No. 322
June 1992

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by

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ABSTRACT

This paper intends to give a global knowledge of marine oil spill cleanup response methods and techniques. It is mostly intended to answer the fundamental questions *when, where,* and *how* to apply the different methods. A brief review of the stages of the oil spill response problem is first presented, followed by the factors that influence the different methods. This is followed by an analysis of some new cleanup methods and improvements to existing methods, specifically: bioremediation, the use of more efficient ships for skimming, the use of fishing nets for heavy oil recovery, and new materials and designs of sorbents. Some cases are also analyzed to evaluate the performance of some methods under real conditions.

1 INTRODUCTION TO THE OIL SPILL RESPONSE PROBLEM

Contrary to popular misconceptions, the world tanker fleet is not spilling more oil recently than it has in past years. Furthermore, tanker accidents contribute only 5 percent of the estimated 2.3 million tons of petroleum entering the seas annually. However, there is much controversy over tanker spills, because such concentrated injections of oil tend to cause significant environmental destruction. (Fig. 1)

The best way to prevent spills is simply to keep the oil in the ship. To do this it is necessary to upgrade traffic control systems, train crews better, upgrade the fleet with safer tanker designs (double hull, double tanks, etc.), and provide incentives to tanker operators to avoid accidents by increasing their liability limits. However, even after taking all these preventive steps, it is difficult to completely avoid accidents, thus efficient cleanup methods together with good contingency planning are needed to minimize damages.

The strategy to minimize oil spill pollution can be divided into:

I Prevention of operational and accidental pollution, and
II Control and abatement of a spill, to minimize the damage.

In part I, we also mention operational pollution, because spills from tankers not only occur because of accidents, but also from mishaps during operations of the vessel such as lightering, loading, unloading, etc. Oil pollution may also be intentional, as a result of operations such as oil tank cleaning.

Prevention by design is one of the most important issues of the spill problem. A good design should minimize the probabilities of a spill. Many advances have been made in this area and research is still going on (double hulls, horizontally divided tanks, etc.). Prevention by optimization of systems like traffic control in heavy traffic areas and global positioning, the most accurate form of satellite navigation, will also help to avoid accidents.

One of the lessons of the "Exxon Valdez" accident was the importance of having well trained, vigilant, and alcohol and drug-free crews. This can be accomplished with training programs, alcohol and drug tests and new regulations about duty schedules. The limit on liability should be high enough to give tanker operators incentive to invest in the above programs.

There are many types of accidents that can occur to a tanker, such as collision, grounding, fire and (or) explosion, striking underwater obstacles, flooding, structural failure, etc. In most cases the master will take immediate action to ensure the safety of his crew and the preservation of the ship and its cargo, and make arrangements for the salvage of the vessel.

The optimal spatial allocation of cleanup resources will help for a faster response. Contingency planning is another very important stage of the oil spill problem and the effects of a lack of coordination were dramatically illustrated in the "Exxon Valdez" spill. The salvager's principal objective will be the successful salvage of the vessel. It is essential that links of communication are established and complete cooperation takes place between all concerned parties, such as the Government departments, the ship and cargo owners, and the salvagers. [1]

Finally, the contingency plan should provide guidelines for the cleanup operations. When an oil spill occurs, one must first act to stop it at its source. Subsequent actions include containment, recovery, and restoration of the oil. The main objective in most of the cases is to prevent oil from reaching the shore.

The cleanup process can be divided into marine and shore operations. Marine operations involve cleanup of oil pollution at sea, while shore operations deal with the cleanup of oiled beaches. In this paper we will discuss cleanup methods applicable to marine operations.

Marine oil spill cleanup methods can be divided into the following groups:

METHOD	PROCEDURE	CLASSIFICATION
Elimination	Combustion Sinking Use of Dispersants	Chemical Procedures
	Bioremediation	Biochemical Procedure
Recovery	Gelling	Chemical/mechanical Procedures
	Use of sorbents Use of skimmers and barriers	Mechanical Procedures

2. CLASSICAL MARINE OIL SPILL CLEANUP METHODS

2.1 MECHANICAL METHODS

We will first analyze the containment and skimming methods (those two actions may or may not be complementary) which are some of the most practical techniques used for primary response. Then we will examine the use of sorbents, which can be used as a secondary or complementary response technique.

2.1.1 Barriers

Oil spreads rapidly on water. Containment is usually achieved with the use of barriers (booms). Containment of oil contributes to cleanup operations in two ways. First, protecting sensitive areas, by preventing oil from entering them. Second, facilitating mechanical removal, it prevents the oil from spreading, confining it in relatively thick layers in which the skimmers recover the oil. Barriers can also be used to encircle a leaking vessel. Additionally, booms may be used during loading, unloading, or lightering operations in the same encircling fashion. [17]

The containment of oil is basically achieved by booms. A boom is a device designed to contain oil floating on the surface of the water. Most booms have the following parts (see Fig. 2):

1. A means of flotation or freeboard to contain the oil and to resist waves splashing oil over the top.
2. A skirt to prevent oil from being carried underneath the boom.
3. A longitudinal strength member to hold the boom together and provide a means of anchoring the boom.
4. A weight to keep the skirt vertical.

Usually the first type of operation (protection of certain areas as beaches) requires the booms to be anchored, as we can see in Figure 3 (a), while for the second type of operation the boom is generally towed by two or more boats. There are several basic boom configurations used [19]:

- "U", "V", or "J" configurations, used downwind or downstream of currents (Figs. 4 a, b and c respectively)
- diversionary configuration, used to prevent the spill from reaching the protected area, (Fig. 3 b)
- encircling configuration (Fig. 5)

The effectiveness of the containment will be threatened by the following factors:

1) The containment effort fails when oil droplets break from the headwave (interfacial waves) and become entrapped in the flowing water as it passes beneath the boom (Fig. 6). This is the most significant cause of leakage from booms. The amount of droplet carryunder is a function of the thickness of the headwave, which is related to water velocity and the specific gravity of the oil. The greater the velocity or specific gravity of the oil, the greater the carryunder. For a given oil and skirt depth (Fig. 2), carryunder will not occur until a critical velocity is reached. This critical velocity decreases as the specific gravity of the oil increases. In general, no boom can retain the oil if the perpendicular water velocity is greater than 1 knot. However, if the angle the boom is carried/moored against the current is changed the critical velocity can be increased, thus allowing its use in worse conditions. For example, if the velocity of the current is 2 knots the boom should be set at 20 degrees angle with the bank. We can see how this velocity varies in the following table [5]:

Angle (degrees)	90	45	28	20	16	13
Velocity (knots)	0.7	1.0	1.5	2.0	2.5	3.0

Increasing the length of the skirt increases the ability of the boom to retain oil, but the advantage is not substantial. Disadvantages of a longer skirt are the increases in weight, cost, and mooring requirements to hold the boom in position. The optimal skirt length depends on the specific gravity of the oil, but in general there is no advantage to making the skirt length greater than 12 inches in slow moving waters. A longer skirt, though, may be required in rough waters.

2) When the sea has waves of short wave length or many wave crests the oil is thrown over the freeboard structure. This type of leakage is called oil splashover. Heavy swells also contribute to reduced performance of the boom.

3) The attachments of different sections of the boom may fail causing leakage.

The characteristics to take into account when evaluating a boom are:

* Capacity to retain spilled oil
* Seakeeping ability
* Structural resistance and durability
* Ease of deployment, handling, and control

It is necessary to have a boom that has flexibility, to follow the seawater motion, but that is stiff enough to retain the oil. Another factor to take into account is the wind velocity because of the force it exerts on the freeboard of a boom. If wind velocity is over 25 knots booms will not be effective.

Types of Barriers [17], [5]

Round solid flotation Boom (Fig. 2)

Advantages:	Disadvantages:
-Easy to deploy	-Bulky to store
-Good seakeeping	-Not easy to clean
-Tows well	
-Allows bottom tension design	

Inflatable Boom (Fig. 7)

Advantages:	Disadvantages:
-Easy to store	-Subject to puncture
-Good seakeeping	-Expensive
-Easy to clean	-Time consuming inflation and deflation

Semi-rigid Boom (Fig. 8)

Advantages:	Disadvantages:
-High critical velocity	-Difficult to clean and deploy
-Good seakeeping	
-Good structural resistance and moderate volume needed to store	

Simple inflatable barrier (Fig. 9)

Advantages:	Disadvantages:
-Excellent seakeeping	-Subject to puncture
-Easy to clean and deploy	-May sink due to its one-piece design

Booms and the Newfoundland oil spill experiment

On September 24, 1987, an intentional oil spill of 18000 gallons was used to evaluate the performance of some standard booms. One of the main questions was whether the boom's ability to contain oil is correlated with its seakeeping ability. If the answer was affirmative, future performance evaluations of offshore containment booms could be restricted to measuring seakeeping capabilities in a range of sea states. The results of this realistic experiment are very interesting and lead to the following conclusions:

* To evaluate performance of offshore cleanup equipment it is necessary to spill large quantities of oil.
* For a good response, extensive practice is required.
* Logistics are also important. To maximize efficiency, the use of helicopters for direct placement of tow vessels and small vessels to control boom conditions is necessary.
* The maneuverability and slow speeds required for a boom's towing necessitate the use of vessels with variable pitch propellers, thrusters and an experienced crew in control.
* It is important to have meteorological and sea condition measurements and forecasts, both in reality and while doing experiments.
* There is a positive correlation between the seakeeping ability of a boom and its ability to contain oil.

Booms should be stored, on the deck of a boat or barge, in a way that will be easy to deploy. Also, using a ramp or roller to assist in launching and recovery greatly reduces deployment time.

The use of booms is limited by the sea state and current. Oil will move under a boom if the perpendicular water current is greater than 0.7 knots. To effectively use the boom in currents faster than 0.7 knots, it should be placed at an angle to reduce the effective velocity. If properly installed, a boom will not only contain the oil, but will cause the oil to move to a selected location where it can be removed by mechanical means. No boom, however, is effective in holding oil in breaking waves. [16]

2.1.2 Skimmers

A skimmer is a device designed to recover the oil or oil-water mixture from the sea surface. This is achieved when there is a thick concentration of oil being contained by a barrier (boom). The greatest disadvantage of the skimmer is that its efficiency is very sensitive to sea state. Small skimmers are typically displaced by waves and larger ones have too much inertia to follow the sea motion. There are some designs and ships, however, that can operate in varying environments quite efficiently. These will be dealt with later. Many designs exist but all of them have the same basic characteristics [5]:

* An oil recovery device
* Flotation elements
* A pump to transfer the recovered oil to a barge
* A device to maintain its level in relation to the sea

Almost all skimmers use one of the following methods for oil recovery:

Recovery by suction

Oil is recovered by a pump. This technique is better for oil with a high viscosity. Skimmers using this method require a high capacity of water-oil separation and also a high containment capacity. Depending on the skimmer size, model, sea state, viscosity, and thickness of the slick, the suction capacity varies between 10 and 250 cubic meters per hour.

Recovery by adhesion

This method uses the adhesive or absorbent (oleophilic) properties of some part of the skimmer's system, which can be a moving belt, drum, disc or rope. Skimmers using this method work better with oil of medium viscosity. Low viscosity oil does not accumulate in enough quantity and the high viscosity oil is hard to remove from the surface. Depending on the skimmer size, model, sea state, viscosity, and thickness of the slick, the suction capacity varies between 10 and 400 cubic meters per hour.

Practical designs of skimmers [5]

From an operational point of view, skimmers can be either integrated into the design of a ship, or attached to the vortex of a "V" configuration barrier (Fig. 10 a & b). Skimmers are used to recover the oil where the spill is thickest, and follow the spill's direction of movement. The advantage of skimmers that are integrated into the ship's design is that they can work in sea conditions that a barrier/skimmer combination cannot.

Vortex skimmer (Fig. 11)
A rotor makes the oil (lighter than water) concentrate in the center of the skimmer and move upward while water flows outward and down where it is discharged. This skimmer is sensitive to sea state, current velocity, and the presence of residues.

Oleophilic Belt skimmer (Fig. 12)
A belt transports the oil upward from the water's surface by adhesion. It is then squeezed into a collection well in the vessel's hull. This skimmer can handle high viscosity oil.

Dynamic Inclined Plane with Belt (DIP) (Fig. 13)
This system forces the oil under the sea surface into a collection well while the vessel moves forward. Once in the well, oil and water are separated because of their different densities. This method is good for medium viscosity oil.

Oleophilic Rope skimmer (Fig. 14)
A mop is dragged, by a rope, through the oil. The mop absorbs the oil, and carries it through squeeze rollers where it is collected in a well.

Disc skimmer (Fig. 15)
The discs rotate through the oil-water mixture. Oil adheres to each disc's surface and is recovered by a wiper which gathers the oil into a central collector where it is pumped to containment equipment.

Mechanical removal methods usually require integrated systems (skimmers, booms, pumps, storing, transporting and logistics equipment) and skilled labor. They are preferable to other methods, however, because they do not introduce additional disturbances on the environment. Their principal disadvantage is that they are limited by the sea state, wind conditions, and high current velocities.

Thus far, however, mechanical removal methods have demonstrated to be one of the best alternatives for quick primary response.

Mechanical methods and the "Exxon Valdez" spill

Skimmers and booms were used extensively in the "Exxon Valdez" spill. The response was slow, however, a quick deployment of booms around the ship, combined with the calm seas and high rate of oil seepage, would have increased the vapor cloud and cause risk of fire and explosion.

2.1.3 Sorbents

Sorbents are materials that use soaking (absorption) or surface adhesion (adsorption) to collect liquids. Oil-specific sorbents are designed to recover oil from water. Sorbents and their methods of application have been refined, but the basic concept remains the same. A sorbent is first spread on the floating slick, where it collects the oil while repelling water. When the sorbent becomes oil saturated, it is removed from the water's surface and either wrung out and reused or disposed of properly. Sorbents are another tool to be used in conjunction with other cleanup methods. Although industrially manufactured sorbents are widely available, it appears that research on sorbents does not attract the interest of organizations dealing with cleanup. [17]

In general, the use of sorbents is more costly than dispersion and mechanical methods (skimming, using booms, etc.). The most costly operations are the harvesting and disposal of the oil soaked material. This is due to inefficient and labor-intensive methods that must be used when applying and harvesting sorbents on oil slicks. Also, sorbent materials generally are not reused for other spills.

Sorbent materials selected for use should have oil-attracting (oleophilic) properties. Efficient sorbents are unsinkable and repel water. Furthermore, a short saturation time, a large capacity for collecting and retaining oil, and enough strength to withstand recovery and handling, are the fundamental qualities of an effective sorbent. Ideally sorbents should also be non flammable, biodegradable, nontoxic, and unaffected by temperature and humidity extremes. Profiles of some sorbent products are shown in Table 1.

There are several ratios used to determine the effectiveness of different sorbents. The *recovery capacity* is the ratio of maximum oil absorption capacity to sorbent weight. Sorbents consisting of very small, porous pieces have a large capacity to absorb oil because of their greater surface area per amount of material. *Recovery efficiency* is the ratio of oil quantity recovered to total quantity of oil and water recovered. This index indicates to what degree the material is oleophilic. Another index is the *oil recovery rate* which measures the gallons recovered per unit time. If the sorbent is reused the overall performance (average) of all the cycles should be considered when calculating these ratios. [7], [19]

Sorbents can be divided into 3 main categories:

Mineral sorbents : common mineral products used as sorbents are carbon powder, volcanic ash, talc, clays, chalk, perlite, etc. The primary disadvantage with using mineral sorbents is that they do not degrade, they are persistent in the environment.

Natural organic sorbents : these are subdivided into two groups;

> *Baled fibrous materials,* such as straw and peat moss, are collected manually. Straw and peat pose difficult recovery and expensive disposal problems.
>
> *Fine particulate sorbents,* such as ground corn cobs and sawdust, are easier to spread than the fibrous materials. A boom should be used downwind to collect both the oil and sorbent for easy recovery.

Although organic sorbents are biodegradable they should be recovered because their decomposition can create a biological oxygen demand which is detrimental to marine ecosystems.

Synthetic sorbents : they include plastic foams (polyurethane and urea formaldehyde) and plastic fibers (polyethylene and polypropylene). These sorbents are the most efficient available. For example, urea formaldehyde foam can absorb up to 25 times its weight in oil.

One new technique that reduces storage and transportation problems is to produce the polyurethane foam on location. The liquid components of the foam are stored in drums and occupy much less space than already prepared foam.

Sorbents are restricted to small spills, spills that cannot be cleaned up by skimmers, or to the final stages of a cleanup operation when only a small amount of oil remains. Unless full recovery of oil-soaked sorbent is assured, sorbents should not be used. Also, it must be kept in mind that sorbents are expensive, time-consuming to use, and have storage problems (sensitivity to humidity, sunlight, and rodents). However, if it is decided that sorbents are to be used for cleanup, pads and sorbent booms are two of the most useful forms. The disposal of sorbents can be handled in the same way as other debris. [7]

2.2 CHEMICAL METHODS

2.2.1 Dispersants

The use of chemical dispersants for response to oil spills has remained a controversial subject in many countries, despite the fact that it is one of the more efficient/proven methods. Concern has been expressed by many marine biologists over the toxicity of dispersants and dispersed oil to marine species. A great deal of research has been carried out, both in laboratories and field tests. Depending on the country, there are toxicity and effectiveness test programs for dispersants and if a product passes the test criteria, it is then placed on an approved list.

When sea conditions are difficult, and do not allow mechanical recovery, dispersants are the only method that will cleanup the oil and prevent it from getting to shore. It must be mentioned that oil treated with dispersants is not recoverable by mechanical methods. Also, dispersants are more cost effective than mechanical methods as the thickness of the oil slick increases. (Fig. 16)

Dispersants are mixtures which reduce the interfacial tension between oil and sea water. This allows oil to break into very fine droplets (less than 100 microns diameter) and be distributed throughout the water. Driving this process is the natural movement of the water itself, and with normal mixing energies, the oil concentration rapidly decreases to background levels. In calm water droplets may slowly rise to the surface, however, the dispersant inhibits reaglomeration and coalescence. Other sources of mixing energy, such as wave action, propeller wash, etc., enhance the dispersion action. Basically, dispersants enhance the oil's penetration into the water column, and thus reduce its tendency to stick to birds, marine life, and other structures. The chance of a fire hazard due to petroleum vapors is also reduced. [7]

Where to use dispersants?

Consideration should be given to water exchange rates and depth. Dispersed oil can have a higher toxicity than dispersant alone, and the use of dispersants for inshore areas is not recommended. The salinity of the water is also an important factor and determines the effectiveness of dispersants. If salinity drops below 12 parts per thousand dispersant effectiveness is reduced.

When should application start?

Spraying operations should be started as soon as possible after it has been decided to use dispersants as part of the response. Many oils form stable water-oil emulsions (called chocolate mousse) which have a higher viscosity than the original oil. The extent of emulsification will depend upon the type of oil, sea state, and water temperature. Viscosity also increases because of the evaporation of lower molecular weight hydrocarbons. Both processes usually take place to a considerable extent within a couple of hours after the spill, and thus dispersant effectiveness may be reduced if application is delayed. Oil slick areas tend to expand linearly with time, and since mousse is very difficult to disperse because of its high viscosity, treatment with dispersants should begin as quickly as possible, before mousse formation.

Application

The best combination of dispersant and application method must be determined for each situation (there are mathematical models and computer programs for this). On the open sea dispersants can be applied from surface vessels or aircraft (fixed wing or helicopter). To determine which type of dispersant is the best, one must consider the previously mentioned variables: the type of oil spilled, the salinity of sea, and the water temperature, because dispersant efficiency is a function of these three parameters. [9]

From surface vessels (Fig. 17): Dispersants are sprayed onto the oil slick by special spray guns or booms fixed with nozzles connected to supply pumps. Sea state will determine if this method of application can be safely and effectively used. Dispersants can be used in their conventional form or a concentrated one. Breaker-boards may be towed behind the spray booms, in calm seas, to supply adequate mixing energy. Some dispersants, however, may not require additional mixing energy. The ship's propeller may also be used, in the absence of breaker-boards, to provide the necessary mixing energy. Concentrated dispersant, if diluted, is done so to 10 times its volume. Dispersant type and spill thickness determine the amount of dispersant needed. A conservative rule for dispersant application rates is to allow the use of up to one gallon of dispersant per acre, per meter of water depth. For an average oil slick thickness of 0.1 mm, 20 cubic meters of oil can be treated per hour. This assumes an application rate of 10 cubic meters per hour (a ratio of about 1:2) for conventional dispersants, and 1 cubic meter per hour (a ratio of 1:20) for concentrates. With an effective spray path width of 20 meters, and at a speed of 5.5 knots, a vessel could cover 200,000 square meters per hour. The nature of the oil and the thickness of the slick will determine vessel speed.

Chemically, dispersants are more effective when applied directly onto the oil slick undiluted. Spray booms are typically mounted on the bow, in this case, allowing the bow wave and wake to provide all the needed mixing energy. Concentrates also permit a wider range of vessel speeds. High speeds can reduce the time of the total operation and lower speeds allow higher dispersant to oil ratios. If the oil slick is near land, application should begin along its landward side, and parallel to the land. An aircraft should be used in this case to direct the spray pattern of the vessel. [9]

From fixed or rotary wing aircraft (Fig. 18): Today the use of ships is considered complementary to the use of aircraft for applying dispersants. With a faster response than vessels, aircraft offer the possibility of rapid oil slick treatment over a large area, and with a better visibility, optimal treatment in critical areas. Aircraft are fitted with spray booms, nozzles, pumps, and tanks. Most concentrate dispersants are well suited for aerial application because of payload limitations. In fact, it would be very inefficient to use diluted dispersants with aircraft. Any fixed wing aircraft with stable low flight characteristics can be used for the response. Droplet size is critical, thus the nozzles and pumping pressures must be carefully selected. The optimum droplet size is (0.4 to 1 mm in diameter). Droplets too small may be blown away from the slick, and droplets too large may pass through the oil layer and be lost in the water column. Payload limitations, flying time, refuelling, and reloading time, make the logistics of aerial spraying very important. An aircraft at a higher elevation should be used to provide guidance and control for the spraying aircraft. Aircraft spraying has been used successfully in a number of spills. [9]

Decision procedures for the use of dispersants

If an oil spill occurs several response options are possible. These include mechanical recovery, use of dispersants, and natural removal. The intelligent use of these options will minimize environmental damage. It may be appropriate, in different areas of the spill, to use more than one option simultaneously. In considering the three major means of oil spill response: mechanical cleanup, dispersant use, and natural removal; decisions should be based on the following issues:

* Which method is more cost efficient? For example, Figure 16 shows how cost varies with slick thickness.
* Which method can be applied with the present sea state and weather conditions?
* The basic question (and the most difficult to answer) "Will the environmental impact of chemical dispersion be less than the environmental impact occurring without chemical dispersion?"

There are many decision procedures available depending on the country and institution. In Figure 19 we can see the decision procedure of the IMO (International Maritime Organization). This flow chart, like many others, guides the user through a series of questions to determine the best possible solution. The user should:

1) Compute the location and size of potentially affected areas.
2) Identify affected resources.
3) Determine the impact, on each resource, of both the treated and untreated spills.
4) Assess the importance of endangered resources and consider predicted impacts. For further information see [8].
5) And finally, compare the predicted impact of a chemically treated spill to that of one left untreated.

In most cases, a combination of chemical dispersants and mechanical methods are used during cleanup operations. However, dispersant use is limited to the first hours of a spill, and is not recommended in very calm seas (lack of mixing energy). In fact, they are more efficient in rough sea states where mixing energies are high.

The long term effects of dispersed oil in the ecosystem are usually less than those of untreated oil. In particular, dispersants may be best suited for use in environments very sensitive to oil. [8]

Dispersants and the "Exxon Valdez" spill

The question still remains whether dispersants should have been used with the Valdez spill as the first line of defense (first hours). Many surmise, that if used properly, dispersants could have prevented much of the oil spill's damage. However, by the time Exxon deployed the dispersants (more than 72 hrs after the spill) the oil had been in the water too long. [13]

2.2.2 Gelling

This method is based on the addition of a chemical agent to the slick that increases oil viscosity. Once the oil slick has been gelled its spread will be reduced and it can be easily removed by nets or other means. The disadvantage of this method is that large quantities of gelling agent and adequate time for the gelling process are required. A product introduced by British Petroleum called Rigidoil turns either crude or fuel oil into a solid sheet that resembles rubber carpeting underlay. In that form the oil can be rolled up and removed easily. This method, which involves spraying the oil with an oil soluble polymer and a cross linking agent, can be used on small and medium size spills. The advantages of this product is that solidification starts in approximately 20 minutes, leaving the surface of the water quite clean. Gellified oil can be taken away for burning or use as landfill. ([18],[19])

2.3 OTHER CLEANUP METHODS

2.3.1 Natural Degradation (or "do nothing" option)

When introduced to the marine environment, crude oil and other petroleum distillate products are exposed to a variety of physical, chemical, and biological changes (Fig. 20 a & b). Ingestion by organisms, as well as microbial degradation, comprise the biological weathering processes. Non-biological weathering processes include evaporation, dissolution, dispersion, photochemical oxidation, water-oil emulsification, adsorption onto suspended particles, sinking, and sedimentation. Changes in the chemical composition and physical properties of the original pollutant are caused by these simultaneously occuring biological and non-biological processes. The changes are important and may influence the rate of effectiveness of biodegradation. [4]

During the first 48 hours of a spill the most important weathering process is usually evaporation, the process by which low to medium-weight crude oil components, with low boiling points, volatilize into the atmosphere. One to two thirds of an oil spill's mass may evaporate away during this first 48 hours. The evaporation rate, however, decreases rapidly over time. In the case of the Amoco Cadiz oil spill, approximately one third of the oil evaporated within the first three days. The composition of the oil, its physical properties, the surface area of the spill, wind velocity, air and sea temperatures, sea state, and solar radiation intensity, all determine the amount of evaporation that will occur. Whenever evaporation does occur, the original oil's specific gravity and viscosity increase. This could cause spilled crude oil to resemble Bunker C, a heavy oil, within a few days. No other non-biological process is responsible for such a significant proportion of the losses from a spill, as is evaporation. However, dissolution is still important because some water soluble components of crude oil (light aromatic compounds) are toxic to various marine organisms, specifically the ones that participate in biodegradation. [4]

Dispersion is the separation of oil, and its passage as small particles from the surface to the water column. This process occurs naturally, however, synthetic chemical dispersants can be used to enhance effectiveness, as mentioned earlier. Dispersion plays a major role in the disappearance of a surface slick. Natural dispersion is driven by sea surface turbulence, the more turbulence, the more dispersion. Dispersion works by increasing the rate of biodegradation. Because they have a greater exposed surface area, dispersed oil particles are more prone to biological attack than undispersed ones. [4]

When seawater becomes entrained with the insoluble components of oil, from heavy wave action, oil water emulsions are formed. Stable mousses are produced when the oil is a heavy crude. Emulsions are more difficult for microorganisms to degrade than oil alone, and thus inhibit natural biodegradation, one of the most important means of oil removal from the marine environment. For a more detailed description of biodegradation refer to chapter 3.1. [4]

2.3.2 Sinking

Sinking usually occurs in a natural way, when oil is attached to sediments. It can be accelerated by adding oleophilic material that attaches itself to oil. Sinking agents are; chemically treated sand, chalk, fly ash, and cement. As we will see later in chapter 3.1, the degradation rate decreases as pressure increases, therefore, sunken oil will remain in the marine environment for a long time. We can conclude that this is not a recommended technique for marine oil spill cleanup.

2.3.3 In-situ burning

This method consists of simply making a controlled ignition (by adding ignition and/or combustion agents) of the oil spilled. It is an unsafe and difficult technique, but if the air pollution trade-off is accepted, burning could get rid of more than 90 percent of an oil slick. Viscous emulsions or weathered oil are difficult to ignite because the light components (which help ignition) are the first to go with evaporation and the water underneath the oil creates a cooling effect. Thus the burning method, if applied, has be used during the early stages of a spill. Furthermore, control of the fire is not an easy task. Special burn-proof booms must be used to effectively contain the burning oil. It is necessary to deploy the booms so that heavy concentrations of oil (the layer of oil must be more than 3 millimeters thick) exist for an efficient burning. The combustion in most cases is incomplete, leaving tar residues in the water and creating air pollution from the intense smoke. [11]

Despite all the drawbacks of this technique, it was indicated as the best method of dealing with the "Exxon Valdez" spill early in the cleanup process. The use of dispersants was not the most advisable because of the calm seas, and the shear size of the spill made removal by skimmers and other mechanical means impractical. However, in the case of the "Exxon Valdez", speed and prior approval were never attained. In-situ burning still remains a controversial method of cleanup, and difficult decisions regarding its use have to be made within a very limited time period.

3 NEW OR IMPROVED METHODS

3.1 BIOREMEDIATION

Petroleum hydrocarbons can, in general, be divided into four broad categories: saturates, aromatics, asphaltenes and resins. Biodegradation rates are typically highest for the saturates, followed by the light aromatics, asphaltenes and resins. As a spill weathers, its composition changes: the light aromatics and alkanes dissolve or evaporate rapidly and are metabolized by microorganisms. The heavier components that are harder to degrade remain. No crude oil is subject to complete biodegradation

The many compounds in oil differ considerably in solubility, volatility, and suceptibility to biodegradation. Some compounds degrade readily; others resist degradation; still others are virtually nonbiodegradable. These different rates of degradation for each of the components of petroleum make it difficult, and possibly misleading, to speak in terms of an overall biodegradation rate.

The "Exxon Valdez" spill gave researchers a rare opportunity to evaluate the feasibility of using bioremediation as a cleanup method. Bioremediation, the process by which oil degrading microorganisms accelerate the natural biodegradation of oil, has been discussed for several years. Only recently, however, have some of bioremediation's problems been addressed. There are still many uncertainties about the use of bioremediation as a practical oil spill response method, as we will see later. Nevertheless, in certain circumstances bioremediation could be appropriate, and further research may lead to enhancing the nation's capability to fight marine oil spills.

We will first give some important definitions :

> *Biodegradation* is the natural process through which bacteria or other microorganisms alter and decompose organic molecules into various substances, such as fatty acids and carbon dioxide.

> *Bioremediation* involves adding substances to oil spill sites and other contaminated environments to accelerate the natural biodegradation process.
> *Fertilization* is a bioremediation method. It involves stimulating the growth of indigenous microorganisms in a contaminated environment by adding nutrients, such as nitrogen and phosphorus. This method is also known as nutrient enrichment.
> *Seeding* involves adding microorganisms to a spill site. Present seeding methods use naturally occurring microorganisms which may or may not be accompanied by nutrients. Although not yet being considered for remediating oil spills, seeding with genetically engineered microorganisms (GEMs) may also be possible. [4]

One of the most important long-term natural processes for the removal of oil from the marine environment, is degradation by microorganisms. Progress has been made in applying the fundamental knowledge of biodegradation to cleaning up terrestrial and enclosed sites polluted with oil. However, very little progress has been made with respect to marine oil spills. Practical problems still exist with applying bioremediation to this area, due to some important differences between the two environments. On land, bioremediation applications have been conducted in closed or semi-enclosed environments. Here microorganisms have little or no competition and conditions can be controlled and monitored. In contrast, the marine environment is a dynamic, open system, that is hard to control. Many additional variables exist in the marine environment compounding the difficulties of using bioremediation techniques.

3.1.1 Environmental influences on biodegradation:

Oxygen, although not a rate-limiting component in the biodegradation of marine oil spills, is nonetheless an important requirement for microbial degradation of hydrocarbons. [4]

Nutrients such as nitrogen, phosphorus, and iron are critical in determining the limiting the rate of biodegradation in marine waters. Slow rates of biodegradation may result from an inadequate supply of these nutrients. Nutrients are added in bioremediation by means of the fertilization method. This is done because, although petroleum is rich in the carbon required by microorganisms, it lacks the minerals necessary to sustain microbial growth. [4]

Temperature of sea water is usually between -2 and 35 °C (28.4 °F and 95 °F). Observed in this entire temperature range, biodegradation occurs the fastest at higher temperatures. Demonstrated in an experiment, a temperature drop from 25 to 5 °C caused a tenfold decrease in response. The reason for this is that hydrocarbon metabolism by microorganisms decreases at low temperatures. Furthermore, microbial activity is suppressed as lighter components of petroleum become less volatile and allow petroleum constituents, that are toxic to microbes, to remain on the surface for a longer time. Low temperatures also cause petroleum to become more viscous, reducing the spreading of an oil slick, and thus the amount of surface area available for colonization by microorganisms. [4]

Other factors such as pressure may also have important effects. For example, oil at great depths in the ocean degrades very slowly because increasing pressure is related to decreasing rates of biodegradation. Salinity and pH do not fluctuate much in the oceans so they do not have important effects on biodegradation of marine spills.

Microorganisms, through the natural process of biodegradation can eliminate many components of petroleum from the environment, given enough time. The basic question, however, is whether bioremediation technologies can enhance this natural process enough for it to be considered practical. [4]

3.1.2 Future of bioremediation

For marine oil spills the usefulness of bioremediation is still being evaluated. Its importance relative to other oil spill response technologies also remains uncertain. Bioremediation could be used as a primary technology in certain non emergency situations (e.g., for cleaning lightly to moderately oiled beaches). However, other cleanup techniques such as mechanical methods, dispersants, and in-situ burning will most likely remain more effective technologies for the initial at-sea spill response. This is especially true when beaches are threatened by a large offshore spill, and the objective is to get the oil out of the water as quickly as possible.

Bioremediation approaches for marine oil spills fall into three major categories:

1) Fertilization
2) Natural Seeding
3) Seeding with GEMs

Fertilization is the approach that has been tested more rigorously. This approach is viewed by many researchers as the most promising one for responding to different types of marine spills.

Bioremediation technologies for beach cleanup have received the most attention. The experiments conducted on pebble beaches fouled by oil from the "Exxon Valdez" indicated that the addition of nutrients at least doubled the natural rate of biodegradation. There is a great promise of bioremediation for oiled beaches. Moderately oiled beaches are the main candidates for bioremediation treatment. It can be a practical tool after the gross amounts of oil have been removed by mechanical means.

Bioremediation has not yet been demonstrated to be an effective response to "at-sea" oil spills as we can see in Table 2. However, bioremediation may have a role in environments such as salt marshes and sensitive ecosystems where the use of mechanical or other approaches might do more harm than good.

No significant adverse impacts related to the use of bioremediation technologies for oil spill cleanup have been identified in recent field applications. However, more development and testing are needed before decision makers for oil spill cleanup will be comfortable advocating their use since they are not willing to experiment during a real spill.

3.2 MORE EFFICIENT SKIMMING SHIPS

As we said before, the most important limitation for skimmers is the sea state, and this is a primary focus of the new designs; to operate in a wider range of sea states. Better recovery capacities are also desired. We will now examine some of the new ships developed to fulfill these two requirements.

3.2.1 Main characteristics of "Valdez Star" and "Shearwater" (Fig. 21)

Displacement	610 Lt
Length	123 ft
Beam	31 ft
Depth	13.5 ft
Draft	10 ft
Oil storage capacity	55,000 gal

"Valdez Star" was designed to operate in Prince William Sound, while its sister ship, the "Shearwater", was ordered for operation in Port Angeles, Washington. "Valdez Star" was ordered before the "Exxon Valdez" accident, however delivery did not occur until 1991.

The first design requirement was to operate in severe weather and sea conditions (like the ones existing in Prince William Sound); winds reaching 50 knots and waves 10 to 15 feet. These parameters dictated the ship's size. Another goal was to design a skimmer with work-boat capabilities. In regards to secondary functions, the ships can transports two small 22 foot boats, store up to 2000 feet of containment boom, are able to provide headquarters for directing spill operations, and give long range support. When not skimming the ships can be used to place containment booms around loading oil tankers or repair docks. They can also tow a 12,000-barrel oil barge.

The oil recovery system onboard these two ships has a collection rate of 1300 barrels per hour with less than 1 percent added water in recovered oil in a range of speeds from zero to three knots. The system consists of a dynamic inclined plane (DIP, explained in chapter 2.1.1, figure 13) at the bow, followed by a collection well and a storage tank amidships. It is housed in a tunnel structure at the bow, which extends to the engine room cofferdam. The forward end of the tunnel structure has a pair of hydraulically controlled bow doors. Oil/water interface sensors in the collection well ensure that virtually oil free of water is transferred to storage by the cargo pumps. Another advantage of the DIP system is that its performance is relatively insensitive to variations in oil viscosity and the limit on relative velocity of the vessel to oil slick is 3 knots with a 23 degree plane incline (much better than the barrier's limit). [15]

3.2.2 The catamaran concept

The design requirements are:

- Capability to recover oil even under adverse sea states
- Low investment and operating costs
- Easy operation by a minimum of crew members
- Ability to be easily pushed or towed by other vessels
- Multipurpose employment capability

This vessel (Fig. 22) has a flexible ramp between the two hulls. It will either be pushed or towed through the oil spill layer, or can be anchored in the current. The oil-water mixture flows over the ramp edge into the unit. This procedure works if there is sufficient current or tow speed, which should not exceed 4 knots. The optimal collection of the oil-water mixture will be influenced by the level of the upper ramp edge, which must be adjusted according to operating conditions (sea state, velocity and oil slick thickness).

The catamaran may also be used as a transport barge or a floating storage facility for bunker and slops. The catamaran design was necessary to make this ship safe and easy for connecting to a tug, since it is not self-propelled because of the low operating cost requirement. [14]

3.3 THE USE OF FISHING NETS FOR HEAVY OIL RECOVERY

Most oil spill containment equipment is not good for use with heavy viscous crude oils like Bunker C. This can be extended to lighter oils which leave viscous emulsions or heavily weathered oil remnants when spilled, because of evaporation and natural processes. For these cases fishing nets have been considered as a containment device, and are now being studied and tested.

The main variables that influence the efficiency of the containment are; the net mesh, the towing speed and the viscosity of the oil. For towing speeds of 0.6 knots a 1/4 inch mesh fish netting was found to be a suitable containment device for heavy oil (viscosity of 3*10^5 cSt at 10 degrees Celcius). The nets weight is only 1 kg/m, a factor that makes them well suited for easy deployment. The towing stresses are lower for the nets than for similar size rigid booms. Floats are sewn into the upper seam to maintain the net afloat, as we can see in Figure 23. The net is submerged when loaded with the oil, which makes it good for moderate waves once the oil has adhered. There are still problems with efficient net recovery once it is soaked with oil due to its weight, and because oil begins to leak off once the net is removed from the water. To fully remove the oil from the net is also difficult, but since the cost is about $25 per meter, it may simply be cheaper to discard the net after each cleanup operation. [3]

3.4 NEW MATERIALS AND DESIGNS OF SORBENTS

Improvements to sorbents have been mainly in the area of materials. A new polymer absorbent is being tested in the form of booms (made of this sponge-like material) that have been designed to sink and remain underwater. The booms are tethered for easy recovery and can absorb any hydrocarbon product with specific gravity greater than one. Once it is saturated it solidifies into a rubber-like mass which is irreversible and nonbiodegradable and can be incinerated or landfilled. This product can be effectively used in harbor areas where standard crude oils that sink are common. A 2.5 inch diameter boom can absorb up to 25 ounces of oil per foot of material.

Another polymer sponge has been tested that will remain afloat indefinitely both prior to contact with oil, and after saturation. It can be produced in either booms or pads. The booms have a 5 inch diameter, are available up to10 feet in length, and can absorb 40 to 50 ounces of oil per foot. This polymer will also solidify (when saturated) forming a nonbiodegradable "rubber" from a process that is irreversible. If not replaced when fully solidified these solidified polymer sponges could become containment booms in low sea states. The sorbent booms can be attached to regular booms to make oil containment more efficient by reducing the potential of free oil escaping. Furthermore, they can be easily retrieved and replaced as they solidify, without interfering in skimmer operations. Any new materials that can reduce the labor-intensive requirement of retrieval and disposal are greatly sought after. There is also room for advancement in designs of innovative boom configurations.[7]

3.5 IMPROVEMENTS IN THE APPLICATION OF DISPERSANTS

The method itself has not changed much but there have been some advances in the chemicals and spray systems. We will mention one of the new spray systems in this section.

A new type of shipboard equipment has been designed for neat dispersant application. This equipment can roughly adjust the dispersant dosage in order to keep a reasonable dispersant/oil ratio in spite of the variations in oil slick thickness. It also can improve the contact between the oil and dispersant. Each spraying boom is independent, with three operating valves and a remote control panel. Two operators run the equipment, adjusting the application rate according to the speed of the ship, the appearance of the oil slick, and the perceptible effect of the dispersant on the oil. This feedback capability is a major advantage permitted by the system's ability to quickly change dispersant flow. It also allows possible treatment even when crossing small, thick patches a few meters wide. We can see a ship with this system in Figure 24.

Other advantages are: oil slicks can be treated in a single application, eliminating additional or redundant spraying; ship evolutions are simplified and less time consuming; and control over the flow rate allows a better distribution of the dispersant, avoiding wasteful overtreatment of low oil thickness areas. [12]

4 CONCLUSIONS

The main cleanup methods discussed in the paper are summarized in Table 3. Of the cleanup methods in use today, none is 100 percent efficient. One of the most important factors for an efficient response is to decide, as quickly as possible, which of the available cleanup method(s) is(are) going to be used. This is the responsibility of the contingency planning team. Some methods, such as dispersants and in-situ burning, require a quick decision/approval process. Since each spill involves not only the oil or shipping company and the relevant state and local authorities, but also environmental groups and public opinion, these decisions are in many cases considerably delayed. Thus the efficiency of these methods is often jeopardized.

We can expect new techniques such as remote sensing (ultraviolet devices can identify oil because it has higher UV reflectivity) to assist classical methods of cleanup. Also, there is room for improvement in methods like bioremediation, which has not yet proven to be efficient for marine oil spills. These methods, however, are hindered by the fact that decision makers of a contingency planning team are normally not going to use techniques with which they do not have experience. Further research and tests are definitely needed to implement these methods. A sound knowledge of all the different cleanup methods and factors involved in a marine oil spill can help the decision makers choose the optimal solution, and therefore minimize the damage caused by the spill.

5 SUGGESTIONS FOR FURTHER RESEARCH

As a practical overview of the different oil spill cleanup methods, this paper has illustrated several limitations of these methods and current oil spill technology. Research and testing, to improve existing techniques and equipment or to discover totally new methods of cleanup, are needed so that environmental damage from oil spills, such as Valdez or recently in the Middle East, can be minimized. Thus, the following areas are suggested for future study.

1) Safer traffic control systems, crew training, new tanker designs such as double hull, etc., and the effects of increased liability on tanker operators, are all important topics to spill prevention. Research in any of these areas could shed new light on the most basic problem, preventing oil spills before they occur.

2) In the area of mechanical removal:
    a) New barrier designs that can withstand greater direct water velocities, are more compact, or have faster deployment.
    b) Conduct extensive testing of new heavy weather skimmers, such as the catamaran design, to determine the vessel's limitations and how oil collection rates vary with seastate.
    c) Determine the limitations of using fishing nets as a method of removing high viscosity oils.

3) In the area of chemical removal methods:
    a) Extensive testing of bioremediation in the marine environment to determine its performance capabilities in an uncontrolled situation.
    b) Identify cost and time savings of the new controllable dispersant application systems as a function of sea state, weather, and other oil spill variables.

4) Identify potential roles for the new aerial, infrared optical scanning system in the detection and cleanup of oil spills. [20]

5) Test the new "glass bead" cleanup method that has just been discovered in a laboratory at the University of Texas, to determine the effectiveness of this technology in the marine environment. [22]

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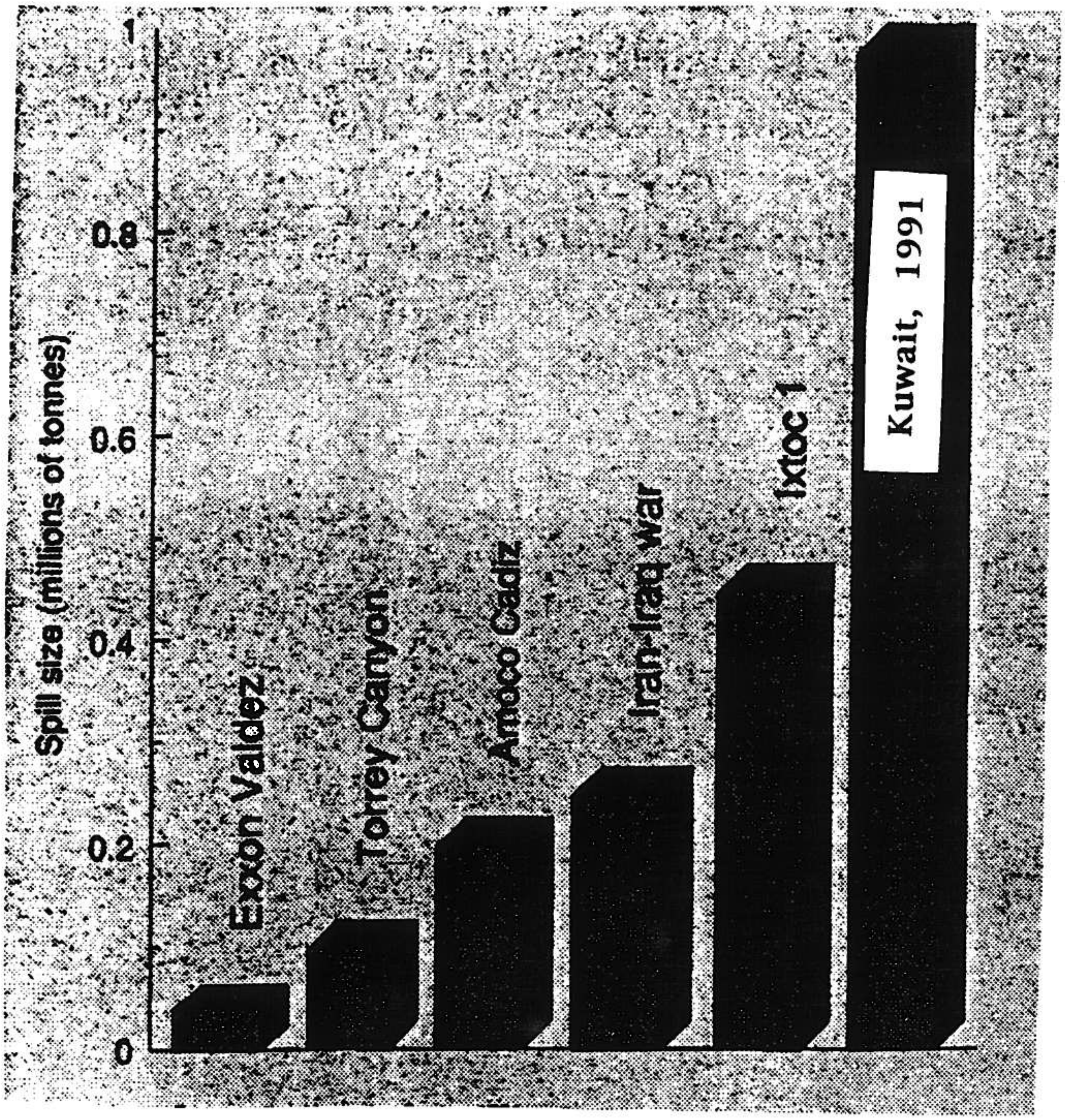
FIGURE CAPTIONS

Figure 1



Major oil spill disasters in recent years.

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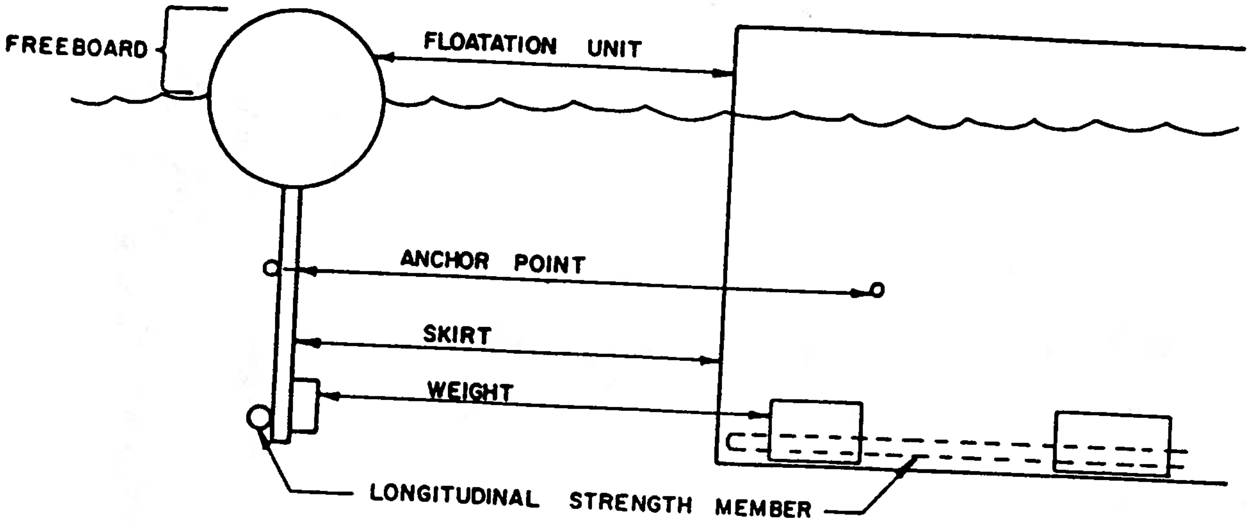
Figure 2



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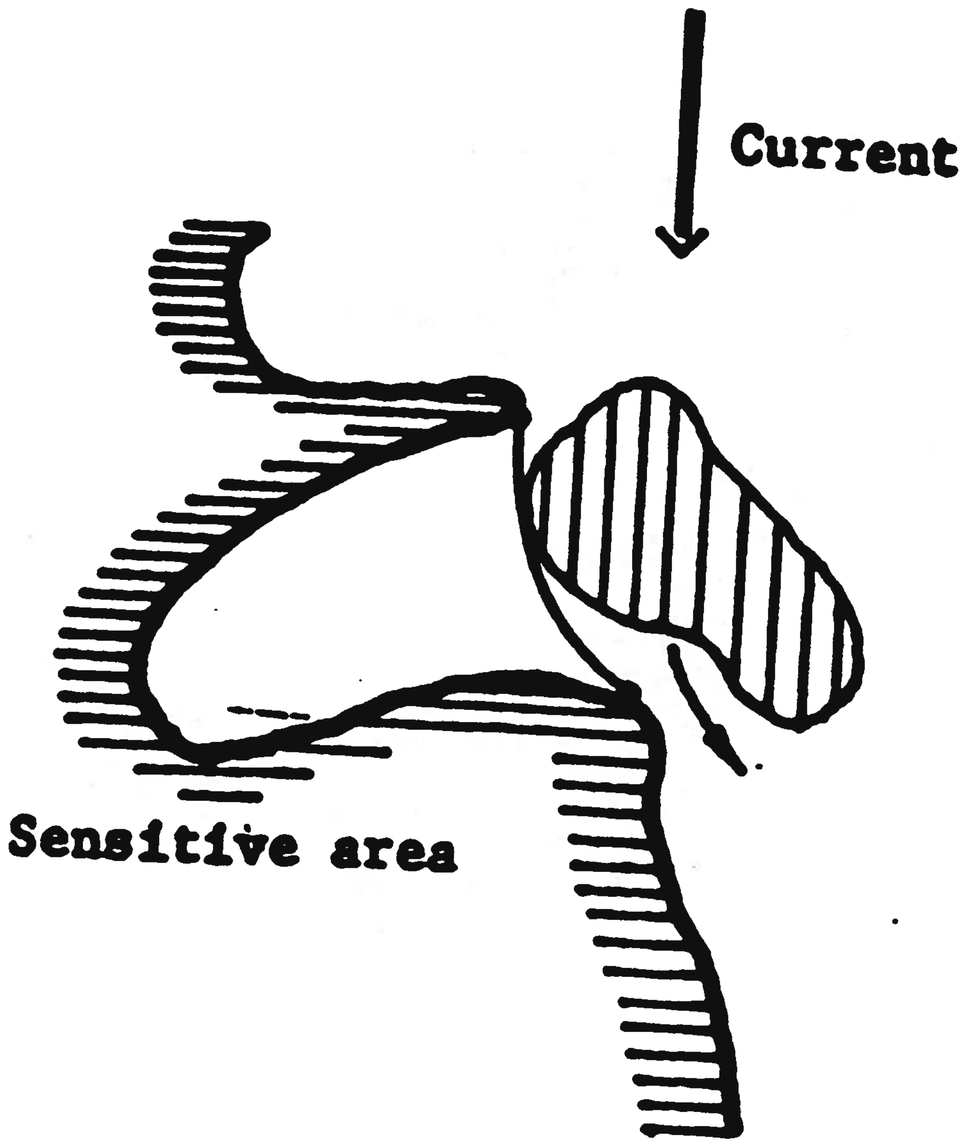

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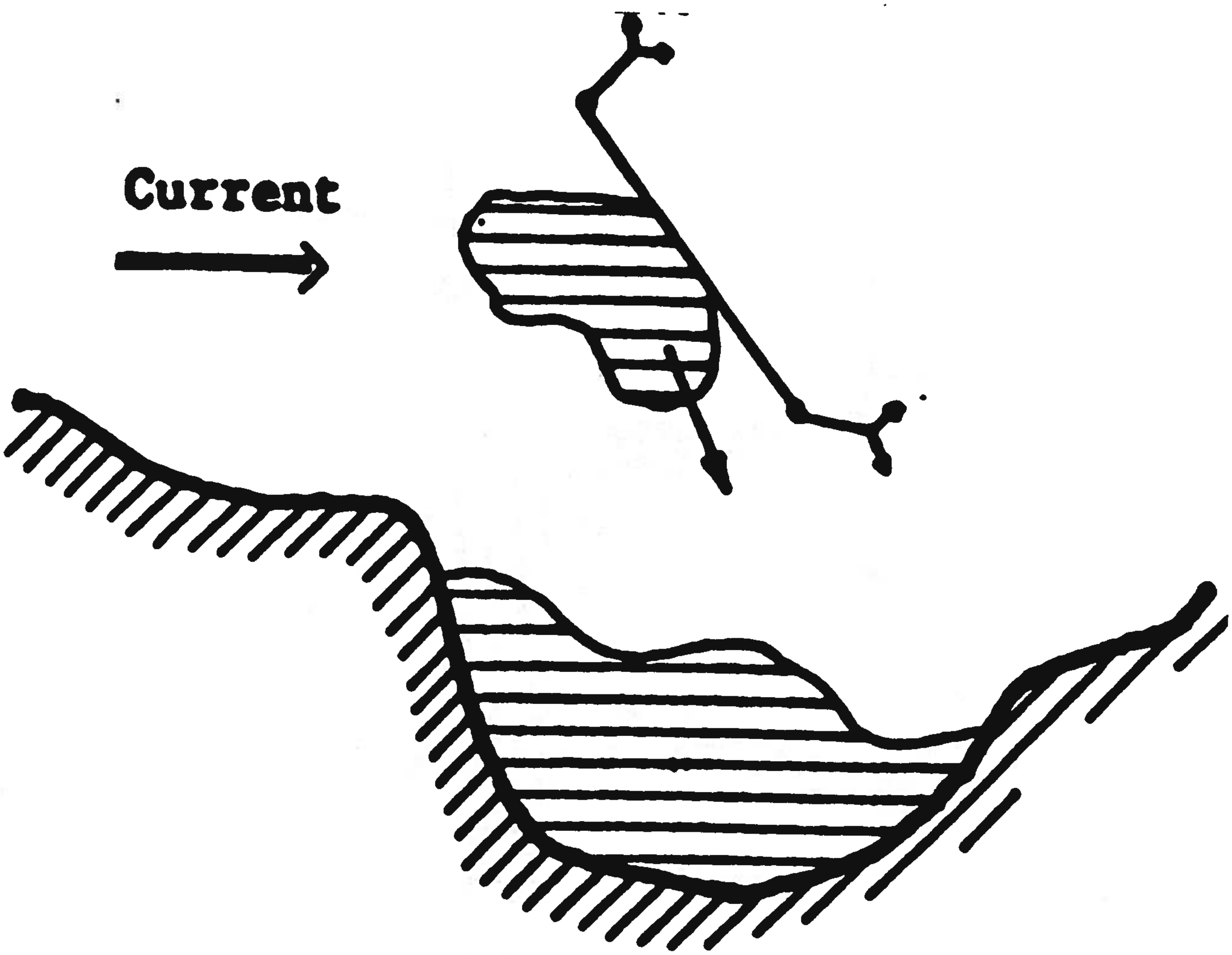

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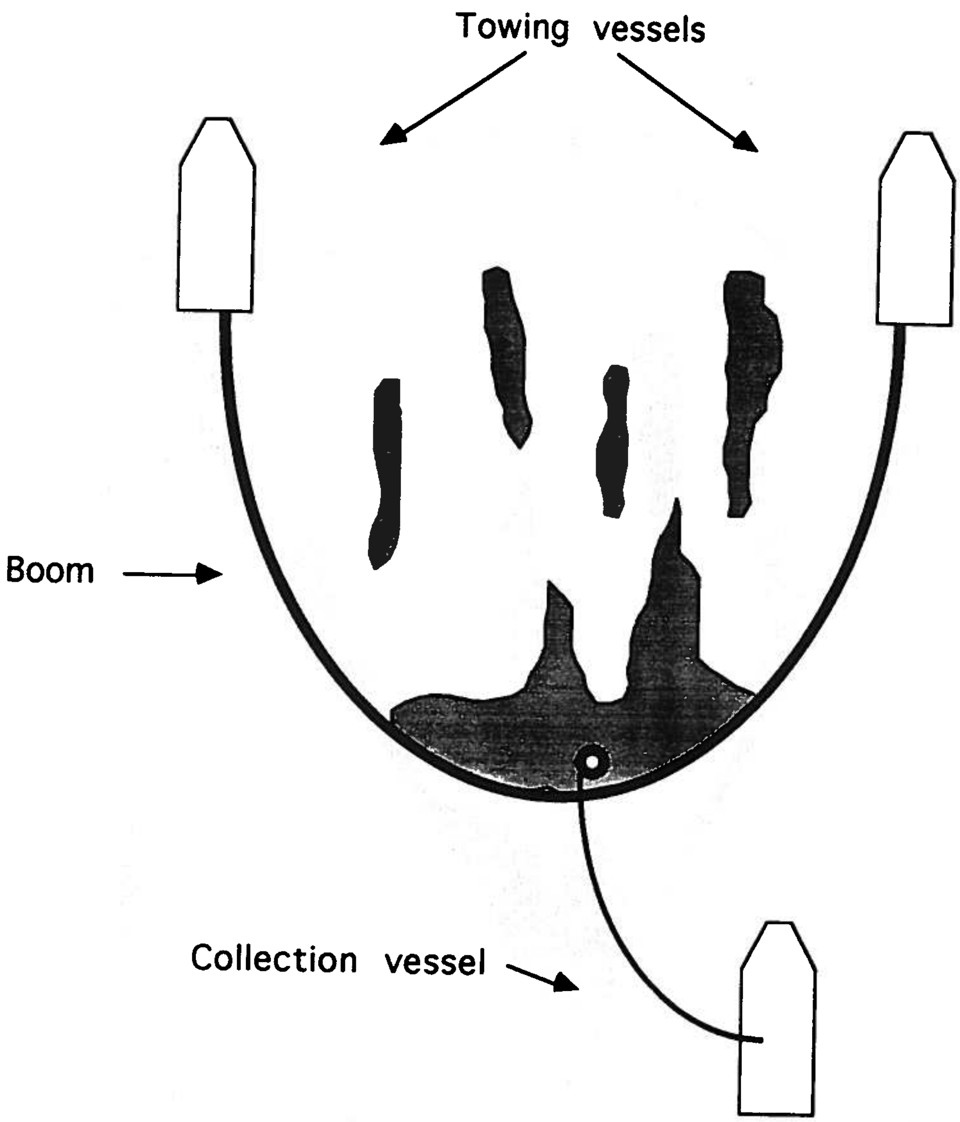

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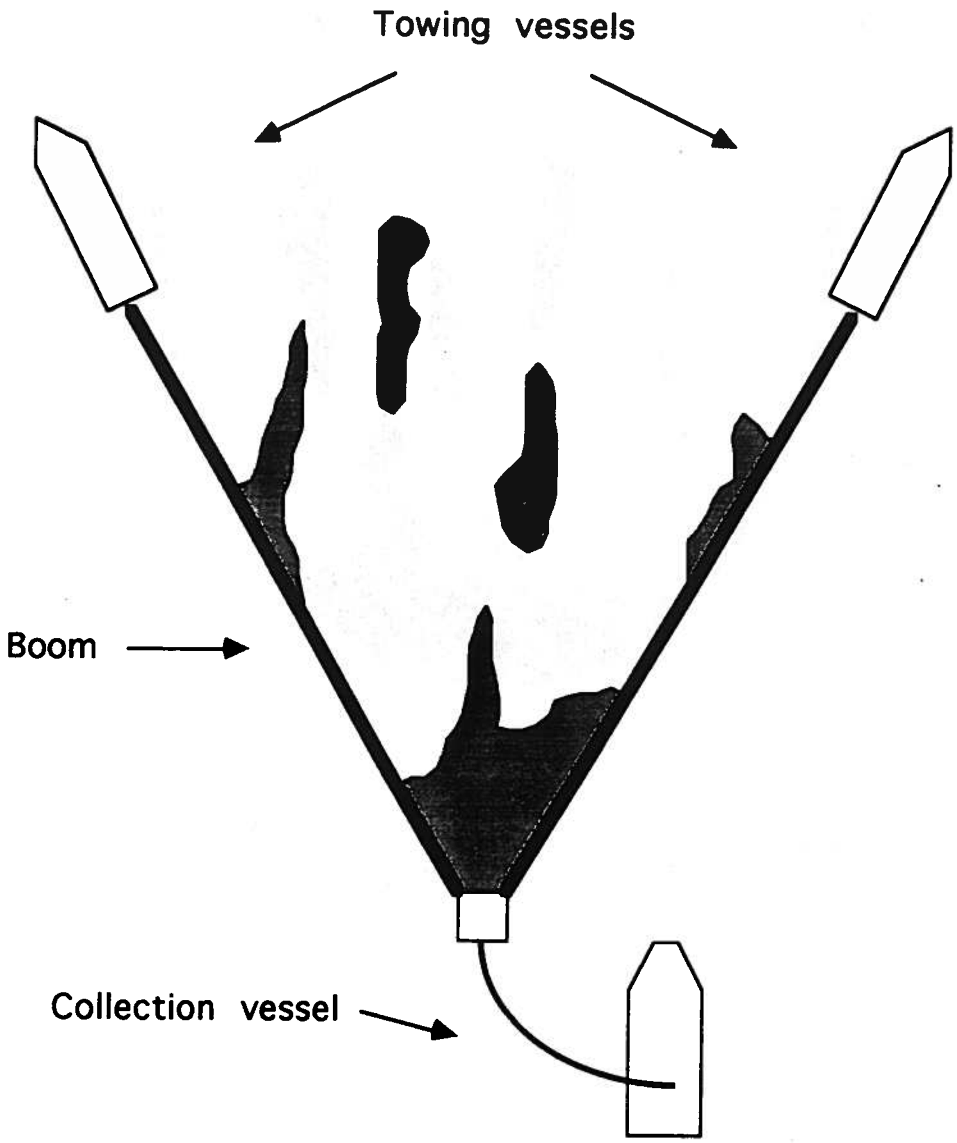

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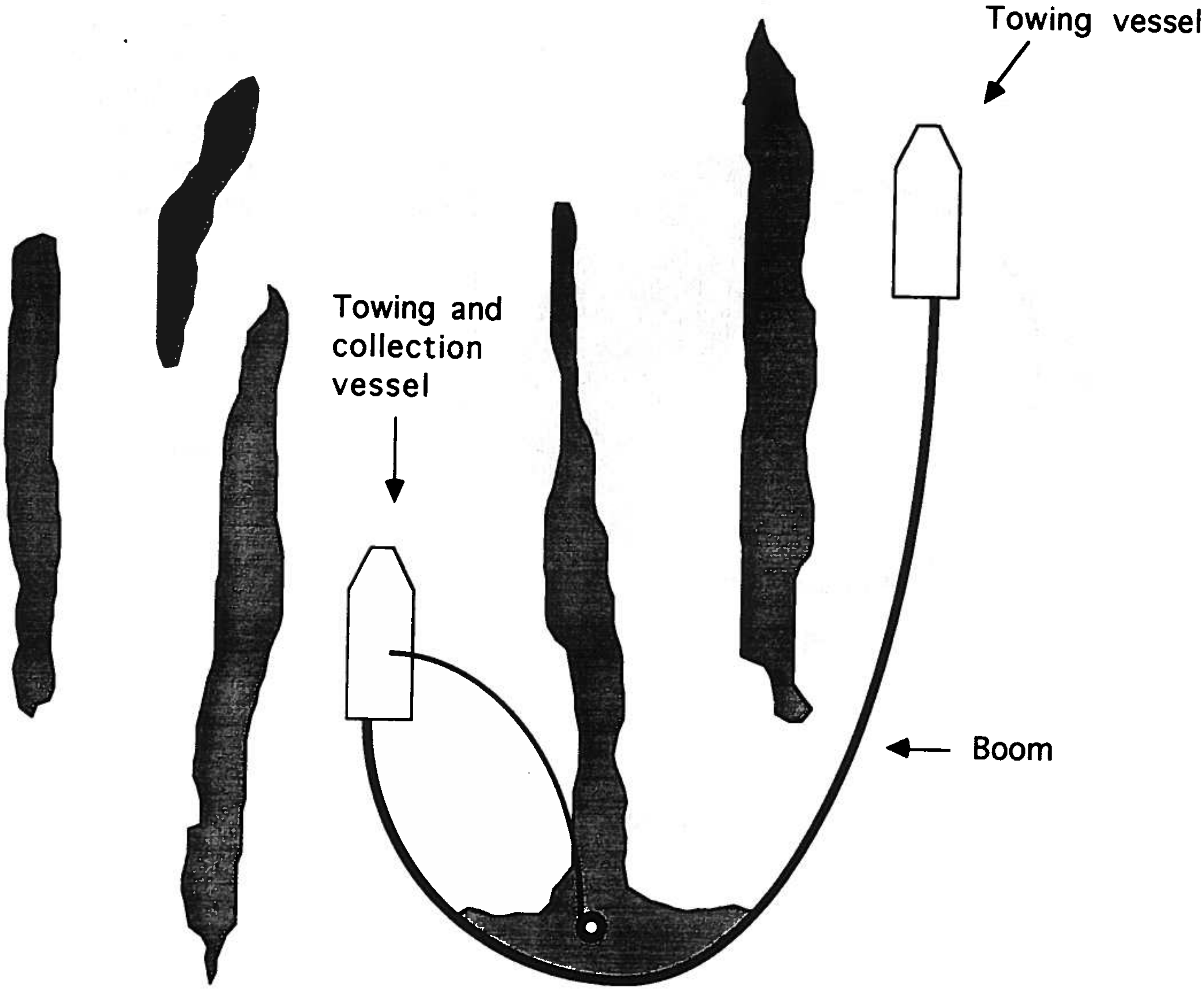

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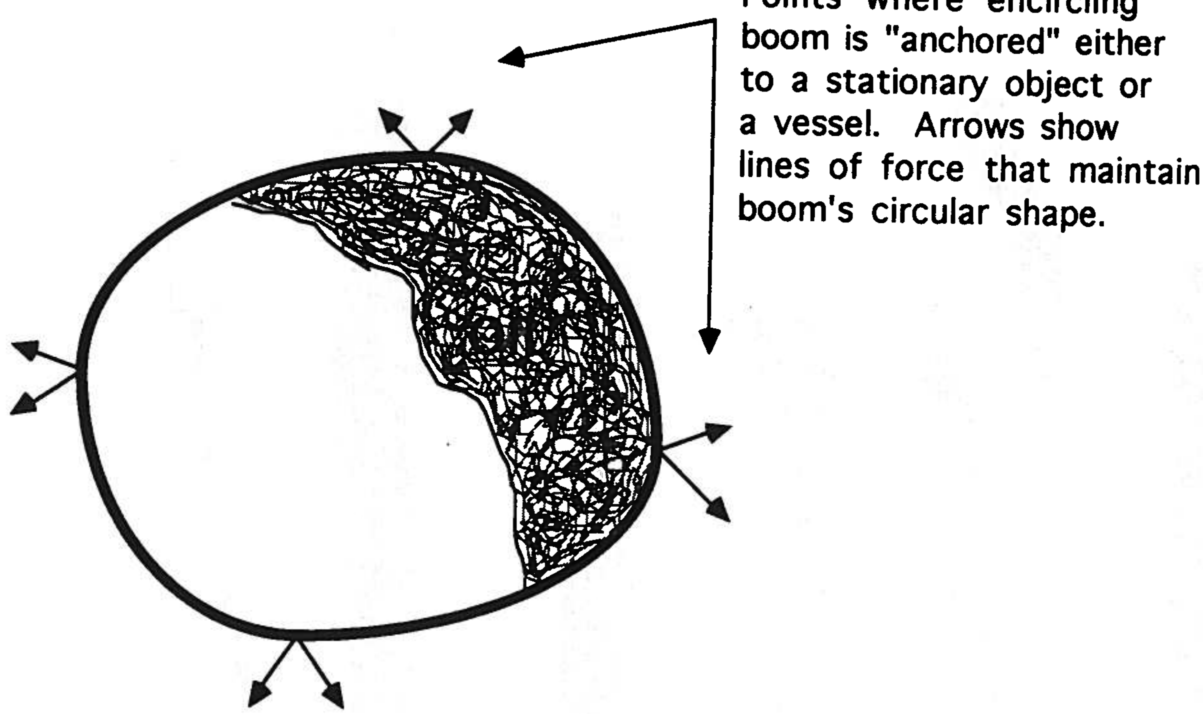

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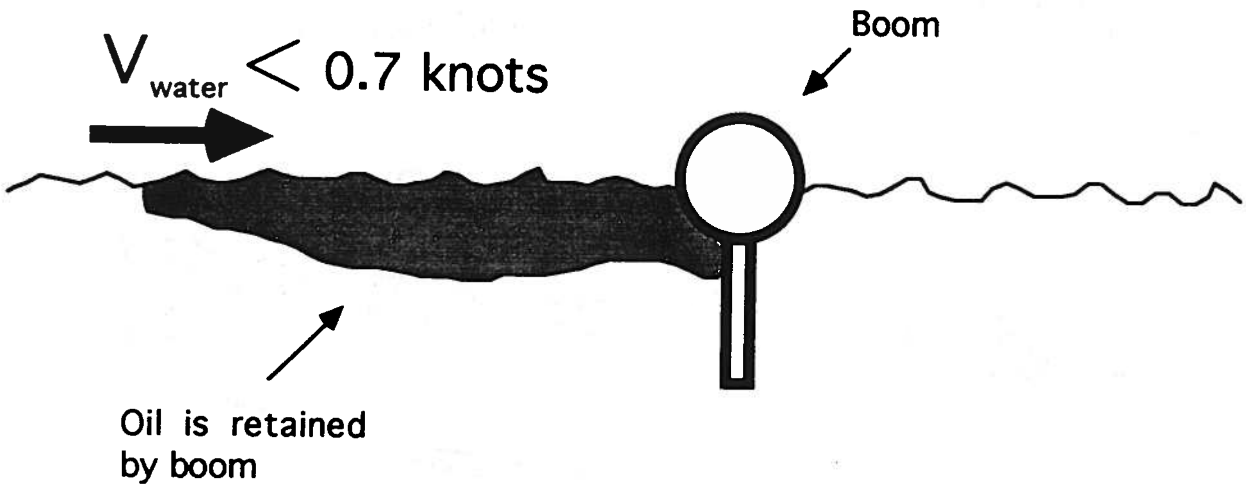

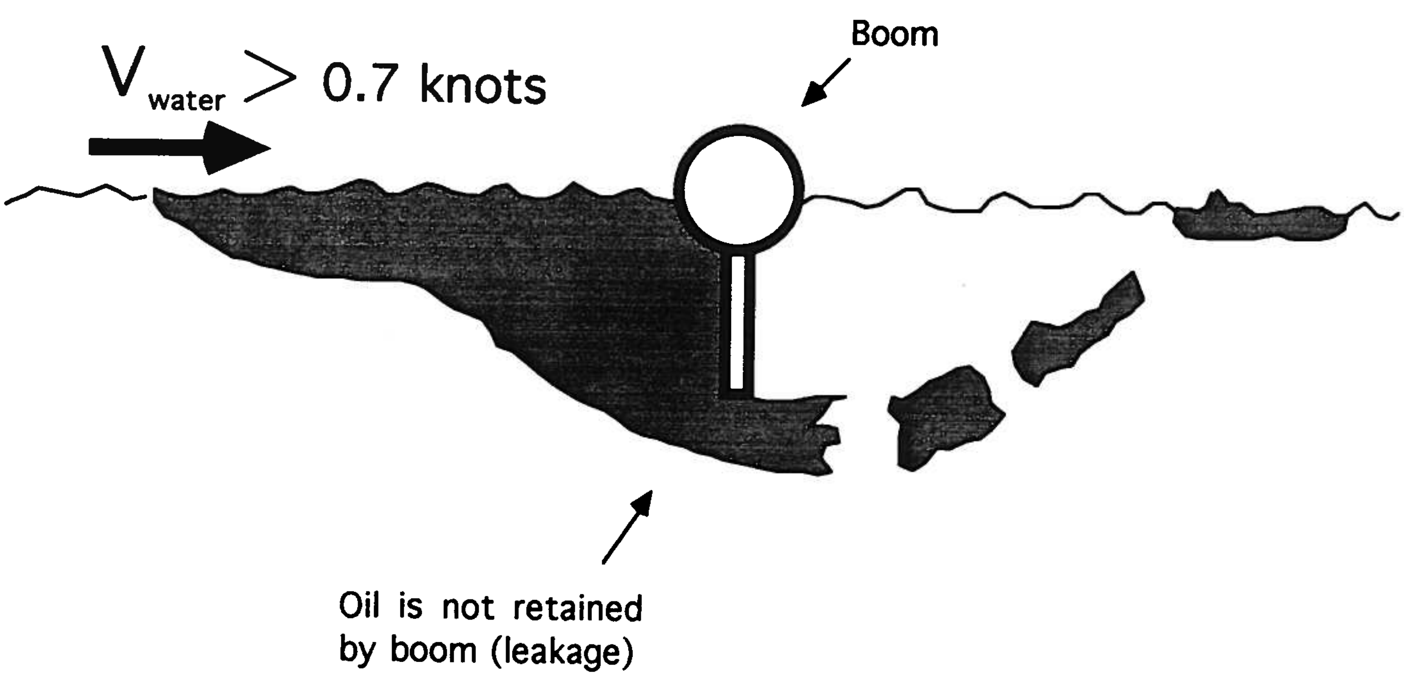

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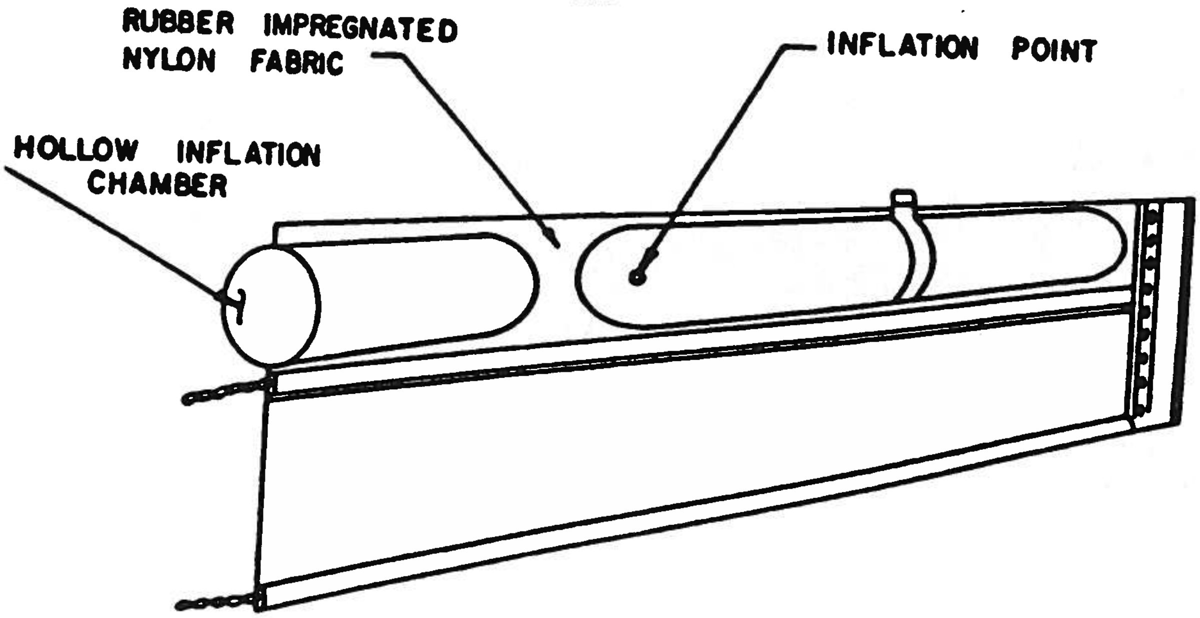

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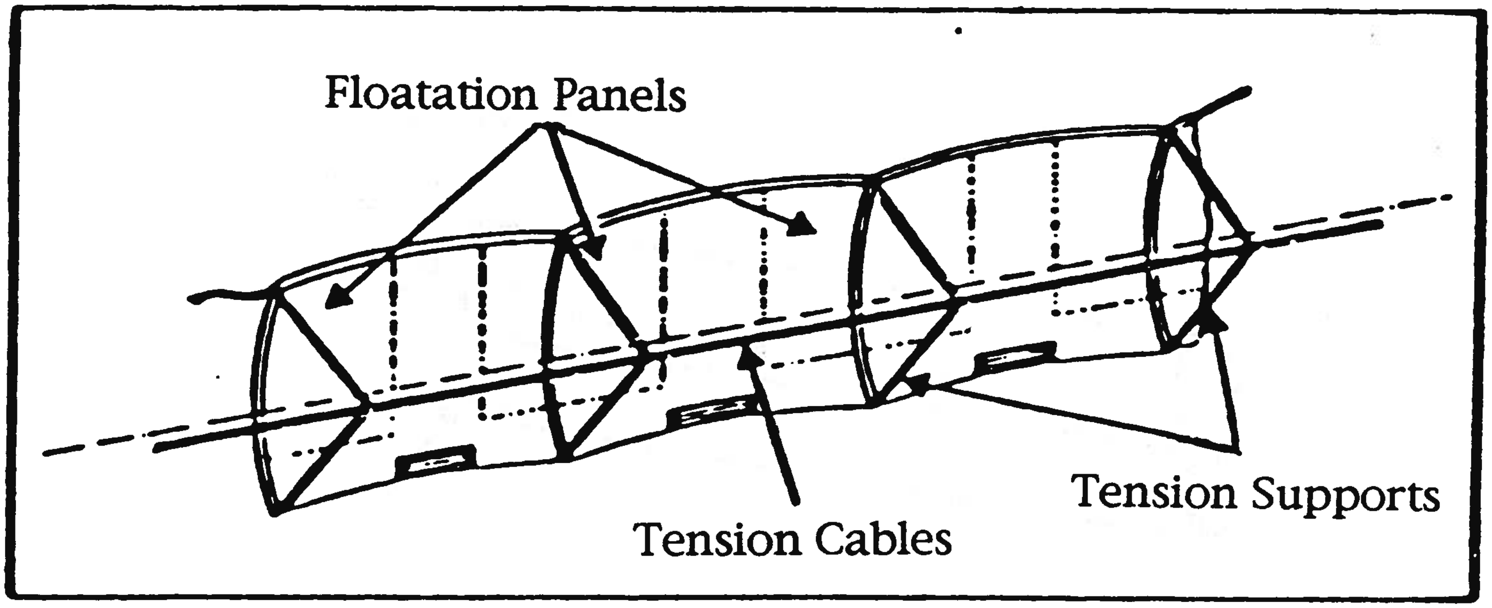

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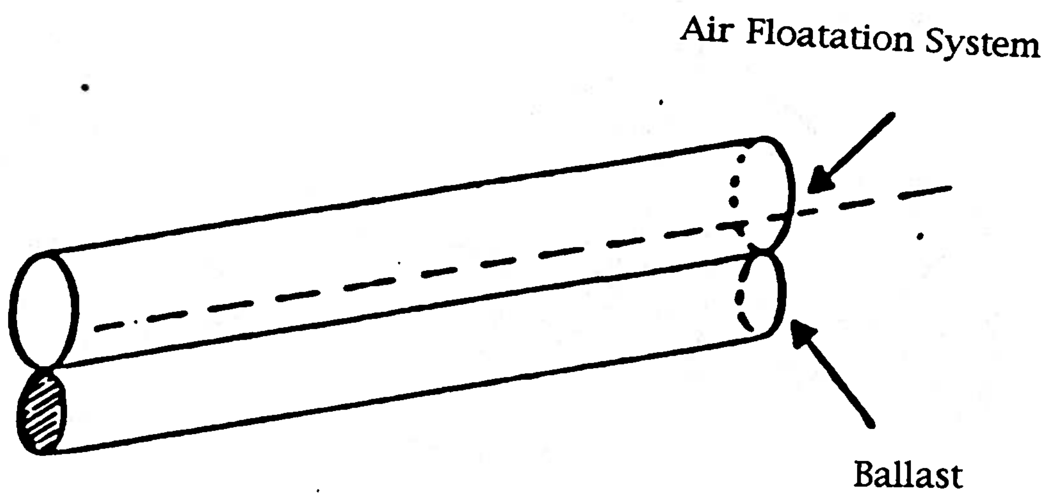

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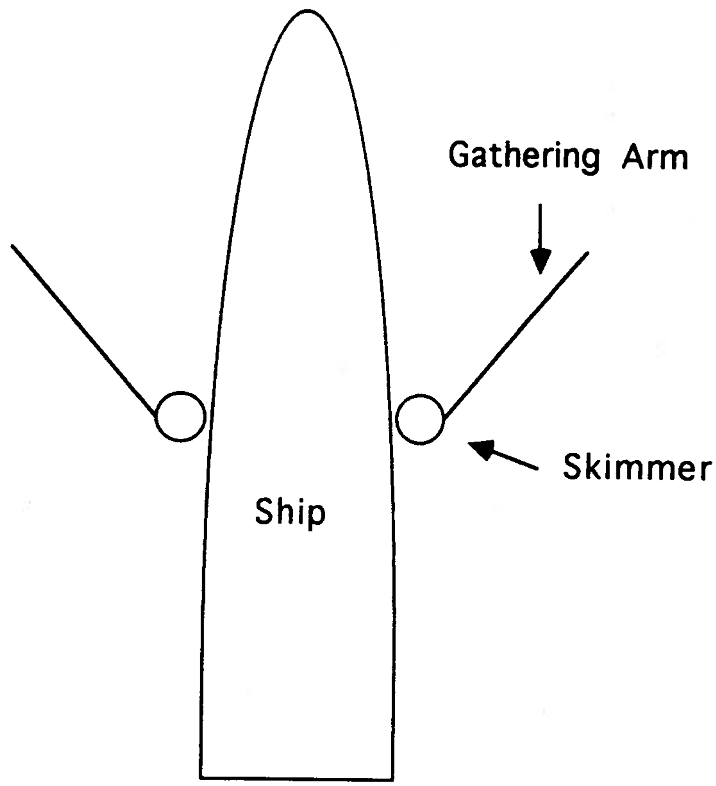

Gathering Arm
Skimmer
Ship

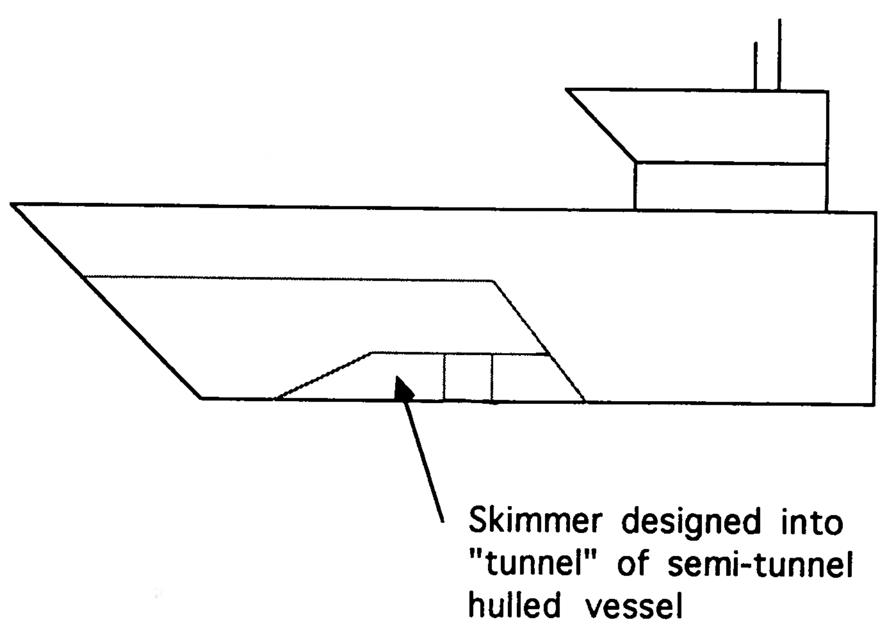
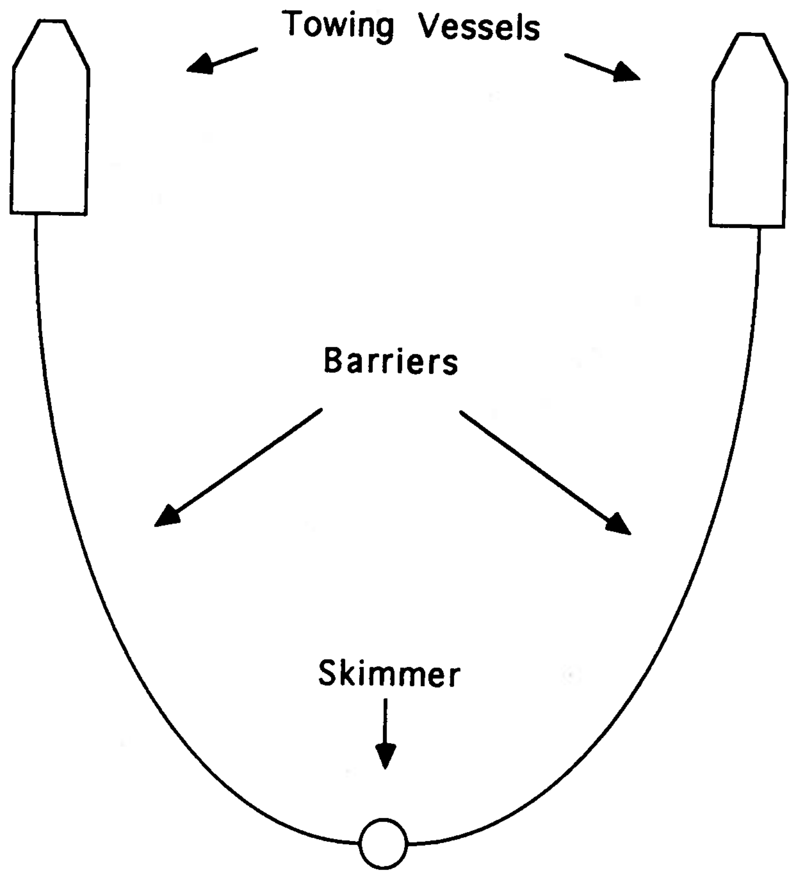

Skimmer designed into
"tunnel" of semi-tunnel
hulled vessel

Figure 10 b



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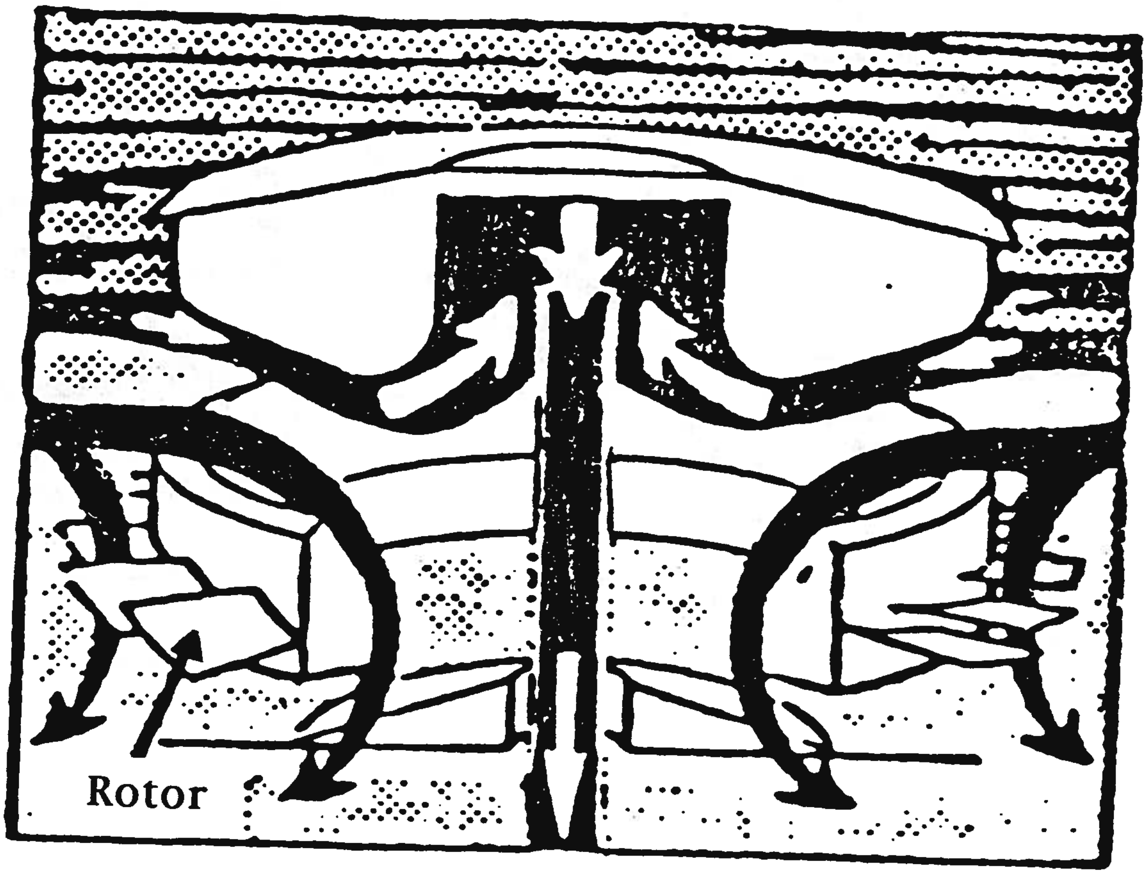

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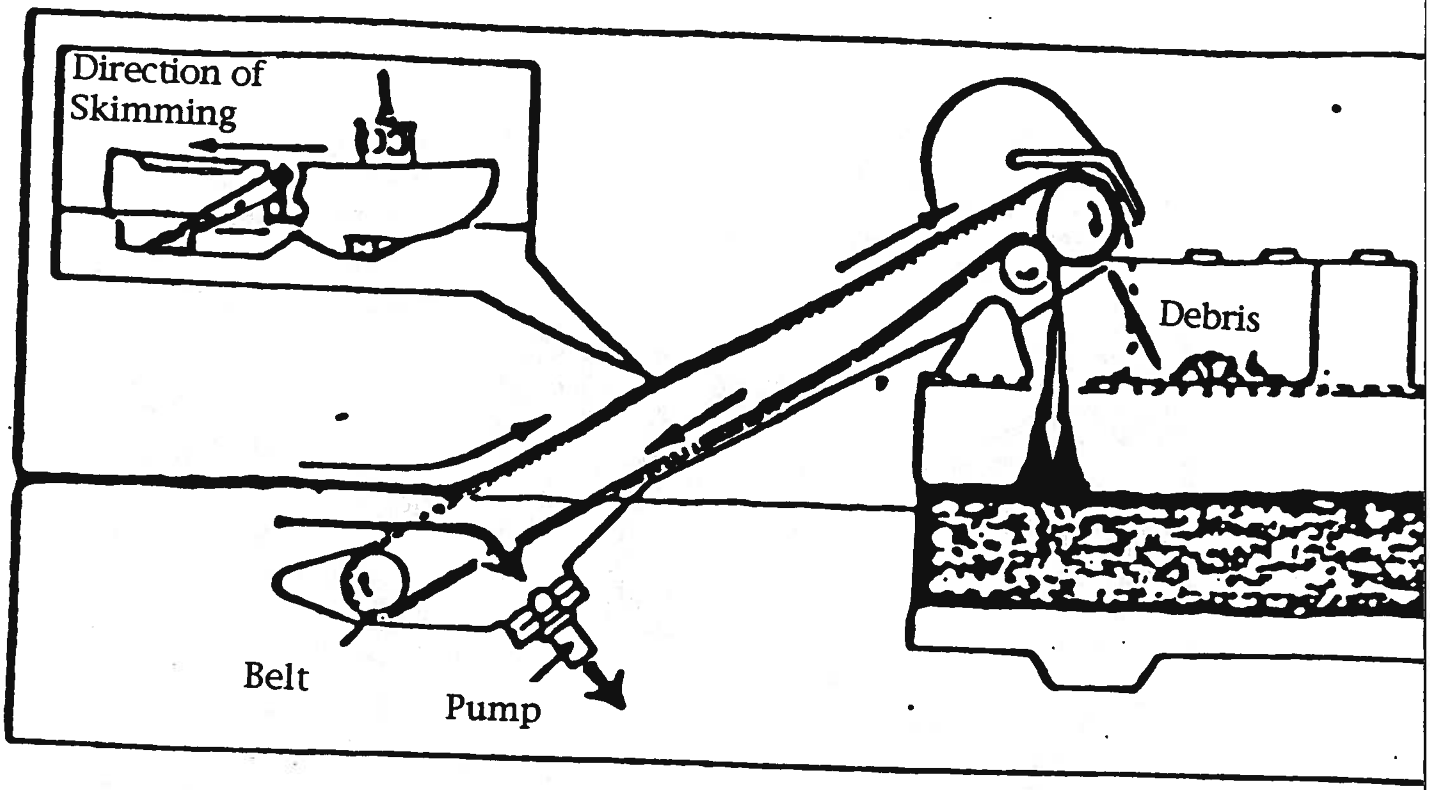

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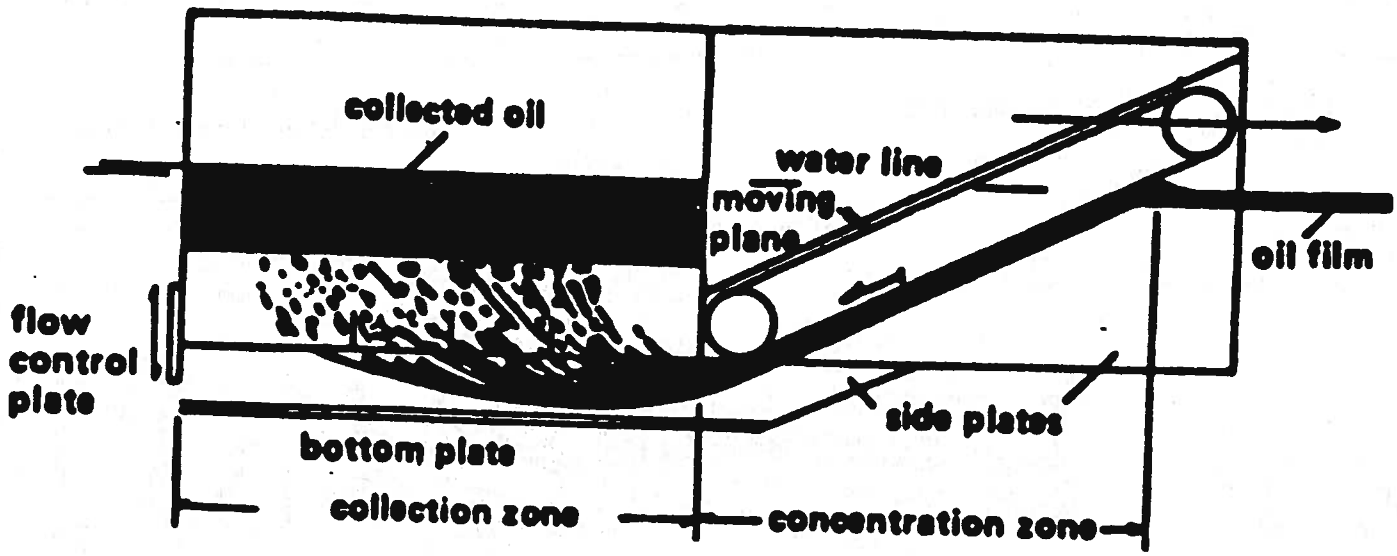

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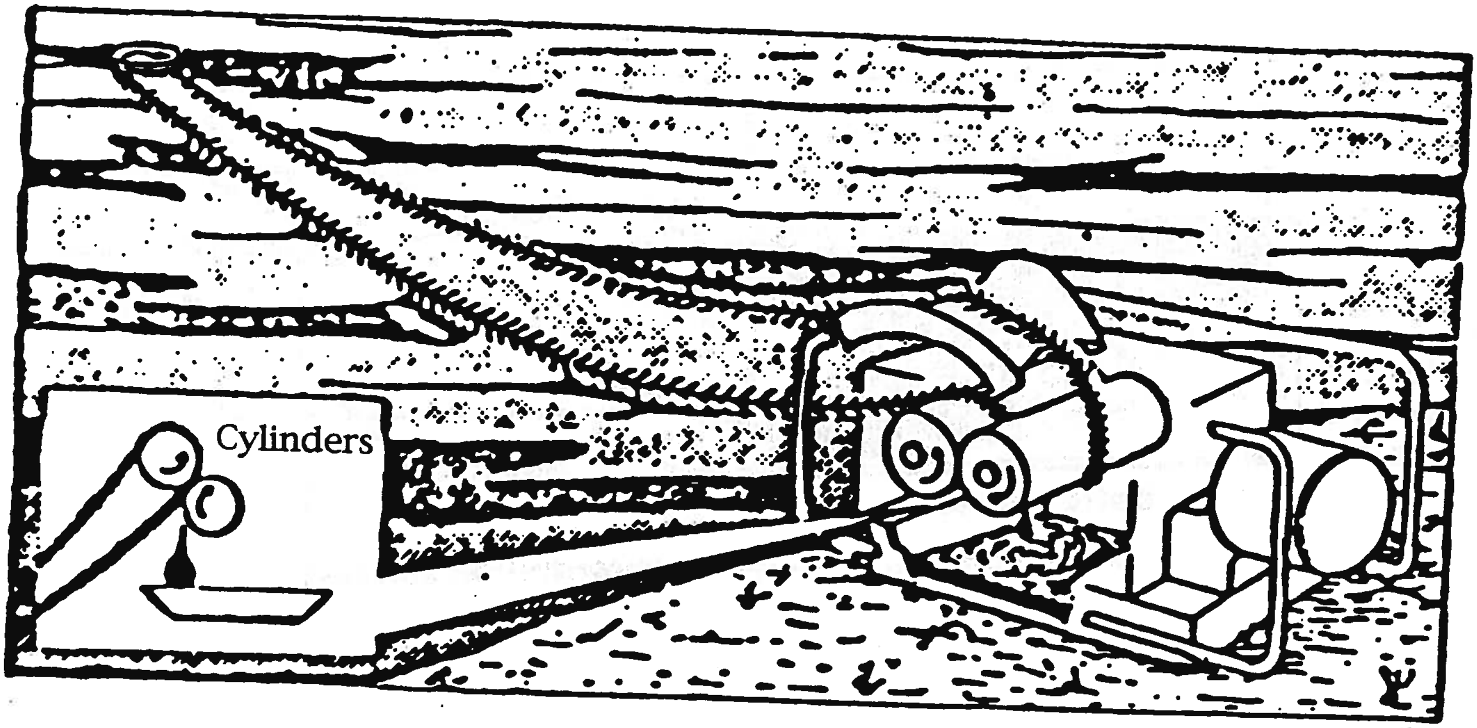

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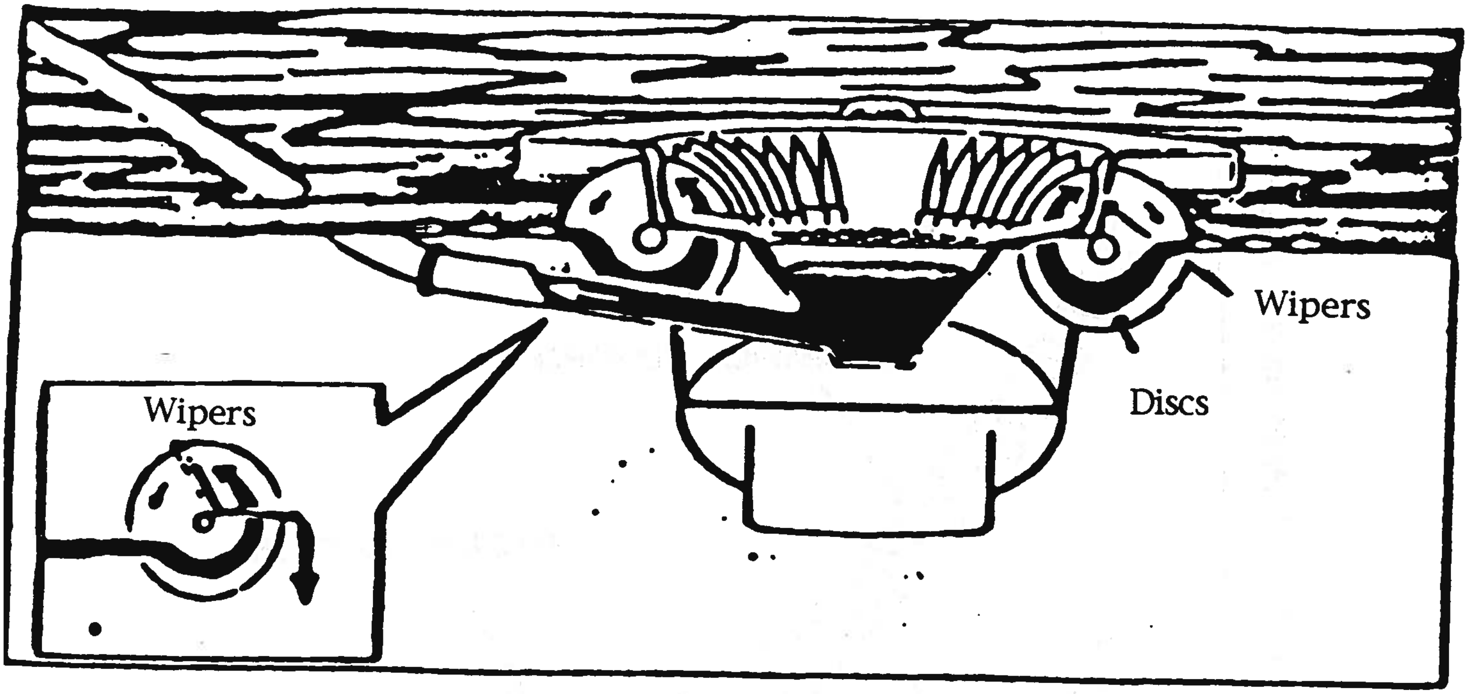

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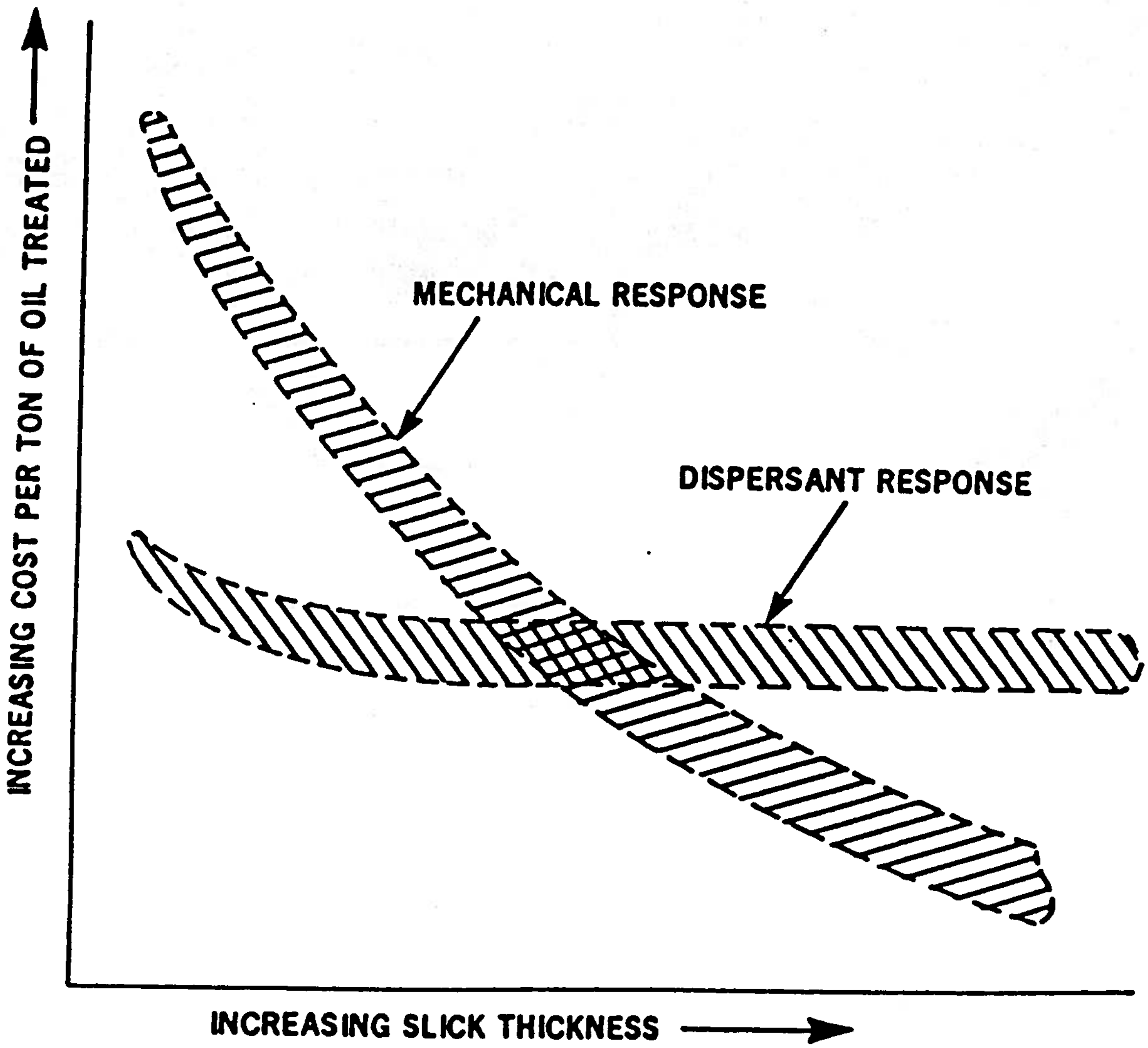

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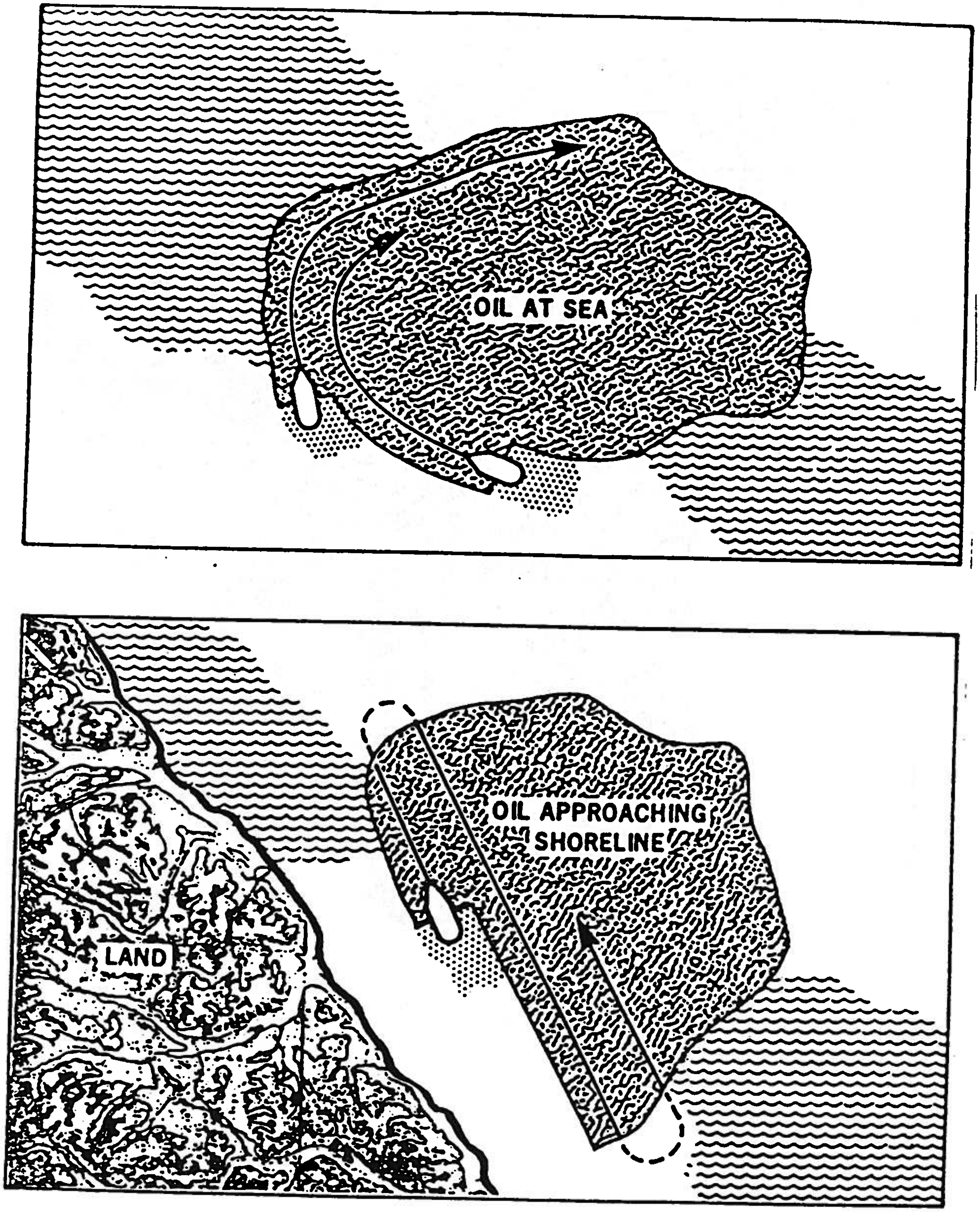

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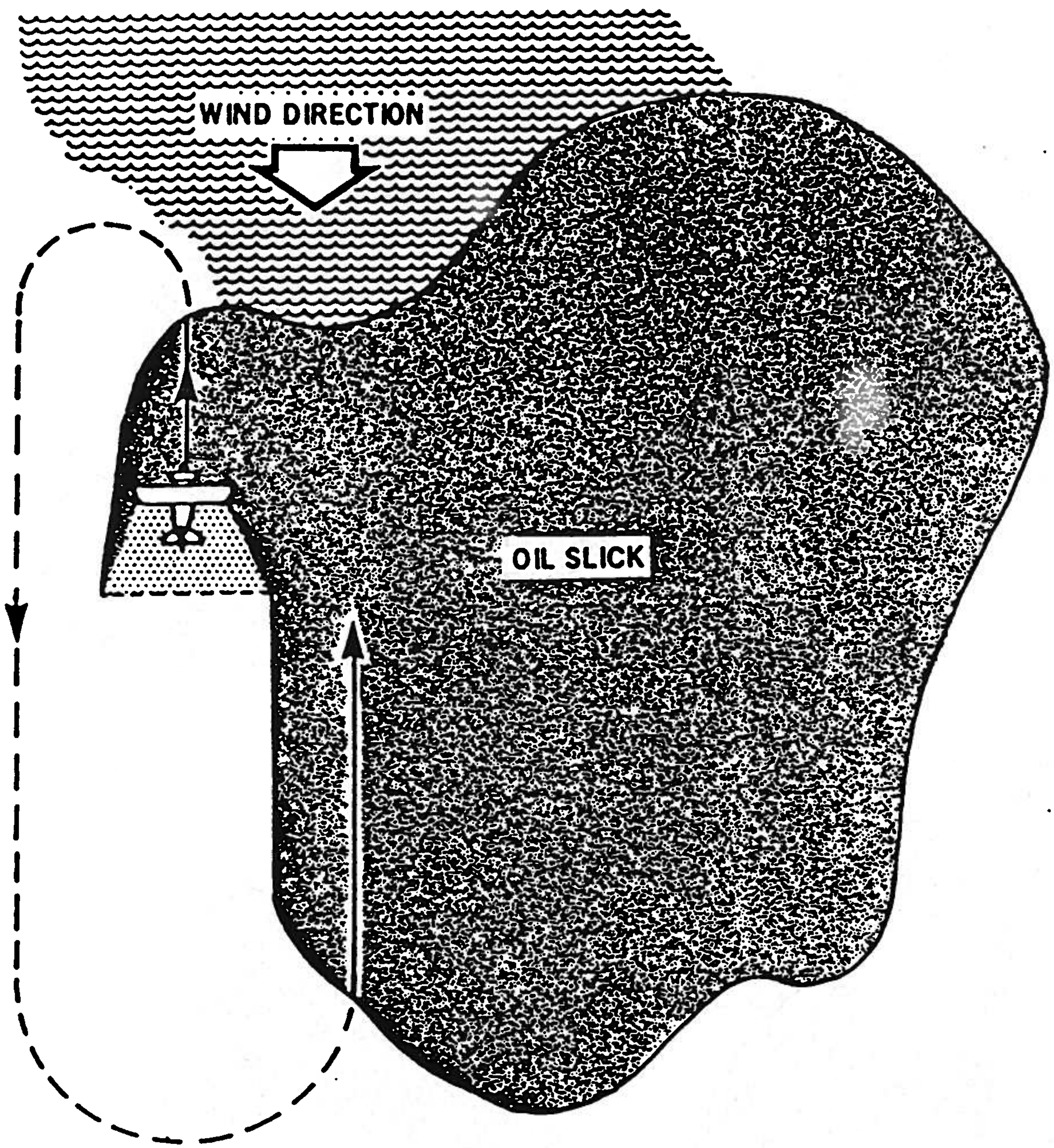

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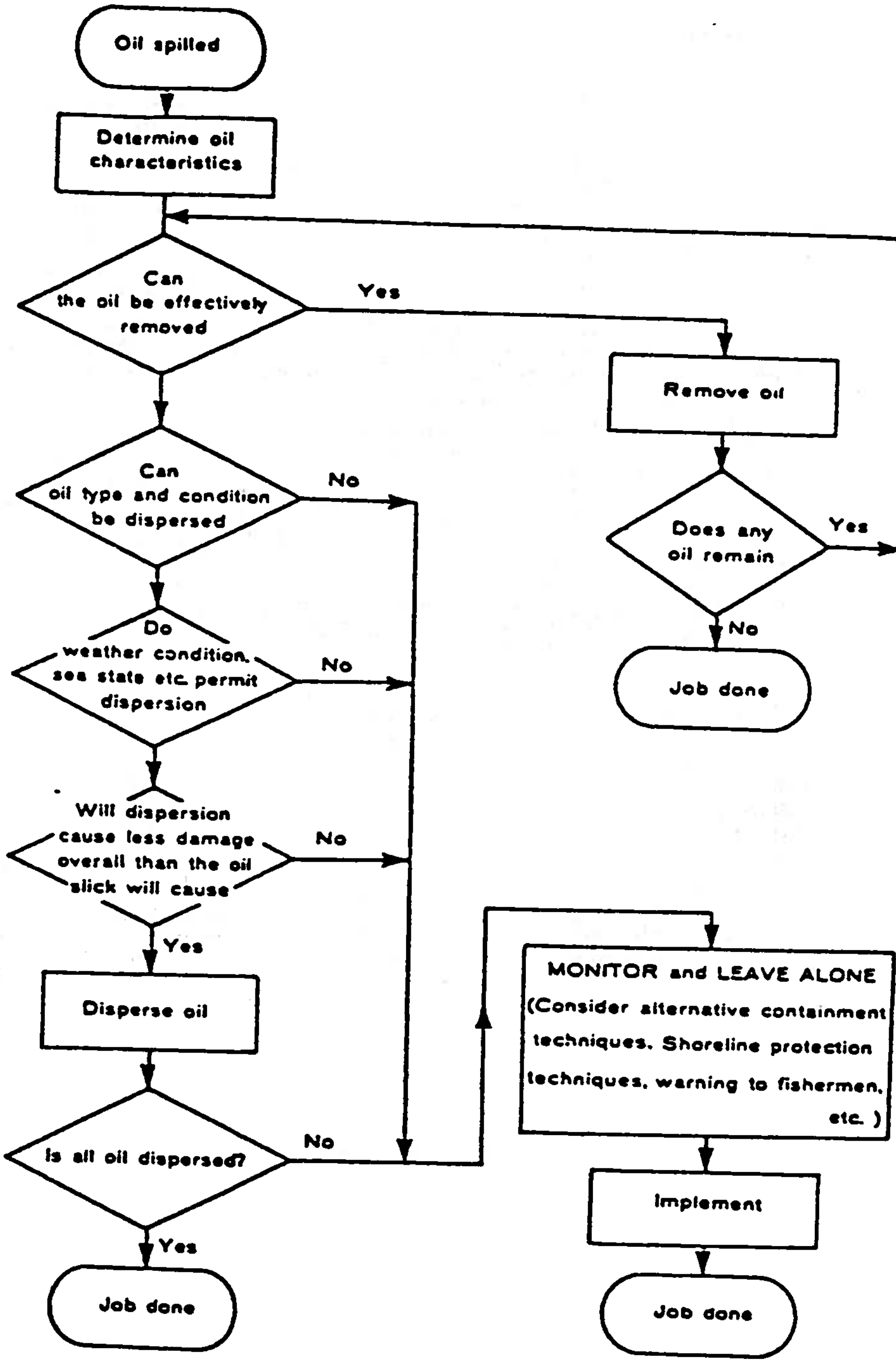

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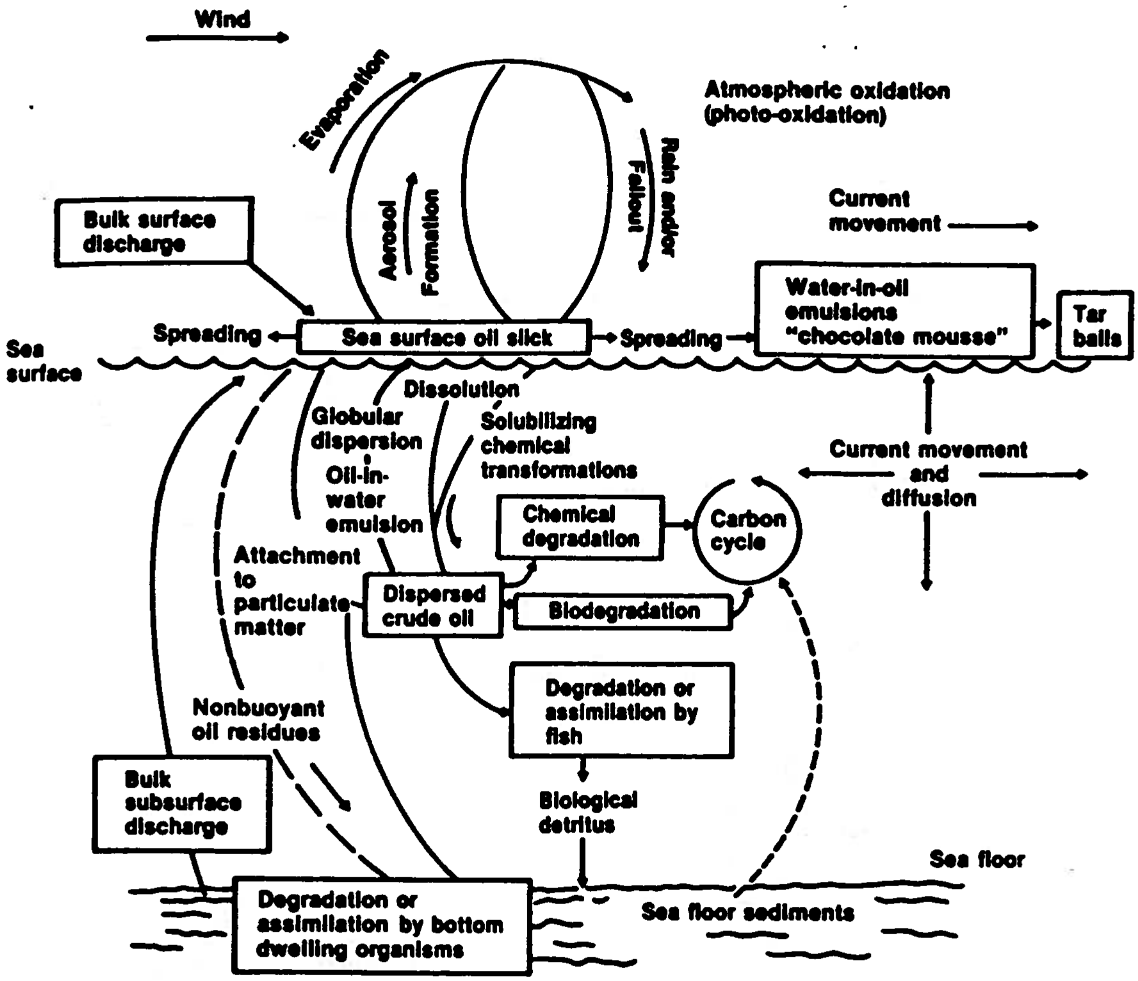

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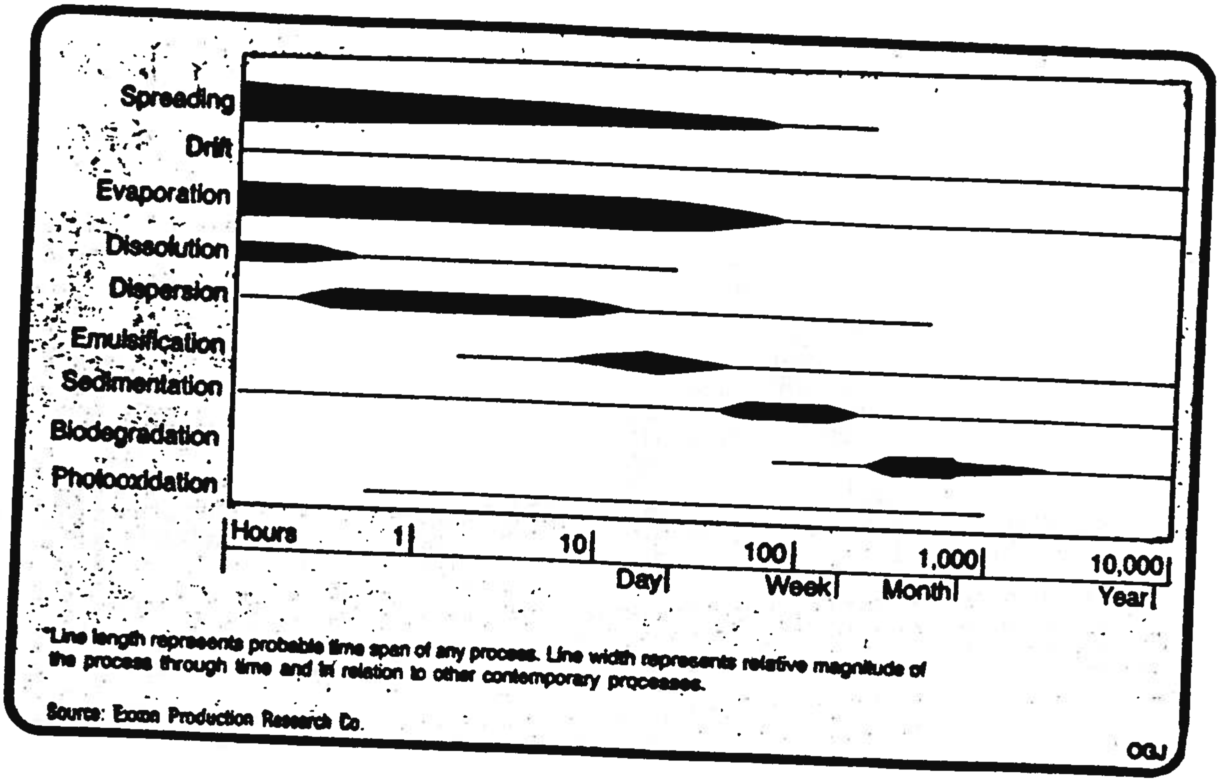

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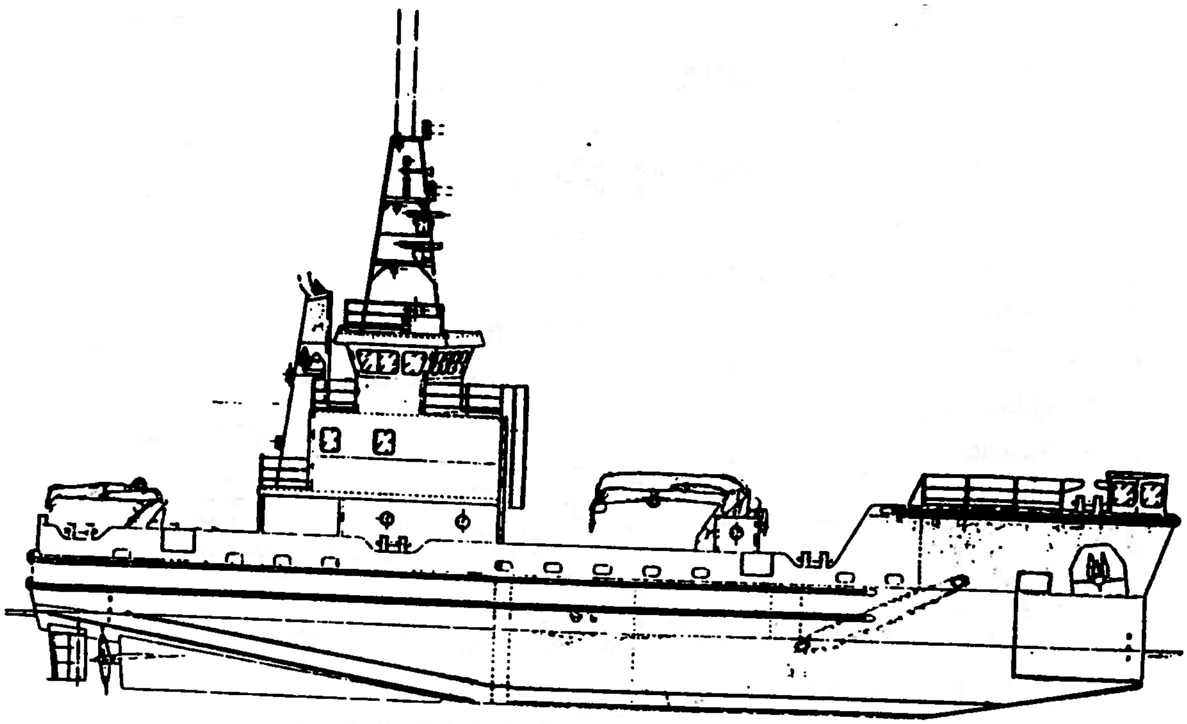
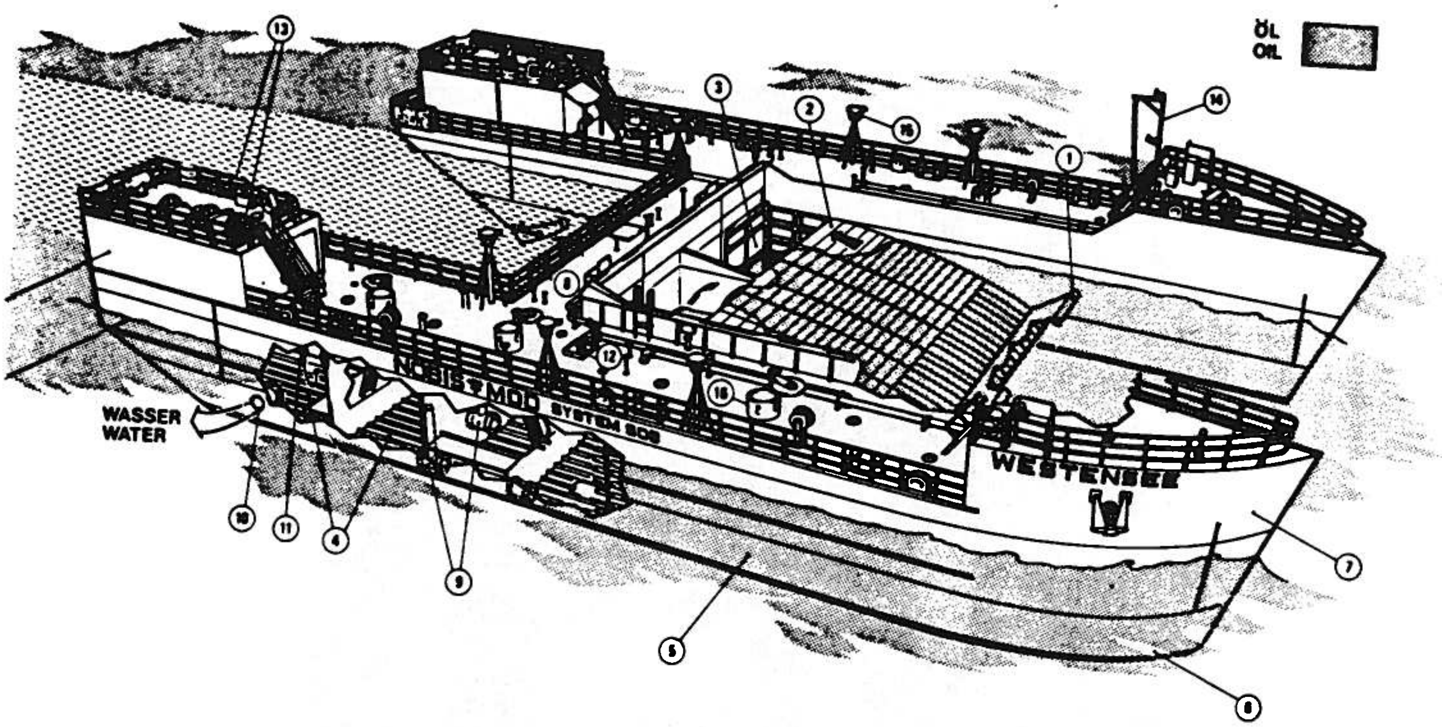
Figure 21



Source: [15]

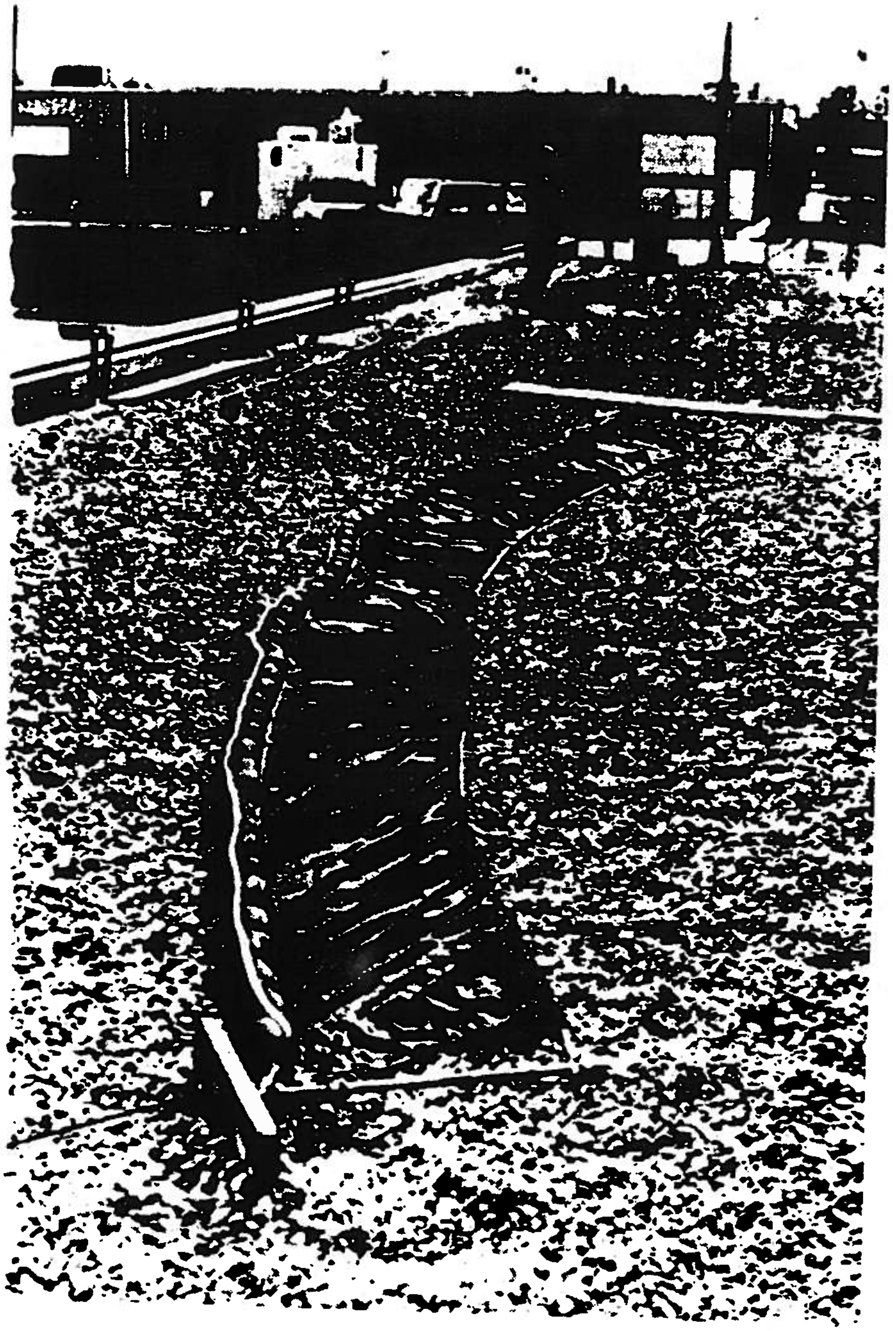
Figure 22



① weir
② ramp
③ collective trough
④ setting tanks
⑤ oil collecting tank
⑥ buoyancy tank
⑦ ballast-trim tank
⑧ box transverse girder with pumproom
⑨ overflow pipes
⑩ draining valve
⑪ floating sucker
⑫ oil transfer station
⑬ mooring equipment
⑭ signal mast
⑮ tank ventilation
⑯ tank hatch

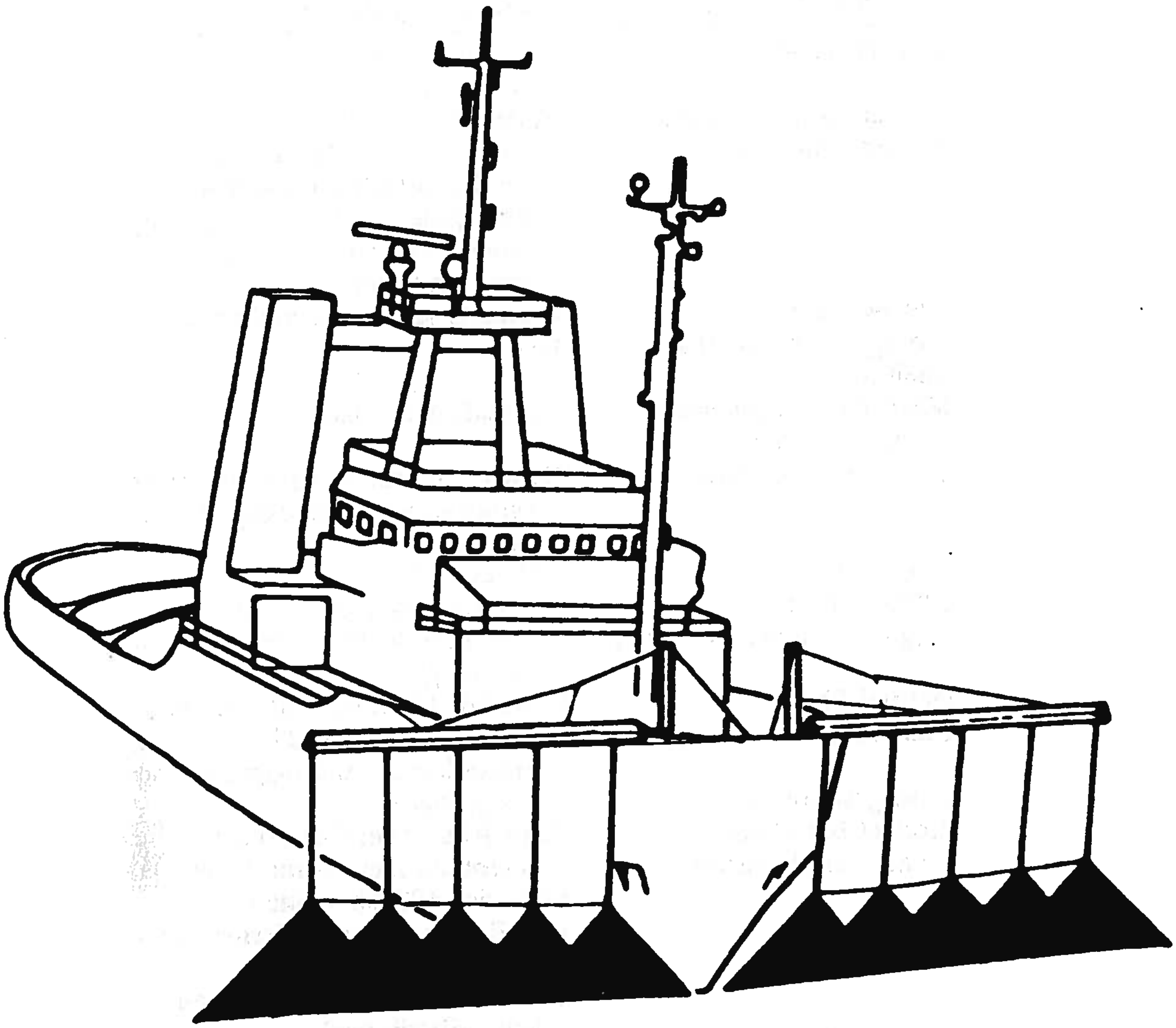
Source: [14]

Figure 23



Source: [3]

Figure 24



Source: [12]

Table 1: Profiles of sorbent products

Sorbent profile:	Natural organic—cellulose/vegetable
Generic products:	Ground corn cobs, sawdust, straw, peat moss
Product configurations:	Particulate, pillows
Recommended use:	Land (One manufacturer offers a biodegradable natural fiber in pad, pillow, boom, blanket, rug, sweep, and strip,which can be used on water.)
Restrictions:	Products sorb water and sink.
Storage requirements:	Dry
Shelf life:	
Methods of deployment and retrieval:	Manual, mechanical
Safety requirements:	Dust respirator and eye protection required when handling particulate form
Reusability:	Not reusable
Effectiveness: (g oil takeup : g sorbent)	5 : 1 (No data available on effectiveness relative to petroleum product viscosity)
Natural fiber:	Low: 26 : 1 Medium: 20 : 1 High: 13 : 1
Comments:	Effectiveness reduced by rain, dense groundcover, and rugged terrain
Biodegradability:	Biodegradable
Product brand names and manufacturers:	High Absorbent Compound (Geotech Development Corp.) Slickwick (Slickbar, Inc.) Lite R Cobs (The Andersons Cob Division) Bedex (Thermo-Cell Insulation, Ltd., distributor) Sorb-oil (Innova Corp.) Sea Curtin Sorbents (Kepner Plastics Fabricators, Inc.)

Source: [7]

Table 2: Bioremediation case histories

	Treatment History				Monitoring		
Incident	Location/Substrate	Type of Oil	Type of Bioremediation	Products	Days Monitored	Endpoints Measured	Application Effective?
Exxon Valdez	Prince William Sound, Alaska shorelines	Prudhoe Bay crude	fertilizer	Inipol Customblen	1989: 99 days 1990: 55 days	oil residue weight GC/MS respirometry microbial counts acute toxicity water quality chlorophyll	yes, partially
Prall's Island	Arthur Kill, New Jersey gravel beach	fuel oil	fertilizer	Customblen	92 days	TPH* GC/MS microbial counts water quality	no
Apex Barges	Galveston Bay, Texas marsh	partially refined (catalytic feed stock)	microbial	Alpha BioSea Miracle-Gro	11 days	TPH percent oil in mousse acute toxicity	inconclusive
Seal Beach	Southern California marsh	crude	microbial	INOC 8162 Miracle-Gro	35 days	GC/MS phenanthrene mineralization respirometry microbial counts	no
Mega Borg	Gulf of Mexico open water	Angolan crude	microbial	Alpha BioSea	7 hours	percent oil in mousse acute toxicity	inconclusive

(Parris and Albrecht 1990; Prince et al. 1990; Texas General Land Office 1990; Exxon 1991; Goodbred 1991; Mearns 1991; Pritchard 1991; Pritchard et al. 1991; U.S. EPA 1991)

*total petroleum hydrocarbons

Source: [10]

Table 3: Summary of the main cleanup methods

Mechanical methods	- Not applicable in rough sea states, very sensitive to sea state - Good from environmental point of view (do not add strange agents to the sea) - Recovery and possible reuse of the oil - Effort increases with the size of the spill more than other methods - There is much experience with its use
Dispersants	- Suitable for large marine oil spills - For efficiency they must be applied during the first hours of the spill - Not very efficient in calm seas - Before use must check potential environmental damage caused by dispersants
In-situ burning	- Suitable for large marine oil spills - For efficiency must be applied during the first hours of the spill - Risk of explosion to the vessel causing the spill - Environmental damage exists, there is a trade-off with air pollution
Bioremediation	- Promising method since it is excellent from an environmental point of view - Takes time to act, not suitable for fast response - There is not much experience with use because it is difficult to measure and control the marine environment