimental | Oil Production & Refining |
| Dong et al., 2014 | Journal | Membrane | Experimental | Oil Production & Refining |
| Furness, 2018 | News Article | Membrane | Experimental | Oil Spill Recovery |
| Gao et al., 2018 | Journal | Membrane | Experimental | Oil Production & Refining |
| Ge et al., 2018 | Journal | Membrane | Experimental | Wastewater |
| Gohari et al., 2015 | Journal | Membrane | Experimental | Oil Production & Refining |
| Gondal et al., 2016 | Journal | Membrane | Experimental | Oil Spill Recovery |
| Gupta et al., 2017 | Journal | Other | Experimental | Wastewater |

| Lead Author & Date | Type of Reference | Sub-Category | Market Readiness | Industrial Application |
|---|---|---|---|---|
| Hardesty, 2012 | News Article | Particles | Experimental | Oil Spill Recovery |
| Hou et al., 2018 | Journal | Membrane | Experimental | Wastewater |
| Hu et al., 2015 | Journal | Membrane | Experimental | Wastewater |
| Jassby, 2016 | Govt. Report | Membrane | Development | Oil Spill Recovery |
| Jiang et al., 2017 | Journal | Membrane | Unknown | Oil Spill Recovery |
| Kavalenka et al., 2016 | Journal | Membrane | Experimental | Multiple |
| Khosravi and Azizian, 2017 | Journal | Membrane | Experimental | Oil Spill Recovery |
| Kong and Li, 1999 | Journal | Membrane | Experimental | Wastewater |
| Kwon et al., 2012 | Journal | Membrane | Unknown | Wastewater |
| Lai et al., 2017 | Journal | Membrane | Experimental | Oil Production & Refining |
| Lee et al., 2017 | Journal | Membrane | Unknown | Wastewater |
| Li et al., 2015 | Journal | Membrane | Experimental | Wastewater |
| Li, J. et al., 2016 | News Article | Membrane | Experimental | Wastewater |
| Li, J. et al., 2017 | Journal | Membrane | Experimental | Wastewater |
| Li, Y. et al., 2017 | Journal | Particles | Experimental | Wastewater |
| Liu, J. et al., 2017 | Journal | Membrane | Experimental | Oil Production & Refining |
| Liu, R. et al., 2017 | Journal | Membrane | Experimental | Wastewater |
| Lo et al., 2017 | Journal | Membrane | Experimental | Oil Spill Recovery |
| Lu et al., 2018 | Journal | Particles | Experimental | Oil Spill Recovery |
| Ma et al., 2017 | Journal | Membrane | Experimental | Wastewater |
| Mahajun, 2011 | News Article | Particles | Market Ready | Oil Spill Recovery |
| Mirshahghassemi et al., 2017 | Journal | Particles | Experimental | Oil Spill Recovery |
| Natural Resources Canada, 2017 | Govt. website | Membrane | Development | Oil Spill Recovery |
| Padaki et al., 2015 | Journal | Membrane | Experimental | Wastewater |
| Pan et al., 2012 | Journal | Membrane | Experimental | Wastewater |
| Peng et al., 2017 | Journal | Membrane | Experimental | Wastewater |
| PennState, 2014 | News Article | Membrane | Development | Oil Spill Recovery |
| Pi et al., 2016 | Journal | Membrane | Experimental | Oil Spill Recovery |
| Qian et al., 2018 | Journal | Membrane | Development | Oil Spill Recovery |
| Shaffer, 2015 | News Article | Membrane | Experimental | Oil Spill Recovery |
| Solomon et al., 2014 | Journal | Membrane | Experimental | Oil Spill Recovery |
| Sultanov et al., 2017 | Journal | Membrane | Experimental | Oil Spill Recovery |
| Tan et al., 2015 | Journal | Membrane | Experimental | Wastewater |
| Tanudjaja et al., 2017 | Journal | Particles | Experimental | Wastewater |
| Tao et al., 2014 | Journal | Membrane | Experimental | Oil Spill Recovery |
| Team Asianet Newsable, 2017 | News Article | Membrane | Experimental | Oil Spill Recovery |
| Tomaszewska et al., 2005 | Journal | Membrane | Experimental | Shipping |
| Tummons et al., 2016 | Journal | Membrane | Experimental | Wastewater |
| Tummons et al., 2017 | Journal | Membrane | Experimental | Wastewater |
| University of Pittsburg, 2010 | News Article | Membrane | Experimental | Oil Spill Recovery |
| Wahi et al., 2013 | Journal | Other | Experimental | Wastewater |
| Wang and Zheng, 2017 | Journal | Membrane | Experimental | Oil Spill Recovery |
| Wang C. et al., 2015 | Journal | Membrane | Experimental | Wastewater |
| Wang et al., 2017 | Journal | Membrane | Experimental | Oil Spill Recovery |
| Wang, J. et al., 2018 | Journal | Membrane | Experimental | Oil Spill Recovery |
| Wang J. et al., 2016 | Journal | Membrane | Market Ready | Unknown |
| Wang, X. et al., 2016 | Journal | Membrane | Experimental | Multiple |
| Wu et al., 2014 | Journal | Membrane | Experimental | Oil Spill Recovery |
| Xu et al., 2018 | Journal | Particles | Experimental | Wastewater |

| Lead Author & Date | Type of Reference | Sub-Category | Market Readiness | Industrial Application |
|---|---|---|---|---|
| Xue et al., 2014 | Journal | Membrane | Unknown | Wastewater |
| Yang et al., 2015 | Journal | Membrane | Experimental | Wastewater |
| You et al., 2018 | Journal | Membrane | Experimental | Oil Spill Recovery |
| Yu et al., 2016 | Journal | Membrane | Unknown | Oil Production & Refining |
| Yu et al., 2017 | Journal | Membrane | Experimental | Oil Spill Recovery |
| Zhang and Seeger, 2011 | Journal | Membrane | Experimental | Oil Spill Recovery |
| Zhang et al., 2013 | Journal | Membrane | Experimental | Wastewater |
| Zhang et al., 2015 | Journal | Membrane | Experimental | Oil Spill Recovery |
| Zhang et al., 2017 | Journal | Membrane | Market Ready | Wastewater |
| Zhu et al., 2013 | Journal | Membrane | Experimental | Multiple |
| Zhu et al., 2017 | Journal | Membrane | Experimental | Oil Spill Recovery |
| Zuo et al., 2018 | Journal | Membrane | Experimental | Wastewater |

## 4.3 Chemical

### 4.3.1 Overview and Trends

Chemical demulsification introduces a chemical substance into an emulsion to separate the water from oil by "breaking" the emulsion. The surface-active compounds migrate to the oil-water interface, rupture or weaken the film, and enhance coalescence. There are many varieties of chemical demulsifiers on the market, and researchers continue to explore new formulas or combinations.

Chemical demulsification technologies only accounted for about 11% of the research reviewed for this report. This does not reflect a lack of research in this area; it is due to the focus of this study on identifying non-chemical technologies that can be incorporated into offshore mechanical recovery operations. Most of the research reviewed was derived from oil production and refining and oil spill recovery.

The chemical technology articles reviewed for this study were not sub-categorized, but Table 4-3 at the end of this section lists the literature reviewed and shows the industrial application for which studies were intended.

### 4.3.2 Demulsifier Technologies

Chemical demulsifiers have been evaluated for their potential to enhance on-water recovery for many years. A series of lab and meso-scale experiments conducted between 1997-2004 evaluated the potential for emulsion breakers to speed up the process of decanting from TSDs, and concluded that while the addition of chemicals would result in some contamination from the demulsifier entering the environment, the overall reduction in oil concentration in decanted water along with the acceleration of the decanting process would merit further consideration. The same studies found that demulsifier efficiency was reduced when free water exceeded 55% of the recovered fluids (SL Ross, 2005; Buist et al., 2005; SL Ross, 2002).

Chemical demulsifiers have also been proposed for use in oil recovery operations by injecting them into viscous emulsions of recovered oil to facilitate pumping (ITOPF, 2012). A study comparing emulsifier performance on water-in-oil emulsions found that amine demulsifiers were more effective than polyhydric and acid demulsifiers (Nour et al., 2007). Recent studies have evaluated ionic liquids and their polymers as an enhancement to non-ionic or anionic demulsifiers, reporting higher efficiencies based on laboratory scale studies (Abullah et al., 2016), and noting enhanced performance in breaking heavy oil emulsions (Ezzat et al., 2018).

Chemical demulsifiers are used in oil and gas production, and there are a number of studies, patents, and promotional materials related to emulsion breaking within the production cycle (Rosstaie et al., 2017; Mueller, 2009; BASF, 2017; Hajivand and Vaziri, 2013). One study (not specific to oil recovery) investigated enhancement such as photo-activated products (Takahashi et al., 2013).

### 4.3.3 Table of References

Table 4-3 shows how each chemical demulsifier technology reference was categorized. A complete reference list is included in Section 7.

*Table 4-3. Categorization of Chemical Demulsifier References*

| Lead Author & Date | Type of Reference | Market Readiness | Industrial Application |
|---|---|---|---|
| Abullah et al., 2016 | Journal | Experimental | Oil Spill Recovery |
| Barillaro, 1997 | Thesis | Experimental | Wastewater |
| BASF, 2017 | Product Info | Market Ready | Oil Production & Refining |
| Belore et al., 2008 | Conf. Proceeding | Experimental | Oil Spill Recovery |
| Buist et al., 2005 | Conf. Proceeding | Market Ready | Oil Spill Recovery |
| Cohen, 1992 | Patent | Market Ready | Wastewater |
| Ezzat et al., 2018 | Journal | Experimental | Oil Production & Refining |
| Hajivand and Vaziri, 2013 | Journal | Experimental | Oil Production & Refining |
| Mueller, 2009 | Patent | Market Ready | Oil Production & Refining |
| Nour et al., 2007 | Journal | Market Ready | Oil Spill Recovery |
| Roostaie et al., 2017 | Journal | Market Ready | Oil Production & Refining |
| SL Ross, 2002 | Govt. Report | Experimental | Oil Spill Recovery |
| SL Ross, 2004 | Govt. Report | Experimental | Oil Spill Recovery |
| SL Ross, 2005 | Govt. Report | Experimental | Oil Spill Recovery |
| Takahashi et al., 2013 | Journal | Market Ready | Unknown |
| Tutien et al., 1978 | Patent | Market Ready | Unknown |
| WVT Industries, 2018 | Product Info | Market Ready | Shipping |

## 4.4 Additional Technologies

### 4.4.1 Overview and Trends

Separation and demulsification technologies described in the literature that could not be categorized based on physical, nanotechnology, chemical, or combined were sorted as "other." Figure 4-7 summarizes the literature reviewed and the manner in which it was sub-categorized and attributed to various industrial applications by the research team. Table 4-4 at the end of this section shows how each reference was categorized.

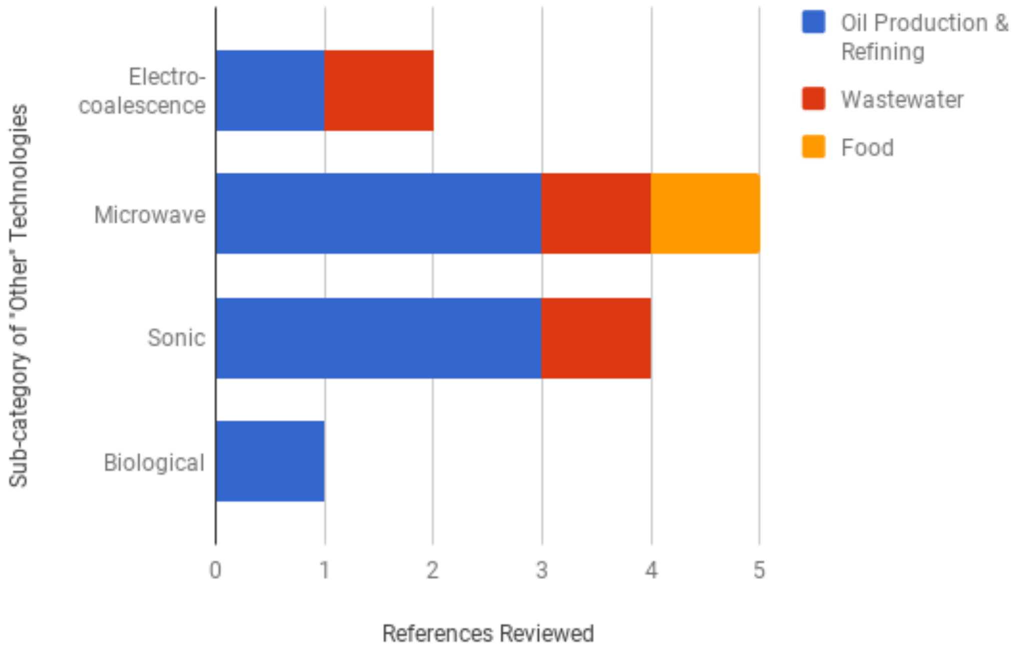


*Figure 4-7. Summary of "Other" Technology Literature Reviewed by Sub-Category and Industrial Application*

Less than 10% of the literature reviewed were characterized as "other." These included sonic, microwave and electro-coalescence technologies. None of these technologies were described in the context of oil spill recovery.

Electro-coalescence technologies apply an electrical current to emulsifications to promote flocculation, with high efficiency reported (Ogutveren and Koparal, 1997; Eow and Ghadiri, 2002). There is a technology on the wastewater treatment market that applies electro-coalescence in a combined separator. Incorporation of electrocoagulation into oil-water separation, discussed in Section 5.2.5, may have some applicability to oil spill recovery (T&T Water Solutions, no date).

The introduction of ultrasonic waves into oil-water mixtures has been demonstrated to enhance separation in laboratory and tank tests (Wang, Z. et al., 2018; Mohsin and Meribout, 2015). An indirect sonic bath technology technique has been developed for potential use in oil production and refining (Antes et al., 2015 and 2017). The technology tested was at laboratory scale, using a 15-cm ultrasonic bath (Antes et al., 2015).

Microwave technology has been used in oil production, wastewater treatment, and food. (Kuo and Lee, 2010; Santos et al., 2017; Xia et al., 2004). Experimental data from oil production research has reported high efficiencies in laboratory tests (Santos et al., 2017; and Xia et al., 2004).

A single biological approach involved mixing fungus spores into a crude emulsion, stirring and then incubating the mixture to promote separation, with high efficiency reported (Vallejo-Cardona et al., 2017).

### 4.4.2 Table of References

Table 4-4 shows how each of the "other" technology reference was categorized. A complete reference list is included in Section 7.

*Table 4-4. Categorization of "Other" Technology References*

| Lead Author & Date | Type of Reference | Sub-Category | Market Readiness | Industrial Application |
|---|---|---|---|---|
| Antes et al., 2015 | Journal | Sonic | Market Ready | Oil Production & Refining |
| Antes et al., 2017 | Journal | Sonic | Market Ready | Oil Production & Refining |
| Chen et al., 2017 | Journal | Microwave | Experimental | Food |
| Eow and Ghadiri, 2002 | Journal | Electro-coalescence | Experimental | Oil Production & Refining |
| Kuo and Lee, 2010 | Journal | Microwave | Unknown | Wastewater |
| Mohsin and Meribout, 2015 | Journal | Sonic | Experimental | Wastewater |
| Ogutveren and Koparal., 1997 | Journal | Electro-coalescence | Experimental | Wastewater |
| Redford, 1993 | Thesis | Microwave | Experimental | Oil Production & Refining |
| Santos et al., 2017 | Journal | Microwave | Experimental | Oil Production & Refining |
| Vallejo-Cardona et al., 2017 | Journal | Biological | Experimental | Oil Production & Refining |
| Wang, Z. et al., 2018 | Journal | Sonic | Experimental | Oil Production & Refining |
| Xia et al., 2004 | Journal | Microwave | Market Ready | Oil Production & Refining |

## 4.5 Multi Method Technologies

### 4.5.1 Overview and Trends

The research team categorized technologies that rely on a mix of physical, chemical, and/or nanotechnology as multi method technologies. Four sub-categories characterized the majority of the multi method technologies: physical and chemical; physical and nanotechnology; chemical and nanotechnology; and physical, chemical and nanotechnology. A fifth category of other combinations was used to capture novel combinations.

Figure 4-8 summarizes the literature reviewed and the manner in which it was sub-categorized and attributed to various industrial applications by the research team. Table 4-5 at the end of this section shows how each reference was categorized.

Multi method technology references accounted for about 12% of the technology-focused literature reviewed for this study. Multi method technologies were predominantly derived from the wastewater and oil production industries. Physical and chemical methods, which are described in literature going back to the 1970s, also apply to the food and shipping industries. Multi method technologies focused on oil spill recovery industry were dominated by studies combining chemical and nanotechnologies. Each of the oil spill recovery technologies reviewed was experimental.

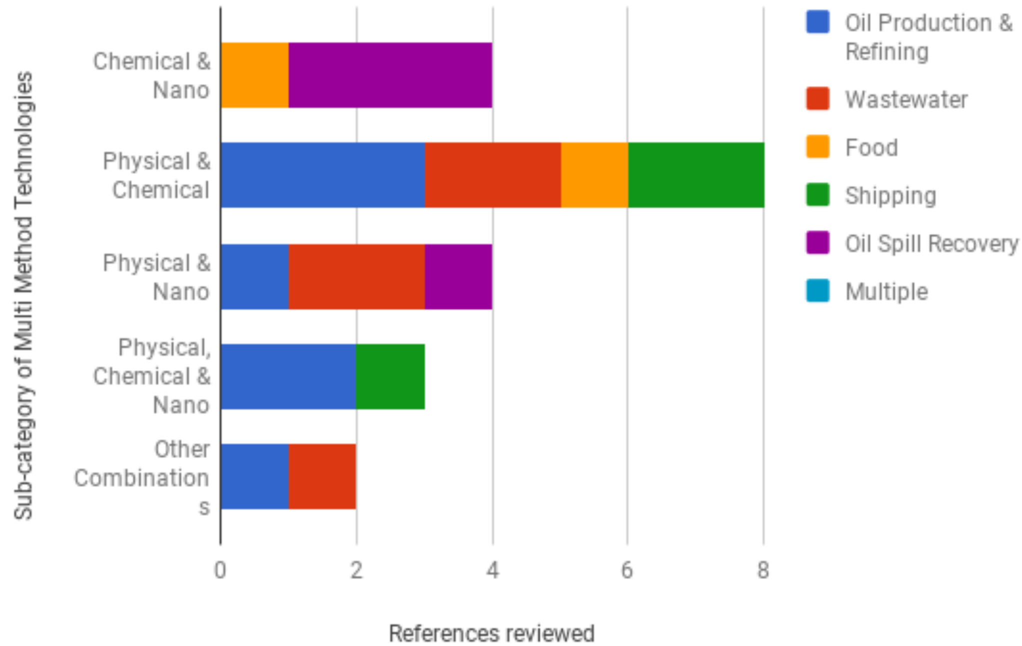


*Figure 4-8. Summary of Multi Method Technology Literature Reviewed by Sub-Category and Industrial Application*

### 4.5.2 Physical and Chemical

Eight of the articles in the literature search were categorized as combining physical and chemical technologies. Combined physical and chemical technologies described for the oil production and refining and wastewater sectors included the use of physical agitation and chemical demulsifiers (Karhu et al., 2014; Bunturngpratoomrat et al., 2013) and freezing and chemical demulsification (Hu, 2016). Research in the food industry has considered the use of a demulsifier and a centrifuge to resolve soybean oil emulsions (Chabrand and Glatz, 2009). Technologies from shipping and wastewater treatment applied gravity separation and emulsion-breaking (Little and Patterson, 1977; Zhang et al., 2008).

Technologies that combine gravity separation with chemical demulsifiers are included in the chemical technologies discussion in Section 4.3.2.

### 4.5.3 Physical and Nanotechnology

The combination of physical and nanotechnology is currently used in the wastewater treatment industry, with a number of technologies on the market that combine gravity separation with nanotechnology filtration. In some cases, nanotechnology filters are combined with an array of physical separation tanks for final polishing of separated water (BATTA Technology, 2016). The major challenge in adapting these technologies to spill response is to match the pace of the nanotechnology polishing to the physical separation rate, and ensuring that both can keep pace with skimming operations.

A Norwegian company is developing a concept that combines physical and nanotechnology, together with the Norwegian Clean Seas Association for Operating Companies (NOFO). The technology involves a labyrinthine process tank where the separation process is based on coalescence, vortex and gravitational effects, and the adhesion to oleophilic materials. The system will have a capacity to treat a volume of 200 m3/h (with 50/50 oil/oilemulsion and water), and separate 2/3 of the free water. This mobile separation unit packs into a 20-foot container, and is designed for use on the deck of a supply vessel, with smaller units planned for smaller vessels. The technology is currently being patented, so there is little information available on its specifications. There are tentative plans to test this unit in the 2018 North Sea Oil on Water Exercise (LossPrevention, 2018).

Earlier technologies (predating modern nanotechnology) utilized membranes to enhance physical separation (Pierpoline, 1996).

### 4.5.4 Chemical and Nanotechnology

The combination of chemical demulsification and nanotechnology has been studied for oil spill recovery application. This includes experiments with nano-coated sponges and polymers (Ferris, 2013) and with surfactants and nano-particles (Ren et al., 2016) or membranes (Kota et al., 2012; Ahmad et al., 2003).

### 4.5.5 Other Combinations

Two studies from the oil production industry considered physical, chemical, and nanotechnologies together. An experimental study evaluated the use of nanoparticles, gravity separation, and chemical demulsifier (Li, Y. et al., 2016). A patent has been filed for a system that includes a membrane, gravity separator, and chemical treatment (Kuki and Matsushima, 2015).

One technique which is currently market-ready combines gravity separation (physical) and electrocoagulation (other) to separate and re-concentrate oil from oil-water mixtures. The system can function in line with a skimmer but requires a constant flow rate, which can prove difficult during operations. The first step is to send the liquid through an electrocoagulation unit and then through a dissolved air flotation unit for a tertiary treatment before decanting (T&T Water Solutions, no date). The system runs on a generator, requiring 230V (50Hz 3-phase) to run the smaller (2,642 gallons per hour) unit and 410-415V (50Hz 3-phase) to run the larger (10,568 gallons per hour) unit. Additional specifications are available through the manufacturer. This system has been successfully used in salvage/lightering operations to remove oil and water from a sunken vessel. U.S. OSROs interviewed for this report indicated an interest in testing this technology as part of an on-water recovery system.

### 4.5.6 Table of References

Table 4-5 shows how each of the multi method technology reference was categorized. A complete reference list is included in Section 7.

*Table 4-5. Categorization of Multi Method Technology References*

| Lead Author & Date | Type of Reference | Sub-Category | Market Readiness | Industrial Application |
|---|---|---|---|---|
| Ahmad et al., 2003 | Journal | Chemical & Nano | Development | Food |
| BATTA Maxi Filter, no date | Product Info | Physical & Nano | Market Ready | Wastewater |
| Bunturngpratoomrat et al., 2013 | Journal | Physical & Chemical | Experimental | Wastewater |
| Chabrand and Glatz, 2009 | Journal | Physical & Chemical | Experimental | Food |
| CMI Marine, 2012 | Product Info | Physical & Chemical | Market Ready | Shipping |
| Deng et al., 2002 | Journal | Physical & Chemical | Experimental | Oil Production & Refining |
| EPA, 2011 | Govt. Report | Physical, Chemical, & Nano | Market Ready | Shipping |
| Ferris, 2013 | News Article | Chemcial & Nano | Experimental | Oil Spill Recovery |
| Hansen and Wolfenberger, 1992 | Patent | Physical & Nano | Unknown | Oil Production & Refining |
| Hu, 2016 | Thesis | Chemical & Sonic | Unknown | Oil Production & Refining |
| Hu, 2016 | Thesis | Physical & Chemical | Market Ready | Oil Production & Refining |
| Karhu et al., 2014 | Journal | Physical & Chemical | Experimental | Oil Production & Refining |
| Kota et al., 2012 | Journal | Chemical & Nano | Experimental | Oil Spill Recovery |
| Kuki and Matsushima, 2015 | Patent | Physical., Chemical & Nano | Unknown | Oil Production & Refining |
| Li Y. et al., 2016 | Journal | Physical., Chemical & Nano | Experimental | Oil Production & Refining |
| Little and Patterson, 1977 | Journal | Physical & Chemical | Market Ready | Shipping |
| LossPrevention, 2018 | Product Info | Physical & Nano | Development | Oil Spill Recovery |
| Pierpoline, 1996 | Patent | Physical & Nano | Unknown | Wastewater |
| Ren et al., 2016 | Journal | Chemical & Nano | Experimental | Oil Spill Recovery |
| T&T Water Solutions | Product Info | Physical & Electro | Market Ready | Wastewater |
| Zhang et al., 2008 | Journal | Physical & Chemical | Market Ready | Wastewater |

# 5 Assessment of Technologies

The literature review and categorization of technology-focused references provided a foundation for assessing technologies based upon a range of factors related to their fitness for offshore mechanical recovery. Within each technology category and sub-category, technologies were assessed for the following: (1) maturity; (2) cost; (3) efficiency; (4) previous use in oil recovery; and (5) potential use as part of an in-line mechanical oil recovery system.

This section describes the assessment factors that were applied to evaluate technologies by category and sub-category and summarizes the results.

## 5.1 Technology Assessment Factors

### 5.1.1 Approach

To evaluate each category of technology, the research team applied a set of criteria to each category/sub-category of literature. Table 5-1 presents the technology assessment approach that was applied to generate an overall evaluation of each technology sub-category against the six assessment factors (maturity, cost, efficiency, previous use, potential).

For each factor, Table 5-1 identifies standard criteria that were compared against the literature reviewed within each technology sub-category. It also outlines additional inputs and considerations that were assessed by the research team based on information in the literature, subject matter expert interviews, and professional judgment and experience. Subsequent sub-sections describe how the assessment factors were applied.

The results of the assessment (summarized in Section 5.2) represent relative – not absolute – values. Technology sub-categories were compared to assign values of low, medium, high for all factors except for previous use in response (which was a yes/no). These relative assessments are meant to facilitate comparison among the technologies described.

*Table 5-1. Technology Assessment Approach*

| Technology Assessment Factor | Value | Literature Review | Additional Considerations |
|---|---|---|---|
| **Maturity** | High | Literature contains multiple articles and indicates full scale applications | Technology is manufactured and marketed for use in oil spill recovery |
| | Medium | Literature describes multiple studies, progression from laboratory scale | Technology is manufactured and marketed for use in other industries |
| | Low | Minimal literature available, all experimental | Technology is still experimental or in early development |
| **Cost** | High | N/A | Sacrificial elements or single use technology, high energy use, high capital costs, high maintenance costs |
| | Unknown | N/A | Not enough information available to assess, or highly variable within technology category |
| | Low | N/A | Durable or low-maintenance technology, low energy use, low capital costs |
| **Efficiency** | High | One or more reference in literature reviewed indicates efficiencies >85% | Technology has exceeded 15ppm discharge standard during oil recovery |
| | Medium | One or more reference in literature reviewed indicates efficiencies between 65% to 85% | Technology has achieved or exceeded 15ppm discharge standard during oil recovery |
| | Low | One or more reference in literature reviewed indicates efficiencies <65% | Technology has failed to meet 15ppm discharge standard during oil recovery |
| **Previous Use in Oil Recovery** | Yes | Literature or interviews confirm that technology has been used during offshore on-water oil recovery (regardless of effectiveness) | |
| | No | Literature or interviews confirm that technology has not been used during offshore on-water oil recovery | |
| | Unknown | No definitive information found regarding past use during offshore on-water oil recovery | |
| **In-Line Mechanical Recovery Potential** | Yes | Technology has potential to integrate into on-water mechanical recovery systems without impacting throughput | |
| | No | Technology unlikely or impossible to integrate into on-water mechanical recovery systems without impacting throughput | |
| | Unknown | Lack of information or high variability among technologies | |

### 5.1.2 Maturity

There are established methods for assessing technology readiness levels (TRL), including an approach designed for oil spill response technologies (Panetta and Potter, 2016). This study could provide a foundation for a full TRL assessment, but the research team did not apply that level of rigor to this study, given the scope of technologies considered.

The research team considered both the literature reviewed and the information collected through expert interviews in assessing maturity. Technologies were considered to have high maturity if the literature indicated full-scale trials or if the technology is manufactured and marketed for use in oil spill recovery. Technologies were considered to have medium maturity if the literature included several studies that described a progression from laboratory scale, or if the technology is manufactured and marketed for use in other industries. Technologies were considered to have low maturity if they were still in experimental stages, as reported by literature or experts.

### 5.1.3 Cost

Even with complete data, the cost of technologies for oil spill response is difficult to assess and compare. There was limited information available about actual costs associated with most of the technologies reviewed, and given that many are still in experimental stages, it would likely be difficult to generate an accurate estimate.

Absent sufficient cost data in the literature to meaningfully compare technologies, the research team considered whether there were elements of the technology that might suggest a higher or lower cost. High cost technologies were characterized by elements such as single use applications, sacrificial elements, high energy use, or high capital costs. Low cost technologies were described as durable, low-maintenance, and multi-use, with low capital costs and low energy use. For the majority of technologies, cost information was not available.

### 5.1.4 Efficiency

The literature reviewed contained a great deal of information about efficiency, which for the purpose of this assessment is used to describe the efficiency with which a given technology separates oil and water. Most of the literature reported efficiency as a percentage, based on the proportion of oil-water mixture or emulsion that had been effectively separated. Very few studies expressed this value as a concentration.

A numeric threshold was applied to evaluate efficiency in comparing technologies where it had been reported. Since there were many technology sub-categories that were described in multiple studies, and because many studies reported a range of values, the efficiency rating was simplified based on the highest efficiency reported for a technology. If the efficiency was measure at above 85% in one or more sources, it was characterized as high efficiency. Technologies for which the highest efficiency was 64% or below were characterized as low efficiency. All others were characterized as medium.

Since many of the efficiency estimates reported in the literature are based on small scale laboratory experiments, it is important to consider that experimental values are not necessarily indicative of how a technology will perform in the field.

A second metric – demonstrated performance in meeting the 15 ppm threshold – was also applied to distinguish high, medium, and low efficiency technologies.

### 5.1.5 Previous Use in Oil Recovery

In evaluating technologies, the research team considered previous use in oil recovery operations (spill response or lightering) to be an important factor to capture, to help BSEE and other readers to appreciate the range of technologies assessed. For technologies where literature, interviews, or professional experience confirmed that they had been previously used in oil spill response (regardless of effectiveness), the assessment indicates "yes." For technologies where literature, interviews, or professional experience confirmed that they had not been used in oil spill response, the assessment indicates "no." If the research team could not determine past use, the entry was "unknown."

### 5.1.6 In-Line Mechanical Recovery Potential

The final assessment factor considered the overall potential for a technology to be incorporated as part of an in-line mechanical oil recovery system. For the purpose of this study, this describes the feasibility of integrating the with offshore skimming operations without significantly altering or impeding the flow of oil from the containment area, through the skimmer head, pumps and hoses, and into the TSD, and without requiring additional time for settling, decanting or offload of fluids in the TSD. This assessment was made based on the professional judgment of the research team, validated by expert interviews for certain technologies.

The research team applied a binary system to assess potential, using a "yes" for systems that the team believed had the potential to be incorporated into on-water recovery and "no" for systems that had clear impediments that would make this unlikely or impossible. Systems for which no assessment could be made were evaluated as "unknown."

## 5.2 Technology Assessment

The assessment factors and approach described in Section 5.1 and Table 5-1 were applied to each of the technology sub-categories, and the results are summarized in Table 5-2.

*Table 5-2. Assessment of Demulsification and Separation Technologies by Technology Category and Sub-category*

| Technology Category | Subcategory | Maturity | Cost | Efficiency | Previous Use in Oil Recovery | In-Line Potential |
|---|---|---|---|---|---|---|
| **Physical** | Gravity | High | Low | Medium | Yes | Yes |
| | Coalescing Surfaces | High | Unknown | High | Yes | Yes |
| | Centrifuge | High | High | High | Yes | Yes |
| | Agitation | Low | Unknown | Medium | Yes | No |
| **Nano-technology** | Membranes | Medium | Unknown | High | No | Unknown |
| | Particles | Low | Unknown | High | No | No |
| **Chemical** | Demulsifiers | High | Low | High | Yes | No |
| **Multi Method** | Physical & Chemical | High | Unknown | High | Yes | Unknown |
| | Physical & Nano | High | Unknown | High | Yes | Unknown |
| | Chemical & Nano | Medium | Unknown | High | Unknown | No |
| | Physical, Chemical & Nano | Low | Unknown | High | Unknown | Unknown |
| | Physical & Electro-coalescence | High | Unknown | High | Yes | Yes |
| **Other** | Microwave | High | Unknown | High | Unknown | No |
| | Sonic | Medium | Unknown | High | Unknown | No |
| | Electro-coalescence | High | Unknown | High | Unknown | Yes |

### 5.2.1 Physical Separation

*Figure 5-1. Freylit mobile oil separator used on spill response in Greece (Hellenic Navy, 2017)*

Physical separation technologies accounted for less than a quarter of the literature scanned, but a majority of the oil recovery-focused research.

Physical separation using gravity separation is the current standard for oil-water separation in most offshore oil recovery systems. OSROs that have oil-water separation systems in inventory report that they represent older technologies that cannot keep pace with high capacity skimming systems. There have been some technology enhancements to integrated systems that reduce the time required for oil and water to separate. The capacity for these systems to keep pace with high-volume skimmer operations has yet to be demonstrated.

Most of the technologies reviewed focus on adaptations that speed up the gravity-driven oil-water separation process within the TSD. The coalescing surface technologies in particular offer very high (99-100%) efficiency rates in trials and experiments. The one system that was reportedly used in an on-water spill response appears to have been trailer-mounted, requiring recovered liquids to be pumped from the TSD and through this system (Figure 5-1). These separators, which are effective on free oils but not emulsions, are being actively marketed for spill response in Europe (Freylit, no date).

Several technologies incorporate oil-water separation within the skimming system, with the goal of reducing water content before transferring fluids to the TSD. One vacuum-based technology reported 99% efficiency in tank tests (ASRC, 2017). This vacuum-based skimming system, the PPR Alaska otter series, has also been used effectively for site remediation, achieving water quality standards for discharge into the Great Lakes. Another system reported 93% efficiency in tank tests (Restco, 2015).

Centrifuge technologies continue to be explored, despite a high-profile failure of a the Ocean Therapy Solutions system during the Macondo spill. Centrifuges are widely used in industrial and laboratory settings, with high efficiency, but do not tolerate the debris that is commonly encountered in on-water recovery operations. The system tested during the Macondo spill had difficulties operating in offshore wave conditions, and experienced decreased efficiency when processing more viscous emulsions. A centrifuge technology that could overcome debris and wave challenges and operate in the offshore environment could have in-line recovery potential.

Hydrocyclone technologies, which were categorized with gravity separation for this study, also show potential, and there are products on the market that have been designed for in-line use in skimming operations, though there is no evidence of deployment or testing during actual spills. These systems, which were developed to deal with oil, water, and sediment, are more debris-tolerant than centrifuges.

Agitation technologies are not readily incorporated into on-water recovery, because of the time and storage space required to operate them. This technology may be better suited to other industrial applications, although one of the combined systems examined includes agitation as a tertiary treatment without compromising system throughput.

### 5.2.2 Nanotechnology

Nanotechnology is a focus area for researchers, particularly in other industries, but its potential applicability for oil recovery is difficult to evaluate. Most of the research to date has been laboratory scale, demonstrating very high efficiency in terms of the percentage of separation, based on low volumes of treated liquids.

Particle technology provides a highly tunable mechanism for adsorption of different pollutants, but the research team could not envision a pathway for introducing particles into on-water recovery systems without disrupting operations. Logistical and operational challenges could include: identifying the type and quantity of particulate needed based on the oil type spilled (if known); storage requirements for clean particulates prior to use; storage; the need to corral or recover contaminated particulates; and transportation and disposal of contaminated particulates.

Membrane technology has greater potential for incorporation into recovery systems, but flow rate through the membrane could be a limiting factor. To be operational, it must be able to filter at a rate equivalent to the skimming system throughput. Ongoing research in Canada is investigating a pressure-driven microfiltration process, derived from oil sands production, as a potential enhancement to oil-water separation during spill recovery.

Utilization of nanotechnologies as a polishing step (secondary, tertiary, or even quaternary) after the oily water is run through physical separation processes shows some promise (see Section 5.2.4).

### 5.2.3 Chemical

Chemical demulsifiers are a proven technology with a high efficiency in breaking emulsions. They have been proposed for use in-line with mechanical recovery to enhance the gravity separation process, but the use of a chemical demulsifier to separate and decant oil from a TSD would result in some of the chemical being released into the environment. In most U.S. jurisdictions, this would require authorizations or approvals. While there are studies that show demulsifiers can speed up the decanting process, their use would still require that the TSD be filled, and there would likely be some disruption to the overall recovery system.

### 5.2.4 Multi Method Technologies

Multi method technologies provide more than one pathway for separation or demulsification, and for this reason are particularly relevant to oil production and wastewater treatment operations, which generally handle more complex waste streams. The potential for a multi method technology to both break emulsions and separate oil and water could enhance response efficiency, but the additional complexity required to implement such a technology in-line with spill response may preclude this.

The use of nanotechnology as a polishing step after physical separation has occurred shows some promise. The pending tests of the LossPrevention system (see Section 4.5.3) during the 2018 North Sea on-water recovery trials will provide more information about the potential for multi method systems incorporating nanotechnology to enhance oil recovery.

#### 5.2.5 Other

Both sonic and microwave technologies have shown some promise in laboratory studies, but neither seem well suited to offshore oil recovery. In order to be effective, sonic waves must be able to propagate appropriately inside a moving TSD or onboard tank, and the operation of this type of technology, which is not standard for oil recovery operations, may require special training. There is also potential for sonic technology to interfere with wildlife. Microwave technology has not been explored for use in offshore oil recovery, and there is nothing in the literature to suggest that this is a realistic technology for in-line operation.

Electro-coalescence requires settling time, which suggests that it might not be easily integrated into offshore recovery. However, electro-coagulation technology has been used to treat oily water removed from submerged vessels, and one vendor suggested that the technology (T&T Water Systems) could be integrated into a fluid recovery system to separate and decant at a rate that matches system throughput. This has not been demonstrated, but several of the OSROs interviewed were aware of and interested in this technology and its potential to enhance oil-water separation during offshore response.

# 6 Conclusion and Recommendations

This section summarizes conclusions based on the research team's findings and offers recommendations for enhancing on-water oil spill recovery capacity by improving oil-water separation in offshore systems. In cases where specific technologies or manufacturers are discussed, the research team is reporting on information collected; no endorsements are intended.

## 6.1 State of Demulsification Technology and Research

The state of technology for oil-water separation during spill response remains relatively simple; gravity separation within the TSD and subsequent decanting of free water are still the favored practice, based on the research conducted for this study. Some of the OSROs have technologies in inventory, or have developed *ad hoc* approaches to enhance gravity separation during spill response operations, but these are not often utilized.

Emulsion breakers have been in use for some time, but their use is limited to treatment of recovered oily wastes during shore side processing; they are not incorporated into on-water oil recovery operations in the U.S. Skimming systems used to support the Norwegian offshore oil industry do include 380-liter tanks of emulsion breakers, which could be applied to the skimmer head to mix with emulsions and promote separation. Experts report that while this technology is in place, it is rarely used or tested.

## 6.2 Enhancing Separation and Demulsification to Increase Response Capacity

Spill response experts understand the challenges associated with managing oil-water mixtures during major spill response. The Macondo spill generated a flurry of research and development activity, both during the response and in the years following, and there have been some advances in on-water recovery systems that have the potential to increase response capacity by enhancing oil-water separation.

The research team identified several considerations that may influence how or whether the U.S. spill response industry adopts new, more efficient oil-water separation technologies. These include operational factors, performance elements, practical considerations, and regulatory drivers.

### 6.2.1 Operational Factors

The transfer of technology from other industrial applications to offshore oil recovery, and the progression of new technology from labs to real world operations, requires that a technology be operable in the environment in which it is intended to operate. A number of factors will influence the operational feasibility of incorporating new technologies into offshore recovery:

- Compatibility with existing on-water recovery system components;
- Suitability to operate in environmental conditions likely to be encountered in offshore environments (sea state, wind, precipitation, temperature, salt water);
- Ability to be deployed and operated by response personnel (or potential that response personnel can be trained to use the system independently); and
- Durability to maintain functionality throughout operational periods, and be reused over prolonged response period.

### 6.2.2 Performance Elements

For OSROs and operators to replace current systems with new designs, they typically expect that the technology will perform reliably. Performance elements may include:

- Overall efficiency of technology (a separation or demulsification technology that did not meet the 15 ppm threshold, for example, could be a liability);
- Throughput (ability of system to process volumes of fluids in pace with other system elements);
- Debris tolerance;
- Ability to process variable waste streams; and
- Dependability.

### 6.2.3 Practical Considerations

There are practical considerations that will influence the likelihood that enhanced separation and demulsification technologies are adopted by the spill response industry. These include:

- Cost of technology;
- Service life of technology;
- Availability in sufficient quantities to provide fleet-wide solutions;
- Portability;
- Storage requirements;
- Maintenance and upkeep; and
- Transportation and mobilization requirements.

### 6.2.4 Regulatory Drivers

International, national, and state laws and regulations establish a framework for the U.S. offshore oil spill preparedness and response system. The equipment that is stockpiled by OSROs, shipping companies, and offshore facilities is measured against planning standards set in federal and, in some places, state statute and regulation. The reality of this system is that spill response equipment decisions are driven by compliance. Federal response planning standards focus on estimated daily recovery capacity (EDRC), which is based on a percentage of the nameplate capacity for the skimming systems in use. Temporary storage requirements are to have enough storage to hold two times the estimated daily recovery volume (33 CFR 155 Appendix B).

OSROs and contingency plan holders who have sufficient temporary storage to meet the regulation do not necessarily have an incentive to enhance their oil-water separation capacity. Without a compliance imperative, it is difficult for OSROs and operators to justify the capital expense of new technology.

## 6.3 Recommendations

This report identifies several areas where technology development could enhance oil demulsification or separation processes. These include:

- Enhancing physical separation within TSDs using coalescing plates;
- Developing systems or components that incorporate hydrocyclone or vortex mechanisms to enhance gravity separation;
- Utilizing vacuum-based skimming systems that separate oil/water within the skimming system;
- Utilizing electro-coalescence as a stand-alone or polishing technique; and
- Incorporating nanotechnologies as a polishing technique in combination with physical separation methods.

This section summarizes identified areas where technology development could enhance oil demulsification or separation processes. Regulatory drivers or incentives that encourage OSROs and their member organizations to enhance oil-water separation as an inline component of on-water recovery would encourage the development and use of new technologies.

### 6.3.1 Enhancements within Technology Categories

For the purpose of this study, separation and demulsification technologies were assigned to various categories. Of these, physical separation proved to be the approach most commonly applied to on-water oil spill response. A number of existing systems and proposed new designs attempt to enhance the physical separation process through use of coalescing surfaces, vacuums, hydrocyclones, centrifuges, and agitation. Of these approaches, the first three – coalescing surfaces, vacuum, and hydrocyclone – appear to transfer most readily to oil spill recovery operations. Centrifuges are very effective oil/water separators, but deployment alongside offshore recovery systems is problematic, as is their lack of debris tolerance. Hydrocyclones and vortexes are a similar technology that overcomes the debris issue, and may be more adaptable for spill response. Agitation may be an option for secondary or tertiary treatment, but as a stand-alone separation technology, it has not been demonstrated to keep pace with the volume of recovered fluids generated during a response.

Nanotechnologies dominate the scientific literature; researchers have focused on their application to wastewater treatment and ship bilges as well as oil spill recovery. Membrane and particle technologies have both been proven highly efficient in both separating and demulsifying oil/water mixes. Nanotechnologies may be used alone or as a secondary or tertiary treatment to polish water that has gone through another system first. Membrane technologies are typically limited by flow rate/batch size; a membrane that could keep pace with skimming rates could be highly effective. Particle technologies can be readily scaled, but face the added challenge or removing the particles from the separated fluids, or dealing with them as a waste stream. Magnets have been introduced in several experiments as a means to coagulate and remove nanoparticles; additional work is needed to demonstrate the use of this technology in-line with spill recovery operations.

Chemical demulsifiers were not a focus of this study, which sought to identify technologies that could be incorporated into on-water mechanical recovery systems. Studies that originated in the 1990s concluded that demulsifiers could enhance oil-water separation and demulsification during response, but that traces of these chemicals remained in decanted water. Demulsifiers continue to have a role in treatment of recovered oily liquids downstream from the recovery operations.

Other technologies examined included microwave, sonic, and electro-coalescence. Of these, electro-coalescence seems to show the most promise, particularly if combined with other methods. In fact, several of the technologies that have been developed or are in development for use in oil recovery operations combine more than one method. Most include physical processes with additional steps to polish the water so that it can meet discharge standards (below 15 ppm hydrocarbons). Section 6.3.2 identifies several combined technologies that show promise.

### 6.3.2 New or Emerging Technologies

Innovative systems that are able to process higher volumes of fluids or produce a more polished (less contaminated) water effluent have been adopted into wastewater treatment and shipping operations, but most are either integrated into shipboard systems or marketed as mobile, stand-alone units. Similarly, technologies used in the oil production industry are typically complex and specialized, and do not suit the need for agile, robust systems to operate in-line with offshore skimming operations.

A few technologies are actively being developed or marketed for enhanced oil-water separation. The research team identified several physical separation technologies that may be suited to operation in-line with offshore recovery systems. These are summarized in Table 6-1.

*Table 6-1. New Physical Separation Technologies With the Potential to Enhance Oil-Water Separation During On-water Oil Recovery*

| Manufacturer or Developer - Model | Technology Type | Description | Reference |
|---|---|---|---|
| Enviro Voraxial Technology - Submersible Voraxial ® 8000 | Hydrocyclone | From manufacturer: Capable of processing up to 7,000,000 gallons of oil-water mixture per day (a rate of 5,000 gallons per minute). Can work at depth or on surface and reduce recovered water by 90%. Designed to work in-line with skimming/recovery systems. Capacity to handle emulsions is unknown based on research conducted. | Voraxial, 2018<br>Hansen, 2011 |
| Freylit – Multiple Models | Coalescent plates | From manufacturer: Can tailor system to match various flow rates. Conceptual diagrams of catamaran and barge-based systems. Used on over 800 oil spills (unclear whether land or marine-based). Not effective on emulsions. | Freylit, no date<br>Braesch, 2017 |
| Loss Prevention – Models Unknown | Coalescence, vortex and gravity | From third party: Mobile concept where the separation unit packs up in a 20-foot container, and is designed to be placed on the deck of a supply vessel. Capacity of of 200 m3/h. Can reduce water content by 66%. Effective on some emulsions. Smaller units for smaller boats are planned. Technology to be tested 2018 North Sea Oil on Water Exercise. | Loss Prevention, 2018<br>Expert interviews – patent pending |
| T&T Water Solutions – Multiple models | Electro-coalescence | From manufacturer: Can clean water to 1ppm. Could be used in-line with skimming system and process up to 10,000 gal/hr with larger (40m3) unit. Can also treat emulsions. | T&T Water Solutions, no date |
| PPR Alaska - Oil-water separator and Otter skimmer series | Gravity (vacuum) | From manufacturer: Dual vacuum chambers separate oil and water, discharging water and moving oil to primary storage. Test tank data demonstrate 99% efficiency at 62 bbl/hr. Debris-tolerant. Prototype systems have been used in spill cleanup and remediation, and open ocean trials demonstrated Otter system could operate in seas up to 6 feet. Vacuum system can break emulsions. | ASRC, 2017<br>PPR Alaska, 2016 |
| Extreme Spill Technologies | Gravity skimmer vessel | From manufacturer: Integrated skimming vessel uses funnel-shape collection chamber (after skimmer head) to promote gravity separation, and when oil reaches top of funnel, it is removed with suction. The design is intended to minimize recovered water, and tank tests in calm conditions recovered 93% oil. | Restco, 2015 |

| Manufacturer or Developer - Model | Technology Type | Description | Reference |
|---|---|---|---|
| Technomar – Multiple Models | Coalescence, vortex and gravity | From third party: Technology works in flow process and does not require long settling times. The separation process is fully automated and controlled by an integrated PLC system. Can separate oil-water mixtures with a maximum oil content of 50%, a maximum viscosity of 70,000 cSt and a maximum density of 0.99 g / $cm^3$. At very high viscosities, throughput decreases. Achieves oil content <15 ppm and the water content in the oil is about 1%. Variability in results depending on oil type. | Technomar Group, 2018 |
| Turbylec | Centrifuge | From manufacturer: Small centrifugal separator with inflow rate of 10 m3/h, autonomous pumping, some adjustability. Proposed for use as part of hovercraft system, but not yet built/to market. | Maj et al., 2014<br>Ylec Consultants, no date |

## 6.4 Conclusion

Across the industries evaluated in this report, a variety of technologies are in use to treat oily water and emulsions, and new research is ongoing. New technologies have emerged in some technology categories including physical separation, chemical demulsifiers, nanotechnology, and combined methods. However, the state of practice in the U.S. remains fairly simple, relying on gravity separation within TSDs as a primary approach.

A large portion of the oil spill recovery-focused research and technology developments have focused on physical methods, including enhancements to gravity separation, coalescent surfaces, centrifuges, hydrocyclones, electrocoagulation, and vortexes. Additionally, nanotechnology has seen a dramatic increase in research over the last few decades, much of it focused on wastewater applications. Nanotechnologies, and particularly membranes, offer a highly tunable and efficient mechanism to separate oil and water, but they have not yet been demonstrated at a scale sufficient to support the volume of oily wastes generated during offshore recovery. Chemical demulsifiers are an effective and mature technology, but the focus of this study was on methods to enhance mechanical recovery. Multi method technologies can also be quite effective, but most are too complex or not sufficiently scaled to work in-line with offshore recovery systems.

Other industries that separate oil and water – wastewater treatment, oil production, shipping, and the food industry – continue to innovate and refine technologies, and some of the technologies identified as having promise for oil spill recovery are derived from these industries. The shipping and oil production industries face many of the same constraints as on-water recovery, such as the need to maximize available deck space and the need to operate in variable sea conditions. Approaches from these industries may be more readily adapted for spill response than wastewater treatment technologies, which are typically designed for fixed facilities and controlled environment.

While researchers and manufacturers interviewed for this study were enthusiastic about their technologies and potential innovations, many of the response professionals did not view innovations to separation technologies as a high priority. The adoption of new, more efficient demulsification and separation technologies by the U.S. oil spill response industry may not occur without a clear incentive or compliance mandate. If improving oil-water separation and demulsification remains a priority for BSEE and other regulators, it is important to examine the policy framework that drives innovation and consider opportunities to encourage new technologies and novel approaches.

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