HANDLING AND DISPOSAL OF OILY WASTE FROM OIL SPILLS AT SEA

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Disposal of recovered oil and debris following an oil spill at sea can present a real challenge to the spill response team: many technical issues and options are involved. The mainly oil component should be kept separate from the mainly debris component of the waste as far as possible. This not only reduces handling problems, but also provides a better opportunity to wash or aerate the debris to allow it to be classified as nonhazardous. Nonhazardous waste landfill remains a potentially cheap option where regulations allow it. Solidification or stabilization techniques may be useful in the future to convert waste oil and debris to a suitable form for landfill. Reclamation of recovered oil is attractive in principle, particularly for large spills; but the presence of contaminants makes it difficult, in practice, for the oil to be recovered. Incineration is technically feasible and mobile/transportable systems are potentially attractive, provided permits can be obtained. A number of biological methods including land farming appear to have promise. Further development work is needed to determine possible techniques for this application.

The disposal of oily waste from any source is becoming an increasing problem as environmental consciousness is being raised and tighter regulations are being introduced. Issues such as the potential for groundwater contamination from landfill sites have resulted in the greater scrutiny of traditional landfill as a disposal route. The classification of some oily wastes as hazardous has limited disposal options and increased costs.

Several specific problems are associated with the disposal of oil recovered following a major spill at sea, which add to the difficulty and complexity of disposal.

- There may be very large quantities of waste collected in a relatively short time.
- The waste is likely to be extremely variable in its physical and chemical characteristics.
- Inevitably, there will be a great deal of public interest and media attention.

The variability in properties of the waste makes it difficult to set watertight contingency plans in place for handling and disposal following an oil spill, because the technical feasibility of any option depends on the properties of the oil. Therefore, it is particularly important for the spill response team to be aware of the issues, to consider segregation of oil and debris at an early stage, to have an appreciation of handling and disposal options, and to understand local circumstances including the regulatory framework within which decisions must be taken. A detailed review of handling and disposal options, commissioned by the Marine Spill Response Corporation, will be published shortly.

Physical and chemical characteristics of oily wastes

The waste can consist almost entirely of weathered oil with minimal associated debris or other contamination, or it can be made up of debris with an almost insignificant amount of weathered oil, or it can be anywhere in between. Indeed, an individual oil spill may well generate waste with properties spanning these extremes. The oil component and the debris component can also vary widely from one spill to the next.

Recovered oil.

A considerable range of crude and refined oils are carried in large quantities at sea. They contain a great variety of chemical compounds in widely varying proportions. No two sources of oil are identical, and oils from individual sources change with time. Carbon and hydrogen make up the major part of the elemental composition of crude oil but other elements present include sulphur (trace to 8 %), nitrogen (trace to 1.6 %), oxygen (trace to 1.8 %), and nickel and vanadium (trace to 1,000 ppm). These elements are combined to form complex mixtures of organic compounds with molecular weights ranging from 16 (methane) to several thousands.

The chemical composition of crude oil spilled at sea changes as a result of the weathering processes, particularly evaporation and emulsification with seawater. The volatile components of the oil are lost quite rapidly by evaporation, for example, 30 percent of Forties crude oil evaporated within one hour and 45 percent within 60 hours following an experimental spill.[6] The more-toxic aromatic compounds, such as benzene, toluene, ethylbenzene, and xylene, can be expected to evaporate rapidly and should be present only in small quantities in recovered oil. The rapid loss of volatiles also results in the flash point of spilled oil generally increasing to above 60 ° C in the first hours after release, thus reducing handling hazards.

The formation of stable water-in-oil emulsions on the sea surface is also particularly significant from a handling and disposal viewpoint. Depending on the oil and the prevailing sea conditions, emulsions can contain in excess of 80 percent water. The volume of recovered waste can therefore be much greater than the volume of oil alone, and significant quantities of salt may be associated with the waste. The combined effects of evaporation and emulsification can result in enormous increases in viscosity. Crude oil viscosities can increase by a factor of 1000 after a few hours on the sea surface. This causes considerable difficulties in handling, pumping, and cleaning operations.

Oily debris.

The floating debris encountered during oil recovery operations at sea comes from a wide variety of natural and man-made sources. In addition, shoreline cleanup operations inevitably result in removal of some of the beach substrate and vegetation.

Oil and debris are subject to the same wind and current forces, and so will tend to move together towards the same places. If the prevailing currents and winds drive the spill against a shoreline, containment wall, or other barrier, the debris already collected there will be thoroughly mixed with the oil.

A detailed survey of debris along the shores of the United States some years ago showed that most of the debris around the coast was wood. A similar survey carried out today would probably draw similar conclusions, although increased regulations may have reduced the quantities of debris found.

The amounts and types of debris collected following some spill incidents are shown in Table 1. This illustrates the significance the debris can have for handling and disposal operations.

Waste handling

The segregation of liquid and solid wastes can be an important part of an oil recovery operation, reducing handling difficulties and simplifying final disposal.

Separation at the sea surface.

One of the most effective approaches is to prevent the oil from contacting the debris. A wide range of equipment can be used to remove debris from the water, particularly in nearshore areas, including wire mesh baskets on articulated hydraulic cranes; front loader baskets; clamshell bucket equipped cranes; debris conveyors; rakes, shovels, pitchforks, dip nets, and the like; log grapples and conveyors; vacuum hoses; special pumps; and kelp harvesters. Predictions of the likely trajectory of an oil slick can be used to help decide where to focus such efforts.

Similarly, oil recovery equipment can be deployed strategically in areas where there is relatively little debris contamination. Aerial reconnaissance may be helpful in identifying the most suitable areas. Mechanical skimmers are commonly used to recover oil from the water surface.

If recovery equipment must be used in areas of mixed oil and debris, a number of measures can be employed to divert debris away from the oil recovery devices. These include water jets, propeller wash from small boats, manual tending, and the use of debris recovery equipment.

Skimmers themselves can generally handle limited quantities of debris. Trash screens are placed to allow oil to pass into the skimmer but to block the debris. Mesh sizes of 1.25 cm (0.5 in) are common although larger meshes may be required for viscous oils and emulsions.

Separation on board recovery vessels.

Simple screens can be used aboard ship to remove large items of debris before pumping the mainly oil and water fraction into storage tanks. The free water separates under gravity and, with further treatment if necessary, may be discharged into the sea. The debris may be shredded, chipped, or ground to reduce storage volumes.

The small water droplets within stable emulsions will not separate under gravity in the time scales required; but the addition of chemical emulsion breakers will reduce the interfacial tension between the oil and water and allow the water droplets to coalesce and settle out. Some recovery equipment enables emulsion breakers to be injected directly into the recovered oil stream thus reducing or eliminating the need for subsequent mixing. The amount of chemical required to break an emulsion varies widely with the type of oil and can range from 0.25 to 5 liters per ton of emulsion.

Separation on shore.

The greater space available on shore provides more opportunities for separation of oil and debris. Some of the options identified below have been used for oil spill response but some require feasibility studies or further development.

- Debris washing - Typically, debris is washed in large pits lined with plastic sheeting, where high pressure water is used to dislodge the oil from the surface of the debris. The oil is carried through a water runoff channel to oil/water separation facilities. Hot water, steam, detergents, or solvents may encourage the release of the oil from the surface of the debris; but there are few reports of their use.

- Decantation washing - This technique is intended for oiled sand and gravel and makes use of readily available concrete mixing trucks. Several tons of solids are loaded into the mixer by means of a hopper mounted on a temporary scaffold. Kerosene is added to the mixer drum during loading and mixed with the oiled solids for several minutes to reduce the viscosity of the oil and facilitate its detachment from the solid surface. The mixer is then filled with seawater and rotated very slowly to allow the oil to separate and float to the surface, from where it flows into a separator tank. Under optimum conditions, in excess of 99.5 percent of the oil may be removed from the solids.[8]

- Screen/trommel washing - Material passing over any screen can be washed by means of dedicated water sprays. Drum and trommel washers have been developed in which kerosene or a hot water containing cleaning agent is added with the material intake.[5,7]

- Submerged spiral classifier - Oiled pebbles have been cleaned by this technique, in which water is sprayed onto a spiral screw through a number of spray nozzles located along its length.[8] The material is fed to the lower end of the classifier through a 25 mm aperture vibrating screen, which removes oversized debris capable of jamming the machinery.
- Size reduction - Hammer mills, shear shredders, wood chippers, and other size reduction equipment may be suitable for oily debris. This can aid handling by conventional processing equipment, liberate oil trapped in items of complex shape or containers, reduce waste volume, and increase surface area to encourage biological breakdown.
- Filtration/centrifugation
- Electromagnetic removal of tramp metals
- Solvent extraction
- Hydrocyclones - For oily water separation or for removal of fine particles from wash waters

Segregation of hazardous and nonhazardous wastes

The difficulty and cost of disposal of oily waste is increased if the waste is classified as hazardous. It is therefore important to minimize the volume of hazardous waste generated following a spill and to keep hazardous waste separate from nonhazardous waste. Treatment of hazardous waste to render it nonhazardous may be cost effective in some circumstances.

Classification of hazardous waste.

Definitions of hazardous waste vary from country to country and need to be considered on an individual basis. However, it is worthwhile considering the situation in the United States, where the handling, transport, and disposal of hazardous waste is controlled by federal and state regulations. Hazardous wastes are defined in Title 40 - Protection of the Environment, of the Code of Federal Regulations, which contains two long and detailed lists, one of wastes from non-specific sources and one of wastes from specific sources. The first list includes petroleum refinery primary and secondary oil/water/solids separation sludge; the second list includes various wastes from petroleum refining. Oily debris and oily waste from marine spills are not included in either list. However, it is conceivable that the processing of such materials could result in a waste similar to one listed, and it might then be classified as hazardous.

Wastes are also deemed to be hazardous if they exhibit defined characteristics of ignitability, corrosivity, reactivity, and toxicity. Ignitability and toxicity may be relevant to recovered oily waste.

- Ignitability - Liquids with flash points less than 60 ° C are considered to be ignitable. Although many crude oils have lower flash points, the rapid evaporation of the more volatile components following a spill will generally result in the flash point rising above 60 ° C within an hour of release. By the time response vessels have begun cleanup operations, it is likely that most crude oils will not be considered hazardous by the ignitability test.

- Toxicity - A waste is considered to be toxic if the extract from a representative sample of the waste contains one of a list of contaminants at or above a stated concentration. The list includes benzene, which has a regulatory level of 0.5 mg/L and which is known to be present in crude oils. However, most of the benzene will evaporate rapidly following a spill and so the oil may not be classified as toxic on these grounds. Unfortunately, crude oils contain such a variety of substances that analysis will be required to ascertain whether any other substances on the list are present.

If the oil with which it is contaminated is classified as hazardous, it follows that the debris will also be so classified. The debris itself, free of oil, is unlikely to be classified as hazardous. In practice, methods to segregate recovered oil from debris are unlikely to remove all the oil. Most states do not specify how effective the segregation must be before the level of oil contamination is regarded as insignificant.

Segregation methods.

The most important steps in segregating hazardous and nonhazardous wastes are to separate the water from the recovered oil/debris and to separate the oil from the debris. Thus, the separation techniques described earlier may also be useful in generating nonhazardous waste components. The following wastes may be produced: recovered oil; heavier than water debris, predominantly sand and shingle; floating debris, predominantly wood; water; and separator sludge in small quantities. Some additional methods that could potentially be used to treat hazardous oily wastes are listed below.

- Aeration - Lightly oiled or washed debris may be rendered nonhazardous by allowing it to stand in loose piles in the open air. Residual volatile toxic components of the oil, notably benzene, will evaporate and be carried away by the natural flow of air through the piles. Care must be taken to ensure that any water flowing through the pile is collected and prevented from entering the groundwater. Turning the debris occasionally may encourage evaporation and natural biological degradation may assist the cleanup process.

- Gas stripping using a packed column - In principle, a packed column might be used to remove volatile components from a relatively fluid, demulsified waste oil. The tower could be packed with small gravel, for example, and the recovered oil sprayed or mechanically distributed over the top surface. Air would be introduced at the bottom and would pass upward through the packing as the oil trickled down. The air would be discharged either directly to the atmosphere or through a biofilter or activated carbon filter. Laboratory and pilot tests are required to demonstrate the method.

- Gas stripping using mechanical agitators - Relatively fluid recovered oil could be aerated using a series of mechanical agitators in tanks. The oil would be first heated to around 40 °

C to increase the volatility of the lighter components of the oil. The performance of agitators is difficult to predict; but preliminary calculations indicate that 3 to 4 tons of oil could probably be treated using four or five agitators of 10 to 20 kW in series to reduce volatile components such as benzene by a factor of 20.

- Air drying - Volatile components may be removed from lightly contaminated debris or shredded debris using a continuous through-circulation dryer. The most widely used type is the horizontal conveying screen dryer, in which the debris is carried along as a layer 0.05 to 0.15 m deep on a horizontal mesh screen or perforated apron while air heated to, say, 40 °C, is blown upward or downward through the bed of material.

Alternative disposal methods

A result of the increasing difficulties and expense associated with landfill disposal of oily waste is that alternative and novel techniques should be considered for technical and economic feasibility. Local circumstances may affect the outcome of such studies but the principles discussed below are of general relevance.

Solidification and stabilization techniques.

The immobilization technologies of solidification and stabilization have been used for many years for the treatment of hazardous wastes, particular for wastes containing inorganic contaminants prior to landfill or construction-related recycling. Solidification techniques involve the addition of reagents to a waste material to reduce its fluidity or friability and physical entrapment to hold the contaminants in the solidified material. Stabilisation techniques involve the addition of reagents to a waste material to convert the contaminants to a more stable form chemically.

In practice, many commercial systems and applications involve a combination of the two processes. These technologies can be grouped into inorganic systems (cement, pozzolans, lime, miscellaneous proprietary agents, bulking agents) and organic systems (thermoplastic and thermosetting). Few systems are reported as having been applied to oil recovered from a spill at sea, but the treatment of oily wastes from other operations within the petroleum industry has been widely documented. Some of the findings are discussed below.

- Cement-based systems - These have proven more successful for inorganic than organic waste immobilization because the presence of organics hinders the cement hydration reactions. Pretreatment techniques have been developed - some of which appear more successful than others and all of which increase the volume of waste and the cost of the treatment.

- Pozzolanic-based systems - Pozzolans are materials containing active silicates or aluminates that will react with lime in the presence of water. The binder-to-waste ratio is normally higher than for cement systems, so that the volume could double or triple. The presence of organic contaminants can reduce the durability of some pozzolanic materials.

- Clays and organoclays - Clay minerals have shown the capacity to bind with organic compounds by the processes of adsorption, intercalation, and cation exchange. The development of organoclays has extended the range of treatable hazardous wastes to include those with a high organic content, especially oils. The clay is converted from hydrophilic to organophilic by modifying its surface by ion exchange using a cationic surfactant. However, these clays have achieved only limited acceptance in hazardous waste treatment because of their comparatively high costs.

- Lime-based systems - In addition to the use of lime in pozzolanic systems, lime is used alone as a stabilizing agent for organic and inorganic contaminants in dispersal by chemical reaction (DCR) technologies.[2] The basis of the DCR process is the controlled hydration of calcium oxide to calcium hydroxide during which the lime adsorbs organic contaminants and disperses them over its large surface area. Some of the waste from the *Amoco Cadiz* spill, which consisted of mixtures of oil, water, and sand, was treated with DCR technology to produce an acceptable soillike fill for the reclamation of an industrial area. Industrial quicklime was also used to treat *Amoco Cadiz* waste containing approximately 35 percent water, 5 percent hydrocarbons, and refuse debris of all kinds including plastic bags, wood, and larger rocks.[9] A number of variants on the basic DCR process also appear to have been used successfully for waste oil treatment.

- Organic binder systems - The system with the greatest potential for oil spill waste involves the use of gelling agents consisting of polymerization catalysts and a cross-linking chemical to convert the oil/emulsion into a soft gel or rubber mat. The comparatively high costs of these agents make them unattractive except for very small spills.

Reclamation

Oil is a valuable natural resource; and potentially it is highly attractive both economically and environmentally to reuse the oil recovered following a spill. This also offers the opportunity for some positive media coverage and public reaction. However, in practice the reprocessing of recovered oil is a complex task involving a combination of logistical, political, and technical problems. The possibilities of disposing of recovered oil to refineries or to reclamation companies are discussed below. It is assumed that the waste oil is mainly liquid with very little associated debris.

- Oil refineries - The main options at refineries for dealing with recovered oil are reprocessing by distillation and reblending. A distillation plant is designed to operate with a feedstock containing a very small proportion of light ends, such as oil recovered from the sea surface, could be accepted. In practice, it would probably be necessary to blend around 5 to 7 percent of recovered oil with the normal feedstock. It could therefore take a long time to process oil recovered from a major spill and suitable intermediate storage would have to be found. The recovered oil would also have to meet strict limits on solids, salt, surfactant, and water content because these contaminants could interfere with the distillation process. It would almost certainly be necessary to process the recovered oil to remove contaminants. This is also the case before recovered oil could be reblended at a refinery for processing or sale. It is therefore understandable that refinery plant management is likely to be reluctant to accept oil recovered at sea.

- Reclamation companies - Companies can be grouped as oil launderers or oil re-refiners. Laundering companies collect used oils and process them to produce reclaimed oil which often meets the original specifications for lubricating, cutting, grinding, or metal rolling oils. The processes used can include settling, centrifuging, or filtering to remove solid particles; treatment with clay or alkalis to neutralize acidic particles; heating/distillation to remove solvents/gasoline/water; clay contacting to remove oxygenated components and spent additives; aeration/biocides to reduce bacteria levels. Re-refining companies may also treat waste oil using one or more of these processes. They then typically subject the oil to vacuum distillation, conventional distillation, and hydrofinishing to produce a high quality product. Both laundering and re-refining companies require a reasonably uniform feed material and additional pretreatment of oily waste recovered following a spill might well be necessary.

Thermal treatment.

The thermal treatment processes of incineration, pyrolysis, gasification, and direct combustion for power generation provide the potential to convert oily waste to flue gas, which can be emitted to the atmosphere, and ash, which can be disposed of in landfill sites. However, pyrolysis, gasification, and direct combustion for power generation are relatively complex technologies and not adapted for heterogeneous material such as oily waste. They are therefore not very promising areas for further development.

- Incineration - There are many different types of incinerator that are designed to deal with liquid, solid, or combined liquid/solid/sludge waste. Thus, despite the wide range of physical characteristics associated with oil spill waste, there is likely to be an incinerator design that can handle it. The rotary kiln incinerator is particularly adaptable and can accept solids, liquids, gases, sludges, and drummed wastes with a wide range of calorific values. Municipal solid-waste incinerators may be suitable for lightly oiled debris. Transportable and mobile incineration systems have the potential advantage of reducing the handling and transportation of the oily waste. Shipboard systems are also available and were selected for use following the *Exxon Valdez* cleanup.[3] However, obtaining permits was a problem. The air curtain incinerator is particularly interesting as a potential technique for oily waste because it can deal with debris in the bottom of an excavated trench that might be prepared for intermediate storage of recovered oil. Air is supplied from a high-volume blower and distributed by a plenum and distribution nozzle. Two air curtain incinerators were tested during the *Exxon Valdez* cleanup, but operating permits were not issued because standard air emission limits on particulates could not be applied to an incinerator without an exhaust stack.[3]

Biological treatment.

Biological decomposition of oil by microorganisms is potentially a safe, robust, and environmentally considerate process, generating recyclable materials such as carbon dioxide, water, and biomass. However, microorganisms may not decompose all the components of the oil, and some may be biotransformed to other organic residues. Treatment methods within solid-phase systems include land farming, composting, and soil banking. Liquid systems include lagoons, stirred and aerated tanks, trickling bed systems, and more innovative methods such as fluidized bed and deep-shaft reactors. Few of these technologies, with the exception of land farming, have actually been used to treat oily waste, and further development work would be needed to prove their suitability for this application.

- Land farming - This is a dependable way to decompose oily wastes that do not contain high concentrations of very toxic or poorly degradable materials. The best working conditions vary between land farming sites and important soil characteristics include texture, pH, salinity, bulk density, cation exchange capacity, organic content, available nutrients, total metal content, and surface microbial populations. Tillage and aeration of the soil are essential to aid decomposition. Land farming of oil industry wastes is practised widely and the techniques required for oil spill waste will be essentially similar. However, the feasibility of dealing with large quantities collected in a relatively short time from a major spill needs further thought.

- Static soil banks - These systems provide an alternative to traditional land farming and involve premixing the waste oil with a soil mass before laying this down in soil banks. Varying degrees of sophistication are possible, but the systems are generally more intensive than traditional land farming and have the potential for process optimization. It can therefore be expected that less time will be required for treating a given waste.

- Composting - Most composting operations involve the use of inexpensive aerated static piles or turned windrows and are designed to operate at higher temperatures than land farming systems. Composting is appropriate for highly contaminated, poorly textured soils. Composting reactors may be used, and these offer a potentially more efficient method because of the opportunities for process optimization and control.

- Treatment in storage tanks/pits - During spill incidents, oily debris may be stored in temporary lagoons and pits that are dug for the purpose close to the spill site. If these storage areas are suitably constructed then it may be possible to use them to treat the debris. Oil and macerated debris (assuming biological in nature) would be blended with water in the lagoon/pit, aerated, and nutrients added. Treatment would continue until biodegradation stops and the effluent can then be removed or discharged or treated further depending on its quality.

- Activated sludge plants - These can be either plug flow or continuous stirred tank reactors and are essentially aerated storage tanks operated in a continuous mode. The oily waste is diluted with water, and should be free of large particulate matter before feeding to the reactor. Normally some of the sludge collected from the downstream settling tank is recycled to enhance degradation. The deep-shaft reactor is a variation of the plug flow reactor and is designed to increase the oxygen content of waste water by passing the liquid down a shaft or well, typically more than 30 m deep.[4] The good mixing and oxygen transfer characteristics result in a high active biomass population thus enhancing degradation rates.

Conclusions

The physical and chemical characteristics of waste oil and oily debris collected following an oil spill at sea can vary widely. A number of techniques are available to recover the mainly oil component separately from the mainly debris component; and the two components should be kept separate as far as possible because disposal of the mixed waste is more difficult.

Washing of oily debris is usually carried out on shore, often by hosing it down in shallow pits. Decantation washing and trommel washing may be useful for separating sand and gravel from mixed oily wastes and for cleaning floating debris, respectively.

Separating nonhazardous from hazardous wastes should reduce overall disposal costs. In most cases the toxic characteristics of the waste determine whether it is classed as hazardous. Oil recovered from spills at sea is usually sufficiently weathered that volatile toxic components of the oil, such as benzene, are substantially removed. The weathering can usually be allowed to continue by aerating the piles of debris.

Little research has been undertaken to develop techniques to separate hazardous and nonhazardous wastes. Aeration techniques using packed towers or mechanical aeration of recovered oil, and air drying of oily debris, appear to have some promise.

Landfill remains an attractive disposal option for suitable material such as debris with little associated oil that can be classified as nonhazardous. Solidification or stabilization techniques may potentially convert hazardous materials to nonhazardous ones but further development work is needed.

Reclamation of recovered oil is attractive in principle, particularly for large oil spills; but it is only feasible if contaminants have been reduced to very low levels. Use of the waste as a low quality construction material, for example for road building, may sometimes be possible.

Established, robust technologies exist for the incineration of oily waste even when large amounts of debris and contamination are present. Mobile or transportable incineration systems could avoid the need to transport the waste over large distances.

Land farming techniques have been widely used to treat oil industry wastes and have potential for disposing of oil spill waste. Some further work is required to establish selection criteria and guidelines for the use of this approach. Other biological methods appear to have promise but further development work is needed.

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Table 1. Debris recovered from oil spill incidents

Location	Amount spilled	Debris recovered
San Francisco	3,000 m^3	140 - 1,400 m^3, mostly wood
Baton Rouge	3,900 m^3	>520 m^3, mostly wood

New Hampshire	8 m^3	60 t, eel grass
Port Angeles	1,080 m^3	2,140 m^3, mostly wood; 2,180 t, logs