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Determination of Efficient Recovery Methods Based on Nature of Spilled Oil

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Abstract: *Oil spillage is one of major disaster that hits the marine ecosystem that stands on par with the natural disaster in terms of the adverse threats it poses. Once oil spill occurs, it poses adverse effects on marine as well as coastal ecosystem. This research paper reviews upon the occurrence of major oil spill, its effects on marine ecosystem and currently used technologies to tackle oil spillage. The measures taken to remove the spilled oil and its effectiveness have been analyzed in the second phase of study. In the third phase of study, major technologies used to recover and cleanup the oil has been studied and merits\demerits of each has been described. The most suitable method for various oil spillage situations is proposed. The scope of emerging technologies in this field is also discussed for future analysis.*

Index Terms : *Marine pollution, Oil spillage*

I. Introduction

OIL or "black gold" is still the largest source of power used by the industry sector. The demand for oil is increasing day-by-day and is substantiated by expanding submarine oil pipelines, distribution of oil and its derivatives by using tankers to carry it to many destinations. This leads to increased chances of oil leakage in the sea either by leakage from submarine oil pipelines or accidents with the tankers. In the past, such miss-happenings lead to major disasters of oil leakage in the high seas. When an oil spill occurs, either in open or confined seas, the ecological damage on the local ecosystem could be huge and irreversible. Birds, fish, sea mammals and several marine invertebrate species are among the groups most impacted, and in some cases the whole food chain is affected [1]. Oil spills can negatively influence the physiology, immunology, and development of some organisms, but their most evident effect is usually an important decrease or disappearance of populations of marine fauna and flora within the affected area. The average quantity of ship-generated oil that ends up in the sea exceeds 350,000 tons per year [2].The occurrence of large and catastrophic spills that can release up to 30,000 tons of oil or even more is relatively rare. The frequency of such events in recent times had gone down perceptibly. But this took a different turn when we experienced the worse and largest oil spill ever recorded in history, the deep water horizon oil spill also known as the Gulf of Mexico oil spill or the BP oil spill [3]. Though some oil spills may not be as extensive or worse like the BP oil spill they still possess the capability to cause serious ecological risks to sea birds and mammals. The result is the long term environmental disturbances that occur in coastal zones. Oil spills also have an impact on the economic activities of the people that depend on the sea for a livelihood. Public outcry over oil spills has led to the coming up of impressive technical, political and also legal experiences in managing oil spills.

II. Environmental Effects Of Oil Spill

The sea includes a wide variety of ecosystems, species, and habitats. When looking at the effects of oil spills, it is convenient to divide these into fish, plankton, benthic invertebrates, exotic organisms, marine mammals, intertidal and shoreline organisms, marine plants, and special ecosystems. Oil spills result in both immediate and long term damage to the environment. Some of the damages that oil spills cause on the environment can last for decades after the spill occurs. There are various notable effects caused by oil spills on the environment. Harsh effects that oil has on the coastline or shoreline are the highly visible parts of an oil spill. Unless a concerted effort to clean up the shoreline is made the oil basically stays on the shore until the weather and time breaks it down a process that is extremely slow. The gooey mass that makes up an oil slick will litter the shoreline with an ugly black tar making it very dangerous since the shoreline is where much marine life is concentrated. Shorelines provide nurseries for fish and marine life, by contaminating the shoreline the oil possess a threat and are dangerous to the marine life in the area.

A. Fish

There is often concern about the effect of oil in fish, from both an environmental and a commercial viewpoint, as fish arean important food source. Both mid-water and bottom-dwelling fish are exposed to toxicity primarily through aromatic hydrocarbons in the water column. Oil exposure can cause a range of physiological and pathological changes in fish. Some of which are temporary and are not a risk to health or survival. Some of the effects noted on fish such as eye cataracts, structural changes of fins, and loss of body weight may be related to the stress of exposure and not directly to the hydrocarbons. Fish species that live or spend time close to the water surface, the shore, or these floor are the most vulnerable to oil spills. Species with eggs or larvae that stay close to the surface and those that feed on organisms near shorelines or on the sea bottom are at greatest risk. Fish that spend most of their life stages in open waters are rarely at risk.

B. Marine Mammals

The effects of oil spills on marine and other aquatic mammals vary with species. Seals, sea lions, walruses, whales, dolphins, and porpoises are discussed here, as well as the effects on polar bears and otters. Seals, sea lions, and walruses are particularly vulnerable to oiling because they live on the shorelines of small islands, rocks, or remote coasts with few options for new territory. Despite this, only the young are killed by severe oiling. External oiling of young seals or sea lions generally causes death because their coats are not developed enough to provide insulation in an oiled state. Oil is often absorbed or ingested and mothers may not feed their young when they are oiled. It was found that polar bears that are oiled ingest oil through grooming themselves, resulting in death or severe illness. Unfortunately, polar bears are attracted to oil, particularly lubricating oil, which they will actually drink. This generally causes temporary illness, but in the case of an oil spill, it could result in death.

C. Marine Plants

Marine plants cover a wide spectrum of plant families and algae. Intertidal algae, macro-algae, and sea grasses are of particular interest during oil spills. Intertidal algae are an important food source for much of the intertidal fauna and like the fauna can be severely affected by an oil spill. Although readily killed by even a moderate oil spill, intertidal algae are usually the first biota to recover after a spill. Plants will show sub lethal effects of leaf loss, color changes, reproductive slowdown, reduced growth, and accumulation of hydrocarbons. They also slowly depurate or cleanse itself of hydrocarbons in clean water. As these plants make up the habitat for complex ecosystems including many forms of animals and other algae, the entire ecosystem can be affected if they are damaged. Recovery for both types of plants and their habitats may take years.

D. Plankton

Plankton are small plants and animals that live in the water and include phytoplankton and zooplankton. Phytoplankton are microscopic plants such as algae and diatoms that live in the top layer of the water as they depend on light for photosynthesis. Zooplankton are microscopic animals that feed primarily on phytoplankton. Plankton are important because they are at the bottom of the aquatic food chain. Thus, oil ingested or absorbed by plankton is passed higher up the food chain, until it is finally ingested by fish and mammals.

E. Birds

Birds are the most visible biota affected by oil spills, especially in the aquatic environment. Oil contaminates feathers when the birds come into contact with slicks on water or shorelines. For sea birds, this is particularly dangerous because when their feathers are oily, their insulation and buoyancy properties are decreased. Once oiled, a bird rapidly loses its body heat, especially at sea and this may cause death. Oiled sea birds may stay on land where their temperature loss is not as great. In doing so, however, they are away from their source of food and may die of starvation. Birds clean their plumage by preening and, in doing so, may ingest some of the oil. Birds may also ingest oil by eating oiled prey. While ingestion of oil may cause death, it is more likely to cause sub lethal effects such as gastrointestinal dysfunction, liver problems, pneumonia, and behavioral disorders. Contaminated birds may transfer oil to their eggs or young. It has been found that only a few drops of fresh oil can kill the young in an egg. Even when birds ingest only a small amount of oil, they may stop laying eggs or the number of eggs may be reduced. A small amount of oil can also affect the hatchability of the eggs. Shoreline dwellers and feeders, which include ducks, gannets, and cormorants, are among the most susceptible birds to oiling.

F. Intertidal Fauna

Intertidal fauna include animals that live in the shoreline zone between the high and low tides. These organisms are the most vulnerable to oil spills because they and their habitat are frequently coated during oil spills. Typical fauna include the mobile crabs, snails, and shrimp, sessile (immobile) barnacles and mussels, and sedentary limpets, periwinkles, and tube worms. Heavy oiling will generally kill most species. The area does recolonize after the spill with the mobile species returning first, but recovery takes months and sometimes years. Decolonization by plants and sessile species is the major factor in site restoration.

III. Methods Of Present Cleanup

G. Surface dispersants

Mode of use: The dispersants are chemicals that are sprayed on the spill site using aircrafts, boats etc. which decompose the oil on the surface to smaller droplets that will degrade away through natural process.

Advantage: The chemicals can be sprayed over a large area within a short time thus enabling to reduce the toxic effects of oil spill .

Disadvantage: The chemical dispersant itself getting toxic in addition to the toxic fuels being spilled [5].

Fig 1.The oil after application of dispersants

B. Underwater dispersants

Mode of use: This method is used when spill occurs underwater. A specialized underwater vessel is used to spray the dispersant under the water.

Advantage: The oil can be decomposed to smaller droplets even before they reach the surface.

Disadvantage: The underwater dispersant may give out toxic substance during decomposition .Also the use of an underwater vessel at extreme depth is not possible [5].

C. Controlled Burns

Mode of Operation: The spilled oil is contained using a fireproof boom and the oil is set to fire in a controlled manner. A picture of controlled burning is shown in fig 1.

Advantage: The oil is removed quickly from the surface of water.

Disadvantage: The toxic smoke coming out from the fire causes harmful air pollution [5].

Fig. 2.The image of a controlled burning procedure.

D. Booms and Skimmers

Mode of operation: Booms are used to contain the spilled oil from spreading to large areas and limit the extent of spillage. Once the oil is contained a skimmer is used to skim off the oil from the surface of water. The skimmer used maybe of different types mainly classified into as Weir skimmers, Lyophilic and Non-Lyophilic skimmers [5], [6].

Fig. 3 the image of a boom deployed in an oil spill.

E. Sorbent Materials

Mode of Operation: According to EPA, sorbents are insoluble materials or mixtures of materials used to recover liquids through the mechanism of absorption, or adsorption, or both. Absorbents are materials that pick up and retain liquid causing the material to swell (50 percent or more).Adsorbents are insoluble materials that are coated by a liquid on its surface. To be useful in combating oil spills, sorbents need to be both lyophilic (oil-attracting) and hydrophobic (water-repellent) [7], [5].

Advantage: The materials can be easily deployed within a short period of time restricting the spread of oil to vaster areas. Combined with a boom arrangement the efficiency of sorbent materials can be increased.

Disadvantage: The materials may absorb not just oil but also water and sink down. This makes it impossible to retrieve them and cause more problems.

F. Manual cleanup.

Mode of Operation: This method is the most basic one in which the oil which washed up ashore is removed by manual labor. Workers are put to work on cleaning the shore using shovels and rakes often using the help of bulldozers and tractors.

Advantage: Little skill and training is required to clean up the shore and with more machinery, the process can be done at a faster rate.

Disadvantage: The use of machinery in excess can lead to destruction of biodiversity in the shores. Also, this technique doesn't prevent the oil from spreading into the shore [5].

Fig. 4. People engaged in manual oil spill cleanup

G. Bioremediation.

Mode of Operation: It is the use of microorganisms which eat up the oil to increase the rate of decomposition of oil. Usually it is the action of bacteria's which help decompose oil. By increasing the amount of bacteria, the same decomposition can be achieved at a faster rate. For rapid multiplication of bacteria's, sulfates or nitrate fertilizers are added to bacterial colony and once the bacteria starts growing it starts decomposing the spilled oil washed up ashore

Advantage: This method doesn't affect the biodiversity much as it doesn't add any chemicals to the environment and the whole things works naturally. Cost effective and safe.

Disadvantage: It is a slow process. [9], [5].

H. Gelling agents

Mode of operation: These are chemicals that solidify the oil into rubber like material which float on water and can be removed using nets, skimmers etc.

Advantage: Easy to use after a spill with less time required for deployment.

Disadvantage: The quantity of chemical solidifiers required very high that it is restricted to be used in small to moderate spills [10].

Fig. 5.Oil spill site after using gelling agent

I. Centrifugal-water oil separator

Mode of Operation: A mix of oil and water is pumped constantly into a cone shaped separating apparatus at an angle, which creates a spinning vortex. The filtration is a result of the force balance that occurs on fluids in a vortex. High density liquids will move to the outside, along with any contaminant, displacing the lower density liquids to the inside (center of rotation). Water, being the more dense liquid, sits on the outside and is removed through a discharge outlet. Any segregated oil can now safely be recovered through a suction orifice at the center. The process will continue to function in this fashion as long as sufficient oil is added to maintain coverage of the suction orifice [11] [12].

Advantage: The low cost of operation, versatility and efficiency are the known advantages.

Disadvantage: To cleanup sea water using this method takes time as it has limited capacity to handle seawater.

IV. Determination Of Oil Spill Cleanup Method Based On Spilled Oil

The nature of oil spill is mainly depended on factors such as quantity of spillage, the type of oil and the weather conditions during an occurrence. Even though we have many oil spill cleanup methods, the efficiency of cleanup varies according to situation. It is not possible to predict the amount of oil spilled or the weather condition before an oil spill. So an understanding of oil property and behavior in water is crucial in determining the cleanup method to be used.

The oil is a chemical which contains many chemical constituents. The chemical composition determines the nature of oil in water. The main classification of oil is given below.

A. Gasoline

It is a petroleum derived liquid that is primarily used in Internal Combustion Engines such as in our automobiles. Also known as "Petrol". Gasoline, as used worldwide in the vast number of internal combustion engines used in transport and industry, has a significant impact on the environment, both in local effects (e.g., smog) and in global effects.

B. Diesel fuel

Diesel fuel is any liquid fuel used in diesel engines, originally obtained from crude-oil distillation (petro diesel), but alternatives are increasingly being developed for partial or total substitution of petro diesel, such as biodiesel (from vegetal oils), and synthetic diesel (usually from a gas fuel coming from coal reforming or biomass, also named gas to liquid fuels, GTL). In all cases, diesel nowadays must be free of sulfur.

C. Light Crude Oil

It is a liquid petroleum product that has low density and flows freely at room temperature. Light crude oil is liquid petroleum that has a low density and flows freely at room, temperature. It has a low viscosity, low specific gravity and high API gravity due to the presence of a high proportion of light hydrocarbon fractions. It generally has a low wax content. Light crude oil receives a higher price than heavy crude oil on commodity markets because it produces a higher percentage of gasoline and diesel fuel when converted into products by an oil refinery.

D. Heavy Crude Oil

Heavy crude oil or extra heavy crude oil is any type of crude oil which does not flow easily. It is referred to as "heavy" because its density or specific gravity is higher than that of light crude oil. Heavy crude oil has been defined as any liquid petroleum with an API gravity less than 20°.It is an oil that is highly viscous and cannot flow easily.

E. Intermediate Fuel Oil

It is a mixture of heavy residual fuel and diesel fuel used primarily as a propulsion fuel for ships.

F. Bunker Fuel

It is a heavy residual oil remaining after the production of gasoline and diesel fuel in refineries and often used in heating plants. Bunker fuel is the generic term given to any fuel poured into a ship's bunkers to power its engines.

G. Crude Oil Emulsion

Emulsion of water in a medium crude oil. An emulsion is dispersion (droplets) of one liquid in another immiscible liquid. The phase that is present in the form of droplets is the dispersed or internal phase, and the phase in which the droplets are suspended is called the continuous or external phase. For produced oilfield emulsions, one of the liquids is aqueous and the other is crude oil. The amount of water that emulsifies with crude oil varies widely from facility to facility. It can be less than 1% and sometimes greater than 80%.

Property	Units	Gasoline	Diesel	Light Crude	Heavy Crude	Intemediate Fuel Oil	Bunker C	Crude Oil Emulsion
Viscosity	mPa.s at 15°C	0.5	2	5 to 50	50 to 50,000	1000 to 15,000	10,000 to 50,000	20,000 to 100,000
Density	g/mL at 15°C	0.72	0.84	0.78 to 0.88	0.88 to 1.00	0.94 to 0.99	0.96 to 1.04	0.95 to 1.0
Flash Point	°C	–35	45	–30 to 30	–30 to 60	80 to 100	>100	>80
Solubility in Water	ppm	200	40	10 to 50	5 to 30	10 to 30	1 to 5	–
Pour Point	°C	NR	–35 to –1	–40 to 30	–40 to 30	–10 to 10	5 to 20	>50
API Gravity		65	35	30 to 50	10 to 30	10 to 20	5 to 15	10 to 15
Interfacial Tension	mN/m at 15°C	27	27	10 to 30	15 to 30	25 to 30	25 to 35	NR
Distillation Fractions	% distilled at							
	100°C	70	1	2 to 15	1 to 10	–	–	NR
	200°C	100	30	15 to 40	2 to 25	2 to 5	2 to 5	
	300°C		85	30 to 60	15 to 45	15 to 25	5 to 15	
	400°C		100	45 to 85	25 to 75	30 to 40	15 to 25	
	residual			15 to 55	25 to 75	60 to 70	75 to 85	
	NR = not relevant							

Fig. 1.The typical properties of various oils are given here.

The above mentioned properties greatly affect the way the oil behaves in water or when it reaches shores through water.

The cleanup method is also depended on these properties. The present cleanup methods has been discussed above.

Though we have cleanup methods to recover the spilled oil, the process may take a while according to the quantity and extent of the spill. During this period between cleanups, some important changes occur to the oil which changes its behavior both physically and chemically. These changes are termed as weathering. The rate of weathering is depended on the conditions at sea as well as time. But weathering is most active just after the occurrence of spill and its rate vary as time passes.

Evaporation is the most important weathering process followed by emulsification. Emulsification is the process of forming oil-water emulsion and lead to drastic physical changes. The rate of evaporation of oil is shown in the column chart.

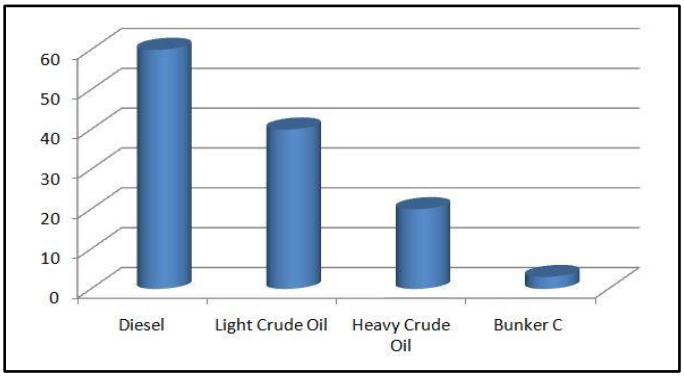

Fig. 1.The rate of evaporation of oil during a time period of 48 hours and temperature condition of 15 degree Celsius.

The major changes that occur in physical behavior include change in viscosity and density.
Therefore the deployment time is crucial in determining the success of recovery. A successful deployment of boom to contain the spill increases the efficiency of any cleanup method.

1) Skimmers

The skimmers can be used most efficiently inside a boom as the oil is more concentrated inside tithe efficiency of skimmer also vary upon type of oil. When skimmers were used to collect Heavy crude oil and Light crude oil got collected more than Diesel or Bunker C oil. Also the efficiency of skimmer is much depended on its configuration. The recovery rate for oil types in cubic metre per hour is shown.

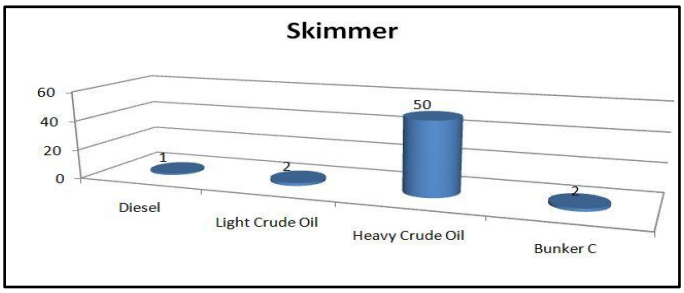

Fig 2.The effectiveness of dispersants

2) Dispersants

These chemical compounds help to break the oil film on water. The rate of their dispersion has been found to be maximum on Diesel and lowest on Bunker C oil. The light crude oil and heavy crude oil stands between the two. Also the effectiveness of dispersant is closely associated with sea conditions and the amount of dispersant used. The effectiveness in high energy sea and low energy sea has been compared.

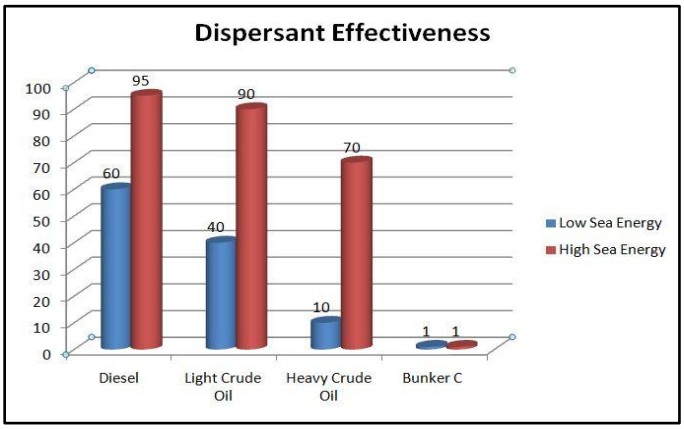

Fig. 3.The effectiveness of dispersants

3) Sorbents

Since sorbents absorb oil as well as water it is necessary to have high Oil Recovery which is the particular weight of an oil compared to the original weight of the sorbent. Also care must be taken to use sorbents that do not sink into water upon absorbing the oil and water mixture. The Oil recovery rate of synthetic sorbents has been compared below. Here the recovery rate is much depended on oil thickness, surface type and other factors.

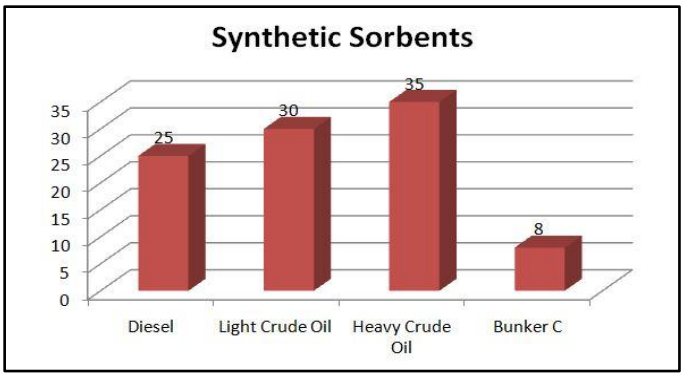

Fig. 4.The oil recovery rate of sorbents.

Here the analysis is conducted for major cleanup methods because other methods are still inferior to these methods. In situ burning is resorted for oil spill cleanup. But they cause environmental issues by emitting toxic gases while cleanup and hence has been avoided from analysis.

It must be remembered that an oil spill cleanup using only one method is never possible. Various methods are used as auxiliary means to help each other.

After checking the results from analysis we can arrive at a table which shows the most effective method for that particular oil.

The formulated table is shown below.

OIL	Cleanup method
Diesel	Surface Dispersant
Heavy Crude Oil	Skimmer
Light Crude Oil	Skimmer
Bunker C Oil	Sorbents

Fig. 4.The best suitable cleanup method is suggested for a particular oil

V. Future Cleanup Methods.

A. Grooved Disc Skimmer Technology

Grooved disc skimmer is an improvement over existing disc skimmers. The skimming discs are provided with grooves which increase the surfaces area resulting in skimming efficiency. This technology is patented by a company named "ELASTEC". The company was awarded first prize in "Wendy Schmidt Oil Cleanup X Challenge" for the innovative technology by recovering at a rate of 17677.87liters per minute with an oil to water efficiency rate of 89.5%.[13]

B. Magnetic Separation Using Nanotechnology

This method uses magnetic nanoparticles and a magnetic field system to collect oil from water. The nanoparticles are water repellent and when poured into oil-water mixture sticks with oil. The surfactants present on the nanoparticles are hydrophobic and lyophilic and thus enables to stick with oil. The process is envisioned to be conducted on a recovery vessel so that a possible mixing up nanoparticles directly with sea is avoided and also helps to calculate the concentration of nanoparticles to be used in the mixture. [14].

C. Basalt Fiber Technology

Basalt fiber is manufactured from basalt rock which is a lava derived rock. Basalt rocks are melted and extruded though small opening to produce basalt fiber. The basalt fibers are lyophilic and hydrophobic which help them to absorb oil up to 75 times their own weight. So when the fibers come into contact with oil, the oil alone is absorbed, which makes basalt fibers usable in oil spills. The oil can be reused and basalt fibers can be recycled and be used for other purposes. [15], [16].

D. Microbes

The use of genetically modified microbes to eat up oil is being tested by scientists. The scientists are looking forward to create microbes which would eat up oil and die after it has been completed thus ensuring safety to the biodiversity. [17].

E. *Swarm Robotic System*

Swarm robotic system is a collection of individual robots working collectively to achieve a desired task. This system could be implemented on sea with each individual robot having a cleaning system on board and being coordinated by GPS during cleanup. The cleaning system may include anything from simple burring to collection and dumping (on to a floating barge) system. The research is going on to create a robot with proper cleaning method that can cleanup oil effectively and efficiently [18].

F. Sponges

As a sponge would naturally absorb water, a sponge that would absorb oil is in the making. The sponge being tested under Switzerland's Material Science lab can hold oil up to 50 times its weight and continue to float in water. The latter combined with absorption capacity hold promising prospects of using such sponge with boom arrangement to attain maximum efficiency. [19].

VI. Conclusion

Recovery of oil from seas is a mandatory process. Even though there are a lot of recovering methods till date we should improve our methods in the path of an effective and efficient scenario. As our history reveals us the fact that most of the oil spill situations were ended with worse conditions just because of ineffective recovery methods. This may due to the behavior of oil towards different recovery systems. This area should be focused and we have to make use of the best recovery method which suits for the nature of the oil.

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