SPILL TECHNOLOGY

NEWSLETTER

ISSN 0381-4459

VOLUME 19 (4)
October-December 1994

OIL SPILLS AND OIL SPILL CLEANUP

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Introduction

Major oil spills can grab newspaper headlines around the world. These incidents have created a global awareness of oil spills and the potential damage they can cause to the environment. Despite the risk of spills, world oil production and consumption continues because oil is one of the necessities of modern industrial society. Oil and its derivatives pervade every aspect of our lives. The risk of oil spills will not diminish in the near future. However, preventative measures have and will continue to reduce the frequency and amount of spills. Continued improvement of cleanup techniques and response capabilities will reduce the impact of spills.

Spills occur at a frequent rate. In Canada, for example, about 12 spills are reported every day to the national spill data base (Beech, 1978). Of these 9 are spills of oil and petroleum products. Almost none of these spills make the news, not even locally, because they are cleaned up rapidly and do not have a major environmental impact. The ability to cleanup small spills has improved significantly in the past 20 years. The ability to cleanup large oil spills, however, has not advanced as rapidly. This is a review of how oil spills are cleaned up - with special focus on spills at sea - and possible future technologies. Particular emphasis is placed on the role of chemical-treating agents.

Overview of Oil Spill Cleanup

Although prevention is the logical means of reducing oil spills, some spills will still occur. Preparation is still a necessary function for both the industry having a spill potential and government authorities. Fast and effective response can also be

This issue features an overview on oil spill countermeasures. Merv Fingas and Brian Mansfield review, in brief, the most common oil spill countermeasures with an appraisal of the effectiveness and future of each.

viewed as a means of preventing further environmental damage. Extensive plans and preparations are needed to effectively deal with an oil spill. The "contingency plan" should be a well-prepared and practised action plan.

No two oil spills are exactly alike. The behaviour of oil on water or land and the ability to contain a spill depends on the type of oil, the location and volume of the spill, weather conditions, and a host of other factors. The most effective cleanup and containment methods vary from spill-to-spill and often vary from site-to-site in a specific spill incident. The efficiency of cleanup equipment and techniques may also change with time, as weather conditions fluctuate and the character of the spilled oil is altered. Consequently, a wide range of cleanup techniques and equipment should be considered. Development and testing of new cleanup techniques and devices is constantly undertaken by government and industry.

The first priority in any spill is to stop the source of leakage. The second priority is to contain the spill so that further environmental damage does not occur. Spills on water can be contained using the many commercial spill containment booms. Booms will contain floating liquids up to a relative current speed of .5 metres per second (m/s) (Fingas, 1979). This is an important limitation because in many situations this velocity is exceeded. Attempts to contain oil directly across a river or tidal bay will be futile. Tidal currents often exceed 1 m/s and can be as high as 4 m/s. Diversionary techniques can be used on rivers and other places where the current exceeds .5 m/s. This technique diverts oil to a collection point along shore or an area of lesser environmental sensitivity.

Once the petroleum or solvent is contained, the usual means of recovery is to pump the liquid to a temporary storage facility. Commonly-used conveyances are vacuum trucks (near shore) or pumps at sea. Skimmers are required for recovering thin oil slicks from the sea surface. Skimmers are available in many configurations and sizes.

Often the oil will reach shoreline, where it will be removed if there is a possibility of further water recontamination or damage to the shoreline ecosystem. A number of shoreline cleanup measures are available for different habitats.

Sorbents are often used to cleanup petroleum and solvent spills. Sorbents are best used to "polish" or cleanup the final traces of the spill on water. Many treating agents are promoted to deal with oil and chemical spills. The most common types are those containing surfactants or soap-like materials. Dispersents are used to put oil or similar materials into the water column in the form of fine droplets. Several other chemical-treating agents are available, but generally have not received wide acceptance.

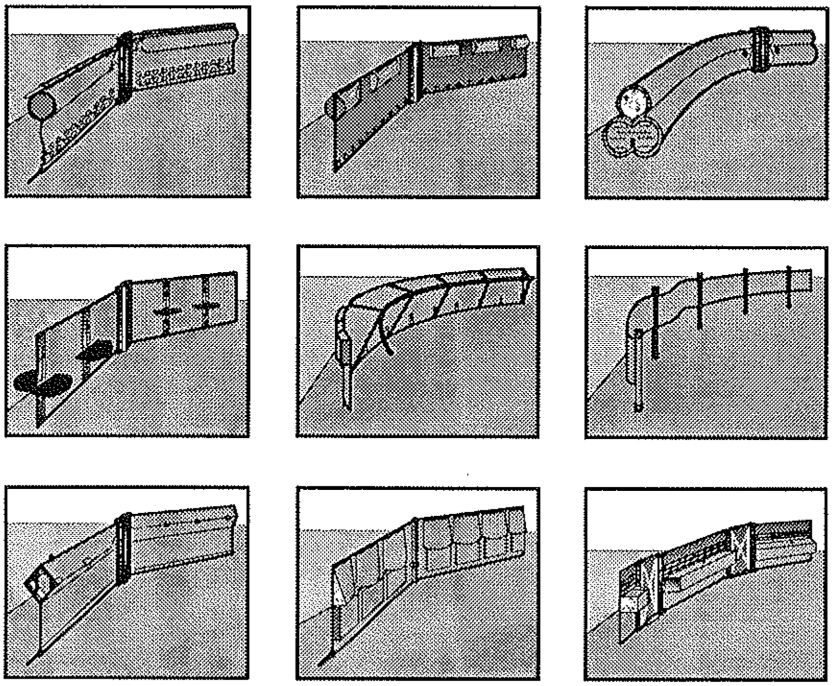
Other cleanup methods are becoming accepted. *In-situ* burning has recently received significant attention. Burning can potentially remove large amounts of oil in a short time. In some environments (i.e., salt marshes) the physical disturbance caused by certain cleanup methods may be much greater than the effects of the oil. In such cases, the "natural recovery", "natural biodegradation", or "monitoring" option is the best choice.

Containment

Containment is the process of confining oil to a specific area. Diversion of oil from a given area is also considered part of the same technology. The primary objective of containment is to concentrate the oil in thick layers so that it can be recovered. The primary objective of diversion is the removal of oil from a given area. Containment is a technology that is reaching maturity. Many commercial booms, capable of containment or diversion, are available and are being used around the world (Schulze, 1995). The configuration of several commercial booms are shown in Figure 1.

Commercial floating booms have four main components: a means of flotation, a freeboard to prevent waves from washing oil over the top, a skirt to prevent oil from being swept underneath, and a longitudinal support member to allow the boom to withstand the forces of wind, waves, and current. In addition, some booms have outriggers or weights to help keep the booms upright. The floatation system of the boom is an important factor and buoyancy-to-weight ratios are specified at approximately 1:20 (ATSM, 1994). This implies that the boom could support 20 times its weight before sinking. These high buoyancy ratios are important for the boom to follow waves. Low-buoyancy-ratio booms have a tendency to ride through waves rather than on top.

Figure 1 *Configurations of Commercial Boom*



There are a variety of boom materials, but boom coverings are typically polyvinyl chloride or chlorinated polyurethane. These materials show reasonable resistance to oil. Floatation material consists typically of polyethylene or polyurethane foam. Self-inflating air booms are also available.

The major limitation of oil spill barriers is their ability to contain oil in a current. The physical limitation is about 0.5 m/s. This is governed by hydrodynamics and only varies marginally with different boom design. At velocities higher than 0.5 m/s, oil will breakaway from the front of the contained slick, a phenomenon known as droplet breakaway. Oil can splash over, or move under, a boom when a boom cannot follow the movement of the sea. Most booms are ineffective at waves greater than two metres and in very choppy waters (it is impossible for the boom to comply with the water surface). Another generic failure is roll-over, which is a function of the boom's tension member and floatation design.

Booms are used in calmer waters to contain oil for recovery, usually by means of skimmers. Booms are sometimes used to divert oil from sensitive areas. When placed at an angle to the current, booms can divert oil from currents faster than 0.5 m/s, depending on the angle. This application is particularly useful in rivers and estuaries where currents are often far greater than the 0.5 m/s limit.

Other types of booms that have occasional application include sorbent booms, used to recover small amounts of oil or to "polish" an area, and air bubble barriers, which are occasionally used to form permanent oil barriers in harbours.

Mechanical Removal

Following containment, the next step in the cleaning operation is recovering the oil from the water surface. In most cases, the containment and recovery operations proceed simultaneously. Recovery is generally performed using skimmers and suction devices. The latter use devices normally used for cleaning sewers and traps to directly recover oil from the surface. The most common of these is the vacuum truck. Oil is often withdrawn directly from the surface with the work hose. Water is usually taken up along with oil. The uptake of water can be reduced by using some of the many specially-designed flotation devices that direct the suction to the water surface.

A skimmer can be defined as any mechanical device designed to remove oil from the water surface. These devices are classified according to their basic principles of operation as: 1) weir-type skimmers, 2) suction devices, 3) centrifugal devices, 4) submersion devices, and 5) sorbent surface devices (Fingas, 1979). In some cases, more than one principle of operation is incorporated in a single skimmer design. The operating principles are illustrated in Figure 2.

Each type of skimmer has its advantages and disadvantages. Skimmer performance characteristics include pickup rate and water pickup rate. The effectiveness of any skimmer depends on a number of factors including: the type of oil spilled; the thickness of the slick; the presence of debris in the oil or on the water; the location of the spill; and the ambient weather and sea

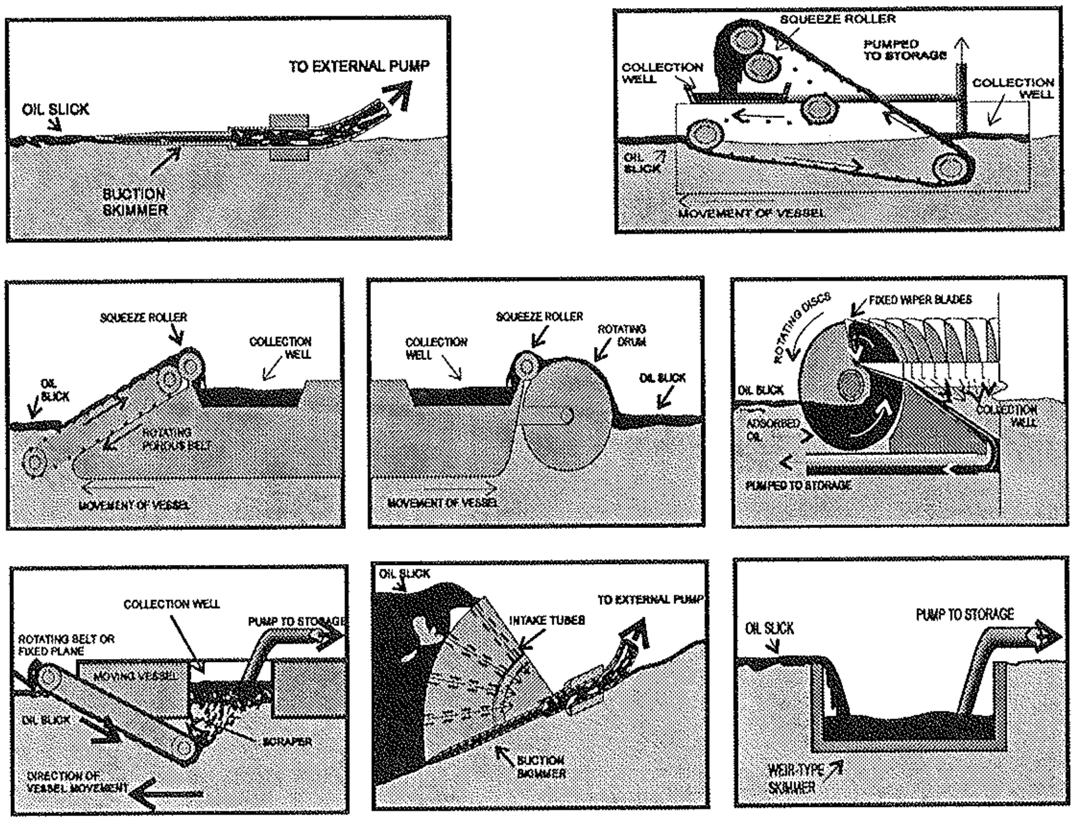


Figure 2
Skimmer Operating Principles

conditions. Most skimmers recover oil satisfactorily when the oil layer is thick. For this reason, containment techniques are important and skimmers are best used in conjunction with these. Boom configurations include placing the skimmer at the apex of the 'V' or at the bottom of the 'J'. Sea conditions have the largest influence on the effectiveness of skimmers. In high seas, many skimmers, especially weir and suction skimmers, take up more water than oil. Actual recovery of oil can cease and containment is difficult, if not impossible. One of the remaining problems in oil spill cleanup is the recovery of oil on the high seas.

There are many types of skimmers available and these generally fall into two categories: simple and more sophisticated devices. The more sophisticated devices use float systems to maintain the edge of the skimmer more precisely at the water-oil interface, and often have positive displacement pumps to handle highly viscous oils. These devices have few moving parts, making them more reliable and inexpensive. The disadvantages include the high uptake of water, especially for the less sophisticated devices. Each type of skimmer has advantages and disadvantages. **Weir skimmers** take advantage of gravity to drain oil from the water surface. Their structure is maintained below the water surface and an edge is maintained as close as possible to the water surface (Figure 2). **Suction skimmers** are simplistic devices designed to be added to simple vacuum or standard suction pumps to minimize the uptake of water. They are cheap and portable, but have little ability to deal with more viscous oils and can withdraw significant amounts of water. **Centrifugal skimmers** operate on the basis of the different densities of oil and water. Under the influence of rotation force or in a vortex, oil can separate and thus be removed. This class of skimmer has been relatively unsuccessful, particularly because the densities of oil and water are often not sufficiently different to yield practical separation. **Submersion skimmers** again use the differential gravities of oil and water to separate oil. The forward movement of a vessel forces oil down a rotating belt. At the end of the belt, the oil floats up into a collection well where it can be removed by a pump. Submersion skimmers are effective if operated in a narrow range of forward speeds and with medium crude oils.

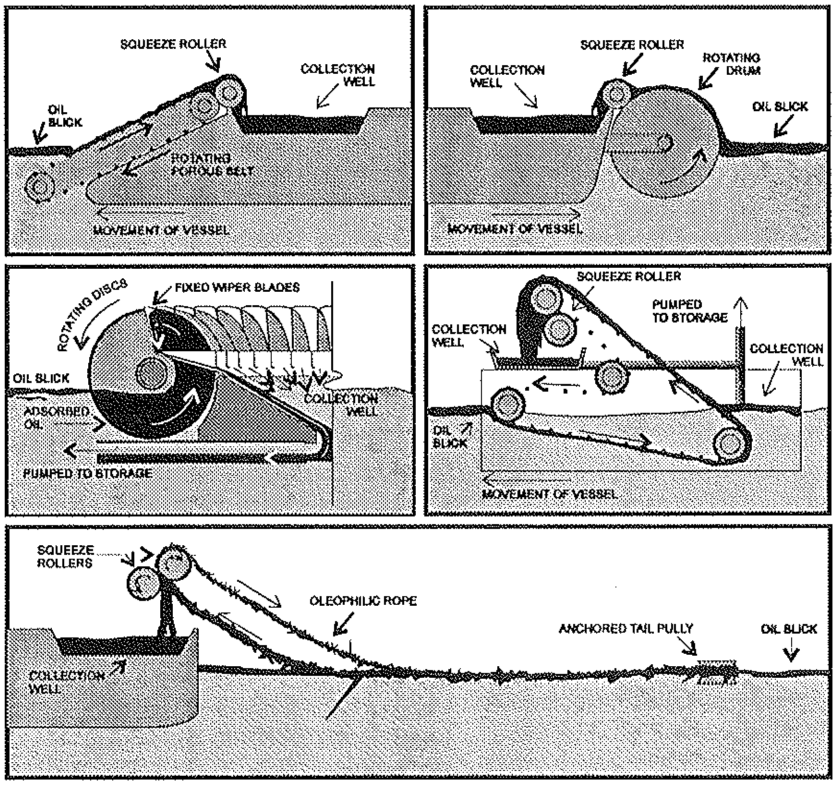


Figure 3 *Oleophilic Surface Skimmers*

The most common skimmers on the market are sorbent surface skimmers. Some of the collection principles are illustrated in Figure 3. In each case an oleophilic surface is introduced to the water-oil interface. This surface is withdrawn and the oil squeezed or wiped off. Surfaces used include drums, blades, belts, ropes, and brushes. Each of these surfaces has a tendency to absorb oil and reject water. Advantages to sorbent surface devices are their relatively low water pickup and their ability to recover even thinner layers of oil. Disadvantages include: mechanical complexity, the limited life time of media such as ropes, and slow recovery rates compared to other skimmers, particularly in thick slicks. Despite these shortcomings, sorbent surface devices remain the most popular skimmers and are available in dozens of commercial varieties.

Sorbents are sometimes used for oil recovery. A large variety of natural and synthetic products are on the market. On water, sorbents, particularly loose products such as peat moss, can complicate a cleanup because they themselves are hard to cleanup and they interfere with skimmers. Synthetic skimmer pads and small booms have found favour among cleanup crews for polishing or removing the last traces of oil from a water surface. Natural sorbents (i.e., peat, wood products) have the advantage of economy but the disadvantages of low oil pick-up capacity, and the potential to sink. Synthetic sorbents have pick-up capacities up to 10 times that of natural products and can be made in useful formats such as pads, wipes, booms, and mops. All sorbents have the disadvantage of becoming a disposal problem once soiled.

The post-recovery treatment and disposal of recovered oil are in themselves very large problems. Depending on the final disposition of the recovered oil, it may have to be treated differently. Sometimes recovered oil can be recycled by sending it to a refinery for re-use. To do so the oil must be dewatered and free of debris. Viscous oils cannot be effectively recycled and are usually disposed of by incineration or by sending the containers to a landfill. Dewatering of oil is performed using devices known as separators. The simplest of these, gravity separators, simply provide a quiescent container where oil is able to rise to the surface. Centrifugal devices use the different gravities of oil and water, and are usually more effective and of higher capacity than gravity separators, but are sensitive to inputs and operator control.

Shoreline Cleanup

Shoreline cleanup is the one area showing significant advances in recent years. This is especially true of the shoreline assessment phase preceding cleanup which has developed into an organized system over the years. Those who implement these procedures are known as SCAT teams for "Shoreline Countermeasures Assessment Team" (Owens, 1994). Key elements of a successful shoreline assessment survey includes both the use of standard terminology and a systematic approach to data collection (with rapid feedback to response decision-makers). Observations provide an accurate picture of the nature and scale of the oiling problem and a foundation for taking the most appropriate response option, determining priorities for cleanup, and evaluating the endpoint of cleanup activities.

Shoreline cleanup is complex because geographic conditions vary considerably. Flat, sandy beaches are the exception rather than the norm. Rocky shorelines are probably more common in the northern hemisphere than sandy beaches. When oil arrives on the shore it may be deposited in crevices or in spaces between rocks. If the oil adheres to the rocks it is difficult to remove using most techniques. The longer oil remains on the beach the more difficult it is to clean. Sensitive beaches or areas particularly difficult to clean might be protected by diverting oil into less sensitive areas.

The most common method of shoreline cleanup remains physical removal using shovels and rakes (Owens, 1995). Care is taken to avoid causing severe physical or biological damage during the cleanup. Using mechanical equipment such as graders, bulldozers, or front-end loaders is generally restricted to sandy beaches where the emphasis is on restoring the beach for public use in a short time. The most common cleaning technique for gravel or rock shorelines is low-pressure cold-water flushing. This technique is effective when the oil is relatively fresh. Hot-water, steam and high-pressure sprays, although useful for man-made shorelines such as piers and jetties, harms biota living on shorelines. It is better to remove the bulk of the oil quickly using cold-water flushing than to clean it thoroughly using a more invasive technique and causing physical or biological damage to the shoreline. In the past few years, highly effective chemical shoreline cleaning agents have been developed. Cleaning agents are not to be confused with dispersants, as discussed later, and are in fact, quite different chemical agents. These are applied on the oil at low tide and the oil flushed later using low-pressure water. The oil is then picked up using skimmers.

Dispersants

Dispersants are chemical agents which create small oil droplets which move into the water column. Dispersants are typically applied from low-flying aircraft rather than from boats. Although boats were historically used, their ability to treat large areas is restricted. A variety of equipment is used from boats and aircraft. Spray units have been designed for many platforms and come as permanent or temporary installations. Dispersants are not diluted when applied from aircraft but are usually diluted with sea water when sprayed from boats. Dispersants are applied to achieve an approximate dispersant-to-oil ratio of 1:10 to 1:20, although slick thickness is hard to judge and no measurement technique is available (Exxon Research Production, 1992).

Dispersants themselves are different from most industrial surfactants. The active ingredients in dispersants are surfactants, specifically designed to operate on oil on open waters. Standard industrial surfactants are too water soluble to function in this application. Aquatic toxicity is a prime consideration and the choice of surfactants is again different from many industrial applications. The hydrophobic-lipophilic balance (HLB) of dispersants is designed to average 10, so that surfactants would be approximately equally soluble in water and oil to be effective. Low (much less than 10) HLB surfactants could result in the formation of water-in-oil emulsions, and high HLB mixtures simply are lost to the water column. The most common formulation uses a three-way mixture of a non-ionic surfactant of high HLB, one of low HLB, and a third ionic surfactant. When these are combined they yield an HLB of approximately 10 (Fingas, et. al., 1995). Crude oils and residual fuels are extremely difficult to treat with surfactants because of the highly-varying composition and the presence of long-chains and functional groups other than hydrocarbons.

The main concern with dispersants is that its effectiveness is primarily dependant on oil type and sea energy. The higher the saturate content of oil, the higher the effectiveness, and vice versa. A minimum of sea energy is required before dispersants function. The higher the sea energy, the more effective the dispersant. These factors limit the applicability of dispersants. Furthermore, as oil weathers, its saturate content becomes lower and its viscosity increases, compounding the difficulty of mixing dispersants with oil. Heavy and highly weathered oils may not disperse at all under certain conditions. Light oils will disperse well, but may also disperse naturally. Laboratory and field test effectiveness values are typically about 30% for a light, 20% for a medium crude, and little or no effectiveness for residual fuels.

Using dispersants is a trade-off between a number of factors; including shoreline protection, protection of birds versus fish, and the realization that only part of the oil would be removed in any case. In most countries, the use of dispersants is either tightly regulated by government agencies or strictly forbidden. Dispersant use has decreased in recent years for a variety of reasons including; strict government regulations, lack of public acceptability of putting oil into the water column, and the limited effectiveness of the technique.

Chemical Treating Agents

Many chemical agents for treating oil spills have been promoted in the past two decades. The compendium on oil spill treating agents prepared for the American Petroleum Institute in 1972 lists 69 dispersants and 43 beach cleanup agents, most of which are also listed as dispersants (American Petroleum Institute, 1972). Only two of these are current commercial products, but both are produced in different formulations. Over 100 surface washing agents have been sold in North America. Six are still commercially available. A number of agents not fitting into the above categories include those that help trace or detect an oil, combinations of the categories described above, and vague items claiming to make oil disappear, become non-toxic, and so on. Approximately 100 of these agents were promoted at one time or another on the North American market. There are approximately 600 agents world wide, but only about 200 were ever tested in the lab or field, even in a limited way (Fingas, M., Kyle, D., Larouche, N., et al.). The quantity of products causes difficulties to the potential buyer and to the environmentalist because they are unable to ascertain which products may actually help the situation and those which can cause further damage.

Effectiveness remains the major problem with most treating agents. Effectiveness is generally a function of oil type and composition. Crude and refined oil products have a wide range of molecular sizes and composition including whole categories of materials like asphaltenes, alkanes, aromatics, and resins. What is often effective for small asphaltene compounds in an oil may be ineffective on large asphaltenes. What is effective on an aromatic compound may not be effective on a polar compound. This leaves little scope for a universally-applicable and effective spill control chemical. The other major factors in agent effectiveness are environmental parameters such as temperature and sea energy. These can be highly dominating and will overwhelm most other factors on occasion.

Toxicity testing is a very important factor. Most vendors of treating agents have not tested their products for aquatic toxicity, although a few have tested their products for mammalian toxicity to meet transportation requirements. Many products tested by environmental agencies have unacceptably high aquatic toxicities. Even tests of natural products have shown unacceptable aquatic toxicities (Fingas, M., Kyle, D., Laroche, N., et al.).

Solidifiers or Gelling Agents

Solidifiers change oil from liquid to solid. These agents often consist of polymerization catalysts and cross-linking agents. Agents which are actually sorbents are not considered gelling agents.

A standard test, developed to assess new solidifiers, consists of adding solidifier to an oil and stirring the mixture continuously until the oil solidifies. Tests indicate that several treating agents require about 15 to 20% of solidifier to completely solidify oil. However, other agents may take up to 200% by weight to complete the task. The aquatic toxicity of these products was measured, and in all cases exceeded the maximum test value. In other word, all products listed are relatively non-toxic. The major problems with solidifiers is the lack of a clear benefit to using the product, difficulties in actual use, and the high amount of agent required. The difficulties in actual use are that once the agent reacts with the first oil it contacts it solidifies, and no more agent penetrates to react with more oil. This implies that complete solidification in actual practise would be difficult, at best.

De-emulsifiers or Emulsion Breakers

Several agents are available to break or prevent emulsions. Most agents are hydrophilic surfactants (e.g., they have a strong tendency to make oil-in-water emulsions). Such surfactants can revert the water-in-oil emulsion into two separate phases. The problem with a hydrophilic surfactant is that it is more soluble in water than in oil and will quickly leave the oil. Such products may not be effective on open water. There are, however, two uses for de-emulsifiers: to break or prevent the formation of emulsions; and to break recovered emulsions in skimmers or tanks on the open seas. In the latter case, the water solubility of the product is not as important an issue.

A laboratory test, under development at Environment Canada, aims to provide a fast, convenient means of assessing emulsion preventers and breakers (Fingas, M., Kyle, D., Larouche, N., et al., 1995) (Fingas, M., and Fieldhouse, B., 1994). Testing of some commercial products, using the initial protocol, shows that these products are effective on stable emulsions at agent-to-oil ratios as low as 1:500. Aquatic toxicities of these products varies considerable from highly to relatively non-toxic.

Surface Washing Agents

The most common treating agents contain surfactants as the major ingredient. These agents are divided into two groups: dispersants and surface-washing agents. Dispersants have approximately the same solubility in water and oil and will disperse the oil into the water in the form of fine droplets. Surface-washing agents remove oil from solid surfaces such as beaches by the mechanism known as detergency. Good surface-washing agents are poor dispersants and vice versa. A test for surface-washing agents was developed by Environment Canada and many commercial products have been tested using this protocol. The test measures how much oil (Bunker C) is removed from a standard test surface when the surface-washing agent is allowed to soak into the oil and then rinsed with water. Results show that the removal rate for the 150 products tested to date varies from 0 to 55% (Fingas, M., Kyle, D., Larouche, N., et al.). Similarly, the aquatic toxicity varied from high to relatively non-toxic. The dispersant effectiveness was also measured and this shows the opposite nature of dispersant and surface-washing effectiveness. Low dispersant effectiveness is a benefit for any surface washing agent because oil can then be recovered rather than dispersed into the water column. Because the two properties of surface washing and dispersancy are orthogonal, highly effective products do not have a significant dispersant effectiveness.

In-Situ Burning

In-situ burning has been used in certain parts of the world, particularly in the Arctic, where oil is thickened by wind herding the oil onto ice. Concern has been expressed about air emissions from burning. Other concerns include residues sinking and containing burning oil on the high seas. The advantages of burning are: oil is removed from the water column, it does not require disposal, and oil can be removed at very high rates, thus preventing shoreline damage. Burning, under the right conditions, can be highly efficient and can result in removal of most of the oil, leaving only a taffy-like residue which can be cleaned manually.

Most oils will burn at sea if they are at least 2 to 3 mm thick and do not contain water in the form of stable water-in-oil emulsions (Fingas, M., and Larouche, N., 1990). The minimum thickness requirements imply that oil must often be contained before burning. To this end, special fire-resistant booms have been designed, but the containment technology is still developing. Tests show that temperatures in the burn can reach 1300 °C and this poses a challenge to material selection (Fingas, M., 1994). Work continues on better fire-resistant boom design and techniques to burn oil with higher amounts of water.

Extensive work has been conducted on analysing the air emissions of *in-situ* burning. Tests show that the primary concern is the release of respirable particulate matter in the smoke (Fingas, M., Halley, G., Ackerman, F., et al., 1994) (Fingas, M., Halley, G., Ackerman, F., et al., 1995). These are particles having diameters of less than 10 µm which affect the human respiratory system. It was also found that the ground level concentrations fall below concern limits, however, the smoke plume can contain particulate matter at concentrations that are a health concern as far as 10 km. The second emission of concern is that levels of volatile organic compounds can be higher than normal as far as 500 m from the fire. However, these levels are generally lower when burning than when not burning. A third concern is the presence of polycyclic aromatic hydrocarbons (PAHs), which can be toxic to most biota. All crude oils contain these substances and it was found that *in-situ* burning actually removes PAHs as well as other compounds in the oil. The soot contains PAHs at lower concentrations than the original oil and is not a concern.

The final issue about *in-situ* burning is the residue. It is generally viscous and contains heavier compounds of the oil, such as metals at higher concentrations. Heavier oils and those that burn efficiently can yield residues that sink. This situation has been observed only a few times out of several hundred burns at sea.

Natural Recovery

In some circumstances, no cleanup is dictated either by the inability to perform such an operation or by the fact that no resources are threatened. In the first case, conventional methods cannot be applied to oil slicks far out at sea and under high-sea conditions. In such cases, no resources (i.e., bird colonies or shoreline) may be threatened. Sometimes the oil disperses naturally before conditions are suitable for a response. In other cases, such as when oil hits a salt marsh or a sensitive remote beach, cleanup may in fact, cause more damage than the oil. There remains the "natural recovery", or the "surveillance and monitoring option" because this is an activity which occurs despite the lack of cleanup. It is always necessary to monitor the track and position of an oil spill for several reasons, not the least of which is the public expectation that this is a minimum requirement. Several natural processes do assist in the cleanup of oil. On shoreline, natural washing and removal occurs as does some biodegradation. At sea, natural dispersion occurs.

Other Technologies

Enhanced Bioremediation

Bioremediation is currently very popular and there are many proponents of the technique and vendors of products claiming to aid in the process. Caution should be exercised in adopting any of these products because bioremediation has only limited application to certain oils and circumstances, and is never as fast as hoped or needed (Hoff, R., 1992). This is not to say that there is no place for bio-remediation, but bioremediation is vastly over-sold at this time and may in fact not be applicable to a number of spill situations.

Spill Treating Agents

Spill treating agents are highly-promoted by manufacturers and many claims are made about their performance. Spill treating agents are usually regulated by government agencies. Guidelines exist for their acceptability and use. Acceptability is usually based on toxicity and effectiveness. Many of the agents, once approved, require specific permission before use. Most spill treating agents do not live up to their promises and do not survive longer than a few months on the market Many agents are toxic or completely ineffective.

This is a brief summary of some spill countermeasure highlights. Please consult the references for detailed information.

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