OIL-IN-WATER SEPARATION

from the state-of-the-art to ZerOil® technology

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1. THE STATE-OF-THE-ART

1.1 INTRODUCTION

Environmental awareness is presently manifesting itself in tightening environmental legislation throughout the world.

Many industries discharge liquid waste contaminated with hydrocarbon or oil-like pollutants. Sources of such waste include petroleum and petrochemicals refining and processing, tramp oils from machine tool coolants, utility operations, sanitary sewage, bilge and ballast water, contaminated surface runoff.

Oil discharges into the environment typically have deleterious effects. Oily waste discharge creates potential safety hazards and consumes dissolved oxygen necessary to aquatic life.

Toxic effects of oil fall into two categories (Laws, 1981):

1. Effects due to smothering or coating of animals or plants with oil. Coating effects are most noticeable when large amounts of free oil are present as in an oil spill. Coating effects are not usually found when only parts per million (ppm) are present, as is the case of an industrial plant effluent.
2. Disruption of animal’s or plant's metabolism due to the ingestion of oil and incorporation of oil into the organism's fatty tissues. Generally, toxic compounds are not water-soluble but are oil soluble, thus tending to accumulate in body fat and damaging animals or human beings.

This paper introduces the oil-in-water separation theory and the basic criteria for selection and design of a separation system, presenting an up-to-date overview of technologies currently available and of their capabilities in terms of achievable discharge levels.

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1.2 BACKGROUND

Oil can exist in water in several forms:

- **Free oil** is composed by oil droplets with a diameter exceeding about 30 microns. It rises quickly to the water surface when given a sufficient quiescent settling period.
- **Mechanical dispersions** are distributions of fine oil droplets ranging in size from less than 1 microns to 30 microns and having stability due to electrical charges and other forces, but not due to the presence of surface active materials.
- **Chemical emulsions** are distributions of oil droplets similar to mechanical dispersions, but which have additional stability due to chemical interactions typically caused by surface active agents present at the oil/water interface.
- **Dissolved oil** is dissolved in a chemical sense; the removal by normal physical means is impossible.
- **Oil that adheres to the surface of particulate materials** is referred to as oil-wet solids.

The degree of an oil/water separation problem depends on the oil droplet size distribution. Separation problems also involve chemicals other than oil, which have an effect on the treatment required.

The degree of the dispersion/emulsion of the oil is difficult to assess, but steps can be taken to discourage its formation by:

a) Preventing from using detergents, which may cause stable chemical emulsions.

b) Ensuring an adequate size piping to avoid the possibility of turbulence and formation of fine droplet dispersions.

c) Avoiding devices such as pumps, especially centrifugal ones, valves, especially globe ones, and other restrictions in flow, such as elbows, tees, etc., or simply unduly small line sizes, which may create shear stresses and enhance the formation of mechanical dispersions. As a matter of fact, where an oil and water mixture has to be presented to the separation equipment, it is of the utmost importance to select a pump which imparts the lowest amount of energy to the mixture, as any excess energy thus created has to be removed by the equipment. For this reason, the use

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of high speed centrifugal pumps, although relatively cheap and small, should be avoided and pumps of low shear characteristics, such as peristaltic or progressive cavity, used.

Ideal inlet conditions for an oil-water separator are:

1. Gravity flow (not pumped) in the inlet piping.
2. Inlet piping sized for minimum pressure drop.
3. Inlet piping straight for at least ten pipe diameters upstream of the separator (directly into nozzle).
4. Inlet piping containing a minimum of elbows, tees, valves, and other fittings.
5. Inlet piping should be as smooth as possible to avoid turbulence caused by pipe roughness. Smooth PVC is preferable to rough concrete. Nevertheless it must be pointed out that a slight amount of turbulence (i.e. at Reynolds numbers close to transition) is likely to increase the probability to coalescence with other oil droplets.

1.2.1 Physical separation

The physical separation of oil from water is governed by the rising velocity of the oil droplet, which follows Stokes' Law.

$$V_p = \frac{g}{18 \cdot \eta} \cdot (D_w - D_o) \cdot d^2$$

V_p = droplet rising or settling velocity (cm/sec)
g = gravitational constant (981 cm/sec^2)
η = viscosity of water (poise)
D_w = density of water (gr/cm^3)
D_o = density of oil (gr/cm^3)
d = diameter of oil droplet (cm).

The hypotheses Stokes' Law is based upon are:

1) The droplet shape is spherical.

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2) The flow is laminar.
3) The Reynolds number is close to unity (always verified if the droplet diameter is small).

Now we can consider the importance of each term included in Stokes' Law in affecting the final oil/water separation.

The importance of viscosity

From Stokes' Law, the lower the water viscosity, the faster the oil rise in water. Increasing the temperature will significantly reduce water viscosity. For example, oil droplets in water at 4°C (40°F) will rise at only half the rate as if they were at 32°C (90°F), if other parameters remain the same.

The importance of specific gravity and oil droplets diameter

From Stokes' Law, the greater the difference in specific gravity between oil and water, the faster the oil droplet rise in water. For example, a fuel oil that has a specific gravity of 0.8 will rise twice as fast as an oil with a specific gravity of 0.9.

The importance of both oil droplet diameter and specific gravity is pointed out in the following table where it may be seen the travel time for a 10 cm (4 in.) vertical distance for various values of the two parameters. Time is expressed in hr.min.sec.

Droplet Diameter (μm)	Specific Gravity 0,8	Specific Gravity 0,9	Specific Gravity 1,15
1	254.50.24	509.40.48	382.15.36
10	2.32.54	5.05.48	3.49.21
50	0.06.07	0.12.23	0.09.17
300	0.00.10	0.00.20	0.00.15
800	0.00.01	0.00.03	0.00.02
1000	0.00.01	0.00.02	0.00.01
3000	less than 1 second	less than 1 second	less than 1 second

Determination of specific gravity, viscosity and oil droplet size

Water viscosities as well as specific gravities of water and oil are readily obtained from literature data. It must be pointed out that, in the design phase of separation

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devices, a wide variety of temperatures (and therefore of viscosities and specific gravities) have to be considered to take into account summer and winter conditions as well as possible process upsets.

Oil droplet size is much more difficult to be determined. The most common way to measure it is by particle size counters such as laser light scattering analyzers.

1.2.2 Mechanical dispersions/chemical emulsions

A mechanical dispersion is a mechanical and apparently homogenous mixture, not a solution, consisting of droplets of one immiscibile fluid dispersed in another continuous fluid. Electric charge may be present on the surface of the dispersed fluid, due to the absorption of ions onto it.

Many mechanical dispersions will separate by gravity if given the necessary time; however some are so finely dispersed by electrostatic forces, that they will virtually never separate if undisturbed.

A chemical emulsion is a chemical homogeneous mixture, not a solution, consisting of droplets of one immiscibile fluid dispersed in another continuous fluid; this mixtures has high stability due to chemical interactions typically caused by surface active agents present at the oil/water interface.

Chemical emulsions, due to the presence of a substance holding the immiscibile fluids bound together, will never separate by gravity.

Processes used to break oil/water stable dispersions or emulsions include chemical and physical methods.

<u>Chemical treatments</u>

Chemical treatments either destabilize the dispersed oil droplets or chemically bind or destroy any emulsifying agent present. Chemical demulsifying processes include:

- Salting out of an emulsifier is achieved by adding a large quantity of an inorganic salt, thereby increasing the dissolved solid content of the water phase.

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- Coagulation with aluminium or iron salts is generally effective, and is in common use even though the resultant hydroxide sludges are difficult to dewater, and limit the reusability of the recovered oil.
- Acidification which cleaves emulsions more effectively than coagulant salts, but are more expensive and the resultant wastewater must be neutralized after the separation.
- Organic demulgators are extremely effective demulsifying agents, but are generally very expensive and specialized.

All these methods, however, give rise to problems regarding downstream water treatment.

The overall cost of them is thus represented by the sum of the cost relative to the use of the proper chemical in the flow and the removal of its undesired effects, as seen previously, for example in the case of acidification.

SPR treatment

Italtraco has discovered a natural food grade molecule, that has the capacity to remove all liquids and solids dispersed in the continuous phase. The reaction takes place in a very short period of time - in the range between few seconds and a minute - and the separation of the clear liquid is obtained, for instance, by sedimentation or filtration.

This process, called SPR, is mostly characterised by the fact that the treated liquid is by no means altered chemically, in that the used molecule is totally insoluble and is thus fully eliminated by filtration and/or other known techniques of liquid/solid separation; this characteristics allow us to re-employ the clear liquids obtained through this process, in the primary cycle from which the liquid wastes originally flew out.

This invention can be efficiently applied to all the polar liquid wastes containing solvated particles, independently from the chemical nature of the particles, since the purification process involved is essentially of the physical type.

This treatment has also proven particularly useful for those effluents that must undergo nanofiltration, reverse osmosis, or electrodialysis processes, because it permits to

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eliminate microfiltration/ultrafiltration treatments, to increase the performances and to prolong the life of the relevant membranes.

Physical treatments

Physical emulsion breaking methods include:

- heating
- high speed centrifugation.

Both this methods, as Italtraco's SPR, work by mean of a physical principle, but they have the main disadvantage to consume a great deal of energy and they are not able to assure the high separation results SPR can easily achieve.

1.2.3 Selection and design of an oil-in-water separator

Several factors must be considered in the selection and design of oil-water separation systems.

Among these are:

1. Flow rate and conditions
2. Required degree of separation and effluent quality
3. Amount of oil in water
4. Particle size distribution
5. Existing equipment
6. Amount of solids
7. Presence of mechanical dispersions
8. Emulsification of oil and presence of surfactants
9. Treated water facilities
10. Recovered oil disposal method.

Relevant physical and chemical properties of each phase are:

- Density
- Viscosity
- Surface tension
- Temperature
- PH.

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The following is a typical example of *TECHNICAL DATA SHEET* allowing to design an oil-in-water separator.

FLOW CONDITIONS:

Normal Flow Rate: ………………… m^3/h
Maximum Flow Rate: ……………… m^3/h
Minimum Flow Rate: ……………… m^3/h
Comments:………………………………
………………………………
………………………………

Operating Pressure: …………………... bar
Operating temperature: ……………... °C
Intermittent Flow: Yes ………..... No
Gravity Flow: Yes ………..... No
Pump Flow: Yes ………..... No
Kind of pump: ....

FLOW COMPOSITION:

Water: …........ %
Oil: ………. ppm Type: ……………................ Specific Gravity: …….....…. g/cm^3
Particle size distribution in µm (to be enclosed)
Solids: ……… ppm Type: ……………................ Specific Gravity: ………...… g/cm^3
Particle size distribution in µm (to be enclosed)
Gas: …………… % Type: …..……………………
Other: …………. % Type: …..……………………
Liquid pH: …………… Liquid Viscosity: …………… cp Specific Gravity: …..…..…... g/cm^3
Comments: ……………………………………………………………………………………
……………………………………………………………………………………

DESIGN PARAMETERS:

Working time: .... hr/day
Area classification: safe area ☐ zone EExd (explosion proof) ☐
Effluent Separation Efficiency Required: Continuous Phase …… ppm Disperse Phase …… ppm
Separator Space Limitations: ………. Lx ……….Wx ………. H(m) Weight: ………... Kg
Below Ground Installation: ……Yes …… No Unit Elevation or Depth: ………. m
Vessel Design Temperature: ………. °C
Corrosion Allowance: …………….. mm. Material: ……........……………………………………
Instrument Air Available: ……Yes …… No Electrical Service: … Volts ….. Phase ….. Hz

CHECK ACCESSORIES NEEDED:

S.P.R. system: ....
Water Pump(s): ………. Oil Pump(s): ………..... Sludge Pump(s): ……….
Control Panel: ……...... Storage Tank(s): ……… Level Control: ………...
Pre-Filtration Unit(s): ………. Filtration Unit(s): ……….
Other: ………………………

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1.3 SYSTEMS AVAILABLE FOR REMOVING OIL FROM WATER

Systems for removing oil from water range from very simple holding ponds to elaborate membrane technology-based systems. Before the advent of ***ZerOil***® it was deemed that, for most applications in removing oil, it was impossible to combine simplicity and performance: the simplest systems are often inadequate (although often used) and the most complicated are either too expensive or too maintenance-intensive. Most of the following discussion will concentrate on methods of separation intended to meet or exceed regulatory requirements with minimum cost and maintenance.

1.3.1 Gravity separation

Gravity separator

The simplest possible way to coalesce a dispersion of a liquid in another, is just to let it sit in place. In most cases it will sooner or later coalesce, settle out and form two distinct layers with the help of gravity. This kind of separator is nothing but an empty chamber with enough volume to contain spills (Figure 1). The effectiveness of a gravity separator depends on the proper hydraulic design and on the period of wastewater detention for a given rise velocity. Longer retention times generally increase separation efficiency. Effective removal of oil droplets with a given rise velocity is a function of the system geometry. The liquid detention time must be sufficient to let oil droplets rising at a given velocity reach the fluid boundary where they can be removed by skimming. Large retention time is provided to heavy flows, by means of very large vessels: they may be 15 ft (4.5 m) to 20 ft (6 m) in diameter and 45 ft (14 m) to 60 ft (18 m) long. Purchasing a gravity separator can be a major capital investment.

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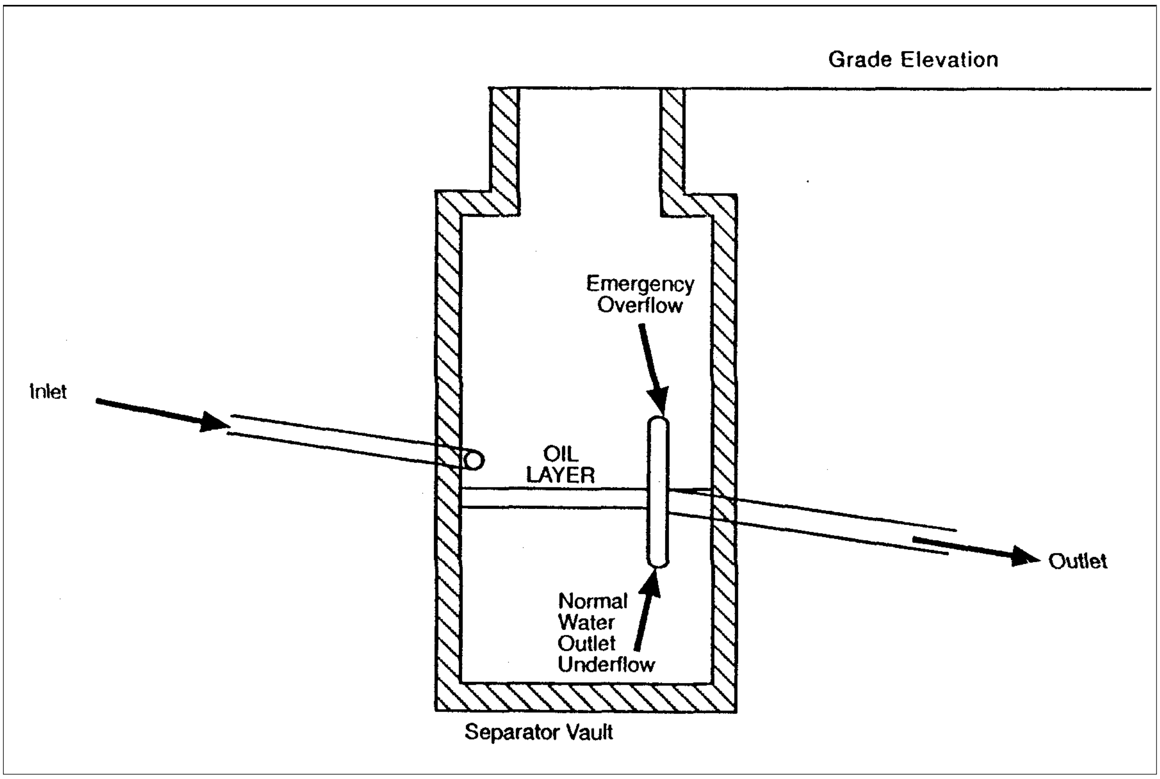

Gravity Separator

API separator

The conventional API separator consists of a channel or channels through which the water passes horizontally at a velocity which allows the oil droplets time to rise to the surface to be skimmed off (Figure 2). API separators are extensively used in oil refineries and chemical processing facilities where waters containing relatively large amounts of oil are present and need to be processed.

API separator design criteria control the velocities within the unit by specifying that:

- The horizontal velocity through the separator may be up to 15 times the rise velocity of the critical (i.e., slowest rising) oil droplet, up to a maximum of 3.0 ft (0.9 m) per minute. Above this limit the effect of turbulence tend to redistribute oil droplets.

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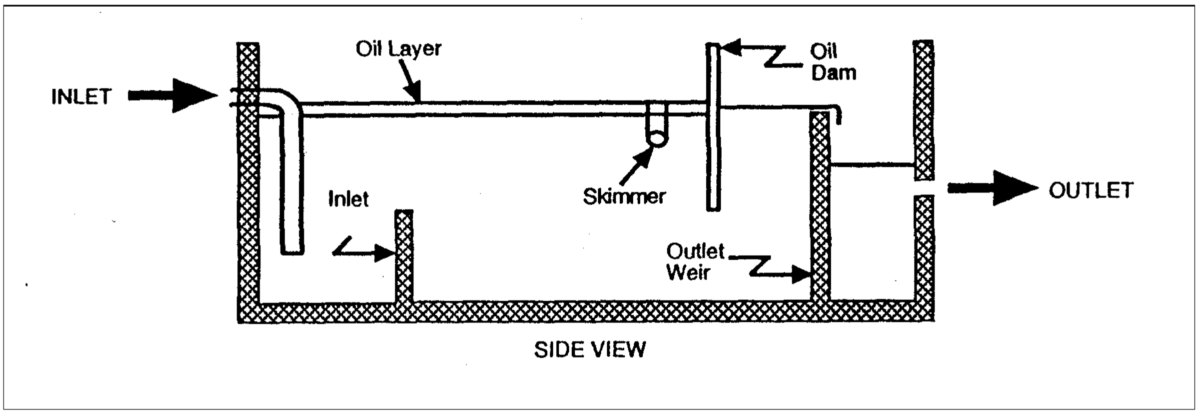
- The depth of flow in the separator should be within 3 ft (0.9 m) to 8 ft (2.4 m). This limits the height that must be traversed by a rising oil globule.
- The width of the separator should be between 6.0 ft (1.8 m) and 20.0 ft (6.1 m).
- The depth-to-width ratio should be between 0.3 and 0.5.
- An oil retention baffle should be located no less than 12 inches (0.3 m) downstream from a skimming device.

The main advantages of these kind of separators are that they are simply designed, cheap, resistant to plugging with solids and require low maintenance.

On the other hand, the standard API separator is designed to achieve the separation of oil droplets of 150 micron diameter and larger. In practice, this means that the effluent will not contain less than 50 ppm of separable oil because a significant proportion of the oil present is below 150 micron diameter. Further, the size and surface area of an API separator allow disturbance of the separation process by wind turbulence and short cutting of the contaminant.



Typical American Petroleum Institute (API) Separator Pit

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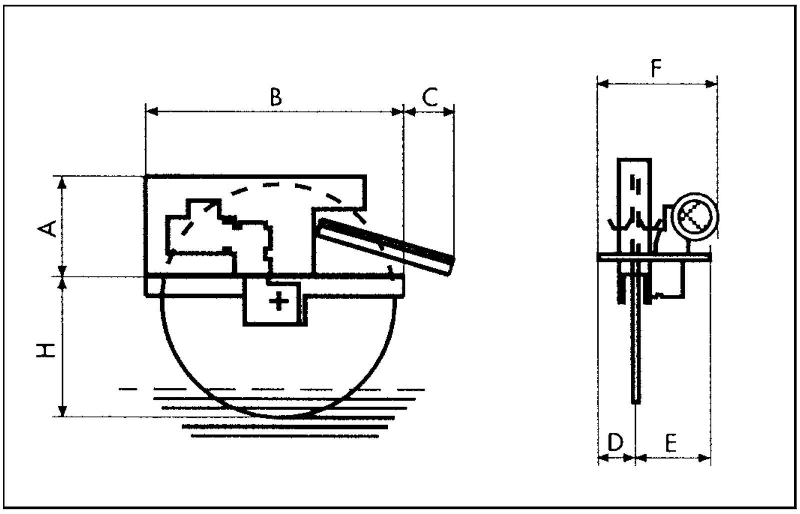
Skimmer

Skimmers, as the name implies, skim oil that have collected on the water surface. There are four basic types of skimmers – belt, collector tube, wheel and aerator skimmers.

Belt and wheel skimmers are probably the most popular forms of oil skimming.



Wheel Oil Skimmer

Inclined plate separator

These systems are usually made in large modules constructed of fiberglass plates packaged in steel or stainless steel frames (Figure 3). The oil droplets entering the system rise until they reach the plate above, then migrate along the plate until they reach the surface. Advantages of this system over API type separators include improved efficiency in removing both solids and oil and resistance to plugging with solids. The improvement is mainly due to the substantial decrease of the effective rise height that must be traversed by a rising oil droplet. On the other hand, these systems are only able to achieve the separation of oil droplets down to 60 microns.

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Flat corrugated (Horizontal Sinusoidal) plate separator

Flat corrugated plate separators often use horizontal oleophilic polypropylene plates stacked one on top of another in vertical stacks and fastened into packs with rods or wires. The system uses a combination of laminar flow, coalescence and oleophilic attraction. Slowing the flow of water to low velocities in laminar flow regime avoids the presence of turbulence which causes mixing of the oil and water and reduces oil droplet size. Stoke's Law states that larger droplets will rise faster and thus separate better. The oleophilic nature of the plates attracts the oil droplets and enhances the coalescence into larger ones, which will rise faster.

The advantages of this system are that the plate packs are modular and relatively small in size compared to the inclined plate modules. Because the vertical rise distance to be covered is less than in inclined plate systems, particles of the same size are separated in less time. Conversely, the same amount of space time provided within the plate area causes effective separation of smaller size particles, down to 45-60 microns. Disadvantages of this system are (apart from the quite poor quality of separation) possible plugging of the plate packs by solids and possible damage to the plates by solvents that could attack the polypropylene plates such as BTEX.

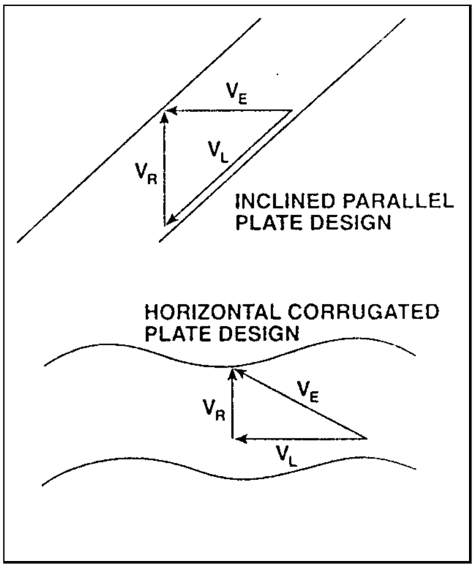


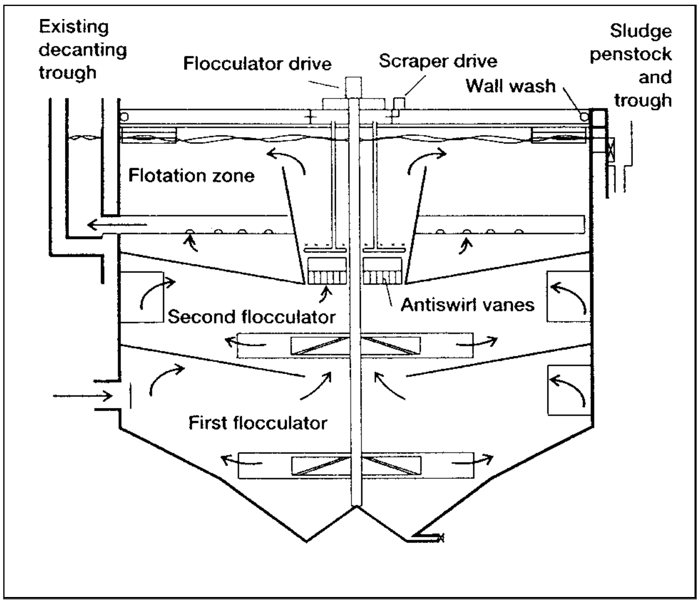
Plate Separators Schemes

1.3.2 Air flotation devices

These systems are used as secondary treatments only and require the injection of air in microscopic bubbles to the effluent stream in such a way that the bubbles stick themselves to the oil droplets. This reduces the effective specific gravity of oil/air droplets in the Stokes' Law formula and thus increases the rising velocity V_p. Air flotation devices are usually located downstream one of the gravity separation techniques described above to remove gross quantities of surface oil and settable solids. This reduces the required volume of dissolved air and flocculating chemicals to economical levels. Two methods are commercially used to form minute air bubbles: the dissolved air flotation and the dispersed air flotation.

<u>Dissolved air flotation</u>

In this process, either the whole flow or a recycled portion is pressurized with air up to 5-6 bar before entering the separation vessel. On entry, the reduction of pressure to atmospheric releases air from solution.



Dissolved air flotation

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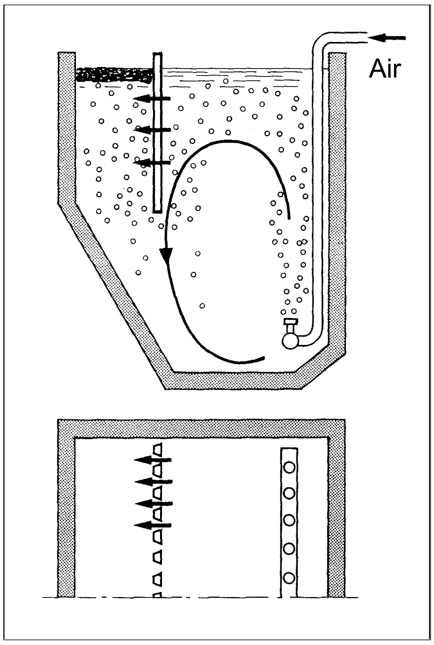
Dispersed air flotation

In this case air is induced into the effluent using a high shear agitator which creates a foaming effect to assist separation of the oil.



Dispersed air flotation

The main advantage of air flotation processes is the enhanced separation of oil. Whereas gravity systems can't separate oil droplets with a diameter under 60 microns, with air flotation we can reach the separation of oil droplets down to 35-50 microns if we use, respectively, dispersed or dissolved air flotation.

But both air flotation systems described above require chemicals and have considerably higher operating costs than the gravity separation procedures. Also, because of the need to pressurize or disperse air into the flow, mechanical breakdown of oil droplets is a serious risk.

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1.3.3 Centrifugal separators

In this technique, the denser water phase is moved to the outer region by means of the centrifugal forces obtained by inducing a rotating fluid flow. The lighter oily materials collect near the vortex core and are subsequently removed. This requires the oil-collecting mechanism to be designed to remove a small column of oil at the center line to be effective in oil-in-water emulsions. The maximum intensity of centrifugal forces is obtained at the outer radial regions, apart from the small column of separated oil.

Hydrocyclone

Hydrocyclone efficiency can only be defined in terms of droplet removal. Colman et al in 1984 developed an empirical expression for the liquid/liquid hydrocyclone in terms of d_{75}; this being the diameter of the droplet with 75% probability of being separated. It was found that hydrocyclone performance could be expressed in terms of two dimensionless groups, the hydrocyclone Reynolds number (Re_D), and the hydrocyclone number (H_{75}). The basic expression for deriving d_{75} is:

$$Hy_{75} = 0.011\ Re_D^{-0.15}$$

Where $Hy_{75} = \dfrac{Q.(d_{75}).^2\,\delta p}{D^3.\mu}$

From the knowledge of d_{75} it is possible to derive either migration probability or grade efficiency curves.

Despite individual supplier claims for their own proprietary hydrocyclone designs, all existing products can be reasonably correlated to the above (Mubarak et al, "Production Separation Systems Conference", 29&30 May 1997, Oslo, Norway). The definition of Hy shows that, once fluid parameters are set (∂p, μ), d_{75} is purely dependant upon flowrate (Q) and hydrocyclone diameter (D).

Hydrocyclone de-oiling efficiency has been found to be mainly influenced by:

- the influent flow rate, which governs the pressure drops through the hydrocyclones and whose fluctuations are admissible only in a range which is proportionally narrower the farther we go from optimal efficiency conditions,

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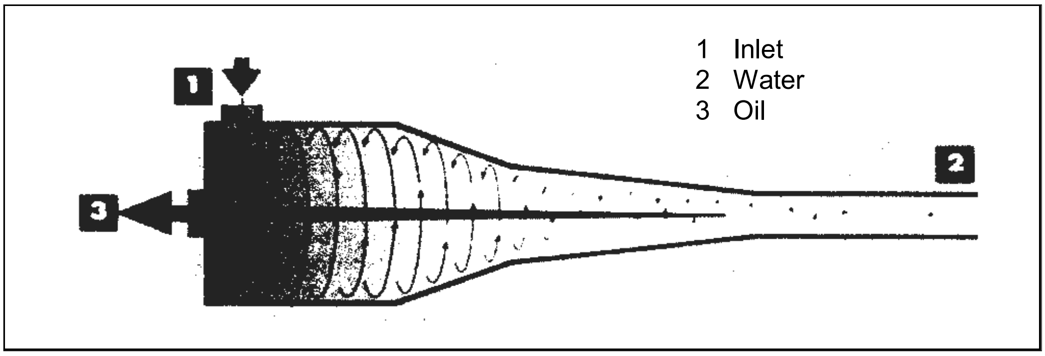
- the diameter and the geometry of the hydrocyclones, the smallest diameters operating, for the same efficiency, with the lowest feed pressures,
- the difference in density between the water and the dispersed hydrocarbons, the greater the latter, the more efficient the separation,
- the viscosity of water (temperature, salinity), the lower the viscosity, the more efficient the separation,
- the dispersion characteristics: sizes (may be influenced by presence in the medium of surfactants) and concentration of hydrocarbon particles,
- some feed pump types which have a high shearing power and are unsuited to feeding hydrocyclone units as they re-disperse the hydrocarbons as particles with diameters incompatible with the efficiency of this technique. Low speed, single stage centrifugal pumps were found to offer an acceptable compromise.

Even in experimental or on site conditions, the yields obtained with only the hydrocyclone units are insufficient, for the types of fluid conventionally found in petroleum fields, to attain the target concentration of 40 ppm. of dispersed hydrocarbons in the water discharge (Gaudebert, 1997).

Effluent qualities averaging 50 to 60 ppm. of oil are reported.



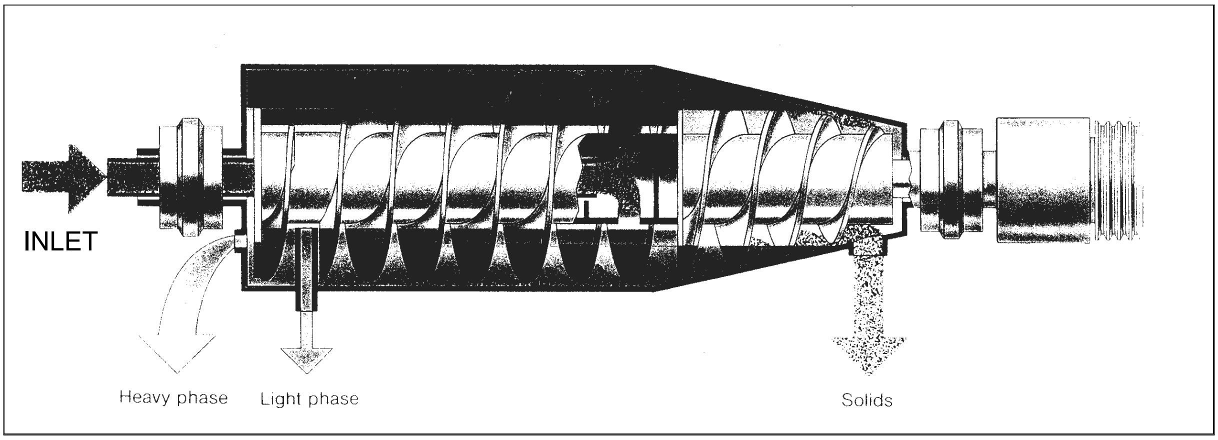
A typical hydrocyclone

Centrifuges

Unlike the hydrocyclone, the centrifuge generates high centrifugal forces by direct energy input. This takes the form of a rotating bowl driven by an electric motor. Bowl rotating speeds are typically 5000 rpm.

The "disk stack" centrifuge is used for the separation of oil from water. The rotating bowl contains a number of conical disks that fulfil the same function as the plates in a plate interceptor, reducing the distance that is travelled by the oil droplets. The oil flows up the plates and is collected from the center of the centrifuge, whilst the water is collected by a central paring disk fed from the outside. Solids are ejected from the bowl at intervals by means of a hydraulic system.

Effluent qualities averaging 40 to 60 ppm. of oil are reported.



Typical 3-phase Centrifuge

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1.3.4 Emulsion separators

Systems that can be used for enhancing oil droplet coalescence are: granular media filter and coalescing media.

Granular media filter

Filtration with granular media pressure filters is routinely used in oily water effluent duties as a polishing stage. The media used may be garnet, sand or crushed nutshells. Media filtration allows the removal of free oil to generally lower levels than flotation, but there are certain severe disadvantages. These disadvantages are all a consequence of media filtration being a batch process:

- Oil handling capacity:
  Oil and solids are physically held up in the filter bed and intermittently back flushed out. There is therefore a strict limit on the holding capacity of a filter bed. In practical terms, to ensure reasonable filter run times and filter bed sizes, the feed oil concentration should not exceed 50 ppm. This means that good pre-treatment is essential. An efficient pre-treatment is hydrocyclones plus degasser. It is important to avoid feeding free gas to the filters.

- Backwash treatment:
  Hydrocyclones and flotation both have a continuous, dilute reject stream which can easily be recycled and reprocessed. By contrast, media filtration has an intermittent, high volume, highly concentrated oil/solids/sludge effluent which has to be reprocessed. Because this stream is intermittent and will be solids laden, it is generally impractical to simply recycle. A separate backwash treatment system is usually installed.

- Response to upset:
  Because of the limited oil handling capacity, a filtration system will be very sensitive to process upsets, and it can be very difficult to recover badly fouled filter beds.

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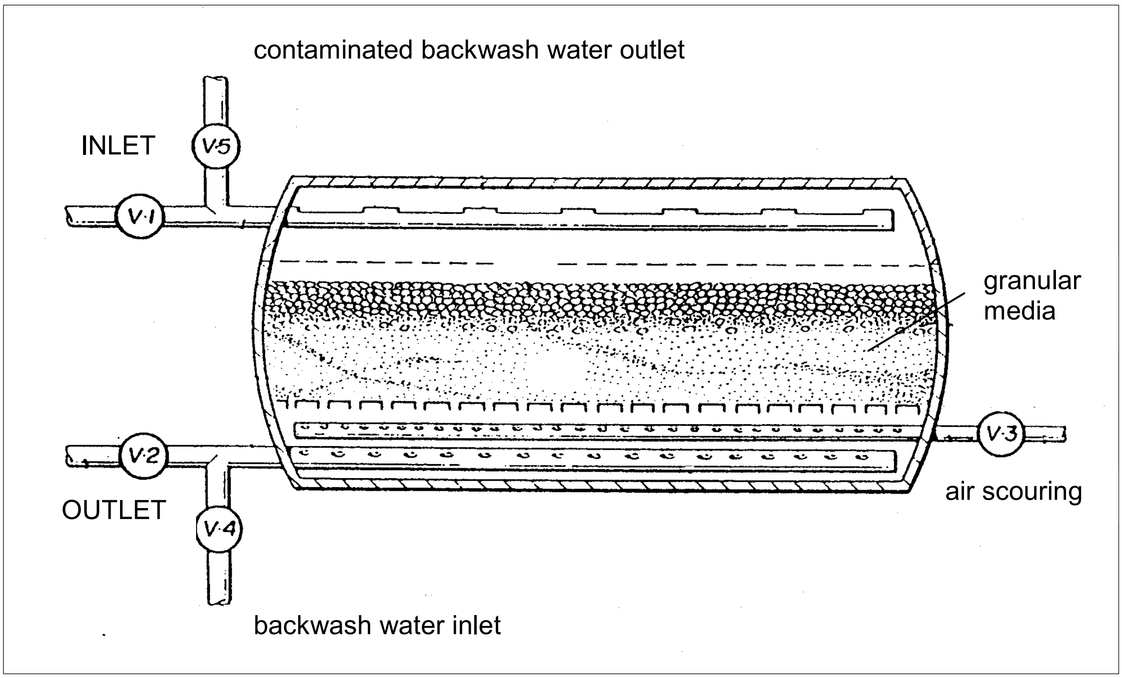
- Control of bacteria:
  Filter media provides an ideal environment for the reproduction of sulphate reducing bacteria (SKB's). Bacterial control is very difficult because many commercially used organic biocides have a deleterious effect on filter performance.
  Effluent qualities averaging 5 to 15 ppm. of oil are reported.



A typical granular media filter

Coalescing media

A number of coalescers are available for oil-in-water separation to provide higher quality discharge. These are basically improved filtration systems using media designed to provide a surface on which the fine oil particles will be retained and collected into larger droplets for separation.

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The small pore size used to create the semi-permeable surface does, however, require the flow to be effectively free from suspended matter which would block the pores.

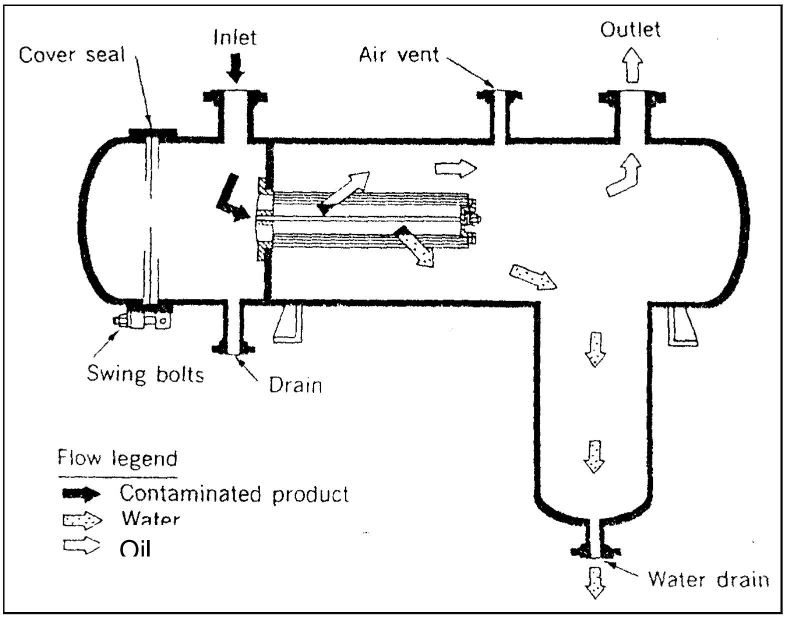
Therefore coalescer must be preceded by filtration, the coalescer material can be a metal gauge of fine mesh, ceramic or polymer based. It is generally produced in a cartridge form.

The major obstacle to good separation is the presence of dirt particles in the wastewater. The oil/dirt particles may not coalesce and will be present in the effluent water contributing to the total oil concentration.

If the oil is viscous, the oil/dirt combination may accumulate on the coalescing media surface resulting in plugging the media.

This technique is very expensive in terms of capital and operating costs and is usually applied for low flow rate oily water duties.

Effluent qualities averaging <10 ppm. of oil are reported.



A typical single-stage coalescer

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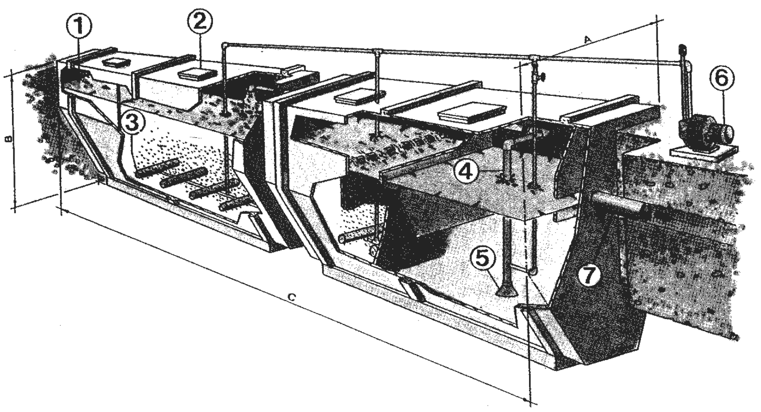
1.3.5 Biotechnology

The treatment of dissolved oils and other types of chemically stabilized emulsions that cannot be destabilized by chemical additions can pose serious problems. Biological treatment with acclimated microorganisms is generally effective in degrading much of this material, and is commonly used in petroleum refineries and rendering plants. However, the systems are only effective if suitable pre-treatment and high dilution can be achieved. Too much oil is a problem in biological systems because it is adsorbed by the microorganisms faster than it can be metabolized.

In trickling filters, oil tends to coat the microbial surfaces and reduce the transfer of more readily oxidizable organics. In activated sludge systems, the adsorbed oil tends to impair sludge settling characteristics. Resulting sludge losses may be so high as to reduce the microbial level in the system enough to cause reduced efficiency and possible system failure.

The microbial metabolism of oil is limited by the low solubility of oil, the chemical configuration of oil molecules, and the microbial surface. Trickling filters can treat oil concentrations of up to 50 ppm. with no effect. Activated sludge systems show no effect if the oil concentration is kept above than 20 ppm. Biologically treated effluents typically contain less than 15 ppm. of oil.



A typical biological plant

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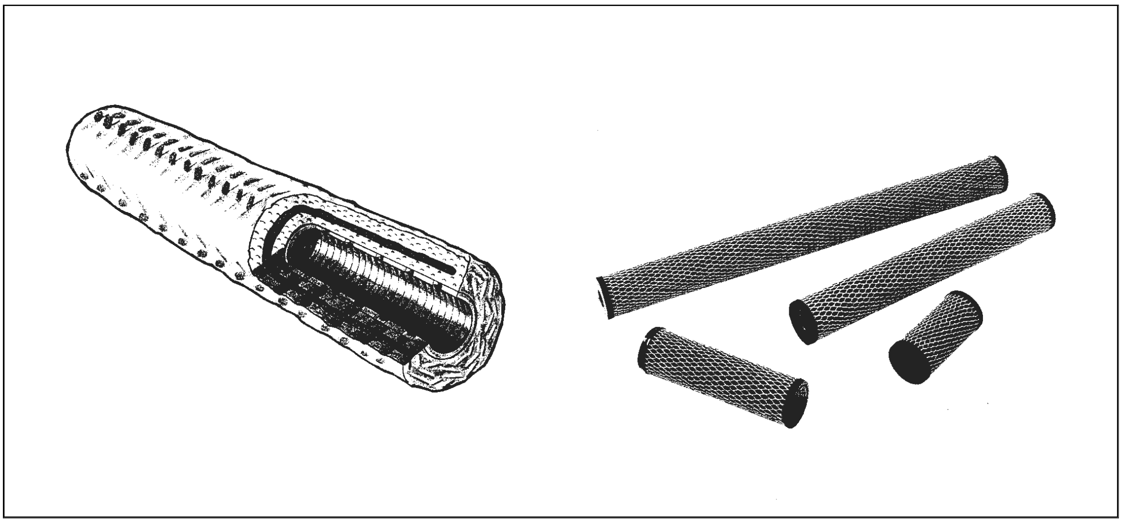
1.3.6 Carbon adsorption

Carbon adsorption has been used extensively as a means of removing trace quantities of oil. Treatment requires a suitable means of regenerating the carbon. Methods that have been addressed include steam, hot water, organic solvents and pyrolysis. Treatment by carbon adsorption also generally requires a large capital investment for carbon inventory and regeneration equipment and has, therefore, not found widespread use in oil separation where high concentrations are involved.



Typical carbon filter tubes

1.3.7 Membrane systems

By taking the coalescer principle further to microfiltration or ultrafiltration, high quality separation can be achieved. On the other hand, very effective pre-treatment is necessary to prevent membrane fouling and frequent backflushing with surfactants is required to maintain peak flux rates.

The system operates under pressure to force water through the membrane with retention of the contaminant. The structure and pore size of the membrane enable separation of emulsified oil from water. However, it is necessary to operate at elevated pressures to achieve the passage of the water phase through the membrane.

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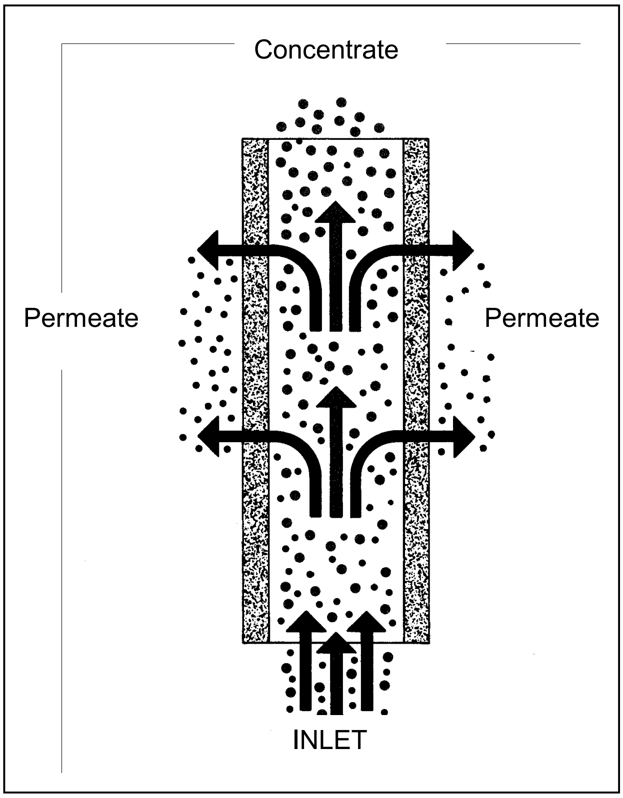
Cross flow systems have a significant power consumption due to the high recirculation rate.

Membrane systems are very expensive in terms of capital and operating costs and usually applied for low flow rate oily water duties.



A typical ultrafiltration membrane

1.4 APPLICATION OF THE DIFFERENT SYSTEMS

In recent years, more stringent effluent requirements have caused the conversion of numerous API separators to more efficient designs. Generally API separators are maintained within the plant, but the separation is bettered providing another and enhanced separation system downstream.

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Plate type separators, systems utilizing coalescing tubes and other enhanced gravity separation systems offer better performance than the simpler systems, but at higher costs . It is often necessary to balance cost versus benefits to ensure that regulatory requirements are met.

In the following table the efficiency of the systems previously discussed is shown:

PLANT PROCESS	Smallest oil droplet removed (average microns)	Comment
API SEPARATOR	150	Very large area and civil works required.
CENTRIFUGES	100	Poor separation quality and require a motor for operation
TILTED PLATE SEPARATOR	60	Large area required, civil works might be necessary.
FLAT CORRUGATED PLATE	45-50	Possible plugging of the plate packs by solids and possible damage to the plates by solvents
DISPERSED AIR FLOTATION	50	Secondary treatment only, high power required; chemicals may be necessary.
DISSOLVED AIR FLOTATION	35	Secondary treatment only, mechanical complexity, high power required; chemicals may be necessary.
GRANULAR MEDIA FILTERS	25-30	Secondary treatment only, chemicals may be necessary, backwash must be treated, power required.
COALESCERS	15	Secondary treatment only, removal of all the suspended solids and power required.
MEMBRANES	<5	Secondary treatment only, high cost, removal of all the suspended solids, cleaning treatment and high power required.

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As it may be seen in the table above, when we are interested in a high separation quality, we have to face elevated costs for sophisticated systems, which are thus delicate and prone to break down. On top of that there may be a lot of other problems, such as plugging with solids, need to use chemicals, impossibility to treat large flows or need to be used as secondary treatment; in the latter case, they need to be coupled with a less efficient system which has to remove gross quantity of oil upstream.

On the other hand, when we chose not to deal with these systems, the quality of separation obtained is very poor and, also in this case, we have to face relevant expenses and sometimes civil works.

When applications require:

- high efficiency oil removal,
- a simple, cheap and easy-to-be-handled system,
- the ability to tolerate solids,
- the ability to treat large flows,

the ***ZerOil***® system is the only one able to grant them.

It shows its ability to perform under very severe conditions and still provides effluent oil concentrations to exceed normal regulatory requirements. Generally, no exotic systems may be required since ***ZerOil***® (as the term states) is able to reach a virtual zero oil level in water discharge.

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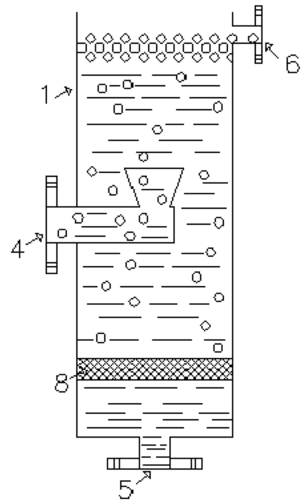
2. THE *ZerOil*® *SYSTEM*

ZerOil®, the new Italtraco's process for the separation of non-miscible liquids, is a revolutionary separation technique based on molecular surface forces and covered throughout the world by national and international patents. Its most important feature resides in the fact that the separation of the non-miscible liquids, being based on physical properties of the liquids themselves, is really complete: in the case of oil-in-water, for instance, the residual content of the oily fraction in the effluent water is, normally, in the range of 1 ppm, but in many cases it has been possible to go further down, to a few parts per billion (ppb) only.

For an essential description of the ***ZerOil***® separator see the sketch.

The separator itself is extremely simple and compact: it consists, essentially, of a static vessel (1) the dirty water is fed into the separator through a nozzle (4); the heavier component (water) is continuously discharged from the bottom through another nozzle (5) while the lighter component (oil/hydrocarbon) will float across the incoming flow and collect at the top surface, from where it is continuously discharged through a nozzle (6); the separating "two phase media" (with this term we indicate the filtering media) is indicated with (8).



The separation of water and hydrocarbons occurs thanks to the molecular and/or elctrostatic actraction/repulsion forces that create an additional surface tension on the upper surface of the "two phase media" as a consequence of the pre-activation of the filtering media, treatment that needs to be effected only once, namely immediately before starting the actual separation process; this pre-activation treatment creates a

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strong, interfacial film, that completely inhibits the passage of the dispersed oily phase through the two phase filtering media.

It's important to notice that just because the separation is not due to some kind of mechanical effect, but solely to natural, strong, molecular and/or electrostatic actraction/repulsion forces, the dispersed oily phase is inhibited to pass through the "two phase media", remaining above the film until macroscopic droplets are being formed by collision with some descending droplets, then buoyancy forces bring them towards the upper surface of the separator, where they will form a layer that is continuously skimmed recovering the oily phase.

Typical applications of the ***ZerOil***® system are presented below:

- ***OIL & GAS PRODUCTION (onshore / offshore):***
  - ◊ production water (oil)
  - ◊ condensate water (gas)
  - ◊ deck washing.

- ***INDUSTRIAL USES:***
  - ◊ power plants condensate and cooling water
  - ◊ petrochemical plants and refineries effluents
  - ◊ rolling oil effluents from any rolling mill
  - ◊ machine tool coolants
  - ◊ oily wastewater from:
    - chemical industry
    - pharmaceutical industry
    - food processing plants
    - mining operation
    - wool and textile industry
  - ◊ mechanical industry:
    - METAL WORKING: water soluble, semi-synthetic, synthetic and biostable fluids used in grinding, turning, and general machining operations;
    - METAL FINISHING: water soluble acid, alkaline and neutral cleaners containing free and mechanically dispersed tramp oils;
    - SCREW MACHINES: tramp oil from water soluble fluids used in screw machine reservoirs;
    - PRIMARY METALS: roll forming, cold heading, stamping and tube mill water soluble fluids used for ferrous and non-ferrous operation.

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- ***MARINE APPLICATIONS:***
  - ◊ bilge water separation
  - ◊ tank ballast water deoiling
  - ◊ oil spill response
  - ◊ sea water deoiling / desalinization plant protection.

- ***POLLUTION ABATEMENT:***
  - ◊ surface water cleanup
  - ◊ ground water cleanup
  - ◊ storm water, rain water runoff cleanup.

- ***SEPARATION PROCESSES:***
  - ◊ diesel / water
  - ◊ kerosene / water
  - ◊ benzene / water
  - ◊ machine oil / water
  - ◊ animal fat / water
  - ◊ immiscible organic chemicals / water.

- ***OTHER APPLICATIONS:***
  - ◊ oily wastewater from:
    - fuels terminals
    - railway yards.

To complete the description of the ***ZerOil®*** system, we want to add that it has been possible to develop a physical model that can explain the high performance capabilities of the system.

This model is based on the assumption that the interaction between the water molecules and the filtering media generates an interfacial film which acts as a real barrier against the oil particles dispersed in the water, through an additional interface tension that depends on the oil-water intrinsic interface tension on one side, and on the dimensions of the incident oil droplets on the other side.

This model has been implemented in a numerical algorithm for the direct simulation of the movement of oil droplets in a laminar water flow.

The results obtained by the model show a complete accordance with the experimental data measured in a number of tests made with oil-in-water mixtures in which the oil

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particulate size distribution was measured using laser light scattering. This accordance is the best proof of the validity of the model and hence of the validity of the hypothesis upon which the model has been developed.

While explaining the extraordinary efficiency of ***ZerOil***® separation process, this model renders also possible a preliminary definition of the parameters for the optimization of any given separation problem.

Further information about the applications and the performances of ***ZerOil***® separation process may be requested directly to Italtraco.

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3. SUMMARY AND CONCLUSIONS

Environmental regulations are steadily becoming more restrictive and requiring lower concentrations of oils and fats in effluent streams. Unfortunately budgets for wastewater treatment are very limited, so it is becoming necessary to provide more effective treatment without increasing capital and operating costs.

Sometimes treatment systems can be as simple and inexpensive as spill control separators. Much often, it may be necessary to provide costly and sophisticated methods of treatment such as membrane systems. The most appropriate method of treatment is the least expensive method that provides the required effluent quality.

In this case, only with the ***ZerOil***® system, we can combine the most accurate purification of water from oil (and thus the possibility to reuse water in the productive cycle) with the need to handle a simple and inexpensive system.

Italtraco's ***ZerOil***® provides the most cost-effective separation to ensure effluent water quality that meets or exceeds the requirements of federal, state, and local regulations. Each system is individually computer designed to meet all customer requirements.

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