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AN OVERVIEW OF CURRENT SPILL CLEANUP TECHNOLOGY

INTRODUCTION

A comprehensive consideration of spill cleanup technology involves a wide range of problems. Consideration must include the nature of the spilled material, the nature of the environment and the state it must be returned to, and the technology available in a variety of related but separate fields. Spill response is not a unified or complete art. Effective response in many cases requires drawing heavily from the knowledge and technology of other fields and piecing together a solution. In most situations the spill response requires a variety of tools, for all are sharply limited and no one will do the whole job.

This paper primarily discusses spills onto or into water -- not on land. It considers only the technology available for cleanup and does not address the often difficult problem of waste disposal after the cleanup. It does not consider radiological or etiological agents, other than the use of bacteria to mitigate problems at spills. It does not consider waste dump sites. The paper first considers the behavior or spilled materials -- whether they float, sink, evaporate, mix into the water, or some combination of these. Then several possible activities for cleaning up the spill are discussed: minimizing the spilled volume, containing the spilled material and preventing its spread, recovering or removing the spilled material from the environment, treating the spilled material so it is no longer a hazard, and temporarily storing recovered materials prior to disposal.

THE BEHAVIOR OF SPILLED MATERIALS

It is convenient to classify products according to their immediate behavior upon being spilled. Products may generally be classified for spill response purposes as floaters, sinkers, vapors, or mixers.

Table 1 - Behavior of Spilled Materials

Product Type	Examples
Floaters	petroleum, vegetable oils
Sinkers	some bunker fuels, ethylene dichloride, carbon tetrachloride
Vapors	volatile hydrocarbons (acetone, freon), LNG, chlorine
Mixers	many acids, water-soluble pesticides

The neatness of this distinction is lost somewhat in practice, however, because some products may display the characteristics of more than one of these four types.

Petroleum oils, for example, are generally regarded as floaters, but it is important to recognize that a significant part of some oil spills may evaporate (vaporize) before and during spill response. Up to 30% of light crudes (the lighter components) may evaporate in 24 hours (Frankenfeld, 1975), and products composed only of light products may evaporate continuously at that rate. Also, some oils are on the borderline between floaters and sinkers. They may float when sufficiently pure or when they have sufficient gas (generally, air) suspended in the liquid phase, but they may sink if they mix with the solids suspended in the water column or if the salinity of the water decreases. This change in behavior can be exploited in spill response. Ammonia acts as both a mixer and a vapor, with a reported partitioning of approximately 60/40% into the water/air (Harsh, 1978). Temperature may also strongly influence which behavior a product exhibits, though materials spilled on water usually quickly adjust to the temperature of the water, which typically falls in the relatively narrow range of -2 to 30 C.

In principle, floaters are perhaps the easiest pollutants to remove from the environment, and they constitute the majority of the spilled pollutants -- primarily oil and other petroleum hydrocarbons. Often, the primary problem with these spills stems from their sheer size: it is uncommon to have spills of hazardous materials other than oil in quantities of 1000 to 100,000 tons.

The available technology that is specifically designed and intended for cleaning up or treating spills of floaters is significantly better developed than the technology for responding to spills of sinkers, vapors, or mixers. This is true primarily because of the variety of equipment developed for responding to oil spills. This equipment generally can be used on spills of any floating liquids or granular, particulate solids, subject to limitations stemming from simple incompatibility of the equipment's materials with the hazardous material. The effectiveness of each device or method may vary greatly for different liquids, however, and some will be completely ineffective on powders.

Sinkers are spilled much less often than floaters, though there are now large quantities in the bottom sediments in some areas because of long term deposition from accidental spills, manufacturing operations releasing pollutants at small rates (sometimes under permit), or a combination of the two. Sinkers include a wide variety of hazardous materials and some oils. Some common chemicals such as carbon tetrachloride, ethylene dichloride, and trichloroethane have specific gravities greater than salt water and will sink.

Sinkers are easy to clean up in principle, but the presence of some sinking chemicals in the water and on all gear that is used underwater may present a serious hazard to divers and topside personnel assisting them. Severe problems have occurred, and solutions are not readily available. The U.S. Government (USCG, EPA, Navy, NOAA) is presently conducting an extensive evaluation of diver safety at spills of hazardous materials. Divers may also be prevented from working efficiently by strong currents, and rough weather may hamper operations topside just as work on floaters is hampered. Although spills of sinkers are easy to clean up in principle, little equipment is available specifically for that purpose.

Materials that vaporize rapidly present the greatest clean-up problems. In many cases, clean-up is not possible at all once the material escapes its container. These materials are typically high hazard materials and may require evacuation of the nearby area or downwind area for some distance. Response measures can be safely undertaken only by experienced personnel working in completely encapsulating suits with self-contained breathing apparatus. Because even this protection is not completely effective, an atmosphere charged with certain highly toxic products like chlorine must simply be avoided entirely.

Mixers probably impact the greatest area or volume but may have the least severe impact. Once partially mixed into the water, relatively modest sources of additional water and mixing will sometimes dilute the pollutant to safer levels. However, a corollary of this is that little can be done except in very low energy environments. The volume of water that the material mixes into represent an ever-increasing volume that must be treated or cleaned. Containment possibilities are sharply limited.

Mixers are often highly hazardous pollutants. The list may include acids, soluble pesticides, etc. that have very low lethal concentration or are highly carcinogenic or teratogenic.

THE PHASES OF CLEANUP

For each of these four types of products, we will try to examine several separate phases of spill cleanup: prevention and minimization, containment, recovery or treatment, and temporary storage.

Table 2 - Phases of Cleanup

Activity	Examples
Prevention and Minimization	patches & plugs, good equipment design, safe operating procedures, lightering
Containment	oil booms, chemical herder
Recovery or Treatment	oil skimmers, sorbents, chemical dispersants, neutralization
Temporary Storage	barges, flexible bags, skimmer's tanks

These examples will be discussed in more detail in subsequent sections of this paper. Note that not all of these activities are possible at all spills. Which ones are feasible and desirable will depend on the behavior of the product, the weather, location, etc.

Prevention and Minimization

Although prevention is not, strictly speaking, a cleanup activity, it is worth noting in this discussion, because it is clearly the most effective action that can be taken. Also, once spilling has begun, the success of the rest of the cleanup operation will be more strongly affected by minimizing the volume spilled than by any other single activity. The response coordinator and crews are often faced with this as their first task.

Devices for minimizing the spilled volume by plugging leaks have been developed but have met with limited success. Magnetic patches are available, and special foam-plug generators (Mitchell, et.al.,1978; Cook and Melvold,1980) have been developed for plugging holes in ruptured containers of hazardous liquids, but these will have trouble coping with the extensive damage that is often caused in maritime accidents. Even for small leaks, inprovisation is sometimes necessary. Methods as crude as wood plugs and plywood patches have been used.

Apparently the most successful method so far is simply some version of lightering: transferring material from the damaged vessel to an undamaged one, or from the damaged compartment to undamaged ones on the same vessel. If divers are not needed during this work, it is no more limited than routine transfer operations, although speed is important to minimize the spilled volume.

Containment

Floaters:

After the material has been spilled and is afloat, early containment is almost always desirable. (At offshore platforms, it may be preferable to disperse spilled oil to lessen the fire risk.) A wide variety of oil containment booms has been developed for containing floaters. Many use elastomeric coatings that are compatible with other hazardous materials besides oil; that is, they will not rapidly degrade and fall apart.

Considering only containment capability, boom designs differ primarily in their ability to contain oil (or even survive) in rough seas. A very few are promising in seas up to 3 m, but most seem limited to seas less than 1-m significant wave height (Corpuz and Griffiths,1978). By design, the typical "harbor boom" is even more severely limited. To improve ease of use and to lower cost, these booms often have low reserve buoyancy and may begin to fail in waves as small as 0.3 m. But what may be the strictest limitation for booms in ports and, especially, in inland waterways is the entrainment failure of floaters in a current. It is well established (Hale, et.al., 1975) that the oil/water interface of oil slicks held by a boom against a current greater than about one knot will become unstable and the oil will break into droplets that are swept away under the boom. The one-knot figure will vary slightly with oil type and may be significantly higher (2 knots ?) for some other hazardous materials. But the response coordinator simply cannot expect to contain floaters in currents greater than two knots, which are commonly encountered in some harbors, estuaries, and rivers.

The variety of booms available is great, and choosing the best for a particular task requires careful study (technical contingency plans), especially if high waves or fast currents must be tolerated. For calm conditions with currents less than one knot, the performance of different booms should not vary significantly (Griffiths, 1981). McCracken and Schwartz (1977) and Freestone, et.al. (1976) have presented test data on small booms acquired using naphtha, octanol, and dioctyl phthalate.

Chemical methods of containment, such as Shell's Oil Herder and other film-forming agents (see Garrett, 1969), are relatively untried. These surface-tension modifiers are applied to the surrounding water to restrict the spread of the pollutant. In some cases they will even push the edges back to concentrate the pollutant slightly, but they cannot restrict its overall drift or develop pools of pollutant several centimeters thick. Other than on the open ocean, where the shoreline is distant, they will not provide containment in the same sense as a boom.

Sinkers:

Containment is rarely possible with sinkers, but it is also rarely necessary. Sinkers will accumulate in depressions on the bottom and will not spread far unless the bottom slopes steeply or unless there is a strong current at the bottom. No special emergency response technology is available for containing sinkers, though any sinkable barrier or subsurface berming should be suitable for local control of sinkers on the bottom (possibly to protect water intakes of important shellfish beds).

Mixers:

Unless the body of water is small and can be closed off, as is possible with ponds and small streams, containing mixers is not feasible. Mixers can be expected to disperse into a large volume of water quickly.

Vapors:

Two modes of containment are possible for some highly volatile liquids. If the material floats prior to evaporating, it may be contained using the floaters' technology. Herding it together on the surface will reduce the vapor emission by minimizing the surface area of the slick. Furthermore, the vapors may then be directly controlled by several methods. Water fogging and foam blanketing are demonstrated methods (Whiting and Shaffer, 1978; Gross, 1978) within the capability of many fire-fighting services. These methods will lower the evaporation rate, thus containing the vapors.

Recovery

Floaters:

If containment of a floater has been successful, the prospects for mechanical recovery of the pollutant are significantly inproved, and recovery is preferable to treatment unless conditions make recovery unsafe or impossible.

Few devices are available for recovery in seas greater than 1 m. Jensen (1976) described several designs developed with U.S. Coast Guard support, but skimmers based on these are not widely available. Apparently only the Skimming Barrier (Milgram and Griffiths, 1977) has enough backup tank test data and field use to defend the claim of up to 3-m seas capability. One other device not described by Jensen, the Shell SOCK skimmer, has also successfully recovered crude oil in tests in seas greater than lm. For 1-m seas and less, numerous devices using conveyor belts, sorbent belts, adsorbing disks, weirs, vortices, etc. become useful. The correlation among size, cost, and performance is very poor, especially if the slick is only a few millimeters thick. High viscosity can also be a serious problem. Good, medium-size harbor skimmers can be expected to recover about 3 to 10 m^3/h of low viscosity product in good weather. Performance results in tests with octanol, naphtha, and DOP for several skimmers in this class were reported by McCracken and Schwartz (1977) and Freestone, et.al. (1976).

Floaters can also be recovered using sorbent materials. Numerous specially treated sorbents have been developed for oil spill cleanup, and some are applicable to other floating hazardous materials. Sorbents come in a variety of forms including loose powders, blankets and pads, and sorbent booms. Sorbents are also used by many skimmers in the form of rotating sorbent belts and sorbent rope mops. Many sorbent materials will adsorb/absorb approximately four to seven times their weight of oil and some foam types will sorb 30 to 40 times their weight. Except for sorbents used by skimmers, application and recovery of sorbents is usually done manually using simple tools such as shovels and forks. This may result in very low recovery rates and substantial safety hazard to cleanup crews. Brugger (1980) has reviewed the effectiveness and chemical compatibility of sorbents for use on hazardous liquids. He noted sorbents' good performance with oil and our present lack of experience with sorbents on hazardous liquids other than oil and, in light of their expected value for cleanup, recommended that we pursue their possible use.

Sinkers:

Dredges appear to be naturally applicable to recovering sinkers. Goodier, Thompson, and Dawson (1980) reviewed the availability of dredges, and Hand and Ford (1978) presented an extensive evaluation of the various types of dredge and their suitability for spill cleanup. Besides the large dredges used for clearing shipping channels, small dredges are available (from car rental companies!) for locations where space or water depth is limited. These pose numerous problems in actual use, however. The problems stem mostly from their tendency to stir up the bottom excessively. As a result they pick up large quantities of bottom solids with the desired pollutant and at least temporarily disperse some of the pollutant back into the water. Thus, the clean-up operation aggravates its own problems of finding and pursuing the spilled material, and large amounts of contaminated sediments may be produced besides the originally spilled material. The U.S. Coast Guard has tried an air-lift dredge to avoid some of these problems on a spill of pentachlorophenol (Thornton and Williams, 1982). In addition, the contaminated materials pose safety problems for the work crews, as noted previously. Diving appears to be necessary to do most jobs properly. Attempts have been made to rebag spilled powders by hand to avoid the above difficulties.

Vacuum systems ranging in size from 55-gallon drums to mobile tank trailers are available for cleaning sewers, sumps, and spills. Though these are not submersible, the suction hoses can readily be controlled by divers, and moderate hose lengths do not seriously degrade their performance. These devices will also tend to pick up water and sediment and mix them with the pollutant.

Vapors:

Recovery of vapors is not feasible after evaporation, so recovery must take place while the material is still afloat or still mixed into the water. The recovery technology for floaters may be useful, or the mixed portion may be treated chemically and rendered less harmful.

Mixers:

Recovery of mixers is possible but very difficult. One may properly consider it beyond the capability of present technology.

If the pollutant (or polluted water) is not contained, it will be impossible to recover all of the mixer. Even if containment is good, presently available methods are likely to be only marginally effective, and these must still be considered experimental.

Schneider (1980) has attempted to recover mixers by applying activated carbon directly to the contaminated water, but he concluded that little could be removed this way because of the poor contact between contaminant and carbon and the necessary long contact times for carbon to work. It is also possible to remove the water, treat it using an appropriate physical or chemical process, and return the treated water to the water body. Ghassemi and Freestone (1980) considered reverse osmosis, ultrafiltration, wet air oxidation, biological treatment, ozonation and UV radiation, and precipitation and coagulation. Huibregtse, et.al. (1978) also considered carbon treatment, ion exchange, and simple gravity separation. The correct process to choose will depend on the chemical contaminant and its concentration in the water. Again, these methods are experimental and have not proved effective or economical on a large scale. Their effectiveness may be minimal in many cases, because the mixer cannot be contained.

Treatment

Floaters:

Several treatment methods have been studied for floaters (again, oil in particular) and are now at least partly effective. Sinking was once considered a possible response to spills of floaters, though this concept has nearly been abandoned as environmentally unsound. Sand, chalk, and other powdered or granular materials were candidates for increasing the specific gravity of the slick. Sinking of portions of the spilled oil from the *AMOCO CADIZ* using chalk was attempted in recent history, but reported to be largely unsuccessful (Bocard and Renault, 1979).

Certainly the most popular and widely studied treatment method for oil slicks has been application of chemical dispersants. Numerous companies now offer different types of chemical dispersant, and both waterborne and airborne spraying equipment have been developed. The effectiveness and toxicity of chemical dispersants remain a matter of debate, though effectiveness has clearly improved greatly and toxicity dropped greatly since the adverse effects at the TORREY CANYON oil spill were noted. Laboratory data demonstrating the potential effectiveness have been developed, but evidence from the field has been contradictory and is therefore inconclusive. Mackay and Wells (1981) have presented a concise review of chemical dispersant use.

Gelling or solidification of floaters is also a possibility. Bannister (1978), for example, has reported an amine carbamate gelling method for oil. This process produced a soft gel from which the oil could be squeezed after the gel was recovered. Meldrum, Fisher, and Plomer (1981) have reported a solidification method that binds oil into a rubbery polymer matrix. A general problem with gellation is that the gel is not often any easier to recover than the liquid oil. Gelling of other floaters has received little study. Michalovic, et al. (1978) have reported a study of a gelling agent on land spills.

The technology of burning oil slicks has improved significantly since the early 1970's. This method is probably not usable on most other pollutants because of the explosion or air pollution hazard, which remains a potential problem even with oil. Special igniters have been developed (Meikle, 1981) that may be dropped on a slick from the air, making them useful in remote locations like the Arctic. If the pool of liquid can be thickened by containment and the water surface is nearly calm, more than 90% of an oil slick can be burned off. The remaining sludge (similar to Bunker fuel) may, however, still present a substantial cleanup problem. In conditions other than calm, burning is not a simple matter. Thin films of water splashed atop the floater tend to douse the flames readily, and the water body acts as an enormous heat sink, inhibiting volatilization. Special fireproof booms have been developed to contain burning oil pools (see, e.g., Buist and McAllister, 1981).

A treatment method showing increasing promise is enhanced biodegradation. Several types of bacteria are ubiquitous (present in waters and soil almost everywhere on Earth) and will gradually break down hydrocarbons, using them as food. Special strains have been developed that act faster or handle particular subsets of hazardous materials.

Like plants, they need a balance of nutrients besides the pollutant, so it may be necessary to add the three primary nutrients (nitrogen, phosphorus, and potassium). Because the bacteria act slowly, it may not be feasible to rely on biodegredation alone.

Enhanced biodegradation is still an experimental method except in certain controlled applications isolated from the environment. It is possible to have highly undesirable products created rather than harmless ones, especially if anaerobic decomposition occurs.

Vapors:

Many vapors are volatile floaters. Sinking them will reduce the vapor hazard. Others may be mixed into the water, using chemical dispersants, if necessary. Unfortunately, with most chemicals this results in trading one problem for another, because some vapors are soluble and highly toxic in the water. Also, this may increase the duration of the hazard, because the chemicals may persist on the bottom or in the water far longer than they would persist as vapors in the air. Furthermore evaporation rates directly from the water may continue to be quite high, so the vapor hazard is reduced but not eliminated. In some cases it may be safe and possible to ignite the vapors, as has been done with the natural gas emissions from uncontrollable oil well blowouts.

True clean-up (i.e., removal) is possible only as long as the material remains a floater. Then, a variety of treatment methods is feasible. These are generally well-known chemical processes such as neutralization, precipitation, flocculation, etc. mentioned elsewhere in this paper.

Mixers:

Most schemes for treatment of mixers require removal of the contaminated water prior to treatment in a controllable facility. Process plants that include carbon adsorption, chemical alteration (neutralization, reduction-oxidation reactions, etc.) have been designed and assembled to handle specific cases, as noted in the section of this paper on recovery of mixers.

In-place treatment of an anhydrous ammonia spill with hydrochloric acid has been described by Harsh (1978). A few attempts at in-place treatment in soil have been reported. In principle, such treatment is a relatively straightforward matter using established chemical methods. However, all face the problem that the mixer is typically uncontained and continues to spread widely, and concentrations are not uniform. As a result, it is difficult to know the right amount of treating chemical to apply and to deliver it to the right place. Thus the potential exists, for example, to be left with both an acid spill and a base spill when attempting to neutralize an acid spill. In-place treatment of mixers in water is a current research topic and must be used very cautiously in the field.

Temporary Storage

Because spills of floaters are sometimes large and because as much water may be taken up as spilled product, a response coordinator's ability to marshall large temporary storage containers is essential to continue the cleanup. Especially hazardous products may need special ISO containers or similar. Skimmers usually have very little built-in storage capacity - 10 m^3 or so in commonly available devices such as JBF DIP and Marco skimmers. Many have none.

For oil spills and many other hazardous materials, this problem is a logistical rather than a technological one. Containers similar to the one that is the source of the spill (another tanker or barge, ballast or mud tanks) are suitable. Inert gassing or foam blanketing in the temporary storage tanks is also feasible but rarely necessary.

An alternative is presented by the various "rubber bags" now available, such as the Dunlop Dracones or Goodyear pillow tanks. These range in capacity from approximately 2 m^3 to 1000 m^3 and are compatible with a wide range of pollutants. Experience with them at actual spills is limited, however, and the results have not been widely reported. The U.S. EPA has also funded development of a special pump and bag storage system for use at hazardous material spills (Hiltz and Roehlich, 1977), but the system is not yet commercially available.

Ideally, the temporary storage container will function as a gravity separator and provide for removal of the water that accumulates under the product. Few presently available storage methods do this with a good degree of control over the separation and water stripping. Flexible bags in particular are not well suited to this.

CONCLUDING COMMENTS

It is difficult to narrow the topic "spill cleanup technology" sufficiently to produce an overview paper without delving into the many intricacies of that technology and the related problems of logistics, legalities, etc. It is particularly easy to gloss over the health and safety aspects of cleaning up a spill of "dangerous cargoes" while trying to ramain on the subject of the cleanup itself. Readers should recognize that safety for response personnel is a major field of study in its own right

I have tried to present mostly the results of recent studies, and hope that the list of references will assist the reader in finding additional sources of new information.

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16. ABSTRACT

A review of the equipment and techniques for responding to spills of dangerous cargoes is presented. Categorizing spilled products as floaters, sinkers, mixers, or vapors provides a convenient viewpoint for discussing response technology, which depends strongly on which behavior the product exhibits. Spills of radioactive and bacteriological agents are not covered in this paper, though the potential use of bacteria for mitigating oil or chemical spills is noted.

The technologies for responding to spills of floaters and sinkers are shown to be the most well developed of the four types. Equipment and techniques in common use by the United States and Canadian governments are discussed to illustrate this. Current technology includes both removal of the pollutant using non-conventional equipment such as booms, skimmers, dredges, or sorbents and in-place treatment such as chemically-enhanced dispersion, enhanced microbiological degradation, or in-place burning. Significant weaknesses are noted, however, in three areas: spill cleanup in rough seas, in fast currents, and in the arctic (or cold climates). Little technology is available for response to spills of mixers or vapors, and a major concern at these spills continues to be the safety of the response equipment operators and divers. Experimental, infrequently-used techniques for in-place treatment and for actual cleanup and removal are discussed.

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