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# Separation of oil and water in oil spill recovery operations*

Knut Gaaseidnes and Joseph Turbeville

*MiljoLab AS, Innherredsveien 10, N-7014 Trondheim, Norway*

*Abstract:* The separation of water from oil that is collected in any oil spill recovery operation is a continuing and necessary requirement during every stage of the effort. Its importance is reflected in the cost of transport and storage of large volumes of oily water, the salvage value of separated oil and the added labor costs associated with long-term recovery operations.

This paper addresses the effects of weathering and emulsion generation which increase the problems normally associated with water extraction. Separation theory, practical separation technology and recommendations for the future direction of research and development are presented.

## INTRODUCTION

Processes for the separation of oil and water are very well known to the oil industry. There are no principal differences in the technology required when separating oil and water mixtures which have been recovered during an oil spill clean up operation. The main difference between separation of oil and water connected to production and handling of oil, as compared to an oil spill recovery operation is that the influent may, and generally does, vary significantly.

The ratio of oil to water collected during a recovery action can vary from as much as 90% oily phase during boom containment and collection in calm water, to as much as 98% oil free water using the same equipment, but with three meter waves. Another problem which exists is that you can never be prepared for all possible scenarios. Spillages of all types of oils occur under all types of sea conditions. The equipment, utility systems and chemicals must be of a general and flexible type that can adapt to all situations.

There are about 50 commercial oil water separators that are marketed for oil spill recovery purposes and can be found listed in the World Catalogue of Oil Spill Response Products [1].

## THE FLUIDS TO BE SEPARATED

Before we begin to discuss separation technology and equipment, it is useful to elaborate on what we are going to separate. Primarily it is water and oil or rather an oily phase. There are two types of water, free water and emulsified water. Most crude oils and intermediate to heavy products will emulsify when spilled at sea, the vast majority forming water-in-oil-emulsions (w/o), often nicknamed 'chocolate mousse'. The w/o emulsions can be stabilized by natural emulsifiers within the oil, by colloidal particles in the sea or from by-products of biodegradation of the oil. This weathering process is very complicated and not too well understood.

### Droplet formation

The initial intrusion of spilled surface oil into the water column on the open sea is caused by agitation from turbulent surface conditions. Primarily, breaking waves provide the largest contribution of energy necessary for the process. However there are other smaller contributing factors such as ship traffic and small craft movement through surface oil. In inland waters where there may be a fast moving flow, the

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movement of oil past piers and rocks or the flow over dams can provide all the necessary energy for the process to occur. This intrusion and diffusion of oil into the water column is called *dispersion* [2]. Evaporation, emulsification and weathering of surface oil can lead to the long-term development of more dense water-in-oil droplets (w/o) which make separation of the collected product more difficult and time consuming.

Studies on water droplet sizes in w/o emulsions have shown that the maximum content of one liquid in another with uniform particle size is about 70% and this is simply a function of geometric packing constraints. By having emulsion particles of different sizes clustered together this ratio can even be larger [3].

It should seem reasonable for the reader to assume that a reverse physical mixing process is possible which produces oil-in-water emulsion (o/w), wherein water is the dispersed substance and oil is the continuous phase. This is indeed the case and sometimes a single emulsion system may include both types of emulsions [4].

## SEPARATION THEORY

We have therefore the situation of separation of either oily droplets from the water (deoiling), or draining of emulsified water from a chocolate mousse type of water-in-oil emulsion. In both cases we are talking about separation, or settling and coalescing of droplets.

When looking into the secret 'black boxes' of the different engineering companies that calculate and dimension separators for oil, water and gas, it is both astonishing and a bit disappointing to see how much they rely on Stokes' law. In-house corrections and experimental factors might be included in the calculations, but still basically they are using his simple equation. This is however, a very good starting point to begin to understand the separation processes.

Stokes' law in its original form in MKS units can be expressed as follows:

$$v = h/t = (D^2 g(\rho - \rho'))/18\upsilon \tag{1}$$

Where: $v$ = terminal velocity of droplet (m/s), $h$ = travel distance of droplet (m), $t$ = time (s), $D$ = droplet diameter (m), $g$ = acceleration due to gravity (9.81 m/s$^2$), $\rho$ = water density (kg/m$^3$), $\rho'$ = oil density (kg/m$^3$), $\upsilon$ = viscosity of the continuous phase (pa·s)

From an analysis of eqn (1) you can determine most of what needs to be done to enhance the separation of the phases.

The droplet diameter is squared and therefore has considerable influence on the rate of separation.

It is important to increase the droplet size. In practical separator engineering this is done by coalescing devices such as oleophilic meshes, porous media, coalescence plates, etc. Applying oscillating electrostatic fields and heat to enhance collisions between droplets, adding surfactants to lower the oil-water interfacial tension destabilizes the natural emulsifiers and lowers the electrostatic repellent forces between the droplets.

Heater treatment units affect the surface chemistry of the complex oil spill emulsions and of oil droplet coalescence processes and are very important to the separation process. The details of these processes are far beyond the aim of this paper, but the interested reader can find an updated review by NN/Separation Technology, 1993.

The droplet separation velocity is also increased if we are able to increase the acceleration beyond that normally provided by gravity (i.e. 9.81 m/s$^2$). This can be done in a centrifuge or hydrocyclone which has been developed for just this purpose. Sophisticated equations have been derived to show separation efficiency and rate centrifuges and hydrocyclones, but for our general analysis it is convenient to put oneself in the position of one of the droplets to be separated and just 'feel' the force produced by the high speed rotation and respond by faster and more energetic separation from the continuous phase. Such devices greatly exceed the normal '***g***' force used in 'gravity' separators. This gives rise to the possibility of construction of very compact separation devices which are able to separate very small droplets. The problem with this type of separation device is the high shear force in a two phase system at the point of entering and leaving the separator. Very often the phases re-mix and the fluid leaves the separator as a milky dispersion product.

The rate of separation is also increased if we can increase the density difference of the phases. This might be done by adding buoyant gas bubbles to the oil droplets or heavy particles to water droplets in w/o-emulsions (chocolate mousse). The application of gas bubble flotation is widely used in the industry and one method for creating gas bubbles is to apply a vacuum above a saturated liquid. This process named *vacuum flotation* forms gas bubbles in the dispersed oil droplets and can be very effective in clearing out oily water. It is believed that part of the reported efficiency of the MSRC oil-water separator is due to this process because of the separators placement at the suction side of the oil cargo pump [5].

The opposite process that of adding heavy particles to an emulsion to adhere to the water droplet and enhance the water droplet separation rate is more rare. This process also has the ability to perforate the rigid interfacial films that are formed when emulsions are weathered, and form channels to drain the water phase from the rigid oily film matrix. The principal author has separated heavy emulsion by adding de-emulsifiers and sand in the size of 2–4 mm with good efficiency. When using this process care must be taken to find the right chemical to prevent the formation of a new waste in the form of oily sand.

Finally the rate of separation of droplets can be increased by lowering the viscosity of the continious phase. When the continious phase is water, little can be done. However in the case of a w/o-emulsion, heating the oil phase will generally lower the viscosity drastically. In the standard heater treatment units used by the petroleum industry to break and separate heavy w/o-emulsions, applying heat both enhances the chemical activity and increases the settling rate by lowering the continious phase viscosity. Continious heating of a large volume of recovered oil spill can be both difficult and expensive.

## PRACTICAL SEPARATION TECHNOLOGY

The current state of the art technology for oil-water separation equipment suitable for maritime oil spill situations which we will discuss has evolved quite naturally from the petroleum production industry. However for future designs, oil spill recovery separators suitable for use with vessels-of-opportunity (VOSS) should attempt to meet the much more difficult set of operating requirements listed below. These were suggested by the US Coast Guard and the Marine Spill Response Corporation (MSRC) after conducting joint tests to evaluate a number of separators listed in the *World Catalog of Oil Spill Response Products* [1].

1. A desired through put capacity for an oil-water separator should be 250–500 gpm. (357–714 BBL/h) or (57–113 $m^3$/h).
2. A desired unit size is one that is relatively lightweight, compact and easily transported. 4000–6000 pounds (1818–2727 kg).
3. A size that will fit within a $(5\times5\times5)\,ft^3$ $(1.52\times1.52\times1.52)\,m^3$ space.
4. An ability to process oil in the viscosity range of 1500–50 000 cSt.
5. Water effluent which is sufficiently clean for discharge directly back into the sea. (The standard acceptable effluent for open sea discharge is $> 15$ p.p.m.)

### Gravity type separators

The simplest separators of this type (Fig. 1) are nothing more than large holding tanks which may be coupled together in series. Debris laden oily water is pumped in and allowed to separate under the action of gravity alone. The surfaced oily flotsam may be skimmed or pumped off and the separated water is drained or pumped off from near the bottom of the tank. When such tanks are coupled in series the oil from the top of the first tank is fed into the second tank and any dispersed water remaining in the oil will have additional opportunity to separate and of course the water quality removed from the bottom of the second tank will exceed that of the first. For cases where the pumping is continuous, the pumping rate determines the residence time and this affects the degree of separation. However it is doubtful if it will be less than 15 p.p.m. at any pumping rate. Figure 1 is an example of coupled separation tanks.

### Gravity type coalescing separators

By creating a situation where oily water is forced to pass through some type of oleophilic medium oil

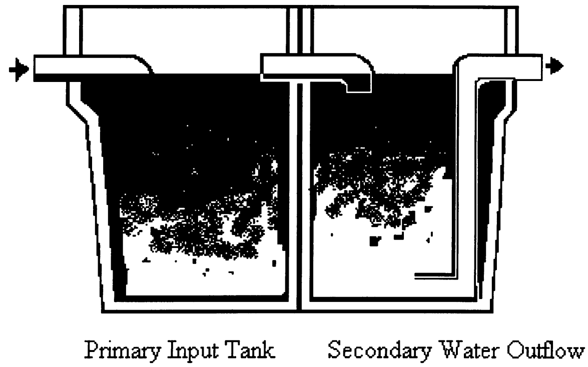


**Fig. 1** Basic type gravity separator.

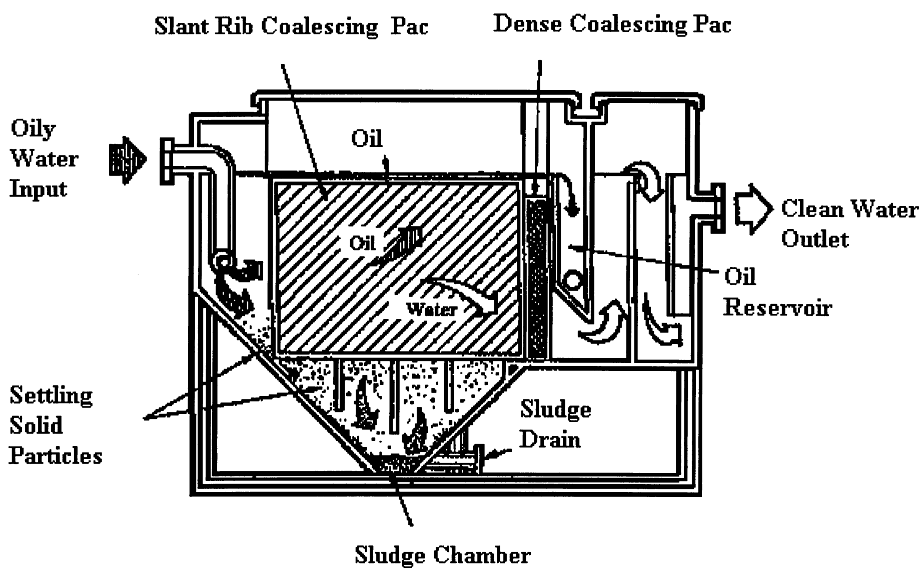


**Fig. 2** Slant rib coalescing separator.

droplets will tend to adhere and collect. They will join together by cohesive attraction thereby increase their overall diameters and reduce the population density of smaller droplets. Since the rate of separation of oil from water is directly proportional to the square of droplet diameter this is the simplest and most significant action which can be taken to separate an oil-water mix. Figure 2 displays an example of such a separator.

This separator is of a type generally employed in the petroleum industry and is very efficient at processing oily waste which is free of large debris and which has a fairly low viscosity (>2500 cSt). Several model sizes ranging from 15 gpm units to 300 gpm (21–429 BBL/h) can be found in the *World Catalog*, however, only the 50 gpm (72 BBL/h) unit falls within range of the suggested weight and size specifications recommended above. Some of the problems presented by this type of separator when used on board a vessel of opportunity such as a barge or ship are:

**1** Severe loss of separation efficiency due to rolling and pitching which causes water to spill over the weir into the oil reservoir.

**2** Ineffective separation when oil or emulsion content exceeds 40–50% of the influent evidenced by an increase of free water in the oil effluent and higher concentration of hydrocarbon in the water effluent [6].

**3** Requires prescreening system to facilitate removal of particles greater than 6 mm in diameter if needed at a particular spill site.

### Inverted cone separators

A unique design for oil–water separation found in the World Catalogue which is also a coalescing device but which differs in the fact that the oily water is pumped in under pressure below the inverted cone and just above the coalescing medium (Fig. 3). Oil which moves into the oleophilic medium of the coalescer slows down and cohesive forces between particles of oil, being greater than the adhesive forces of the oil and the oleophilic medium, cause oil particles to join together diminishing the population density of the smaller oil droplets. Both the separated oil and water exit the unit by gravity flow.

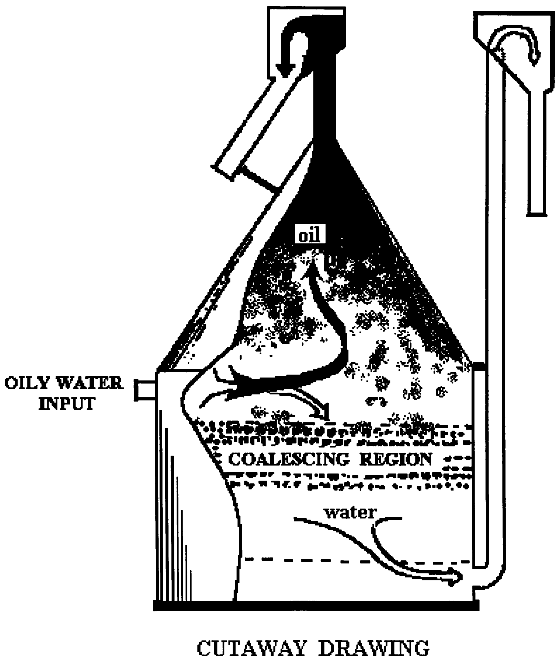


**Fig. 3** Inverted cone separator.

A significant difference between this device and the others discussed so far is that separated oil collects in a deep vertical column assuring that little if any water will exit with the separated oil even when employed on a moving platform such as a ship or barge. Even though the weight and size of the listed available units exceed the targeted future expectations for water borne separators, the manufacture specifies that they can be used on board vessels larger than 65 ft (20 m) in length. Both the through put capacity and effluent quality are shown to be reasonably close to the desired values.

### Skimmer/separators

An oil skimmer concept which has been on the market for many years is now listed in the chapter on oil/water separators in the *World Catalog* [1]. Quite possibly it might be called a floating oil-water separator as it would seem to eliminate some of the obvious problems that exist in trying to develop suitable transportable separators (Fig. 4).

For example there would be no need to be concerned with size and weight of the separator as it is an integral part of the skimmer design. The flow capacities of the two units listed in the World Catalog are ambiguous and have no relation to the desired throughput capacities listed in the first paragraph of this chapter. A search of early product literature from this company reveals that the recovery rate for the 33 ft (10 m) unit '1000 gpm (1573 BBL/h)' is based on a vessel speed of 3 fps (1.8 knots) and a slick thickness of 1 inch (25.4 mm). The recovery rate for the 66 ft (20 m) unit '3300 gpm (4905 BBL/h)' is based on a vessel speed of 4.7 fps (2.8 knots) and the same slick thickness. No 'effluent' measurements are provided because 'the water phase is in open communication with the surrounding sea' [1].

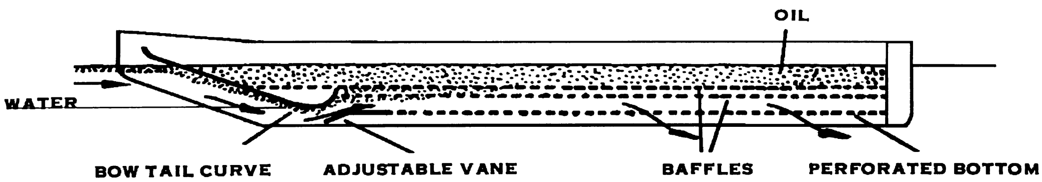


**Fig. 4** Combination oil skimmer/separator.

It would seem to the authors that some means to sample and efficiently test the ‘effluent’ directly beneath these vessels on a continual basis should be required before these units are classified as oil separators, without which they are only collectors of spilled oil and emulsions.

### Centrifugal separators

One of the centrifugal oil-water separation units tested by the US Coast Guard and MSRC was *Vortoil*, an oil spill separation system made by Conoco Specialty Products. It employs a surge tank for its first stage and hydrocyclones in the final two stages. The initial stage provides gravity separation and emulsion breaker treatment. From there oily water is pumped from the tank bottom to the first hydrocyclone. These are long conical devices designed for continuous flow through operation wherein the oily mixture is caused to rotate at extremely high angular velocities causing a radial separation to occur with the most dense medium being pressed to the outer wall and the least dense forming a central core where it is systematically extracted and returned to the surge tank. The water and any oil it may retain due to the extraction process are then fed to the second hydrocyclone for further separation, thereby reducing the water effluent to its lowest possible hydrocarbon level.

By the very nature of their design hydrocyclones function best when the influent oil/water ratio is under the 25% range. At a 25% oil/water ratio, the central core of oil in the hydrocyclone occupies half the overall radius. When the influent oil/water ratio rises to 50% the central core of oil will move to occupy approximately 70% of the radius. In one test of the unit where the oil content of the influent was 76%, the water in the effluent oil went up to an unacceptable level of 86%.

When tests were run with mousse mixtures (25 932 cP) where the influent mousse/water ratio ranged from 15 to 61%, the water effluent ran from 103 to 122 p.p.m. oil and an oil effluent 1–2% water.

The performance of the *Vortoil* system was rated as successful for cases where influent oil/water ratios were kept below 50%. Such ratios could be easily maintained at a spill site by selection of the proper skimming or pumping systems.

## CONCLUSION

The systems described in the previous section were selected because they are typical examples of state-of-the-art oil–water separation devices which are in use today. Adaptation and modification of some of the concepts are necessary and ongoing processes which will allow the improvement of all phases of an oil spill recovery operation.

The possibility of developing floating oil-water gravity separators which can be maneuvered by on scene response vessels has not gone without mention in the literature [1]. The addition of emulsion breakers to floating separators would also help reduce the quantity of water collected thereby further improving oil collection efficiency. This would greatly reduce time loss attributed to transfer operations of recovered oily water. This includes skimmer down time while transfer is made to a barge or shuttle tanker.

The reduction of water content in recovered product also is reflected in the reduction of the number of trips required to move the oil ashore and likewise a reduction in the number of onshore tanks required to hold the oil. All of which go to greatly reduce the costs necessitated by a recovery operation.

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