



**Technical University of Crete**  
**School of Mineral Resources**  
**Petroleum Engineering Msc Course**



## **Diploma Thesis**

# **Oil-in-Water emulsions: Techniques and processes for maximizing the oil recovery in high water cut oil wells**

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*To Sofia, Dimitris and Kiara*

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## Abstract

One of the most challenging issues in the oil production industry is the treatment of oil in water emulsions. Such emulsions may occur during enhanced oil recovery methods, workover of oil wells, or even during the conventional steady state production process. Incomplete resolution of the emulsions results in loss of conventional steady state production process. Incomplete resolution of the emulsions results in loss of production and environmental hazards from the disposal of the production water.

The present thesis is focused on the methods and equipment used for the treatment of oil in water emulsions. Initially the mechanism for the emulsion formation is explained, as well as the characteristics of each type of emulsions. Subsequently, a detailed description of the separation stages is provided along with the type of equipment used and processes that take place during the emulsion separation. The chemical additives that facilitate the treatment are analytically presented. Both the equipment and chemicals can vary between each case depending on the oil and water characteristics and the regulatory restrictions in each country. Newly introduced chemicals, equipment and processes are presented along with the established ones.

A major role in the success of such treatment plants plays the continuous optimization of both the equipment's orientation conditions, as well as dosage and types of additives used for the resolution of the oil in water emulsion. The scope of such optimization is always the minimization of the cost and the improvement of the separation efficiency. The process' economics is the most important factor, so information related to the costs of treatment plans of oil in water emulsions is presented in the last chapter.

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## Introduction

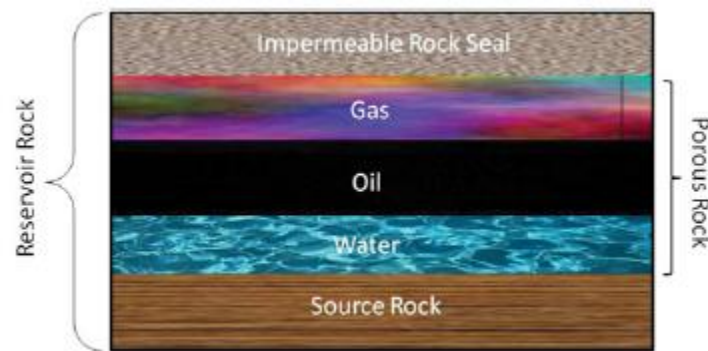
Consumers of petrochemicals are usually unaware of all the processes involved until the final product reaches them. The producing lifeline of an oilfield can be divided into 3 periods of different recovering method. Primary recovery takes advantage of the natural pressure regimes which move the oil to the wellbore and then to the surface. The secondary recovery, which involves water injection scheduling, is the most common method to keep the oil flowing through the rocks to the wellbore by maintaining the pressure sufficiently high. Tertiary recovery is the last period, also named as enhanced oil recovery (EOR) which involves chemical flooding or steam injection, targeting on changing the oil-rock properties so as to maximize the production. Enhanced oil recovery can be categorized in thermal, gas and chemical injection recovery. Thermal recovery targets to the reduction of oil viscosity by the application of heat in the form of steam in the reservoir. Flow to the surface is then easier. Gas injection technique aims similarly in the alteration of oil viscosity and the extraction of oil by the introduction of natural gas, nitrogen or carbon dioxide in the reservoir. Chemical injection is the least used method and it involves lowering the surface tension of the oil in the well and increase the water flooding efficiency.

All three periods can produce up to 80% of the total oil in place. Produced water, solids and other chemicals are brought up to the surface together with the oil and they create serious problems. Water can be produced either as "free" water that will settle out easily during the separation process or as an emulsion. Emulsions in oil industry can be a dispersion of oil in water or vice versa. In more complicated situations a combination of those two categories can exist. They are mainly formed due to the reduction in the interfacial tension between oil and water caused by the presence of additives and chemicals related to EOR. In some cases dilute oil in water emulsions are injected into the reservoirs for the enhancement of production of high viscosity oils (de Farias et al. 2016).

Emulsions are a concern for the producers, transporter and refiners since they can be formulated at each stage of the oil production and processing. Breaking the emulsions is difficult but vital for the oil recovery industry. Large amounts of oil can be recovered through this process while at the same time the production water gets cleaned. Among the different categories of emulsions that are common in oil industry, this work focuses in oil in water type of emulsions. It will be extensively discussed how this type of emulsions forms and how it can be treated in order to recover as much crude oil as possible, without any chemical additives if possible, and clean water that its quality complies with the legislation standards.

## Chapter 1 - Origin of produced water, oil recovery and environmental concerns

The water that is produced on the surface during oil and gas extraction operations is the water trapped in the underground formations and it is referred as "connate water". This water contains a mixture of organic and inorganic compounds, it is slightly acidic and it is located at and below the hydrocarbons' reservoir media, as it shown in Figure 1 (Igunnu and Chen 2012). American Petroleum Institute has estimated in 2012 that the average water to oil ratio was 10 barrels of water for every 1 barrel of oil produced, with daily costs for water treatment reaching \$125,000 in certain oilfields (Kelland 2014). The water to oil ratio production of well varies widely from essentially zero to more than 50, e.g. 98% water and 2% of oil (Neff et al. 2011). The source of this water can lie above, within or below the hydrocarbons zone. Another source can be the water injected during production activities and in this case additives and injection fluids will be present.



**Figure 1** - Sketch of a typical Reservoir (Igunnu and Chen 2012)

During production, a mixture of oil, water, dissolved or suspended solids, injected fluids and additives comes to the surface. As a result produced water's characteristics can vary depending on the geographic location, the geological formation and the type of hydrocarbon produced. Water's composition may even vary between different production zones of the same field. Dissolved, suspended and precipitated solids, sand, dissolved gases and toxicants are the main constituents of the produced water along with the liquid hydrocarbons that can be in dispersed or dissolved form.

Oil and grease are the most important pollutants of produced water for both offshore and onshore operations while salinity is of high importance for the offshore operations. The oil which is "trapped" in the water consists mainly of non-emulsified oil and emulsified state while insoluble solids are also present. The total organic carbon (TOC) in produced water can range from 0.1 to 11,000 mg/L. Organic acids

are present in the produced water in the form of mono- and di-carboxylic acids (-COOH) and of saturated and aromatic hydrocarbons. Table 1 illustrates the concentration range of several classes of naturally occurring organic chemicals in the produced water (Neff et al. 2011).

Chemical Class	Concentration Range
Total Organic Carbon	$\leq 0.1$ - $> 11,000$
Total Organic Acids	$\leq 0.001$ - $10,000$
Total Saturated Hydrocarbons	17 - 30
Total Benzene, Toluene, Ethylbenzene and Xylenes (BTEX)	0.068 - 578
Total Polycyclic Aromatic Hydrocarbons (PAH)	0.04 - 3
Total Steranes/Triterpanes	0.14 - 0.175
Ketones	1 - 2
Total Phenols (Primarily C <sub>0</sub> -C <sub>5</sub> -Phenols)	0.4 - 23

**Table 1** - Concentration ranges (mg/L or parts per million) of several classes of naturally occurring organic chemicals in produced water worldwide (Neff 2002)

An additional difference in characteristics occurs if waterflooding operations have been conducted for unconventional oil liberation. Water produced after such operations can include corrosion inhibitors, oxygen scavengers, scale inhibitors, emulsion breakers and clarifiers, coagulants, flocculants and paraffin solvents. Toxicity of water can be affected from these chemicals as well as the oil/water partition coefficient. It is of high significance for the industry to measure and evaluate the characteristics of produced water so that proper scale inhibitors and well treatment chemicals are applied.

After production, oil, gas and water are fractionated into distinct streams at the separators' facility. After the primary separation, water can still contain emulsified oil which requires a secondary treatment stage in order to be removed. Common treatment methods for this case involve the application of heat and introduction of emulsion breaking chemicals while processing the mixture in specialized equipment.

In most of the cases chemical addition is needed in the treatment facilities and that is due to the conditions applied to the fluids during their transportation from the well to the treatment site. Cold conditions and pressure drop may cause emulsions.

Legislation restrictions can make the treatment of the emulsions very intense and costly and in many cases are the reason why production projects are rejected. (Veil et al. 2004). Each country has set its own regulations concerning the disposal of produced water. The latest regulations in some countries demand that the hydrocarbon content of the disposed water should be between 15 and 50 mg/l, as shown in Table 2. In general, two processes take place during the produced water treatment. A gravity separation of the oil occurs naturally and removes the non-emulsified oil portion. At the second stage chemical treatment (emulsion breaker) is applied for the emulsified

portion of the oil (Becker 1997). The emulsion breaker should be introduced the earliest possible in the production process. In practice the wellhead is the best possible option. To achieve this, a chemical pump and a chemical injection line in the well line need to be installed. Different wells can face different emulsion problems thus there is not a unique solution for all.

Country	Limit
Ecuador, Colombia, Brazil	30 mg/L
Argentina and Venezuela	15 mg/L
Indonesia	25 mg/L
Malaysia, Middle East	30 mg/L
Nigeria, Angola, Cameroon, Ivory Coast	50 mg/L
North Sea, Australia	30 mg/L
Thailand	50 mg/L
USA	29 mg/L OCS water Zero discharge inland water
Canada	30 mg/L
Mediterranean Sea	40 mg/L

**Table 2 - Regulations for oil concentration in water effluent (Modified from Stewart and Arnold 2011 and Neff 2011)**

The salinity of the produced water can range from a few parts per thousand to that of a saturated brine. In most cases the produced water is more saline than the seawater, with high concentrations in sodium and chloride ions (Neff et al. 2011).

## Dissolved solids

Dissolved solids are inorganic and they are mainly  $\text{Na}^+$  and  $\text{Cl}^-$  and to a smaller extend  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ . Rarely  $\text{Ba}^{2+}$ ,  $\text{K}^+$ ,  $\text{Sr}^+$ ,  $\text{Al}^{3+}$  and  $\text{Li}^+$  (Igunnu and Chen 2012). Bicarbonates, carbonates and sulfates can be present also. Depending on the characteristics of the reservoir, dissolved solids can exist in ranges from 100 to 300000 mg/l. In general, the higher the temperature of the reservoir, the higher the dissolved solids concentration. Accurate estimation and measurement of the composition of those solids are very important to avoid precipitation from scales and corrosion (Stewart and Arnold 2011).

## Precipitated solids

With the change in pressure, temperature or composition some ions can form precipitates, which tend to deposit in the equipment and create operational problems. Calcium carbonate ( $\text{CaCO}_3$ ), calcium sulfate ( $\text{CaSO}_4$ ) and iron sulfide ( $\text{FeS}_2$ ) are very common scales. The first two can be treated with hydrochloric acid but iron sulfide cannot due to its high toxicity. Barium and Strontium sulfates can be removed only by mechanical means and their disposal is difficult since they are considered as

radioactive materials. Prevention of scale can be achieved by using scale inhibiting chemicals. These chemicals tend to slow down the growth of scale. The most common scale inhibitors are inorganic phosphates, organic phosphate esters, phosphates and polymers (Stewart and Arnold 2011).

### **Sand and other solids**

Sand, clays, stimulation proppants and corrosion products are also very common in the produced water. In general the size of the particles and their oil affiliation is a decisive factor for the intensity of the separation problems. If those particles attract the oil droplets, the formulated emulsions will be very stable due to prevention of coalescence. Moreover, the specific gravity of the combined oil/solid droplet can be equivalent to that of water, rendering the gravity separation impossible. Solids are mostly oil coated so their direct disposal is prohibited. Chemical treatment is required to reduce the attraction of solids and oil droplets. The oil measurement should not be affected by the presence of solids (Stewart and Arnold 2011).

### **Dissolved gases**

Water in the reservoir can be saturated with natural gas, hydrogen sulfide and carbon dioxide. Primary separators and stock tanks remove most of those gases. Separation pressure has a proportional relation with the quantity of dissolved gas while temperature is inversely proportional to this. Natural gas components show an affinity to oil and this is crucial for the gas flotation equipment. Hydrogen sulfide can be also present in certain water stream. It is very dangerous for the personnel highly corrosive so special equipment is required for its treatment. Its corrosion product, iron sulfide, is also a potential fire hazard. Carbon dioxide is also present in most of the cases and it can cause precipitation of  $\text{CaCO}_3$ . Another cause of corrosion is the oxygen that gets absorbed by the water during its atmospheric exposition. A natural gas blanket can prevent this. Oxygen and carbon dioxide are also present in sea water which is sometimes used in injection processes and they should be removed before injection (Stewart and Arnold 2011).

### **Petroleum Hydrocarbons**

The two main groups of petroleum hydrocarbons contained in the produced water are the saturated and the aromatic hydrocarbons. Their solubility is inversely proportional to their molecular weight with aromatic hydrocarbons being more water soluble. They both appear in dissolved or dispersed form (emulsions) in the water. Single ring aromatic hydrocarbons such as benzene, toluene, ethylbenzene and xylenes (BTEX) are the most abundant type present in produced water. Table 3 illustrates their

concentration in different production areas in Indonesia and in Gulf of Mexico (Neff et al. 2011).

Compound	Gulf of Mexico concentration (mg/L)	Indonesia concentration (mg/L)
Benzene	0.44 - 2.8	0.084 - 2.3
Toluene	0.34 - 1.7	0.089 - 0.8
Ethylbenzene	0.026 - 0.11	0.026 - 0.056
Xylenes (3 isomers)	0.16 - 0.72	0.013 - 0.048
Total BTEX	0.96 - 5.33	0.33 - 3.64

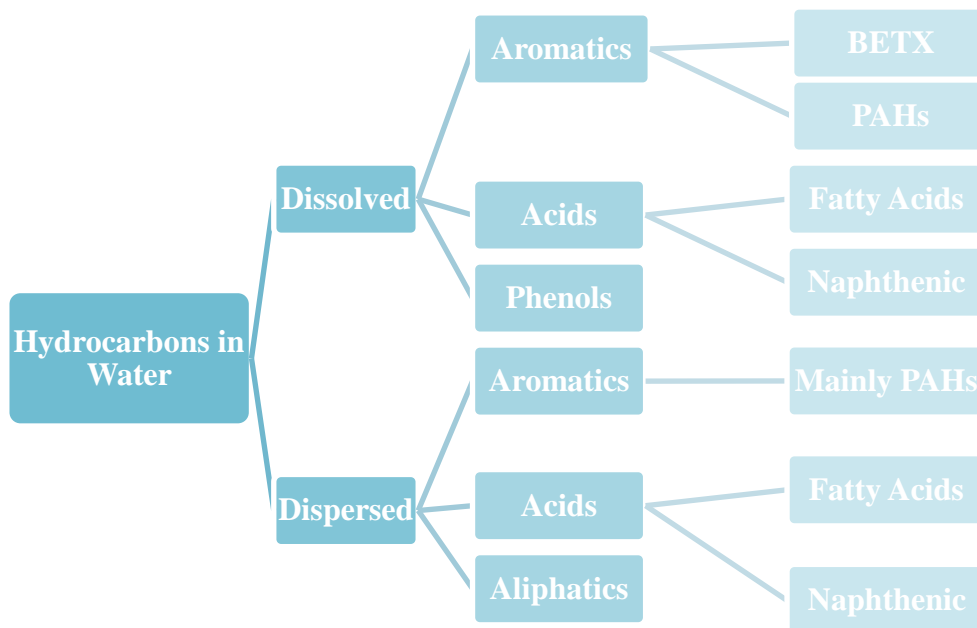
**Table 3 - Concentrations (mg/L) of BTEX in produced water from US Gulf of Mexico and Indonesia production facilities (Neff 2002)**

Polycyclic aromatic Hydrocarbons (PAH) are also contained in the produced water. Their toxicity is high, so that makes them a primary environmental concern for the disposal of the treated water. Their concentration can range between 0.04 to 3 mg/L and they consist of 2 and 3-ring PAH such as naphthalene, phenanthrene and their alkyl homologues. 4 to 6 ring PAH are rare, but their low water solubility promotes the creation of oil in water emulsions. Table 4 illustrates PAH concentrations in different production areas in the Gulf of Mexico, Sotian Shelf, North Sea and Grand Banks in Canada. Phenols are also found in produced water at concentrations of less than 20 mg/L (Neff et al. 2011). Oil in produced water can be either dissolved or dispersed as it is shown in Figure 2

Compound	Gulf of Mexico	North Sea	Scotian Shelf	Grand Banks
Naphthalene	5.3–90.2	237–394	1,512	131
C1-Naphthalenes	4.2–73.2	123–354	499	186
C2-Naphthalenes	4.4–88.2	26.1–260	92	163
C3-Naphthalenes	2.8–82.6	19.3–81.3	17	97.2
C4-Naphthalenes	1.0–52.4	1.1–75.7	3.0	54.1
Acenaphthylene	ND–1.1	ND	1.3	2.3
Acenaphthene	ND–0.10	0.37–4.1	ND	ND
Biphenyl	0.36–10.6	12.1–51.7	ND	ND
Fluorene	0.06–2.8	2.6–21.7	13	16.5
C1-Fluorenes	0.09–8.7	1.1–27.3	3	23.7
C2-Fluorenes	0.20–15.5	0.54–33.2	0.35	4.8
C3-Fluorenes	0.27–17.6	0.30–25.5	ND	ND
Anthracene	ND–0.45	ND	0.26	ND
Phenanthrene	0.11–8.8	1.3–32.0	4.0	29.3
C1-Phenanthrenes	0.24–25.1	0.86–51.9	1.30	45.0
C2-Phenanthrenes	0.25–31.2	0.41–51.8	0.55	37.1
C3-Phenanthrenes	ND–22.5	0.20–34.3	0.37	24.4
C4-Phenanthrenes	ND–11.3	0.50–27.2	ND	13.2
Fluoranthene ND–	ND–0.12	0.01–1.1	0.39	0.51
Pyrene	0.01–0.29	0.03–1.9	0.36	0.94

C1-Fluoranthenes/ Pyrenes	ND–2.4	0.07–10.3	0.43	5.8
C2-Fluoranthenes/ Pyrenes	ND–4.4	0.21–11.6	ND	9.1
Benz(a)anthracene	ND–0.20	0.01–0.74	0.32	0.60
Chrysene	ND–0.85	0.02–2.4	ND	3.6
C1-Chrysenes	ND–2.4	0.06–4.4	ND	6.3
C2-Chrysenes	ND–3.5	1.3–5.9	ND	18.8
C3-Chrysenes	ND–3.3	0.68–3.5	ND	6.7
C4-Chrysenes	ND–2.6	ND	ND	4.2
Benzo(b)fluoranthene	ND–0.03	0.01–0.54	ND	0.61
Benzo(k)fluoranthene	ND–0.07	0.006–0.15	ND	ND
Benzo(e)pyrene	ND–0.10	0.01–0.82	ND	0.83
Benzo(a)pyrene	ND–0.09	0.01–0.41	ND	0.38
Perylene	0.04–2.0	0.005–0.11	ND	ND
Indeno(1,2,3- cd)pyrene	ND–0.01	0.022–0.23	ND	ND
Dibenz(a,h)anthracene	ND–0.02	0.012–0.10	ND	0.21
Benzo(ghi)perylene	ND–0.03	0.01–0.28	ND	0.17
Total PAHs	40–600	419–1,559	2,148	845

**Table 4 - Concentrations of PAH or alkyl congener groups in produced water in various production areas (ND: Not Detected) (Neff et al. 2011)**



**Figure 2 - Dispersed and dissolved oil scheme**

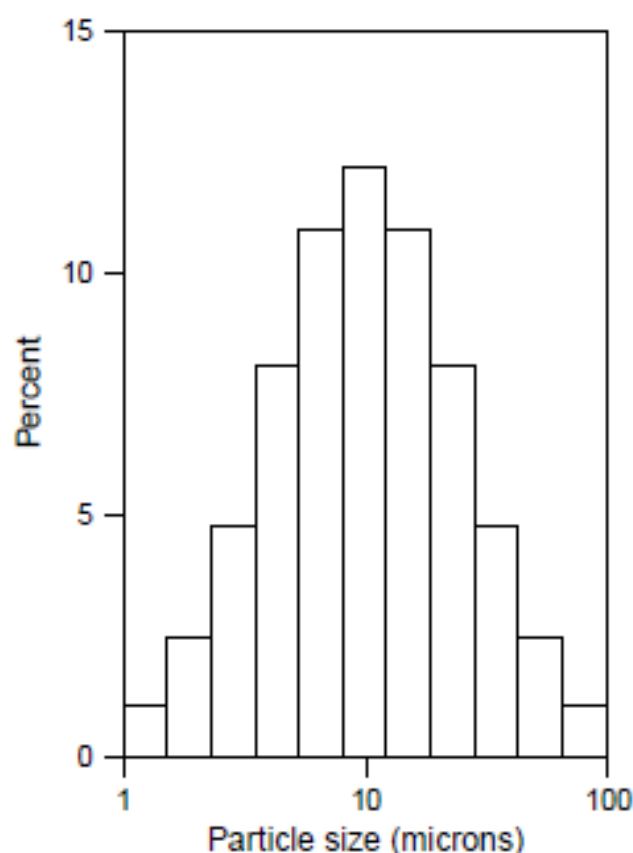
### *Dissolved Oil*

If water is produced together with a gas condensate, the dissolved oil in water will be in greater quantities. This oil is defined as "soluble oil" and consists of hydrocarbons that are soluble in the produced water. Gravitational separation methods cannot remove this type of oil. Bio treatment, adsorption filtration, solvent extraction and

membrane techniques targeting to the enhancement of the separation are still on experimental stage. Solubility is not affected dramatically at the temperature conditions of the usual treatment (77-167 F°). To reduce the oil concentration a saltiest brine can be introduced to the produced water. This will salt out the lighter hydrocarbons and it will force the heavier ones to coalesce. Extra care should be taken for the toxic aromatics of the BTEX scheme (Benzene, toluene, ethyl benzene and xylenes) which are highly soluble in the water (Stewart and Arnold 2011).

### *Dispersed oil*

The diameter of the dispersed oil droplets in oil-in-water emulsions ranges from 0.5  $\mu\text{m}$  to 200  $\mu\text{m}$  and it is a key factor for the water treatment. Stokes law governs the relation between the oil droplet diameter and the settling velocity and it has great effect on the efficiency of the separation equipment used for removal of the oil droplet from the water. The greater the size of the droplets, the higher the efficiency of the equipment, which is crucial for the disposed water to be in compliance with the standards and regulations. An example of oil droplet distribution is shown in Figure 3. A distribution curve can be drawn, connecting the midpoints of the tops of the bars (Stewart and Arnold 2011).



**Figure 3** - Oil droplet distribution histogram (Stewart and Arnold 2011)

Different oil droplet sizes can be encountered in the same water system. Interfacial tension, turbulence, temperature and shearing are decisive factors for the size distribution.

## **Toxicants**

Special care should be taken for the toxicity effects of the produced water in the environment and on marine organisms. The toxicity is estimated by a number of tests on organisms treated by water effluents at given concentrations. Mortality and reduction of birth rate are the main measurements. Water treatment methods such as the removal of emulsions contribute to the reduction of toxicity (Stewart and Arnold 2009).

## **Potential Uses for Produced Water**

Treated produced water can be used in a number of applications. It can be used for non potable uses, aquifer recharge storage and recovery, surface water discharge, irrigation, wildlife maintenance and enhancement, dust control, fire protection and others. Especially in the US, the beneficial uses of produced water are an important part of the oil and gas industry water management policies (Drewes 2009). For direct discharge, where the produced water is discharged directly in accordance to the regulation norms, the cost varies from \$0.03 to \$0.05 per barrel. For reuse in oil and gas processing industries the cost varies from \$0.04 to \$0.07 per barrel, while for converting it into an asset the cost varies from \$0.25 to \$2.00 per barrel. (Duraismy et al. 2013).

## ***Injection of oil in water emulsions in the reservoirs as an Enhanced Oil Recovery Technique***

A technique involving the injection of oil in water emulsions into reservoirs for the production of high viscosity oils have been applied in various production sites as an alternative to polymer and surfactant flooding. A characteristic example of this case is Midway Sunset Oilfield where 33,000 bbls of 14% oil in water content in the form of emulsions were injected, leading to an estimated additional oil recovery of 55,000 bbl (McAuliffe (1973 a and b). Recent studies (Sarma et al. 1998, Mandal et al. 2010, Baldygin et al. 2014 and de Farias et al. 2016) support the idea that higher percentages of oil can be recovered using this process instead of conventional waterflooding.

Karambeigi et al. 2015, describe the related mechanism. It is based on the hypothesis that capillary forces are responsible for the entrapment of the oil into the pore space when the pores constrain the water-oil interface to a high degree of curvature. Viscous

fluids flow are counteracting the effect of capillary forces and this results in the displacement of the entrapped oil. The capillary number, which is defined as the ratio of viscous forces to surface tension, determines how strong is the entrapment of the oil in the porous medium. It is a dimensionless quantity which can be calculated by Equation 1.

$$Ca = \frac{\mu Q}{\sigma A}$$

Where:

$\mu$  = the dynamic viscosity of the liquid

$Q$  = the flow rate

$A$  = the transversal area

$\sigma$  = interfacial tension between the two fluid phases

**Equation 1** - Capillary number formula (Guillen et al. 2010)

To mobilize this oil a small difference in the interfacial tension between oil and the displacement fluid is needed (Karambeigi et al 2015). Emulsion formation is also favored by low interfacial tension. A reduction of interfacial tension causes a reduction of the capillary forces that leave the oil behind any immiscible displacement and lead to additional oil recovery (Mandal et al. 2010). The proper selection of the dispersed hydrocarbon phase has been under research in various studies and it depends on its stability under the reservoir conditions, efficiency, cost effectiveness and environmental compatibility (Karambeigi et al. 2015).

## Chapter 2 - Emulsions

The word "emulsion" comes from the ancient Greek word “ἀμέλγω” (to milk) since milk itself is an emulsion of fat, proteins, lactose and other solids dispersed in water. As an emulsion we can describe a heterogeneous system that consists of at least one immiscible liquid dispersed in another liquid in the form of droplets, with diameters that generally exceed 0.1 micron. Emulsions are a sub-category of colloids, which in general are derived as mixtures composed of dispersed insoluble particles or droplets of one substance within a fluid which is considered as the continuous phase and are stabilized under the presence of an emulsifier. Emulsifiers or emulsifying agents are substances that cause the formation of interfacial films around the dispersed oil droplets, preventing the coalescence process (Bai and Bai 2012). Two immiscible fluids, water and oil, are involved in the formation of emulsions in the oil industry. In case oil is the dispersed phase and water is the continuous one, the emulsions are called oil in water as shown in Figure 4. Usually they are formulated when watercut exceeds 80%. Water droplets in oil continuous phase is the most common emulsion in the oil industry. Their formation depends on the volume fraction of the phases and the type of the emulsifier and they are usually formed at watercuts of up to 80%. There are also multiple or complex emulsions for watercuts higher than 95%. In this case water in oil in water or oil in water in oil emulsions can be formed. Emulsion formation occurs under high shear stresses in certain parts of the equipment such as the bottomhole and the transfer pumps. Flow through tubes, wellhead, manifold and flowlines promotes the formation of emulsions as well as during the high pressure drops through chokes and valves (Bai and Bai 2012).

Summarizing, three types of emulsions can be confronted in oil industry - oil in water, water in oil or complex emulsions of oil in water in oil or water in oil in water. The type of emulsion formed depends on the volume fraction of the phases. The boundary between the continuous and the dispersed phase is called interface and many characteristics of the emulsions depend on its attribute. Its thickness  $\delta$ , defines an area that has different properties from water and oil. In particular, the free energy of the surface between the phases, called as "surface tension" or "surface energy", is a decisive factor for the characteristics of an emulsion. The Gibbs-Deuhem Equation 2, explains mathematically the correlation between the surface free energy, entropy, interfacial energy and composition.

$$dG^a = -S^a dT + Ad\gamma + \sum n_i d\mu_i$$

where for constant temperature and composition

$$dG^a = Ad\gamma$$

$$\gamma = \left( \frac{\partial G^a}{\partial A} \right)_{T, n_i}$$

where:

$dG$  = The total differential of the Gibbs free energy

$S$  = Entropy

$T$  = Temperature

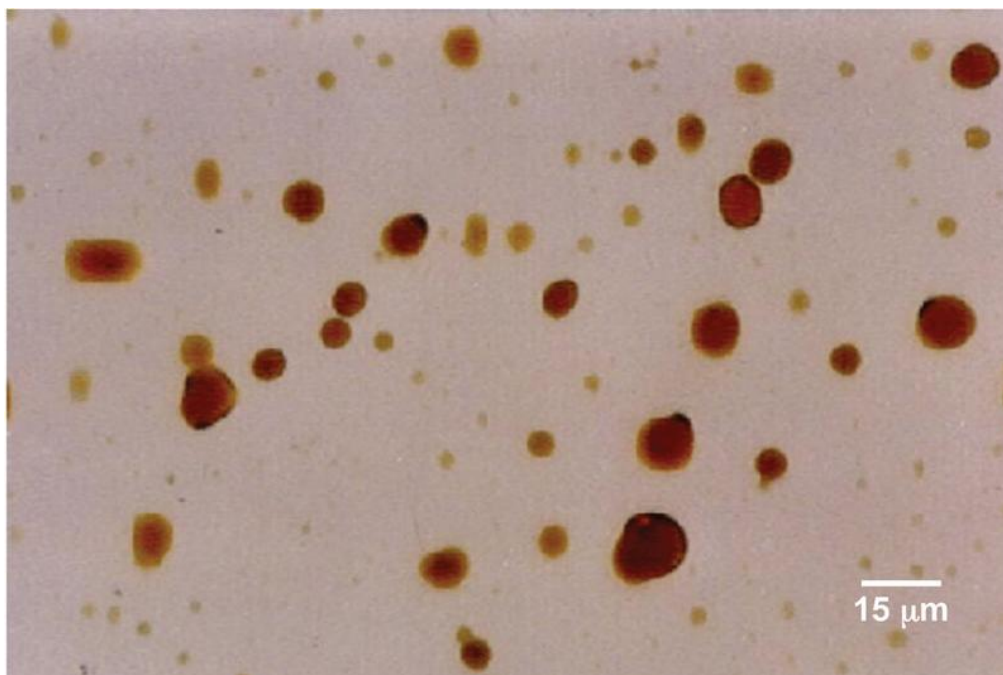
$A$  = area

$\gamma$  = Interfacial tension

$n_i$  = The number of moles

$d\mu_i$  = The infinitesimal increase in chemical potential

**Equation 2** - Definition of free energy



**Figure 4** – Photomicrograph of an oil-in-water emulsion. (Oil emulsions. Retrieved from: [http://petrowiki.org/Oil\\_emulsions](http://petrowiki.org/Oil_emulsions))

Free oil in the wastewater stream will rise to the surface due to gravity and form an oil layer. Emulsified oils will not rise on the surface by gravity alone. Oils can be either mechanically or chemically emulsified. Mechanically emulsified oils are produced with water at high shear forces in parts of the equipment like centrifugal pumps. Mechanically emulsified oils will eventually separate by gravity. Chemically emulsified oils are produced by the action of soaps, detergents and degreasers. Cutting lubricants are a form of oil water emulsions which are used to cool and provide lubrication for the cutting tool. This type of emulsions are more difficult to treat as the emulsifier is selected based on its strength to hold the oil in an emulsified state. If pH is greater than 8.5 the oil is chemically emulsified and will not separate by gravity. (Alther 2001)

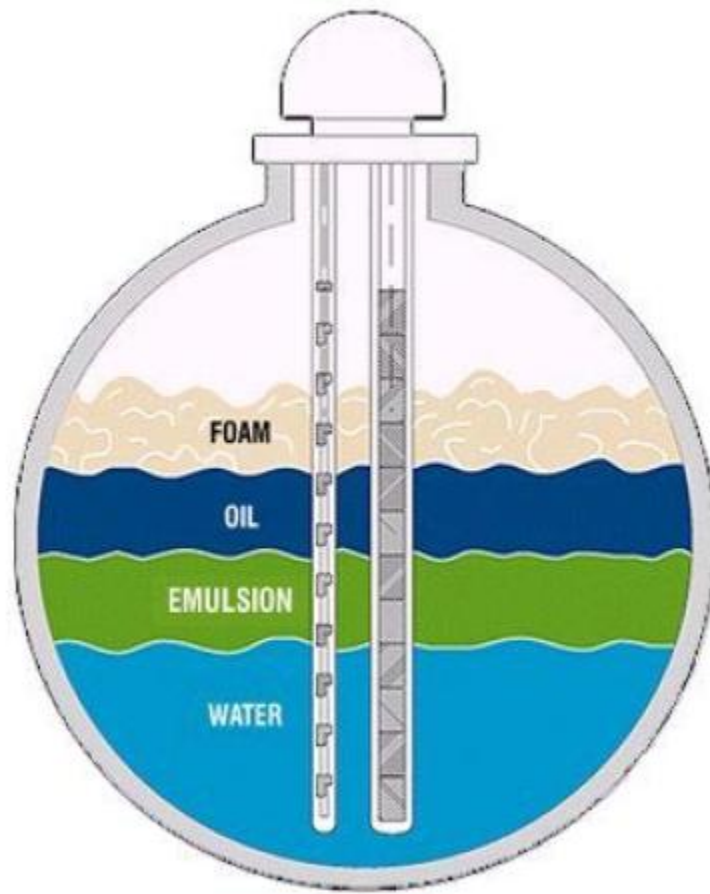
Another categorization for emulsions is related to the size of the droplets spread within the continuous phase. Macroemulsions' droplet size is greater than 1μm while microemulsions' ones are lower than that. Most of the emulsions that we encounter in oilfields belong in the first category and they are characterized by thermodynamic

instability, since the phases tend to separate over time due to the reduction in interfacial energy. Microemulsions on the other hand are considered thermodynamically stable and they are formed due to extremely low interfacial energy. Interfacial energy or interfacial tension is defined as the tendency towards the minimization of the surface area between two liquids or a liquid and a solid (Alther 1997).

Emulsions can be also classified according to their degree of stability as loose, medium and tight emulsions. Loose emulsions can be separated within a few minutes, medium ones need approximately ten minutes while tight ones within hours, days, weeks or not at all (Fink 2012).

## Formation of Emulsions

The ratio of water and oil as well as the presence of emulsifiers are decisive factors for the formation of an emulsion. Mixing can occur during flow through the reservoir rock, through the production pipeline, through the surface equipment and as a result of the release of gas bubbles. The more extensive the mixing, the smaller the size of the droplets. Emulsifiers are critical for the formation of the emulsion. Naturally-occurring emulsifiers include surface active agents and finely divided solids. The most common type of emulsifier in the oil industry is ions such as  $\text{OH}^-$  that are adsorbed on the droplets, producing a charge which causes electrostatic repulsion (Tadros 2013). Low stability emulsions, which can be easily resolved, are expected in case of low concentrations of such emulsifiers. Organic acids, bases, asphaltenes and resins are partly soluble both in water and oil due to their hydrophobic and hydrophilic parts. They have a tendency to concentrate at the interface of oil and water and form films which lead to the reduction of interfacial tension and enhance dispersion, thus promoting the emulsification process. In some cases surfactants coming from drilling fluids, stimulation chemicals, corrosion and scale inhibitors, waxes and asphaltenes control agents may be present. Fine solids can also act as stabilizers of the emulsions and they also have hydrophobic and hydrophilic parts. They can come from clays, sand, silt, asphaltenes, waxes, corrosion products, shales, mineral scales and drilling muds. Water, oil and emulsion configuration in a tank is presented in Figure 5.



**Figure 5** - *Schematic view of the different layers of foam, oil, emulsion and water in a tank*  
(Lees 2005)

## Properties and characteristics of emulsions

The emulsification system involves a continuous fluid phase a dispersed one within the first and the interface. Interface consists of emulsifiers which keep the emulsions stable by binding the continuous phase and the dispersed one together and doesn't permit the oil droplets to coalesce. It is not a "single molecule line" but a region whose thickness can vary and its properties are different than oil and water phases. Temperature, composition and droplet size distribution affect the properties of emulsions Their characteristics can change at various stages and that is due to absorbable materials contained in various oils, adsorption rate of the emulsifier, temperature changes, pressure changes and the degree of agitation (Tadros 2013).

### Color

Depending on the geometry of the interphase, the light passing through, will give a cloudy color impression due to the in general non-equally scattering of the light. The most common colors of emulsions range between dark brown to lighter brown,

however depending on the oil/water content and its characteristics, other color impressions can be formed. In case of equally scattered light, a white color impression will appear. In two special cases – microemulsions and nanoemulsions (droplet size < 100 nm) the appearance will be semitransparent. This happens because the droplet size is significantly smaller than the wavelength of the visible spectrum of light (ranges between 390 and 750 nm), permitting it to pass through the emulsion without being scattered. Overall, if large diameter droplets of oil exist then the color will be darker while for small diameter of droplets it will be lighter. (Chantrapornchai et al. 2008)

## Viscosity

Emulsion's viscosity can be a lot higher than the one of water or oil, due to non-Newtonian behavior which is caused by the high concentration of droplets or structural viscosity. Structural viscosity depends on the flow rate and it is typical of disperse systems. During the flow of liquids the work done by external forces, not only overcomes the Newtonian viscosity but also destroys the structure of the liquid and re-orientates the particles in the flow. This viscosity that is related to the structure of the liquid is called "structural" viscosity and it plays a key role in the flow of the liquids (Kokal 2005).

Dispersed phase's droplet size and the oil-water ratio are two critical factors for the viscosity (Arirachakaran et al. 1989). The highest viscosity value will occur at the point of phase inversion. Phase inversion occurs when agitated oil in water emulsion of certain composition reverts to water in oil emulsion and vice versa (Preziosi et al. 2013). The composition of the interface is similar to the critical phase inversion composition and this fact combined with the high viscosity value will slow down the separation process. Up to 80% of watercut, the viscosity raises along with the percentage of watercut. In contents of water higher than 80%, where actually oil in water emulsions are formed, viscosity declines (Figure 6). Interfacial viscosity is also an important property of the emulsions. The interface is a 2D insoluble viscous monolayer which is independent of the 3D fluid space. In case of high interfacial viscosity, there will be a delay in the liquid drainage rate which will have a stabilizing impact on the emulsion. It is suggested by studies (Calderon et al. 2007) that it plays a key role in the demulsification process. Interfacial viscosity can be defined by Equation 3.

$$\sigma_s = \eta_s \gamma$$

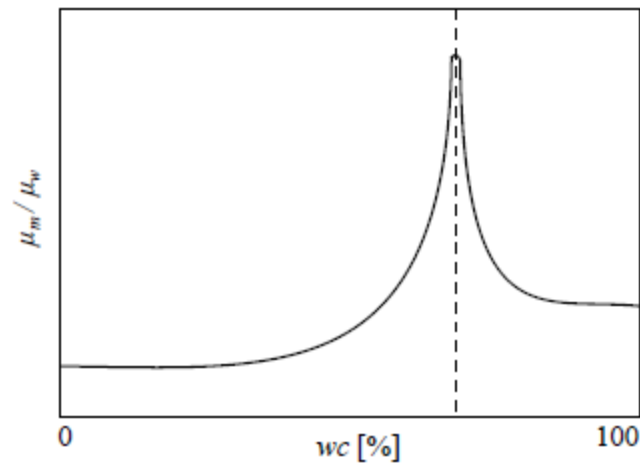
where:

$\gamma$  = shear rate

$\eta_s$  = interfacial viscosity in  $\text{Nm}^{-1}\text{s}$

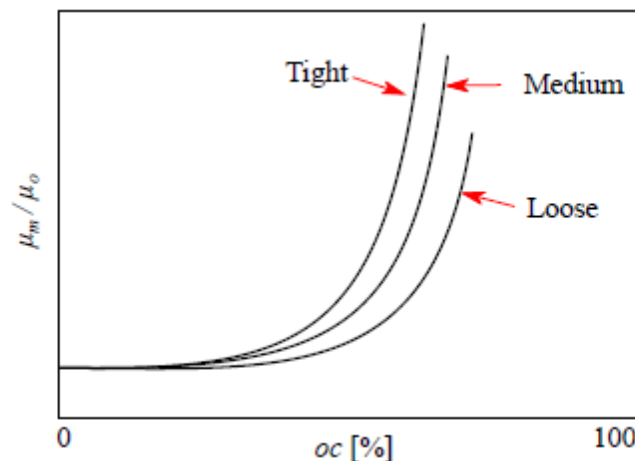
$\sigma_s$  = interfacial stress

**Equation 3 - Viscosity calculation (Oil emulsions. Retrieved from:**  
[http://petrowiki.org/Oil\\_emulsions#Viscosity\\_of\\_emulsions](http://petrowiki.org/Oil_emulsions#Viscosity_of_emulsions))



**Figure 6** - Relative viscosity (mixture viscosity over the viscosity of pure water) in oil-water emulsions as a function of watercut. The phase inversion point is represented by the vertical dashed line. (Arirachakaran et al.1989)

Smaller droplets make "tighter" emulsions while larger ones make more "loose" emulsions. Thus the smaller the droplets are present in the emulsion the higher the viscosity of the mixture as it moves towards the phase inversion point. This effect is depicted in Figure 7. Crude oil characteristics and the degree of turbulence in the separator are decisive for the droplet's size. Viscosity can further be affected by flowrates and other variables during the separation process, creating a reduction of the separation rate.



**Figure 7** - Relative viscosity (mixture viscosity over the viscosity of oil in oil-water emulsions as a function of oilcut for three emulsions with different tightness. (Woelflin 1942)

Woelflin in 1942 suggested that oil-water ratio of the mixture is of greater importance than that of tightness. Nevertheless, despite the large variety of formulas for the prediction of viscosity of emulsions, none of them can be applied for all the oil fields due to different conditions existing in each one.

## Emulsification

Two main interaction forces act for the stabilization of emulsions: electrostatic and steric repulsion forces.

### *Electrostatic stabilization repulsive forces*

Electrostatic stabilization is caused by mutual repulsive forces that act when electrical charged surfaces approach each other. A charged layer is formed at the interface by ionic or ionisable surfactants and is neutralized by counter ions in the continuous phase for the case of oil in water emulsions. The term "double layer" is used for the charged surface and the counter ions (Urrutia 2006). Electrostatic repulsion can be produced by the adsorption of ionic surfactants as illustrated in Figure 8. The surface potential, defined as  $\psi_o$  decreases linearly to  $\psi_d$  (stern or zeta potential) and then further decreases exponentially as distance ( $x$ ) increases. A double layer is formed which extension depends on the proportional relation between electrolyte concentration and valency. Repulsion occurs when oil droplets in dispersion approach each other in a way that the double layer begins to overlap. Limited space doesn't permit complete potential decay and the double layers cannot develop further. Equation 4 defines the repulsive interaction. As  $G_{el}$  is defined the repulsive interaction,  $\epsilon_r$  is the relative permittivity,  $\epsilon_o$  is the permittivity of free space and  $\kappa$  is the Debye-Huckel parameter. The extension of the double layer is defined as  $1/\kappa$  and is given by Equation 5, where  $k$  is the Boltzmann constant,  $T$  is the absolute temperature,  $n_o$  is the ions per unit volume,  $Z_i$  is the valency of the ions and  $e$  is the electronic charge (Tadros 2013)

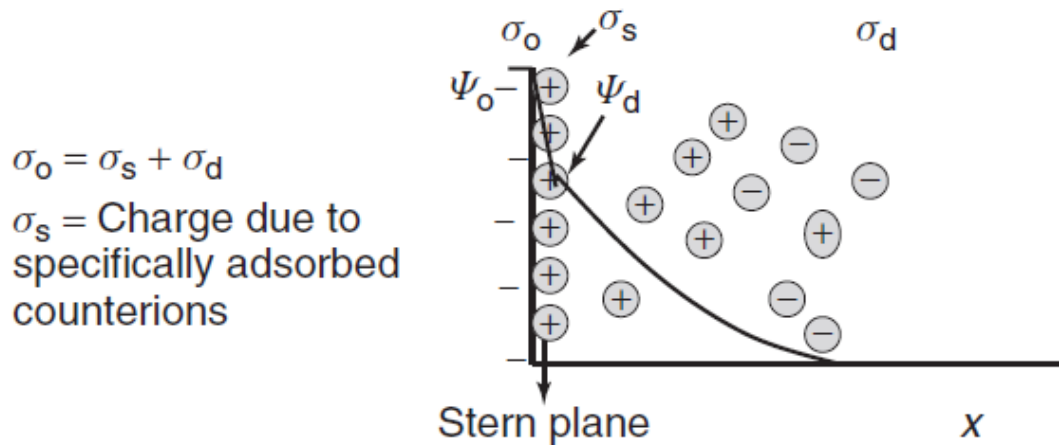
$$G_{el} = 2\pi R \epsilon_r \epsilon_o \psi_o^2 \ln[1 + \exp(-\kappa h)]$$

**Equation 4 - Repulsive interaction (Tadros 2013)**

$$\left(\frac{1}{\kappa}\right) = \left(\frac{\epsilon_r \epsilon_o kT}{2n_o Z_i^2 e^2}\right)$$

**Equation 5 - Extension of the double layer (Tadros 2013)**

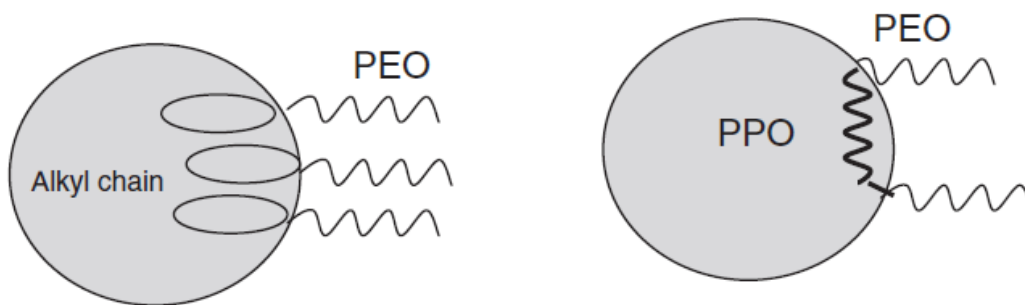
The extension or thickness of the double layer is inversely proportional to the electrolyte concentration, which means that repulsion will decrease for increasing electrolyte concentration. When repulsive interaction energy is at its maximum then flocculation is prevented. This occurs for high values of surface potential and low electrolyte concentration and valency (Tadros 2013).



**Figure 8** - Schematic representation of double layers produced by ionic surfactant (Tadros 2013)

### *Steric stabilization repulsive forces*

Steric stabilization is the result of a physical barrier to coalescence. Non ionic surfactants (e.g. Alcohol ethoxylates or Polyethylene oxide - Polypropylene oxide - Polyethylene oxide block copolymers as illustrated in Figure 9 form thick hydrophilic chains and produce repulsion forces due to unfavorable mixing of the surfactant's chains or entropic, volume restriction and elastic interaction. The total energy of the interaction is the sum of the free energy produced by non favorable mixing, the energy of the repulsive interaction and the attractive energy between the droplets.

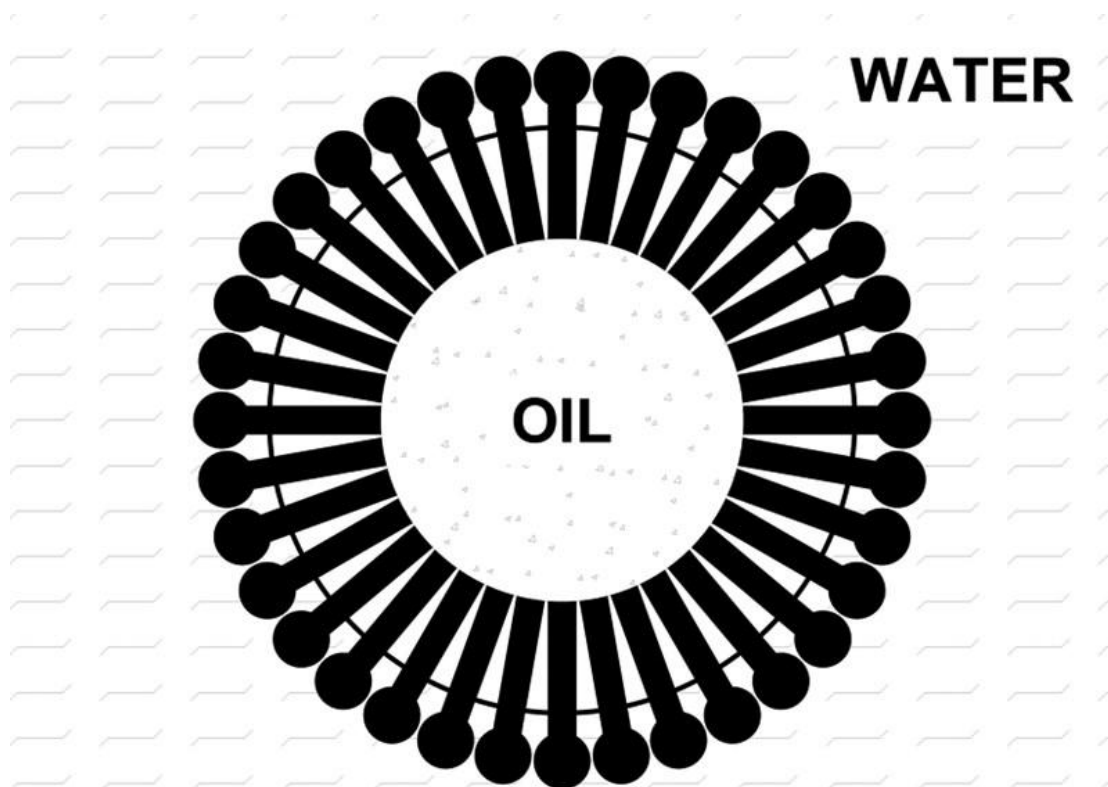


**Figure 9** - Schematic representation of adsorbed surfactants that lead to steric stabilization of oil in water emulsions (Tadros 2013)

### *Emulsifiers*

Emulsifiers are substances such as surfactants or soaps that can be present to the inflow of water and oil and they increase the stability of an emulsion due to interfacial action by causing heterogeneity on the surface. Their ability to reduce the interfacial

tension is crucial for the formation of emulsions due to the fact that it produces charges on the surface by their adsorption to the interface of oil and water. As adsorption is defined the attraction of one substance to the surface of another while absorption is the penetration of a substance into the inner structure of another. Emulsifiers can be present in small amounts or form polymolecular aggregates called micelles. Emulsifiers have molecules with hydrophilic and hydrophobic portions. When they migrate to the interface of oil and water, their hydrophobic portion will adhere to oil droplets while their hydrophilic one will stay in water forming a barrier around the dispersed phase of oil droplets as shown in Figure 10. Finely divided solids can act as emulsifiers due to the fact that oil droplets coat these solids leading to the formation of emulsions. (Alther 1997).

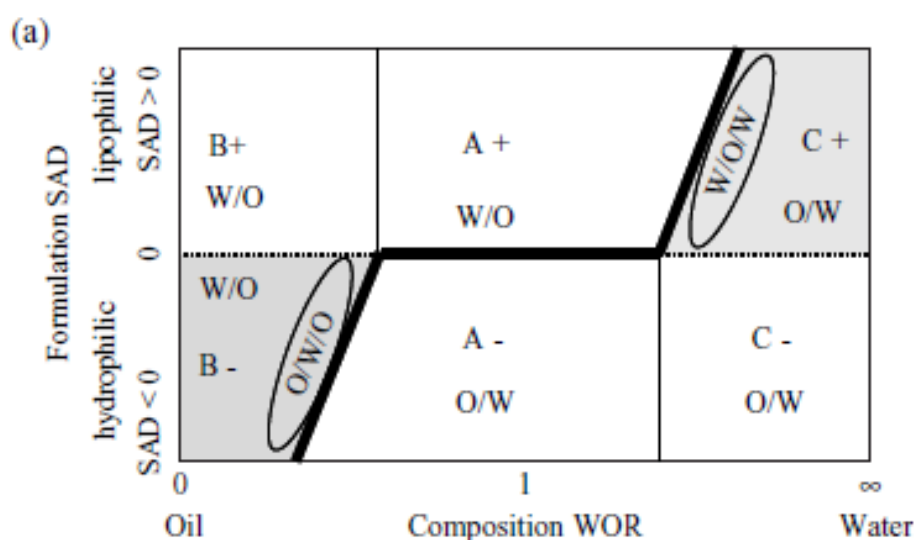


**Figure 10** - Oil in water emulsion, surfactant orientation towards the oil-water interface. Thick black head represents the hydrophile end of the surfactant while its tail represents its hydrophobic end (Retrieved from: <http://www.processingmagazine.com/emulsion-stability-basics/>)

### *Spontaneous Emulsification*

When two immiscible fluids are in contact but not in physicochemical equilibrium, droplets can be formed. The process can be accelerated by stirring but is referred in the literature also as self-emulsification exactly because it can be initiated without external energy input (Shi et al 2015). Mostly this phenomenon appears in oil in water emulsions and various mechanisms have been proposed (Solans et al. 2016).

An example of spontaneous emulsification is the phase inversion phenomenon. Oil in water emulsions or water in oil emulsions can be inverted from one to other due to changes in physicochemical parameters such as salinity, temperature and pH. Those parameters need to be taken into account and that's why Surfactant Affinity Difference (SAD) (Calderon et al.2007) has been introduced. SAD is an empirical number which characterizes the surfactant for certain values of the parameters mentioned before. In Figure 11 the effect of SAD in the formulation of the emulsions is shown. Positive SAD implies surfactant's affinity for the oily phase, negative SAD implies surfactant's affinity for the water phase while zero SAD implies affinity to both water and oil. All the above are valid under the consideration that oil and water volumes are equal. When oil content is high, water in oil emulsions are favored and respectively for high water content oil in water emulsions will occur. Nevertheless it is possible that double emulsions are formed. This phenomenon is considered as abnormal because although it is in accordance with volumetric requirements it is against the formulation ones. This can lead to double emulsions of oil-in-water-in-oil (Calderon et al. 2007)



**Figure 11** - Schematic formulation-composition map. SAD is positive for surfactants with oil affinity and negative for water affinity ones while grey zones are considered as abnormal. Regions with letter "A" have equal content in oil and water while regions with letter "B" have high oil content and letter "C" high water content. Areas that are colored in gray are considered as abnormal and double emulsions can be formed there (Calderon et al. 2007)

### HLB Value concept

The Hydrophilic - Lipophilic Balance number (HLB) was introduced in the late 40's as a scheme which aids in the determination of the surfactants-emulsifiers present in an emulsion. It shows the balance of the size and strength of the hydrophilic (polar) and the lipophilic (non polar) groups of the emulsifiers. The surfactants are assigned a

number based on their solubility in the water as illustrated in Table 5. High HLB values indicate the presence of hydrophilic surfactants that stabilize the oil in water emulsions and their value can range between 8-18. Although the HLB constitutes an empirical approach, it is very simple and popular in the industry (ICI Americas INC 1980). The HLB value is calculated using Equation 6 where m is the number of hydrophilic groups in the molecule,  $H_i$  is the value of the  $i^{\text{th}}$  hydrophilic group and n is the number of the lipophilic groups in the molecule. The HLB values of common hydrophilic and lipophilic functional groups are presented in Figure 12.

HLB Range	USE
4-6	W/O Emulsifiers
7-9	Wetting Agents
8-18	O/W Emulsifiers
13-15	Detergents
10-18	Solubilizers

**Table 5 - HLB Values concept (ICI Americas INC 1980)**

$$HLB = 7 + \sum_{i=1}^m H_i - nx0.475$$

**Equation 6 - HLB value calculation (Kanicky et al. 2001)**

Hydrophilic group	HLB	Lipophilic group	HLB
-SO <sub>4</sub> Na	38.7	-CH-	-0.475
-COOK	21.1	-CH <sub>2</sub> -	
-COONa	19.1	-CH <sub>3</sub> -	
Sulfonate	~ 11.0	-CH=	
-N (tertiary amine)	9.4	-(CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -O-)	-0.15
Ester (sorbitan ring)	6.8		
Ester (free)	2.4		
-COOH	2.1		
-OH (free)	1.9		
-O-	1.3		
-OH (sorbitan ring)	0.5		

**Figure 12- HLB values of common lipophilic and hydrophilic groups (Kanicky et al. 2001)**

## Resolution of Emulsions

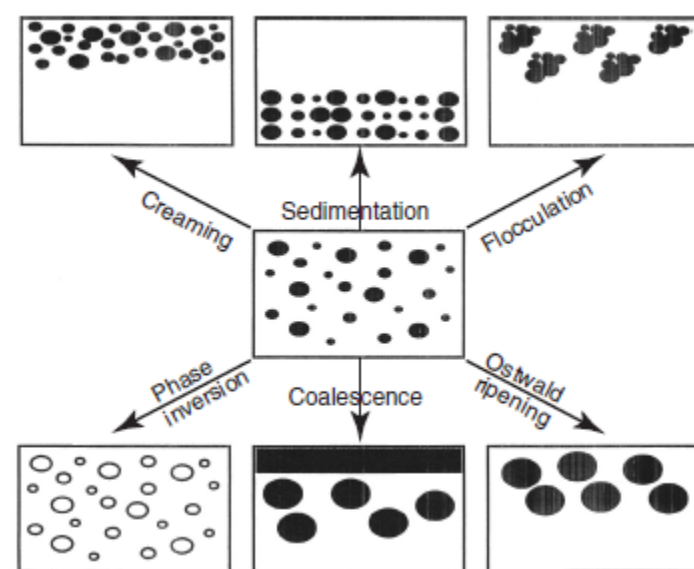
### Van der Waals attraction forces

In absence or neutralization of repulsion forces, van der Waals attraction is the main mechanism causing the coalescence and flocculation of oil in water emulsions. Van der Waals attraction can be categorized in three different categories: dipole-dipole, dipole-induced dipole and dispersion interactions. Different orientation of dipoles tend to cancel the first two categories of van der Waals attraction since they are

defined as vectors. Thus dispersion interactions (London) that arise from charge fluctuations are acting for emulsion resolution (Tadros 2013).

### *Processes of separation*

Gravitational or centrifugal forces overcoming the thermal motion of oil droplets are the main cause of emulsion resolution. Processes that take place during the phenomenon of emulsion resolution are creaming, sedimentation, flocculation, phase inversion, coalescence and ostwald ripening as illustrated in Figure 13. Flotation which will also be described in a later chapter of this work is an industrial process that aids the resolution of emulsions. As demulsification or resolution of emulsions is defined the separation of oil and water into two distinct parts after neutralizing the stability factors of the emulsion. The main target of a demulsification process is the destruction of the interface by driving the emulsifier either to the water or the oil phase.



**Figure 13 - Demulsification mechanisms (Tadros 2013)**

### *Sedimentation and Creaming - Gravity Separation*

Sedimentation is caused by the gravitational forces which act due to density difference between the continuous and the dispersed phase of the emulsion. Centrifugal forces are the cause of these processes also. The simplest and the most common separation equipment is based on gravity principles. When centrifugal or gravitational forces exceed the thermal motion of the droplets, a concentration gradient will build up in the system forcing the larger droplets to rise vertically to the top. Drag force resists droplets' vertical movement (Tadros 2013). In the point where drag force and gravity force are equal, the constant velocity is reached and it can be

computed by Equation 7. Equation 8 is used to calculate the gravitational buoyancy force. The term  $g$  represents the gravitational acceleration. In case of some other driving force it can be replaced. Frictional force  $F_d$  is calculated by Equation 9 (Stewart and Arnold 2009).

$$a) V_o = \frac{1.78 \times 10^{-6} (\Delta SG)(d_m)^2}{\mu_w}$$

where:

$V_o$  = Rising vertical velocity of the droplet (ft/sec)

$d_m$  = Droplet diameter in microns

$\mu_w$  = Viscosity of the water (cp)

$\Delta SG$  = Difference of specific gravity between oil and water

**Equation 7** - Constant velocity equation - (Field Units) (Stewart and Arnold 2009).

$$F_g = V_d(\rho_d - \rho_m)g$$

where:

$F_g$  = Gravitational force

$V_d$  = Volume of droplet

$\rho_d$  = Density of droplet

$\rho_m$  = Density of medium

$g$  = gravitational acceleration

**Equation 8** - Calculation of gravitational buoyancy force - SI Units (Stoke's law. Retrieved from: [https://en.wikipedia.org/wiki/Stokes%27\\_law](https://en.wikipedia.org/wiki/Stokes%27_law))

$$F_d = -0.5 C_D A_d \rho |v|v$$

where:

$C_D$  = Drag coefficient

$A_d$  = Reference area

$v$  = relative velocity of the object surrounding the fluid

$\rho$  = density

**Equation 9** - Frictional force calculation (Ishii and Zuber 1979)

Equation 7 for rising velocity is based in the following observations. The first one is that the larger the size of the oil droplet the greater its vertical velocity. That means that bigger oil droplets have smaller times of settling in the surface and thus they can be treated easier. The second observation is that the greater is the difference in specific gravities the greater will be the velocity of the oil droplet. This means that lighter crude oils are easier to treat. The last observation is that since viscosity depends on temperature, on higher temperatures there will be greater droplet

velocities. This means that treatment of water is easier in high temperatures. Theoretically Stokes law acts for oil droplets of 1-10  $\mu\text{m}$  diameter. In practice, 30  $\mu\text{m}$  is the lower limit for the size of the droplets that can be removed. Below this limitation the oil droplet rise to the surface depends on other factors than gravity like vibrations and pressure fluctuations (Stewart and Arnold 2009).

### *Flocculation*

During this process droplets are attracted close to each other but still they don't form a bigger droplet due to a thin film of continuous phase between them. Van der Waals forces attract them together but electrostatic or steric repulsion prevent the unification. Flocculation thus occurs when there is not sufficient repulsion to keep the droplets apart to distances where the van der Waals attraction is weak. This process though accelerates sedimentation and it can be "strong" or weak" depending on the magnitude of the attractive energy involved (Tadros 2013). Negative charge of oil droplets need to be neutralized to overcome steric repulsion forces. Anionic / non ionic polymeric flocculants aid this process since they bring together and agglomerate the micro flocs formed by the coagulants (Lee et al. 2014)

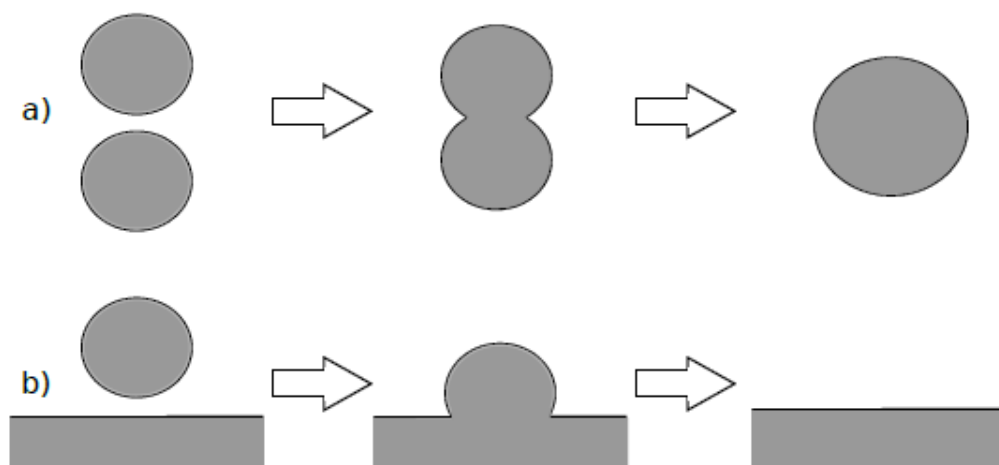
### *Ostwald Ripening*

This process is a result of finite solubility of the liquid phases. Often immiscible fluids have comparable solubilities which leads to dissolution of smaller droplets in the continuous phase and deposition into bigger droplets leading to larger droplet size distributions (Tadros 2013).

### *Coalescence*

Coalescence is the process of thinning and destruction of the film between the droplets and their merging into larger droplets. The driving force of coalescence is the surface and film fluctuations which result in close approach of the droplets (Tadros 2013). Coalescence mostly occurs in the separators, either between two droplets who mix, forming a new larger droplet or when a droplet reaches the interface of the continuous phases (Figure 14). Coalescence is caused by the different velocities between the droplets which leads to collisions. The difference in velocities depends on the droplets' size. Eventually coalescence is dependent on the kinetic energy of the droplets and the attractive or repulsive forces acting between them. During coalescence the droplet size increases and that makes the separation easier. In the event of high interfacial tension, coalescence will be promoted close to the interface since the droplets will accumulate in that area. The energy input to the system should be low enough to permit the coalescence process. In case of high energy inputs, dispersion will occur. On the other hand the energy input should be high enough to promote frequent droplets collision or else the whole process will proceed at a very low pace. In most treating vessels coalescence depends on gravity forces. Flotation

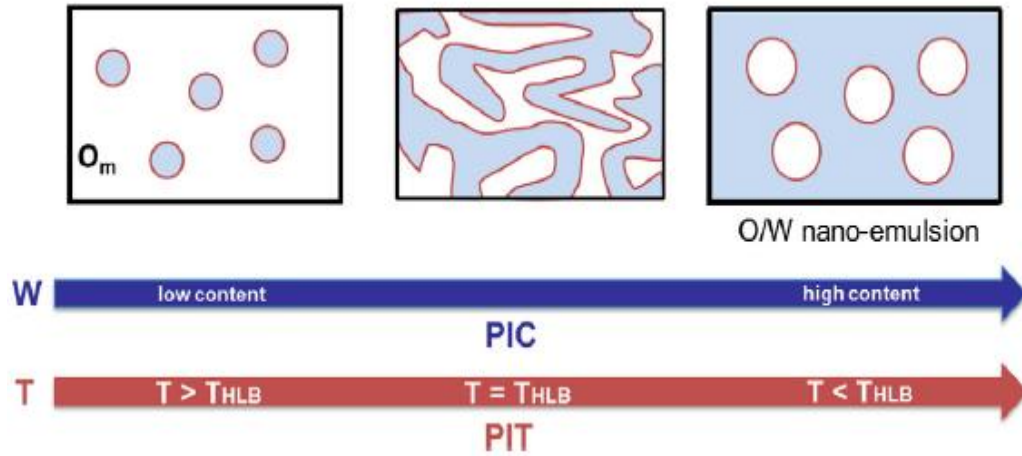
units and hydrocyclones are exceptions to this rule. Those vessels are nicknamed as "deep bed gravity settlers". Experiments conducted both with flotation units and hydrocyclones show that there is only a 10% size increase in the droplets if residence time is doubled and that the more dilute is the oil the greater is the residence time needed (Stewart and Arnold 2009).



**Figure 14** - a) Coalescence between two droplets, b) Coalescence between droplet and continuous phase.(Tyvold 2015)

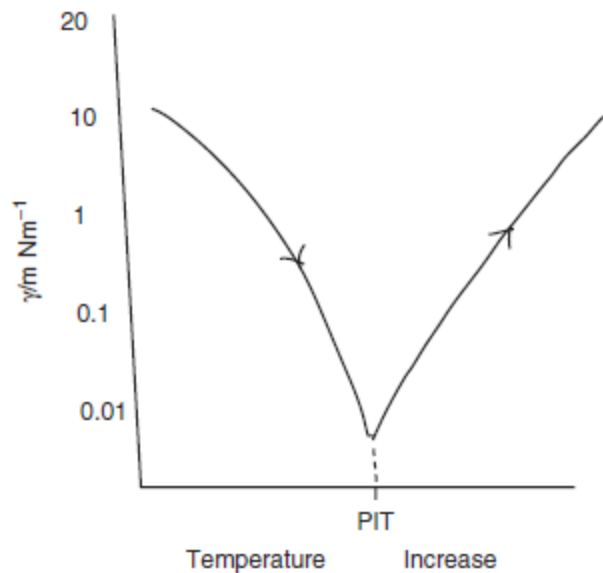
### *Phase Inversion*

An exchange between disperse and continuous phase can occur leading to transformation of oil in water emulsions into water in oil emulsions (Tadros 2013). This process can occur during the accumulation of oil droplets into flocs at the interface. The phase inversion temperature (PIT) (Shinoda and Saito 1968) and the phase inversion composition (PIC) concepts are mechanisms leading to phase inversion of the emulsions caused by changes in temperature or composition respectively. Studies (Solans and Sole 2012, Roger et al. 2010, Roger et al. 2011 and Morales et al. 2006) have shown that both methods are based on the fact that a temperature increase (or composition change respectively) results in a proportional increase of the conductivity of the oil in water emulsions until PIT is reached and an inversely proportional decrease in its solubility in water as shown in Figure 15. That means that emulsions close to their phase inversion temperature are less stable and can be easily resolved due to the fact that interfacial tension decreases as temperature is closer to PIT (Figure 16). Emulsification through this mechanism demands changes in the spontaneous curvature of the non-ionic surfactants.

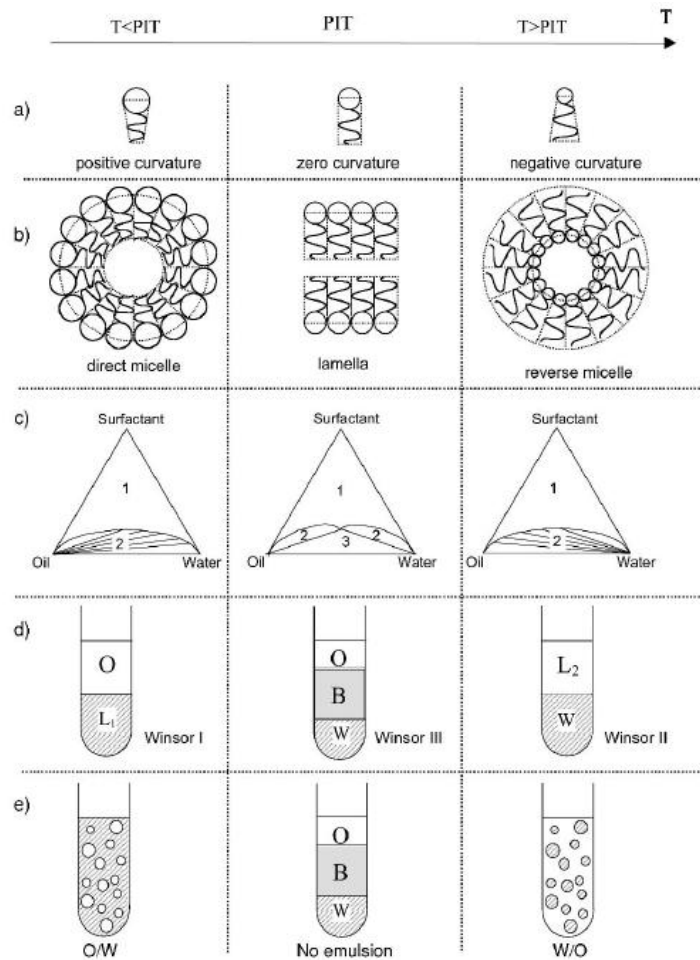


**Figure 15 - PIC and PIT methods emulsification process (Solans et al. 2016)**

For lower temperatures the surfactant is soluble in water. Hence an aqueous rich-in-surfactant phase ( $L_1$  in Figure 17) and an almost pure oil phase will be obtained (Winsor I). Surfactant's spontaneous curvature is positive and upon stirring oil in water emulsions can be formed. The same mechanism gives water in oil emulsions in higher temperatures due to negative spontaneous curvature of the surfactant. Water in oil emulsions are formed after stirring the oil phase containing the surfactant ( $L_2$  in Figure 17) and pure water (Winsor II). For spontaneous curvature close to zero emulsions get destabilized and destroyed and thus as we can see on Figure 17 we have the presence of three phases, B (bicontinuous or liquid crystalline phase), water and oil (Winsor III) (Calderon et al. 2007). Spontaneous emulsification is important for EOR methods as proposed by studies (Salager et al. 2013 and Shi et al. 2015)



**Figure 16 - Variation of interfacial tension with temperature increase for an Oil in Water emulsion (Tadros 2013)**



**Figure 17** - In case of non-ionic surfactant, it is shown the different situations formed with the change of temperature on (a) the spontaneous curvature and surfactant morphology, (b) self-assembly, (c) phase diagram, (d) coexisting phases, (e) emulsions formed for each case (Calderon et al. 2007)

## Favorable conditions for emulsion breaking

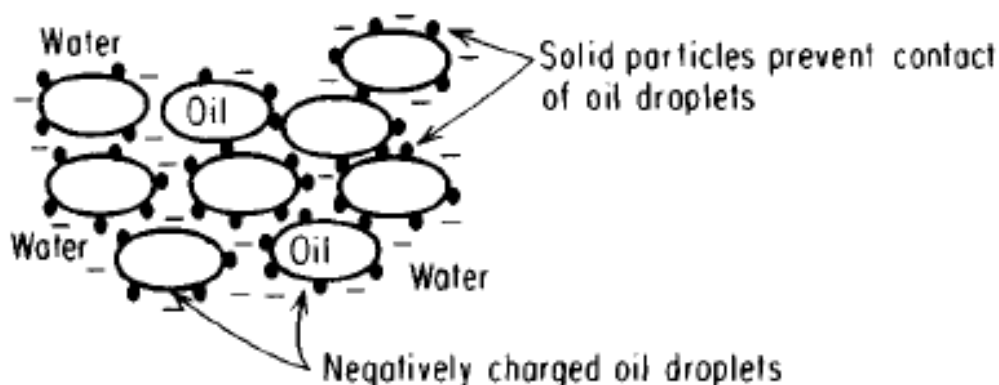
Favorable conditions for emulsion breaking include an increasing temperature profile since it decreases viscosity and increases the Brownian motion. In this way the particle collisions rate also increases. If residence time is long enough, different breakdown mechanisms can act and addition of demulsifiers promotes flocculation which will be examined later on in this work.

As it was previously mentioned there are two common types of emulsions, the oil-in-water and water-in-oil. They can be easily differentiated visually. The main focus of the present work are oil in water emulsions which appear as dirty oily water. They can contain different oil types and concentrations. Cutting fluids, lubricants, tars, crude oils and grease can be found in water together with various contaminants that can be present in emulsions such as solids, metal particles, soaps, silt and residues. All of them need to be removed both for reasons of oil recovery and water cleaning.

Charged oil droplets in an ionic environment constitute the colloid Oil in Water emulsions. In case of intense mixing or shearing a dispersion of those oil droplets throughout the water bulk will take place. Friction between oil and water phases acts as a stabilizing factor since static electric charges are developed and gathered in the oil-water interface.

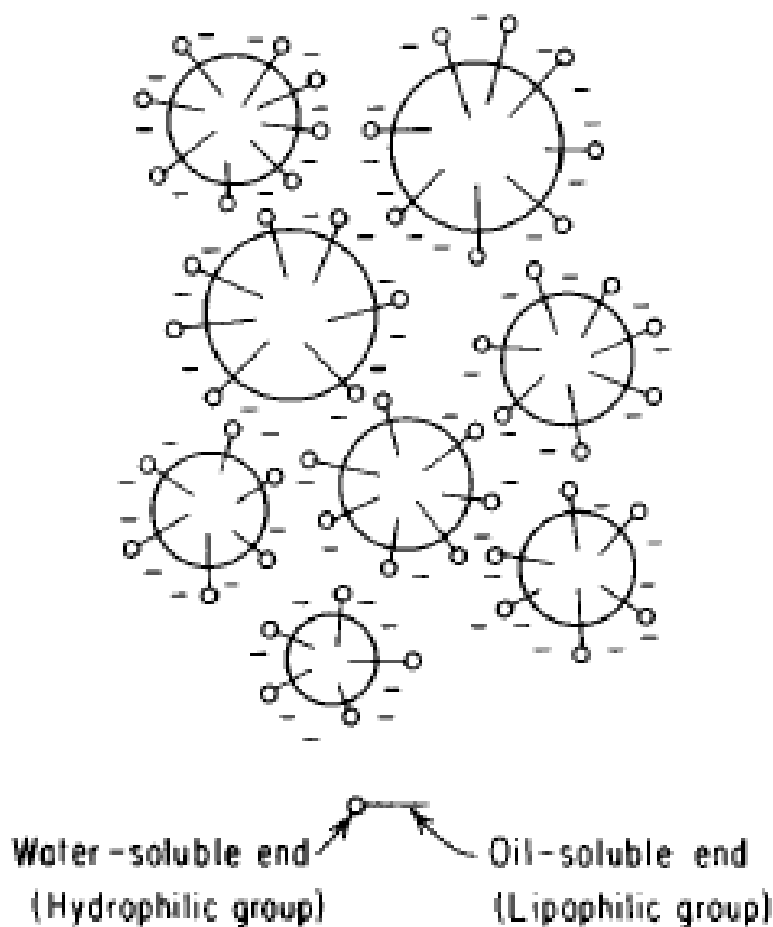
Ionization, which is provoked by surface-active agents is one of those mechanisms. The electric charge of organic materials attracts them to the oil-water interface of the droplet. Due to accumulation of charges, the emulsion stabilizes under repulsion of the common charges (Schramm 2005). Electrically neutral surfactants can also act as stabilizers since their molecules are both water-friendly and hydrocarbon-friendly. This utility acts as a bridge in the interface and a stabilization factor.

Solid particles of certain size and quantity may also act as stabilizing factors for the emulsions (Figure 18). The interfacial film is reinforced by those particles which results in blocking the coalescence between the oil droplets. The most stable emulsions occur when the contact angle between them and the particles is close to 90°.



**Figure 18** - Solid particles acting as stabilizers of Oil in water emulsion (Kemmer 1988)

A hydrophilic molecule or portion of a molecule is one whose interactions with water and other polar substances are more thermodynamically favorable. Proportionally as lipophilic are defined the molecules or portions of a molecule whose interactions with oil or other hydrophobic solvents. Complex molecules called surfactants with a hydrophilic group at one end and lipophilic at the other can act as stabilizers for the emulsions (Figure 19). Surfactants are compounds that lower the surface tension (or interfacial tension) between two liquids or between a liquid and a solid. Their affinity to both oil and water makes possible the dispersal of oil droplets in water phase despite the act of coalescence. The "tail" of most surfactants are fairly similar, consisting of a hydrocarbon chain, which can be branched, linear, or aromatic. They can be anionic surfactants or non-ionic. Some emulsifiers can act as stabilizers also. An example of such anionic emulsifiers is the petroleum sulfonates and the sulfonated fatty acids while non-ionic emulsifiers which act as stabilizers are ethoxylated alkyl phenols. A list of such emulsifiers is presented in Table 6.



**Figure 19** - Surfactants with hydrophilic and lipophilic groups acting as stabilizers (Kemmer 1988)

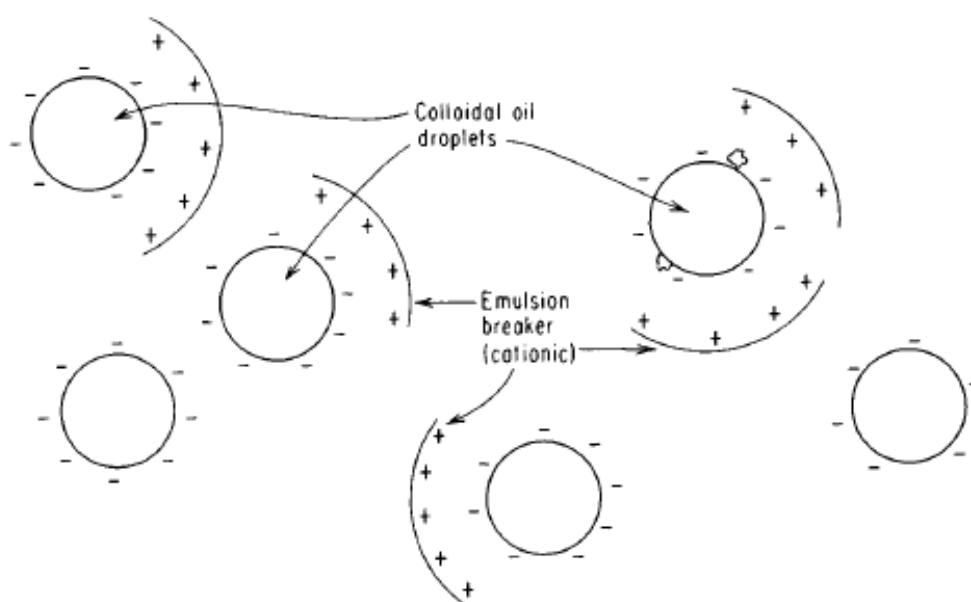
Type	
Formation	Soaps dispersed in water phase
Ionic emulsifiers	a. Sodium, potassium soaps and sulfides
	b. Sodium naphthenes and cresylates
Stabilizing electrolytes	c. Precipitated sulfides and surfactants
	d. Organic amines
	a. Salts or univalent cations
	b. Salts of di- and trivalent cations

**Table 6** - emulsifying agents for oil in water emulsions

As previously mentioned the oil in water emulsions are droplets of oil dispersed in a continuous water phase and are known as "reverse emulsions". The unstable oil in water emulsions can break within minutes due to coalescence. In case of stable emulsions chemicals, heat, settling time and electrostatic forces are used for breaking.

If not treated properly, emulsions can remain unresolved for weeks. Emulsion breakers used for oil in water emulsion treatment are water soluble and are added to the stream after the first oil-water separator in concentrations of 5 to 15 ppm. After the breaking of the emulsions, the oil droplets that will form, will coalesce into bigger ones and due to gravity they will float as an oil layer.

In order to break the oil in water emulsions chemical or physical methods can be applied. Chemical treatment is more commonly applied to oily wastewaters and for enhancing the efficiency of mechanical treatment. The main focus is to neutralize the stabilizing factors and thus to permit the evolution of the coalescence process between the emulsified droplets. To achieve this, the introduction of opposite charges to the ones existing in the system must occur (Figure 20). Oil droplets carry negative charges due to the dielectric characteristics of water and oil (Alther 1997).



**Figure 20** - Schematic view of cationic emulsion breaker neutralizing surface charges (Kemmer 1988)

Theoretically a perfect breaking of the emulsion will yield a clear water layer and a clear oil layer. In practice this is rarely achieved and in most cases a scum is formed in the interface by the remaining solids and neutralized emulsifiers. Normally this is achieved in two steps:

1. Coagulation: Neutralization of the charge of the oil droplet which leads in deprivation of emulsifying properties of the surface active agent
2. Flocculation: Neutralized droplets form agglomerate. It can occur when Van der Waals attractive energy exceeds the repulsive energy as discussed in previous chapter.

In general acids are more effective in breaking of emulsions but a major drawback in this case is that the acidic wastewater demands special treatment of neutralization. Salts of iron or aluminium can also be used instead of acid, aiding the agglomeration

process. A problem occurs though since both aluminium and iron salts form hydroxide sludges that need special treatment to dewater.

Giving better results than inorganic demulsifiers, the organic ones can be considered as much better emulsion breaking agents. For the same treatment program, less dosages of organic demulsifiers are needed than those of inorganic demulsifiers. The effluent quality is much better with the use of organic breakers. In Table 7, four examples of breakers are presented (Kemmer 1988).

Main type	Description	Charge
Inorganic	Polyvalent metal salts - alum, $\text{AlCl}_3$ , $\text{FeCl}_3$ , $\text{Fe}_2(\text{SO}_4)_3$	Cationic
Inorganic	Mineral acids - $\text{H}_2\text{SO}_4$ , $\text{HCl}$ , $\text{HNO}_3$	Cationic
Inorganic	Adsorbents - pulverized clay, lime	None
Organic	Substituted copolymers of polyamines and polyacrylates	Cationic

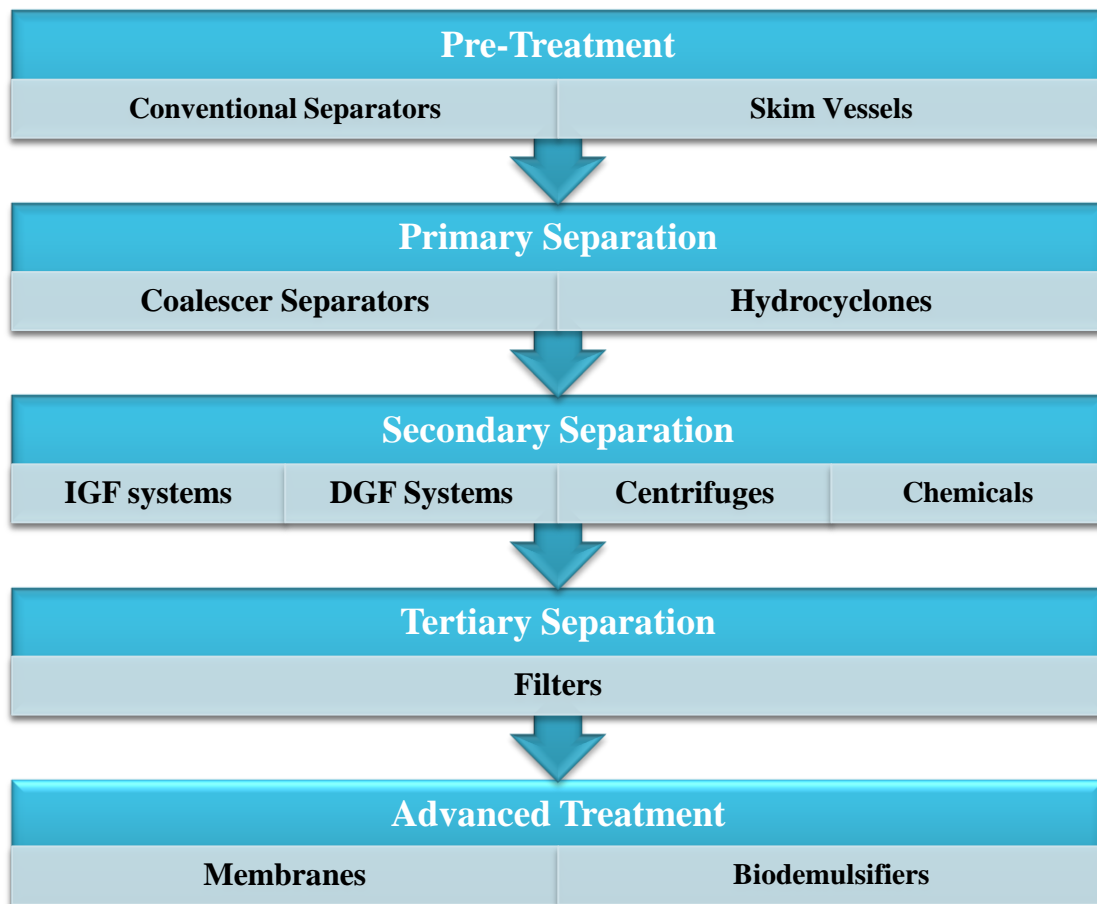
**Table 7** - types of emulsion breakers for oil in water emulsions (Kemmer 1988)

## Chapter 3 - Specialized Techniques and Equipment used for oil in water emulsion resolution and oil recovery - General Information

Various methods and vessels are used in water treatment for the removal of oil. This is due to the fact that multiple sources of water streams can be encountered during the oil production operations. Mainly brine water or surface water is encountered. In Table 8 some examples are presented while in Figure 21 an example of treating system configuration is presented. Depending on the concentrations of the substances need to be removed a secondary, tertiary or advanced treatment may be necessary. Treating systems need to be selected considering their efficiency and space available for minimization of expenses.

Method	Equipment Type	Approximate Minimum Drop Size Removal Capacities (μm)
Gravity separation	Skimmer tanks and vessels API separators Disposal piles Skim piles	100-150
Plate coalescence	Parallel plate interceptors Corrugated plate interceptors Cross flow separators Mixed flow separators	30-50
Enhanced coalescence	Precipitators Filters/coalescers Free flow turbulent coalescers	10-15
Gas flotation	Dissolved gas Hydraulic dispersed gas Mechanical dispersed gas	10-20
Enhanced gravity separation	Hydrocyclones Centrifuges	15-30
Filtration	Multimedia membranes	1+

**Table 8 - Treatment equipment for water (Modified from Stewart and Arnold 2009)**



**Figure 21** - *Treatment stages of oil in water emulsions*

A critical factor for decision making concerning the method applied in each case is the droplets' sizes. Different mechanical methods can treat different sizes of droplets as seen in Table 8. The basic principle on which the water treating scheme is based is the removal of oil droplets and oil in water emulsions from the water. Dispersion and coalescence of oil droplets starts during their flow towards the wellbore, control valves, chokes and the process equipment. Small concentrations ( $<100\ \mu\text{m}$ ) of free hydrocarbons need to be treated further after the primary water treatment or, oil in water emulsions pre treatment, which usually is two or three phase separators and skim vessels. The more energy is put in the system the smaller are the droplets. When energy is low coalescence is promoted. Gravity separation, flotation and coalescence are the basic phenomena aiding the treatment. Gravity separation devices include skim tanks, API separators, plate coalescers and skim piles (Juniel and Rawlins 2007). Primary oil in water emulsions treatment involves CPI and cross flow modified separators while Secondary treatment involves induced and dissolved gas flotation units and centrifuges. Further treatment of the oil in water emulsions involve the tertiary separation which includes walnut shell, media, cartridge and activated carbon filters while the last stage of treatment called "Advanced Treatment" are membranes and biodemulsifiers. Chemical treatment can be applied in all stages for the promotion of coalescence of oil droplets but usually chemicals are introduced in the secondary treatment stage. All stages of the treatment procedure will be discussed in the

following chapters. It is critical though for the design and application of a proper treatment scheme to use monitoring and simulation techniques. Characterization of emulsions is crucial also.

## **Characterization of Emulsions**

It is essential for the design of the appropriate treating scheme to characterize the emulsions that are to be treated. Several techniques are available in the industry.

Studies (Vandaraj et al. 2007) have shown that emulsion stability can be determined according to their flow through porous media in a rapid and convenient assay through Micro-percolation test. If the emulsified sample passes completely through a porous media, then it can be centrifuged in two distinct phases. The greater the proportion of pure water phase that is formed after this treatment the less stable is the emulsion. The value range is between 1 (maximally unstable) and 0 (maximally stable).

Field Bottle or Jar test is another technique used in the industry. This technique has been in use for more than 60 years (Kirkpatrick et al. 1960), with various alterations proposed by studies (Leopold 1992, Manning et al. 1995, Poindexter 2009) but it hasn't been standardized so far. The main idea of the procedure is to put a sample of emulsion in a gal, drain off all free water and determine sediments and water of the emulsion. After this add in different precipitation bottles 100 ml of emulsion and emulsion breakers and shake them for a given time in constant temperature. In the end a sample of oil is removed from each bottle and further analysis is performed on it. This method is considered as a multivariate one and statistical analysis of it has shown that although solid content is the most important indicator, several crude oil parameters should be evaluated to predict emulsion stability (Poindexter et al. 2006). A more detailed review of the method will be presented in a following chapter.

## **Monitoring techniques for oil in water emulsion treatment**

Engineers need to design a treatment scheme that complies with each state's requirements for effluent quality. Configurations of the treatment line are subjected to the strategy that each engineer would adopt. This depends absolutely to the experience of the engineer and the circumstances. Evaluation of data is really important for the design of this treatment line. Sometimes values have to be assumed in case they are missing. Basic information needed for the design of a proper treatment line is the flow rate, specific gravity and viscosity of the produced water, concentration of oil in the produced water and its specific gravity at flowing conditions, concentration of soluble oil in the effluent, oil droplets size distribution in the produced water and rainfall rate and flow rate of washdown water (Abdel-Aal 2003). Industry has introduced various techniques to obtain this data.

### *Colorimetric method*

This technique is based in the measurement of absorption of energy in the visible light. It is recommended for heavy oils mainly and it is based in the correlation of the examined water sample to another with known concentration of oil. Calibration of the sample of the oil is required. This technique can have large uncertainty concerning the final oil in water measurement. HACH company provides portable test kits for the implementation of tests using this method as shown in Figure 22 (Daigle and Cox 2012).



**Figure 22** - CEL/890 Advanced portable laboratory (Daigle and Cox 2012)

### *Direct Weight Measurement*

This technique is used for the US EPA and it is known as Method 1664. It involves the acidification of a liter of water sample to pH lower than 2 and the extraction of its n-hexane. N-hexane is evaporated and the remaining residue is weighted, obtaining a direct measurement of concentration in mg/L (Daigle and Cox 2012).

### *Infrared Method*

Carbon - Hydrogen bonds adsorb infrared energy at 3.41 micron wavelength. Instruments that are used in this case are correlating the absorption of IR energy to the oil concentration in water. Calibration of fluids for each sample is needed and it is not so popular in the oil industry lately due to the fact that it is error prone method (Daigle and Cox 2012).

### *Particle Counting Method*

This method involves measurement of turbidity, Coulter counter and visual recording of particles and their characteristics. Turbidity limits justify the maximum size of the particles. Coulter counter is used for the determination of the oil droplets size, but it can be error prone due to the fact that it doesn't differentiate between oil droplets and solid particles. Microscopic visual recording through micro cameras can lead to safe

determination of the volume of the oil droplets within the water volume and determine the oil's concentration. JM Canty and Jorin are two industrial companies that employ successfully this method (Daigle and Cox 2012).

### *Ultraviolet Fluorescence Method*

This method targets the aromatic compounds which absorb the UV radiation. The principle of use of this method is related to the infrared one since the amount of fluoresced light measured can give an estimation of the oil concentration in the water sample. Technology is continuously improving and enhanced monitoring methods are used in the industry today. Advanced Sensors company has manufactured monitoring equipment which involves the use of both the UV technique along with particle counting methods for the part per million oil in water calculation. An industrial installation of this technology is shown in Figure 23 (Daigle and Cox 2012).



**Figure 23** - *Advanced Sensors Inline Probe Measurement (Daigle and Cox 2012)*

New experimental methods have been evolved lately for the efficient monitoring of the oil in water. The use of inductance, microwave and NIR absorption sensors has been introduced lately. Photometry also has been used by Optek while NIM Tech has introduced SonicGauge Sensor System which provides ultrasonic frequency measurements to track the chemical fingerprints of oil emulsions in water (Daigle and Cox 2012).

## Simulation techniques for oil in water emulsion treatment

Approximation models have been proposed for the simulation of emulsion resolution. Coalescence depends on the contact time and interface characteristics of the phases, thus its frequency can be estimated by correlation of collision frequency and coalescence efficiency (Almeida-Rivera and Bongers 2012). Computational Fluid Dynamics (CFD) codes are used for the simulation of fluid flow of immiscible fluids in three dimensions based on the population balance equation (PBE). CFD softwares can simulate compressible, non-isothermal, non-Newtonian, multiphase and porous media flow for laminar and turbulent flow regimes. Two commercial examples of CFD software used for the simulation of oil in water emulsion treatment are ANSYS fluent and OpenFOAM. Simulations aid in the understanding of surfactants' role in the stability of emulsions also, although computational restrictions due to large number of processes involved exist. This is due to the fact that the potential of molecular interactions is time dependent since the coalescence of oil droplets reduces the interfacial area of emulsions. Continuous calibration of the model is needed though since interfacial properties and intermolecular forces of droplets are changing with time (Urbina-Villalba 2009).

## Chapter 4 - Specialized Techniques and Equipment used for oil in water emulsion resolution and oil recovery - Pre Treatment Stage

The primary level of water treatment for oil production can be considered as the pre-treatment stage of emulsions due to the fact that all the free oil is removed from the stream. Dispersed and dissolved oil remains in the water and needs to be treated by specialized equipment and chemicals in various stages depending on the stream's characteristics and discharge regulations.

### *Conventional Separators*

An oil-water separator is a chamber designed to provide flow conditions sufficiently quiescent so that globules of free oil rise to the water surface and coalesce into a separate oil phase, in order to be removed by mechanical means. The base of oil-water separation theory is the rise rate of the oil globules (vertical velocity) and its relationship to the surface-loading rate of the separator. The rise rate is the velocity at which oil particles move toward the separator surface as a result of the differential density of the oil and the aqueous phase of the wastewater. The surface-loading rate is the flow rate to the separator divided by the surface area of the separator.

In an ideal separator, any oil globule with a rise rate greater than or equal to the surface-loading rate will reach the separator surface and be removed. An ideal separator is assumed to have no short circuiting, turbulence, or eddy currents. The required surface-loading rate for removal of a specified size of oil droplet can be determined from the equation for rise rate. The mathematical relationship for the rise rate is provided by a form of Stokes' Law:

$$V_l = \left( \frac{g}{18\mu} \right) (\rho_w - \rho_o) D^2 \quad (1)$$

Where:

$V_l$  = vertical velocity, or rise rate, of the design oil globule (cm/s)

$g$  = acceleration of gravity (981 cm/s<sup>2</sup>)

$\mu$  = absolute viscosity of wastewater at the design temperature (P)

$\rho_w$  = density of water at the design temperature (gr/cm<sup>3</sup>)

$\rho_o$  = density of oil at the design temperature (gr/cm<sup>3</sup>)

$D$  = diameter of oil globule to be removed (cm)

The vertical velocity of an oil globule in water depends on the density and diameter of the oil globule, the density and viscosity of the water, and the temperature. The oil globule's vertical velocity is highly dependent on the globule's diameter, with small oil globules rising much more slowly than larger ones. There are two fundamental principles that should always be kept in mind when designing and operating oil-water separators. The performance of the separator will depend highly on the difference

between the specific gravity of the water and that of the oil. The closer the specific gravity of the oil is to that of the water, the slower the oil globules will rise. Since the oil globules' rise rate is inversely proportional to the viscosity of the wastewater, oil globules will rise more slowly at lower temperatures.

As stated above, oil-water separators are designed to remove free oil. If the oil is emulsified or dissolved, additional downstream treatment is required. A principal function of the oil-water separator is to remove gross quantities of free oil before further treatment. In this capacity, the oil-water separator protects more sensitive downstream treatment processes from excessive amounts of oil. Since separator skimmings are typically recycled and the oil which is not recovered can end up as sludge, efficient recovery results in minimization of waste. In a treatment scheme, simple separators are acting as a pretreatment for the minimization of emulsion formation and the removal of as much free oil possible.

The performance of gravity oil-water separators varies with changes in the characteristics of the oil and wastewater, including flow rate, specific gravity, salinity, temperature, viscosity, and oil-globule size. Performance is also a function of design and operational constraints and of the analytical methods used to measure performance. However, the data indicate that increasing separator size, as measured by surface-loading rate, results in improved performance, as measured by effluent oil and grease. Unit design needs to take into account the impact on downstream oil removal processes (for example, dissolved-air flotation) to determine whether incremental improvements in performance can be justified.

Parallel-plate separators are based on a newer technology. They require less space than do conventional oil-water separators and are theoretically capable of achieving lower concentrations of effluent oil. Petroleum industry data are insufficient to conclude that parallel-plate units offer overall superior performance.

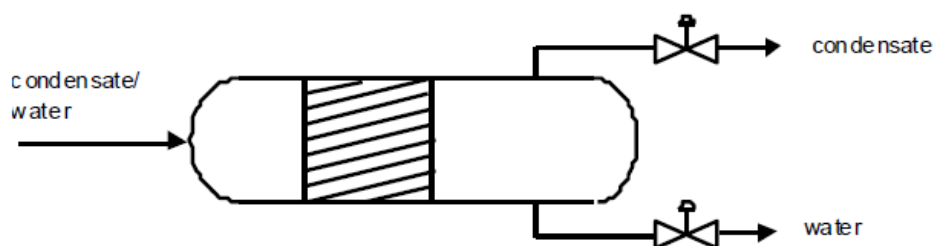
There are petroleum industry applications in which oil-water separators are the only end-of-pipe treatment provided. These are usually cases in which the only effluent restrictions specified are for oil or suspended solids and the wastewater in question consistently contains sufficiently low amounts of emulsified and dissolved oils. In some applications, the oil-water separator is provided as a protective device for containment of spills and leaks (for example, on once-through cooling water). Another example is an instance in which a stream is discharged to a publicly owned treatment works and the oil-water separator is used to ensure compliance with requirements for pre-treatment of oil and grease.

It should be stressed that whenever an oil-water separator is considered for an application where it must stand alone, the amount of emulsified and dissolved oils in the wastewater stream must be properly quantified, because these oils will not be removed by the separators.

One aspect of oil-water separator design that is sometimes overlooked is that whether intended to or not, an oil-water separator also functions as a sedimentation basin. Solid particles more dense than water (for example, soil and coke particles) will tend to settle out in the separator. Provision must therefore be made to deal with the removal of settleable solids that accumulate in the separator.

### *High pressure water condensate separator*

This vessel (Figure 24) operates approximately at the same pressure as the primary production separator, in order to avoid the exposure of the water-condensate mix to large pressure drops which lead to the formation of emulsions. Special valves are regulating the pressure levels and emulsion formation can be reduced at least by 20% by the use of this vessel. Corrosion inhibitor's use should be avoided since in combination with high pressure it can promote the formation of emulsions (OSPAR Commission 2013).

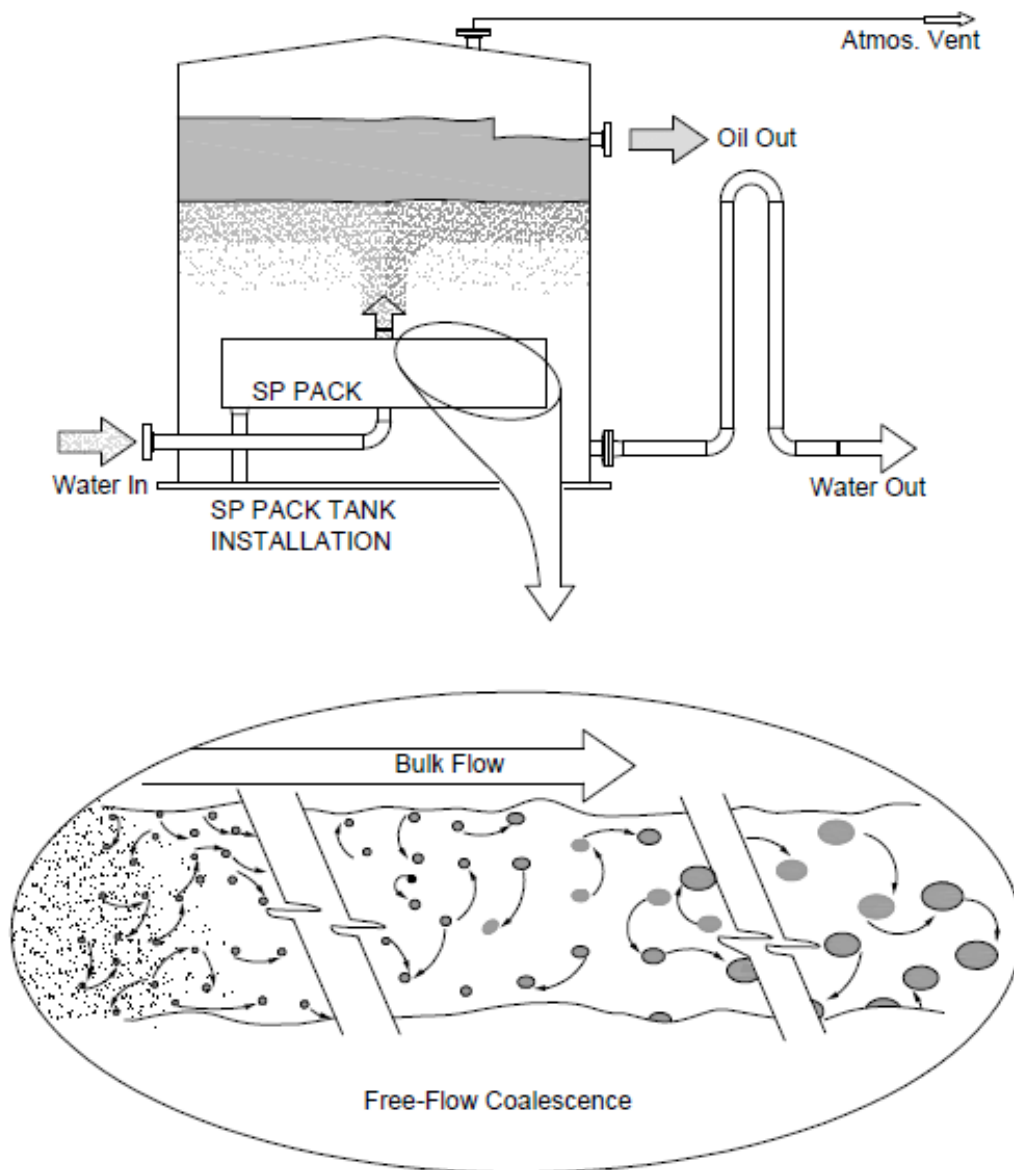


**Figure 24** - High pressure water-condensate separator (OSPAR Commission 2013)

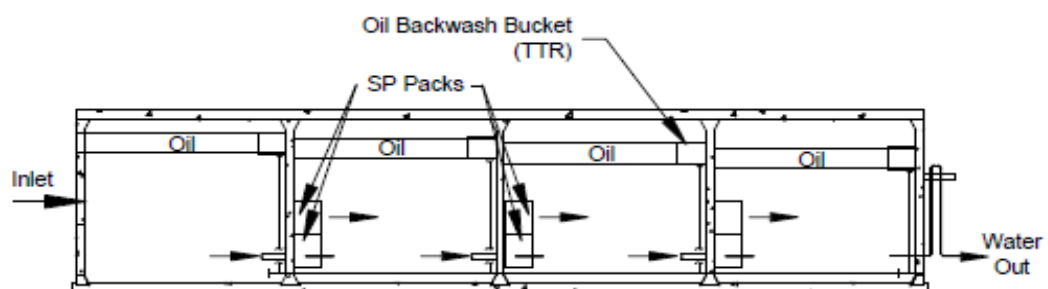
### *Free flow turbulent coalescers (Serpentine-Pipe Packs)*

SP packs is the common trade name used by the industry for those devices. They can be cheap for onshore applications where space is not a problem but for offshore applications they can be used only for small water rates depending on the space available (Stewart and Arnold 2009). Laminar flow and closely spaced plates are needed for plate coalescers to promote gravity separation and coalescence. Plugging can easily occur under those circumstances. The idea for the confrontation of this issue is the forced flow of the water through a serpentine path which will create turbulence and coalescence will be promoted as shown in Figure 25. Sizing plays an important role in this case since shearing of oil droplets must be avoided. Maximum drop size needs to be of 1000  $\mu\text{m}$  for efficient gravity settling (Abdel Aal 2003) Their pipes are created for Reynolds number up to 50000 and they include 180° bends. When diameters are increased from the typical value of 250  $\mu\text{m}$  to 1000 $\mu\text{m}$ , the use of skimmer is reduced. Retention time is also not so important since coalescence has

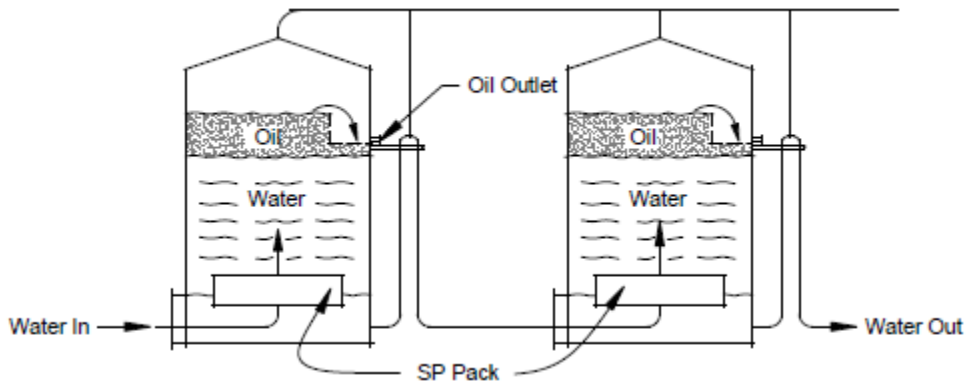
occurred before skimmer. (Stewart and Arnold 2009). Serpentine pipe packs can be 50% more efficient than simple gravity settling devices.



**Figure 25 - SP Pack operation principles.** (Stewart and Arnold 2009)



**Figure 26 - SP Packs horizontal configuration** (Stewart and Arnold 2009)



**Figure 27** - SP Packs in a series of staged tanks (Stewart and Arnold 2009)

They are installed inside gravity settling devices like skimmers, clarifiers and plate coalescers as shown in Figure 28 and they can be staged in series causing successive coalescence as shown in Figure 26 leading to enhancement of oil removal efficiency as shown in Figure 29. They can be put between skim vessels constituting two stages of coalescence and separation. The first one will deal with larger droplets and the second one with smaller as shown in Figure 27 (Abdel-Aal 2003). More than two stages can be used in the coalescence and removal process. Their efficiency for each stage is calculated by Equation 10.  $C_i$  is defined as the inlet concentration while  $C_o$  is defined as the outlet concentration (Stewart and Arnold 2009)

$$E = \frac{C_i - C_o}{C_o}$$

**Equation 10** - Efficiency calculation of each stage for SP packs (Stewart and Arnold 2009)

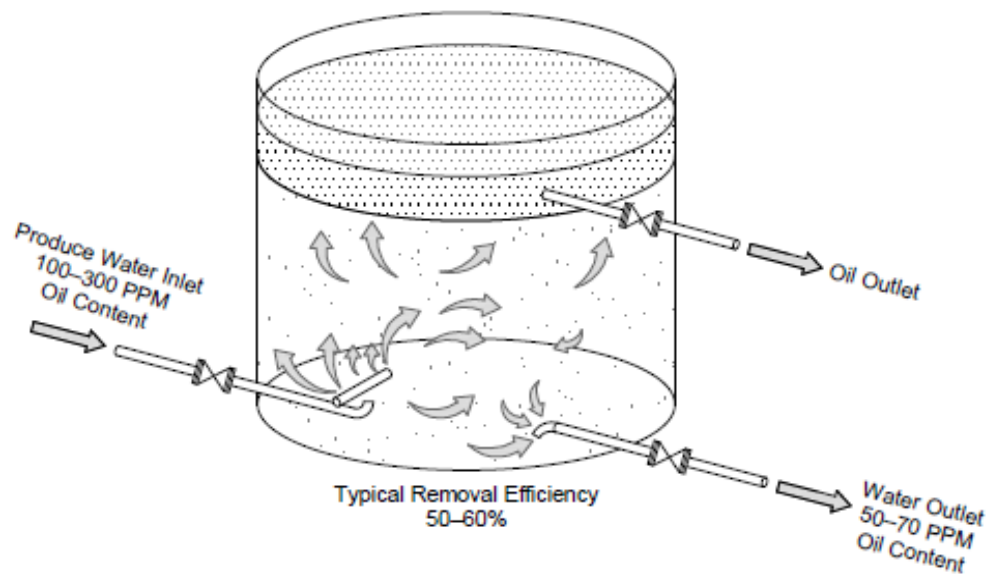
Efficiency can also be calculated, assuming that the drop size distribution constitutes a straight line by Equation 11 where  $d_m$  is the drop size that can be treated and  $d_{max}$  is the maximum size drop created (1000  $\mu m$ ). The overall efficiency can be estimated by Equation 12 where  $n$  is the number of stages. Increased oil removal efficiency is depicted in Figure 30 for SP Packs installed in different sized tanks. (Stewart and Arnold 2009)

$$E = 1 - \frac{d_m}{d_{max}}$$

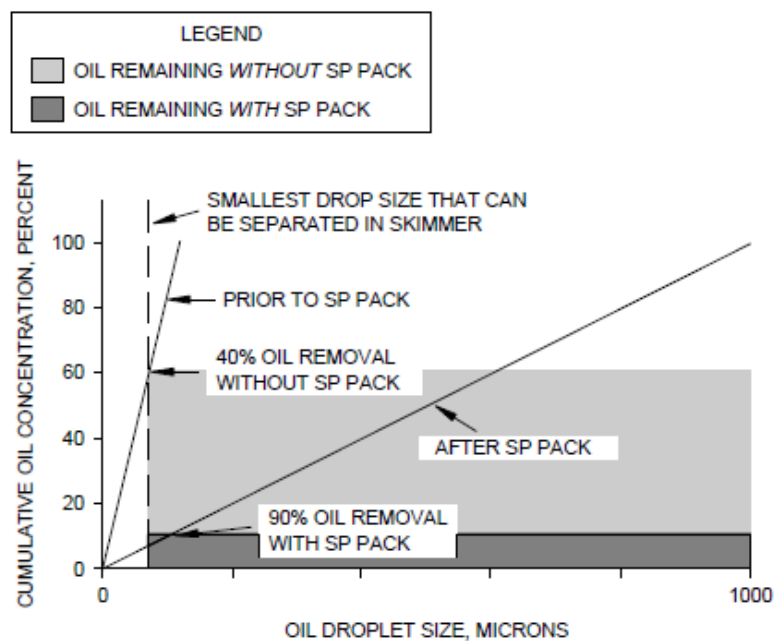
**Equation 11** - Efficiency as a function of oil droplets size (Stewart and Arnold 2009)

$$E_t = 1 - (1 - E)^n$$

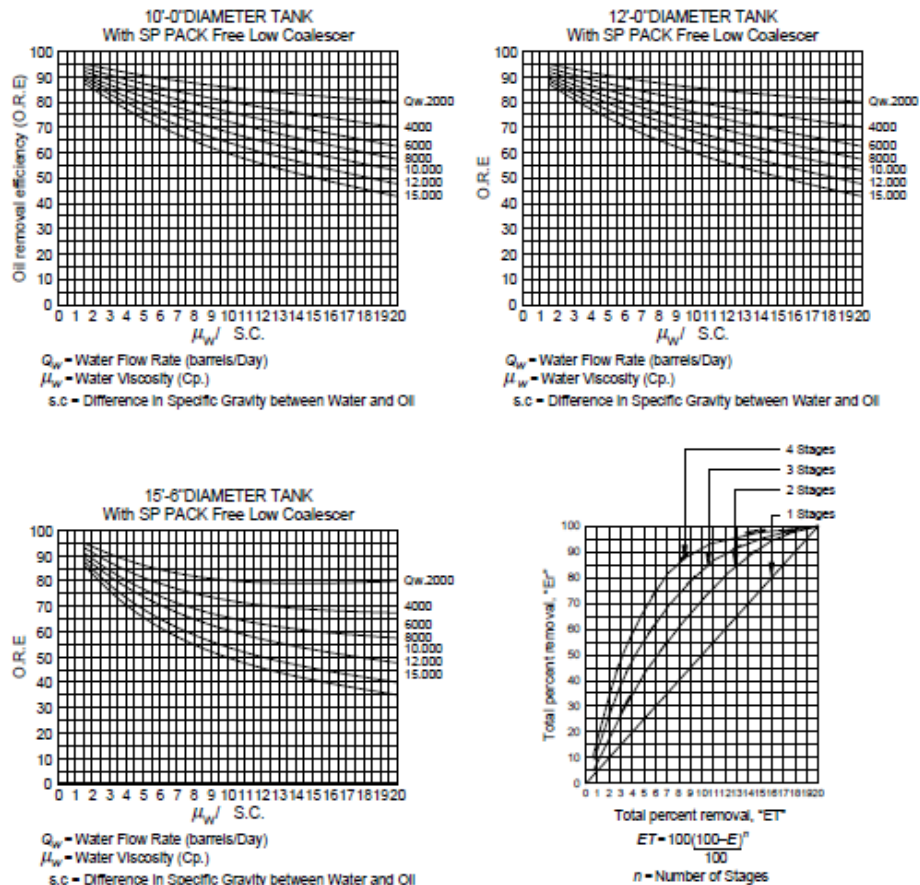
**Equation 12** - Overall efficiency estimation (Stewart and Arnold 2009)



**Figure 28** - SP Pack inside a clarifier tank (Stewart and Arnold 2009)



**Figure 29** - Distribution of droplet sizes by the use of SP packs and its effect to the skimmer (Stewart and Arnold 2009)



**Figure 30** - Oil removal efficiency using SP Packs in various sized tanks (Stewart and Arnold 2009)

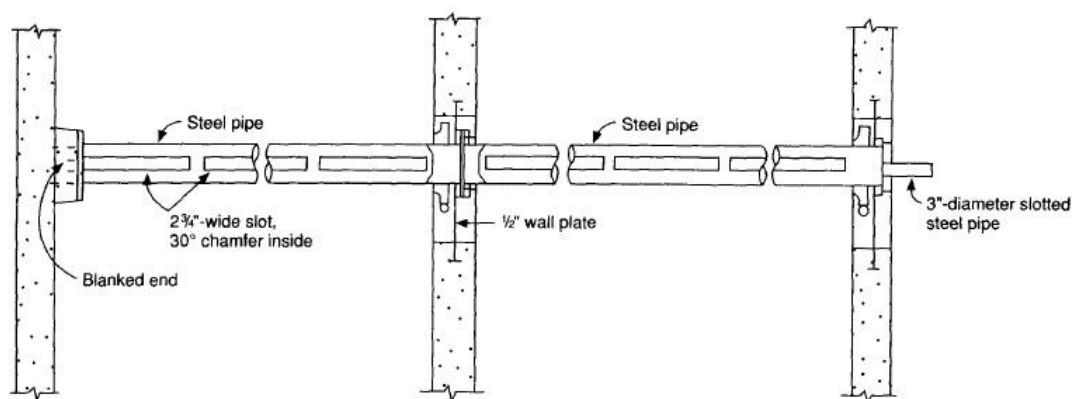
## Skim vessels

Skim tanks are not the so-called settling tanks. Skim tanks are used for the removal of dispersed oil while settling tanks are used for the removal of solids. They are the simplest treatment equipment vessels and they provide large residence times to aid the coalescence and gravity separation and they can be either pressure vessels or atmospheric tanks with vertical or horizontal configuration (Juniel and Rawlins 2007).

Another category, the "wash tanks" are used as FWKO vessels for incoming streams of 10%-90% oil fractions. After the separation of oil and water in those vessels, water is guided to the skim vessels. Skim tanks are the most common and simple treating equipment. Long residence times are provide for the promotion of gravity separation and coalescence. Atmospheric pressure regime prevails in those vessels and they are placed upstream of the rest water treatment equipment. If the oil outlet concentration can be accurate predicted, the vessel's dimensions can be theoretically determined. Vibration, short-circuiting and turbulence effects cannot be neglected. Their

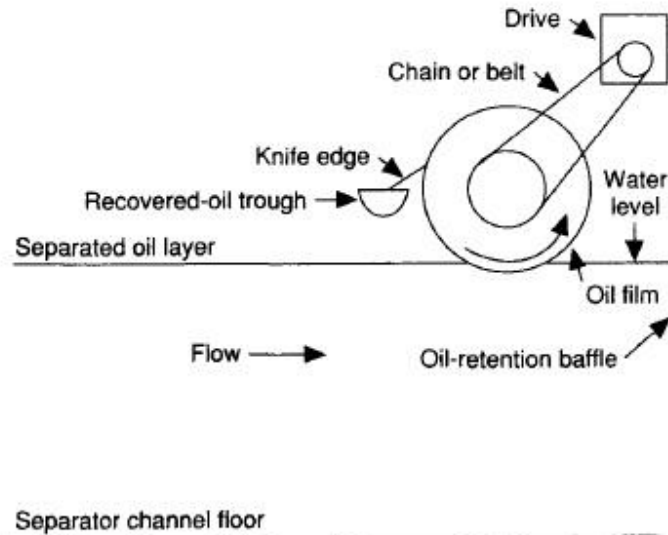
configuration can be either horizontal or vertical while several types of those devices are in use such as the rotatable slotted pipe skimmer which is the most common, the rotary drum skimmer and the floating skimmer. (Stewart and Arnold 2009)

The rotatable slotted pipe skimmer which is shown in Figure 31. The proper skimming level can be adjusted by rotation of the pipe and it should have the ability to be rotated backwards and forwards over a range of 180 degrees so that the separated oil that is collects between the skimmer and the oil retention baffle can be recovered. This is a simple device and is usually manually adjusted, but it can have the disadvantage of picking up a relatively large volume of water along with the skimmed oil unless the slot elevation is properly set. It can be made to operate automatically by providing the proper control and actuating equipment. The amount of water included with the skimmed oil depends on the care exercised in submerging the slot and on adjusting it during the skimming operation. When used in a multiple, parallel-chamber separator installation, rotatable slotted-pipe skimmers are connected end to end in a line that drains to a sump located at one side of the installation. The oil skimmed from the channel farthest from the sump must flow to it through each of the succeeding skimming pipes. As a result, each succeeding downstream skimmer pipe should be large enough to allow collected oil from other channels to flow by gravity to the sump.



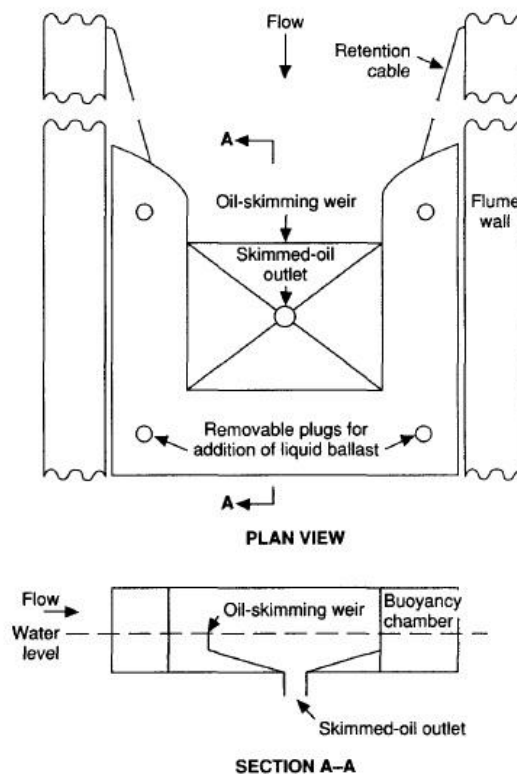
**Figure 31** - General arrangement of Rotatable Slotted Pipe skimmer (API 1990)

The rotary-drum skimmer (Figure 32) is available in both floating- and fixed-level modes. The principle of operation is the same for both types. Skimming is accomplished by a drum that rotates with the flow and picks up a thin film of oil, which is scraped off and drained into a collecting sump. The drum can be made of carbon steel, stainless steel, aluminum, or plastic. The optimal tangential velocity of the drum is on the order of 0.5-1.5 feet per second, with a submergence of 0.5 inch or more. The optimal rotational speed depends on the amount of oil to be removed and its viscosity. Submergence is not critical as long as the drum is in contact with the oil layer. The advantages of this unit are that the recovered oil contains relatively little water and its operation can be made automatic.



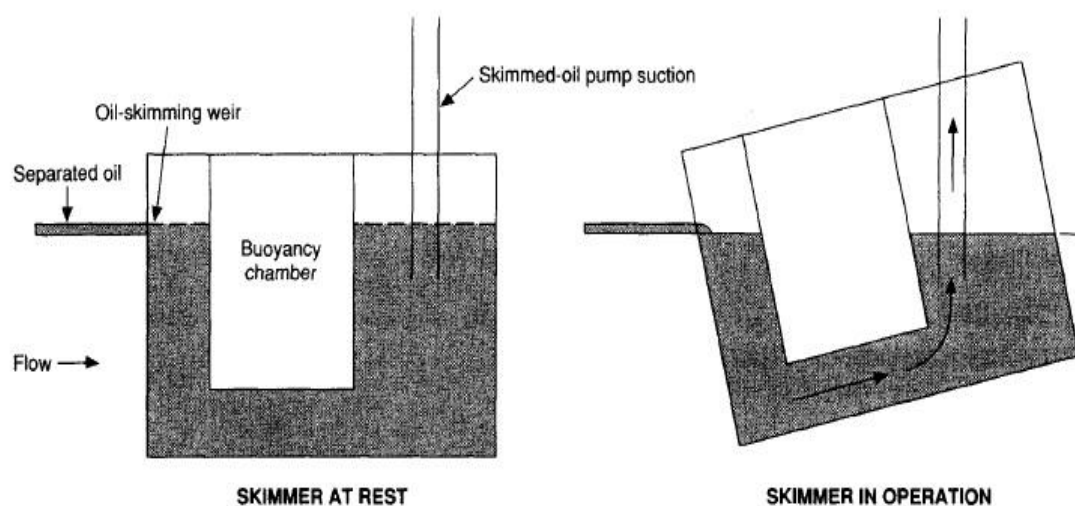
**Figure 32 - Rotary-Drum Oil Skimmer (API 1990)**

Several types of floating skimmers are also available. The horseshoe-type floating skimmer (Figure 33) consists of a buoyancy chamber, a skimming weir, an oil-collecting pan, and a discharge orifice attached to a hose that conveys skimmings to a sump. The self-adjusting floating skimmer (Figure 34) is a box within a box, with the inner box serving as a buoyancy chamber.



**Figure 33 - Horseshoe-Type Floating Skimmer (API 1990)**

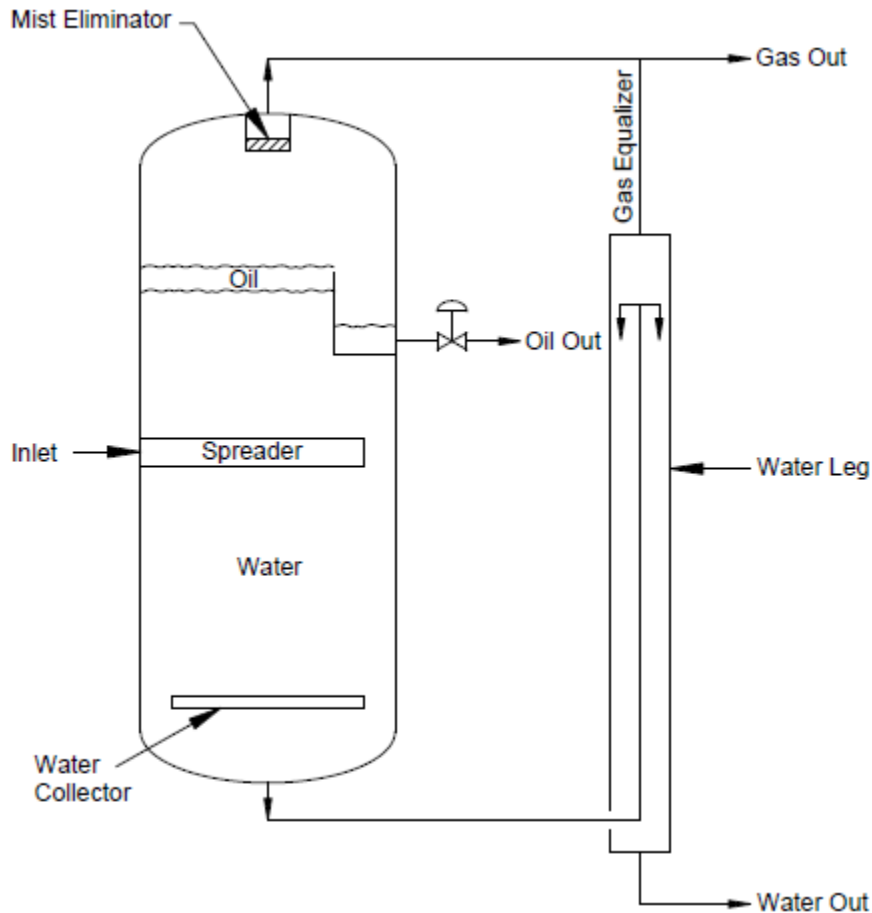
During the skimming operation, liquid must be removed by pumping from the rear of the outer box. When this is done, buoyancy is upset, causing the front of the outer box to tilt forward and submerge the skimming weir. When pumping is stopped, the skimmer returns to its normal inoperative position. Neither of these floating skimmers is frequently used in refinery separator installations.



**Figure 34 - Self-Adjusting Floating Skimmer (API 1990)**

### *Vertical skim vessels*

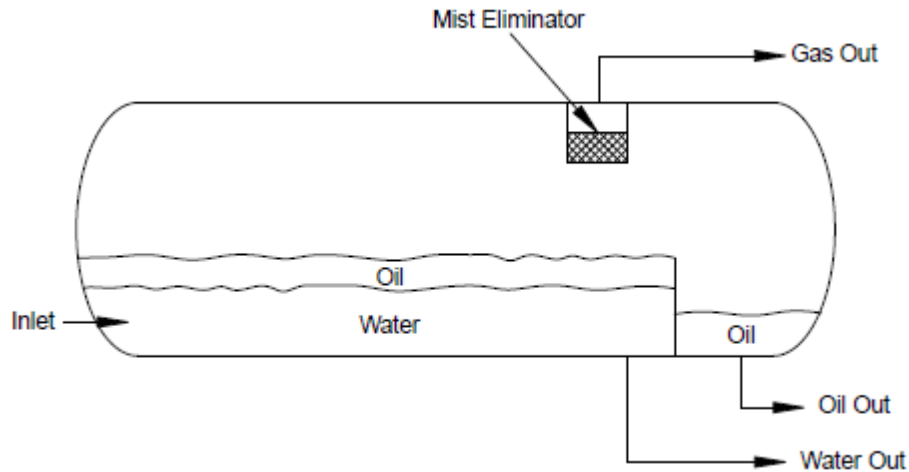
In vertical skim vessels the water flows downwards while the oil droplets motion is countercurrent due to buoyancy. They are less susceptible to high level shutdowns caused by liquid surges (Juniel and Rawlins 2007). In some cases the existence of inlet spreaders or outlet collectors make a better distribution of the flow (Figure 35). The inlet fluids must be introduced below the oil-water interface. Gas that is liberated from the water promotes the movement of oil droplets towards the interface. Coalescence occurs in the span between the spreader and the water collector. An oil layer will be formed in the surface and will be skimmed off. An interface level controller needs to be used to keep control of the relative heights of oil weir and water leg (Stewart and Arnold 2009). PROSKIM by PROSEP is an industrial commercial example of vertical skimmer. It is motion insensitive and requires residence times of 5-15 minutes.



**Figure 35 - Vertical skim vessel scheme** (*Settling Tanks and Skimmer Vessels Retrieved from: <http://www.oilngasprocess.com/oil-handling-surfacefacilities/produced-water-treating-system/water-treating-equipment/settling-tanks-and-skimmer-vessels.html>*)

### *Horizontal skim vessels*

In horizontal skim vessels (Figure 36), the water enters the vessel in a horizontal flow line. Oil droplets rise flow is perpendicular to the water flow. As in vertical skim vessels, gases that are liberated from the water promote the flotation of oil droplets in the top of the surface. Flow can be normalized by baffles. All other principles are same like in the vertical separation vessel. Horizontal vessels though are more efficient than vertical ones due to the fact that oil droplets dont have to rise countercurrent but perpendicular to the inlet flow. They are used also for sand and other solid particles handling. Sand and other particles sink in the bottom of the vessel and they are removed. Sand drains design though is expensive and has enjoyed limited success in field operations. Another issue that can occur in horizontal vessels is the waves that can occur in the surface of the liquid due to surging. A major drawback of the horizontal vessels is the spacing issue which makes difficult their operation offshore. (Stewart and Arnold 2009)



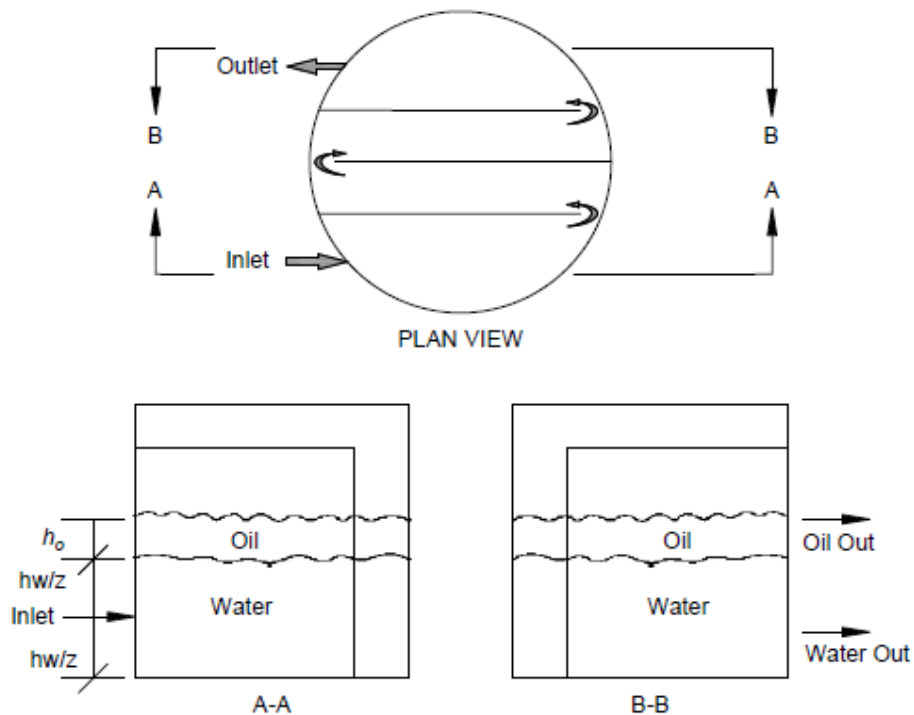
**Figure 36** - Horizontal skim vessel scheme (Settling Tanks and Skimmer Vessels. Retrieved from: <http://www.oilngasprocess.com/oil-handling-surfacefacilities/produced-water-treating-system/water-treating-equipment/settling-tanks-and-skimmer-vessels.html>)

### *Pressure versus atmospheric vessels*

This type of vessel is recommended when too much back pressure can be created in the atmospheric vent system due to potential gas blow-by through the upstream vessel dump system (Stewart and Arnold 2009) and when the water needs a higher level treatment through a pump. Those vessels are more expensive and are used downstream of three phase separators.

### *Retention time*

Oil concentrations can vary from 500 to 10000 mg/l into the skim tanks during the primary water treatment - pre treatment stage for emulsions. The minimum retention time for those quantities range from 10 to 30 minutes while the minimum size droplet removal is in 100-300  $\mu\text{m}$  range. Short circuiting can be eliminated with the introduction of baffles (Figure 37) and spreaders which improve the flow distribution (Stewart and Arnold 2009). Large skim tanks though exhibit poor behavior and short circuiting due to density and temperature differences, deposition of solids, corrosion of spreaders and flow dynamics (Juniel and Rawlins 2007).



**Figure 37** - Example of a vertical skim tank with baffles (Stewart and Arnold 2009)

### Performance

Several designing factors affect the performance of a skim tank. Inlet and outlet distributors should be designed to improve the performance of a skim tank. Temperature of the inflowing water should be pre-raised on levels that will reduce the oil viscosity significantly enough to promote removal. Short circuiting should be avoided by the use of baffles. Usually a single vertical baffle is enough for great reduction of short circuiting. Maximum benefit though can occur if they are installed as close to horizontal as possible. Shorter and wider tanks must be preferred to tall and narrow ones so that the gravity forces will provide the less possible resistance to the rising of the oil droplets. The dosages of chemicals introduced for the treatment of water should be carefully computed so that the formation of a froth layer in oil water interface is avoided. Malfunction of the level controller can occur due to this froth leading to spills.

Skim vessels are appropriate when downstream installed equipment requires pressure drawdown for safety reasons and for cases where degassing of water is needed. They should also be used when the inlet of oil concentration needs to be reduced for further treatment or solid contaminants exist. Their use should be avoided on the other hand when droplet sizes below 100  $\mu\text{m}$  are encountered, outer factors can create waves in the vessel or water temperature is very low (Stewart and Arnold 2009)

## **Chapter 5 - Specialized Techniques and Equipment used for oil in water emulsion resolution and oil recovery - Primary Treatment Stage**

### **Coalescer Separators**

Gravity separators called the coalescing oil water separators are used by the process industry for liquid-liquid or liquid-gas separation before the application of chemical treatment. That happens due to the fact that free oil and solids consume chemicals unnecessarily which has an economical cost. Their design is based in the physical properties of water and oil and especially in their density. In this way free oil droplets rise at the top due to smaller density as is the case with skimmers. Theoretically they would follow a linear rise according to Stokes law but in practice this is not the case due to turbulence and short circuiting. Coalescence is induced also and separation is improved in this way. Coalescers are preferable for the industry over gravity separators since they require less space and they can confront with higher efficiency mature emulsions. Coalescers use mats, beds or layers of porous or fibrous material whose properties are especially suited for coalescing purpose. The settling process can be enhanced considerably by passing the dispersion through a suitable coalescer pack or providing electrical energy. Electrostatic and mechanical coalescers are the two types of coalescers that are more usual in the industry (Nageshwar 2013). Multiple configurations of coalescers including Parallel Plate Interceptors (PPI) and Corrugated Plate Interceptors (CPI) are available also.

#### ***Electrostatic coalescers***


Electrostatic force of weak electric charges is used in those vessels to break oil in water emulsions. Offshore production facilities use those vessels due to their small size. Settling velocity of oil droplets in water depends on their radius and oil's viscosity and density. The coalescence of oil droplets is dependent on electrostatic induced forces, rheology and collision frequency (Nageshwar 2013).

#### ***Mechanical Coalescers***

Baffles are used in those vessels to promote coalescence of small droplets. Those baffles are made of knitted polymers, corrugated sheets or fiberglass fibers. The liquid stream passes through the baffles or filters causing oil droplets to coalesce and gather in the surface of the baffle. This type of coalescers can be used to separate hydrocarbons from water phases such as oil removal from produced water. Coalescers typically will have a service life of 1 to 2 years when protected adequately by prefiltration (Nageshwar 2013).

## Coalescing Media

Selecting the right coalescing media for the duty depends on many factors. The most important are the droplet size distribution and the targeted efficiency. The most common coalescing media are polyester, nylon, fluoropolymer, fiber glass, polytetrafluoroethylene fibres, polyurethane foam, fired boards of saffil fibers, polyamide fibers, matrix of stainless steel wool, multistage filter with cotton polyester and aspen wood fibers, aluminum or steel fibers coated with vinyl acrylic, polyethylene, or PVC, copolymer of acrylonitrile and methyl acrylate matrix, oleophobic/hydrophobic treated media, etc. Table 9 shows some real life examples of coalescing media (Nageshwar 2013).

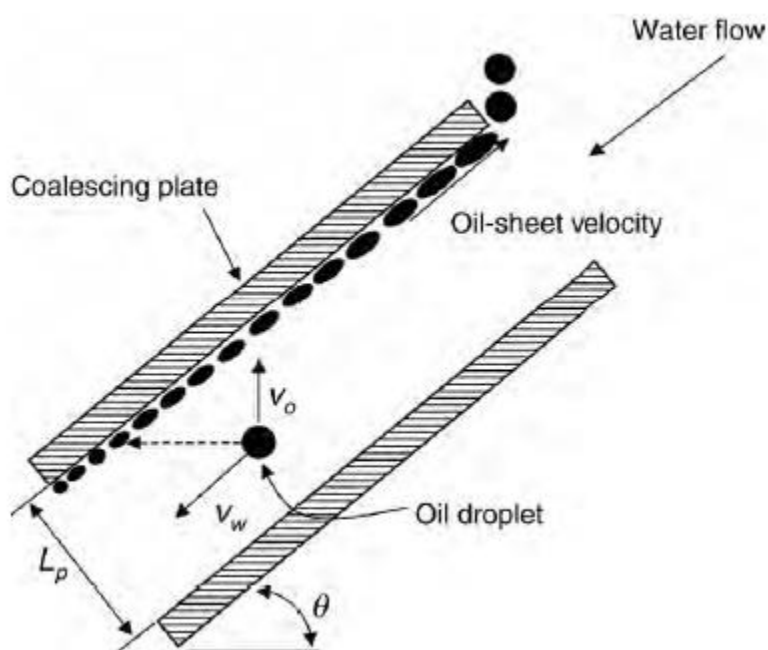
Droplets size distribution	Coalescing Media	Example
40-1000 $\mu\text{m}$	Corrugated sheet and proprietary packing	
20-350 $\mu\text{m}$	Wire wool and proprietary packing	
10-250 $\mu\text{m}$	Knits of wire and polymer	
1-30 $\mu\text{m}$	Knits of fiber glass and other materials	

**Table 9** - Examples of coalescing materials (Nageshwar 2013)

## Plate coalescers

Flow through parallel plates improves gravity separation. Various configurations have been proposed for the plates but the two dominating ones are parallel plate interceptors PPI and corrugated plate interceptors CPI. Plate coalescers are enhancing

the coalescence between the droplets by increasing their rising velocities. That means that less cross sectional areas are required and space is saved. The basic principle is that flow of the water is forced to split between parallel plates which distance from each other is 0.5 to 2 in (1.2-5 cm) as shown in Figure 38. Those plates usually have an inclination which promotes the formation of films of oil droplets which are guided to the interface of oil and water. Mixing with water is prevented due to the formation of those films. Stokes' law governs the motion of oil droplets higher than 30 microns. That means that oil droplet velocity will be the same as the water bulk's velocity. Using this correlation we can estimate the diameter of the rising droplet of oil. Below this limit other factors affect the rise of droplets to the interface (Stewart and Arnold 2009)

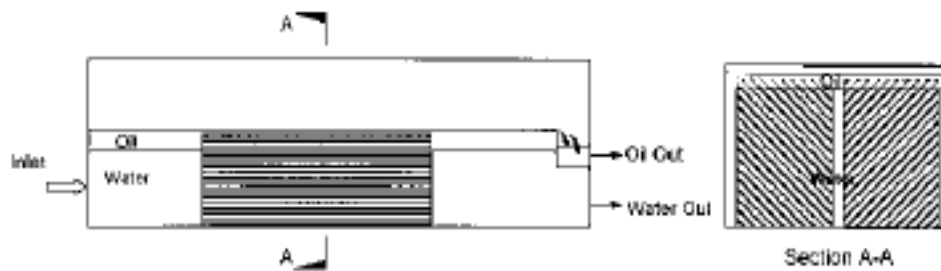


**Figure 38 - Oil droplet flow in a plate coalescer** (Juniel and Rawlins 2007)

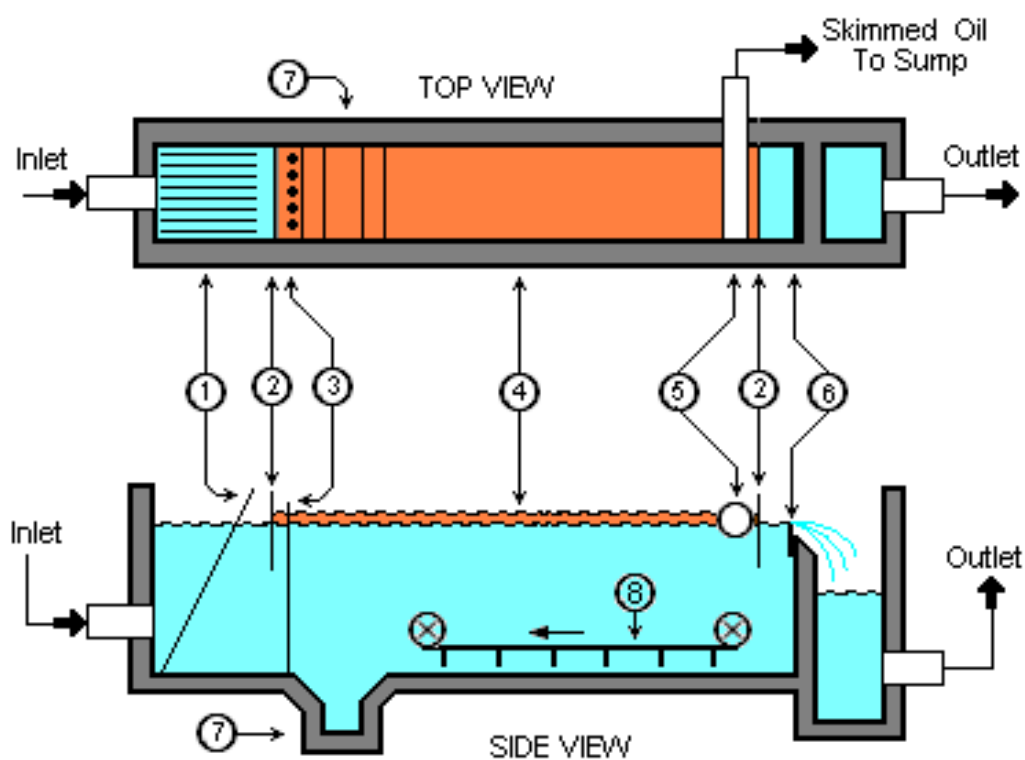
### PPI - Parallel Plate Interceptor

Initially the plate coalescers were designed according to the configuration of PPI. The design of a PPI separator (Figure 40) is based on Stokes law and the specific gravity difference of the fluids. It's a configuration of an API separator with series of inclined plates installed (Abdel-Aal 2003). The plates form a "V" scheme perpendicular to the flow axis so that oil is forced to migrate to the upper side and water and solids to the down side as shown in Figure 39. The number of plates should be adequate enough to guarantee a maximized area for the coalescence of oil droplets but not so big that a danger of blocking from particles would arise. A distance of 3/4 in. is mostly used and the angle inclination is 45° (Stewart and Arnold 2009) Most of the solids that exist in the fluids will settle in the bottom of the separator and will form a layer of sediments. The water will be the middle layer and above it the oil. The

bottom sediments are continuously removed by a chain or similar device while the oil that rises in the surface is sent to a recovery unit (Abdel-Aal 2003).



**Figure 39 - PPI separator plates pattern (Abdel-Aal 2003)**

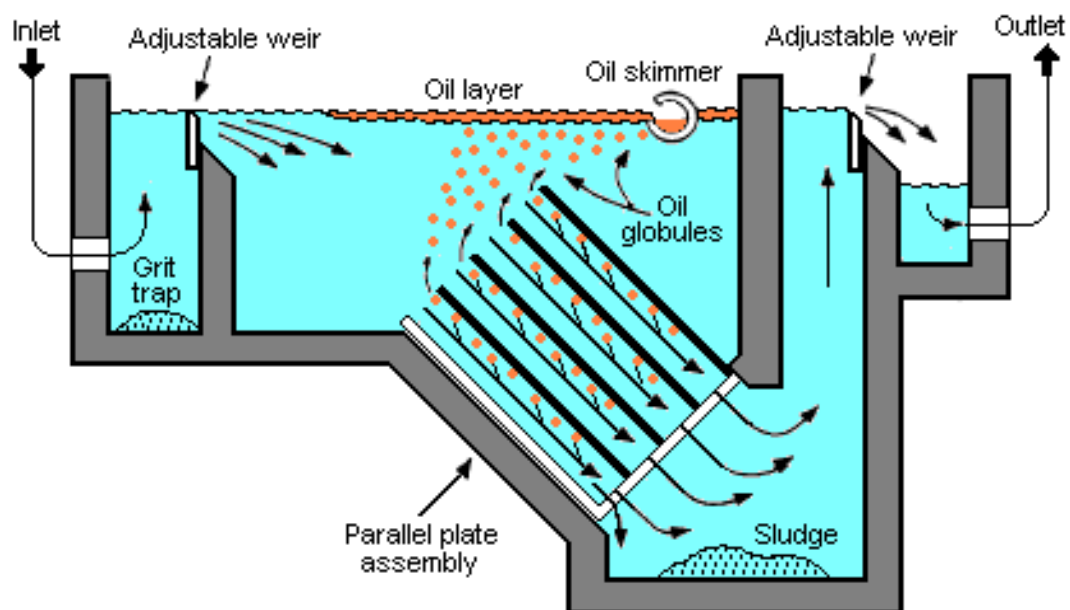


- 1 Trash trap (inclined rods)
- 2 Oil retention baffles
- 3 Flow distributors (vertical rods)
- 4 Oil layer
- 5 Slotted pipe skimmer
- 6 Adjustable overflow weir
- 7 Sludge sump
- 8 Chain and flight scraper

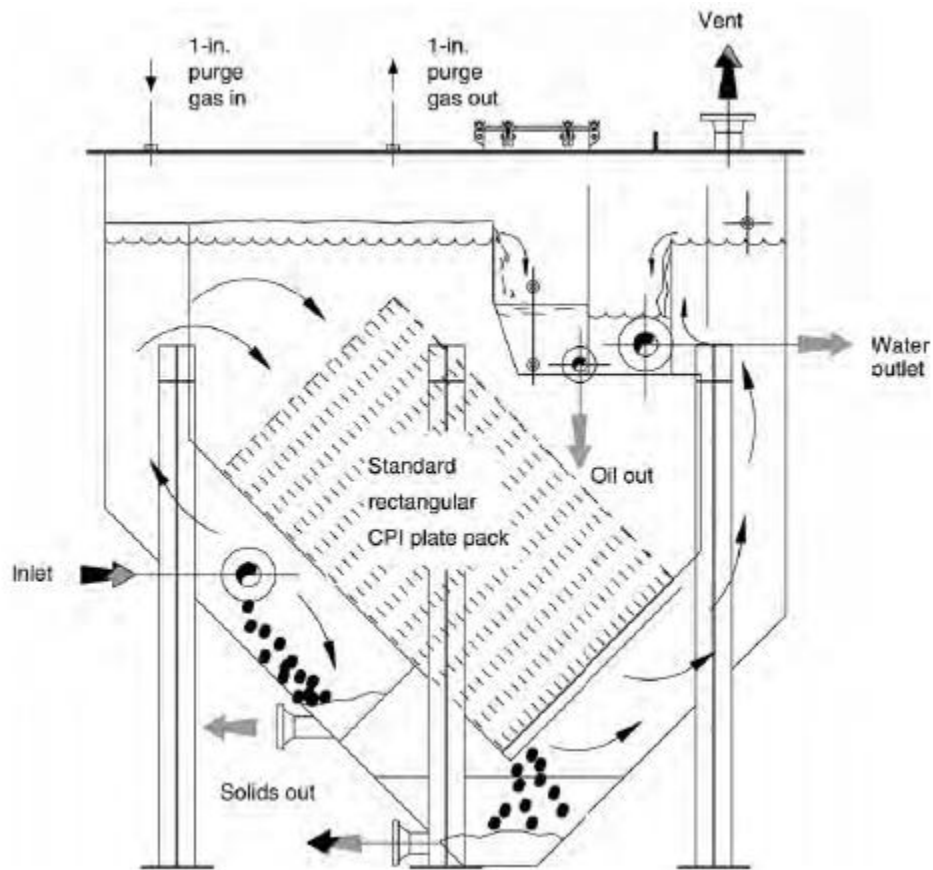
**Figure 40 - PPI separator operational scheme (API oil-water separator. Retrieved from: [https://en.wikipedia.org/wiki/API\\_oil%E2%80%93water\\_separator](https://en.wikipedia.org/wiki/API_oil%E2%80%93water_separator))**

## CPI - Corrugated Plate Interceptor

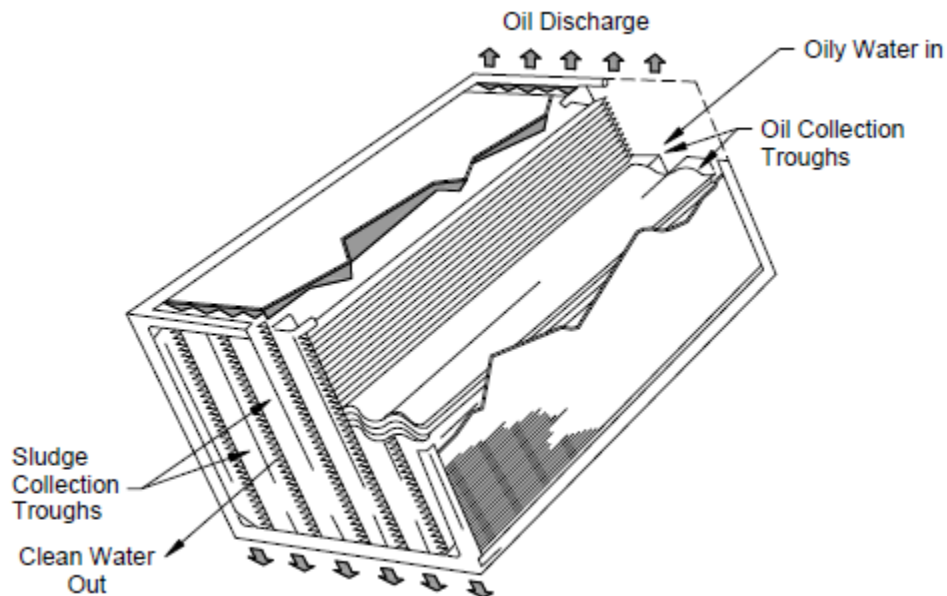
The CPI separator (Figure 41) is the most common PPI configuration and is made of corrugated plates which are inclined and mounted parallel to each other in a distance of 1.9 to 3.8 cm and inclination angle of 45°. Their number can vary from 12 to 48 and a typical CPI pack is shown in Figure 43. It is actually a hybrid of PPI that is more efficient in particle separation and is cheaper. During the flow of the wastewater downwards through the CPI pack, as shown in Figure 42, the lighter oil will float into upper corrugations and will coalesce leading it through plates into weep holes and then to the floating layer of oil (Abdel-Aal 2003). This layer of oil is removed by an adjustable weir. Solids and sludge are generated to the lowest plates surfaces and they are removed. In some cases gas blanket operations can take place if a gasketed cover is configured in the system (Stewart and Arnold 2009).



**Figure 41** - CPI separator operational scheme (API oil-water separator. Retrieved from: [https://en.wikipedia.org/wiki/API\\_oil%E2%80%93water\\_separator](https://en.wikipedia.org/wiki/API_oil%E2%80%93water_separator))



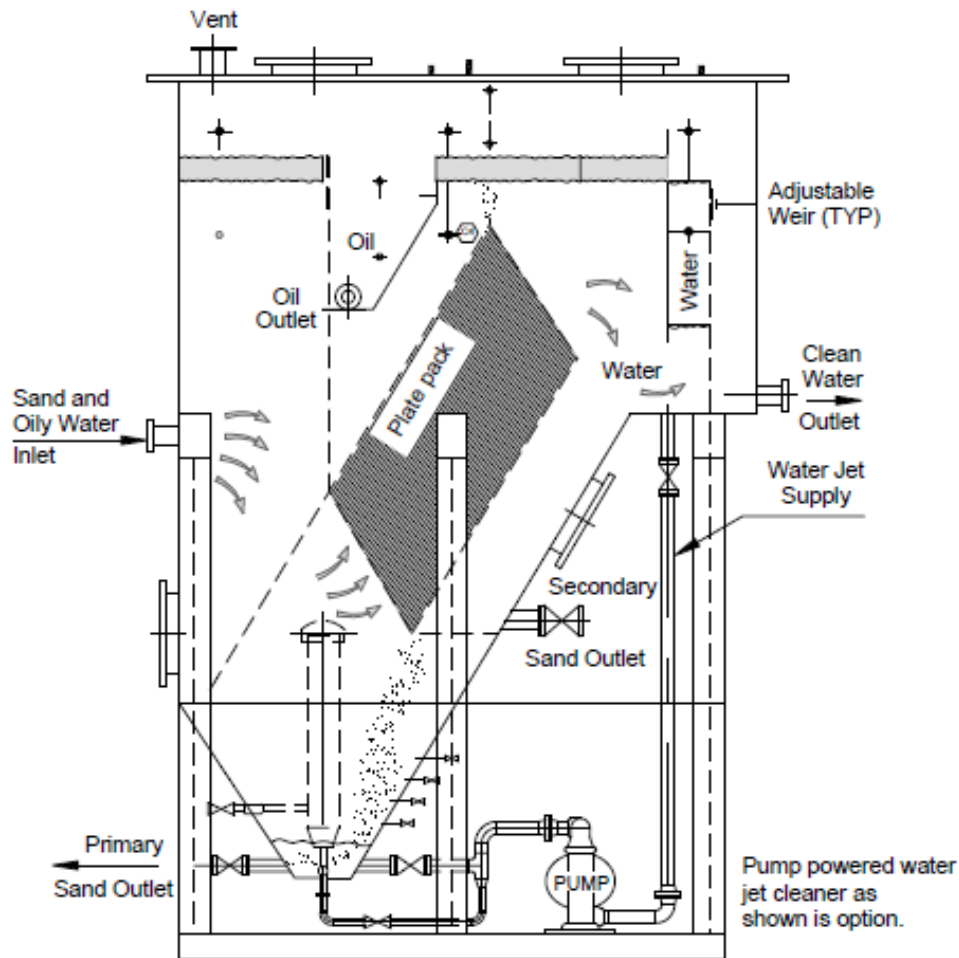
**Figure 42 - CPI flow pattern schematic** (Juniel and Rawlins 2007)



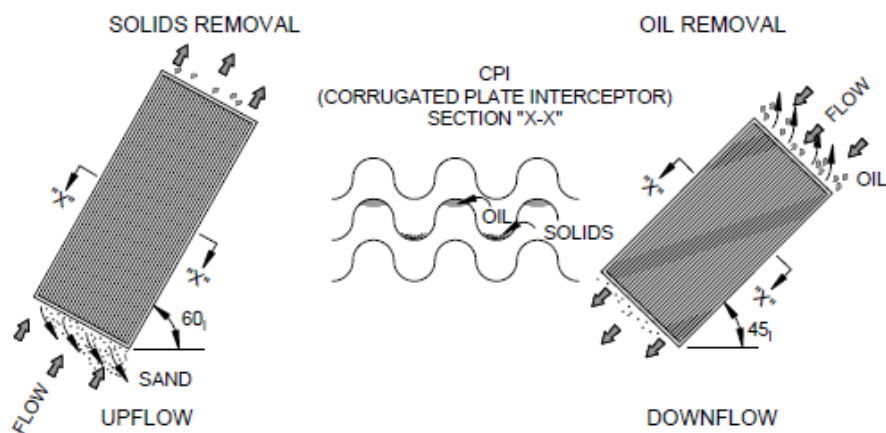
**Figure 43 - Typical CPI plate pack** (Stewart and Arnold 2009)

Atmospheric conditions are demanded for the operation of both configurations. Due to laminar flow regime and the 45° inclination, problems related to sediment settling can be created, especially in cases where oil-wet sand is present. This can be confronted using an up-flow configuration of CPI (Figure 44) units. Inclination of 60°

to horizontal one is used. Furthermore plate packs are installed into pressure vessels. This is causing a perpendicular flow to the axis of corrugated plates, while water jets for the removal of sand are installed (Abdel-Aal 2003). Figure 45 shows a comparing scheme between the two configurations of CPI pack. (Stewart and Arnold 2009)



**Figure 44** - Upflow configuration of CPI (Stewart and Arnold 2009)



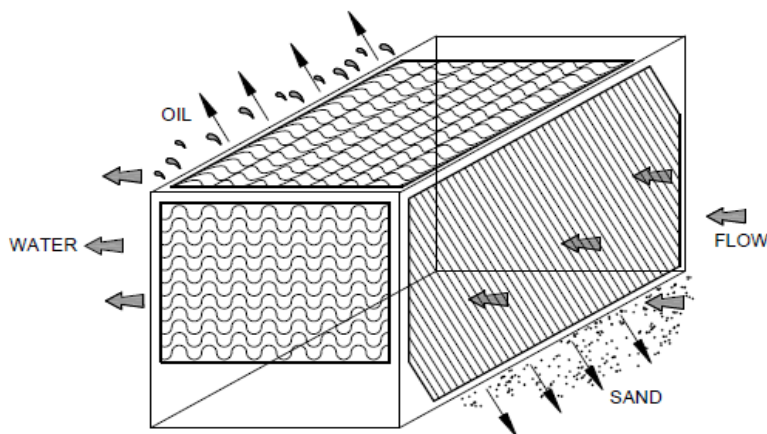
**Figure 45** - Upflow versus downflow configuration of CPI flow patterns (Stewart and Arnold 2009)

CPI base and internals are made of carbon steel and the edges are welded while epoxy paint is used for the surfaces. The plate packs are made of chlorinated polyvinylchloride (CPVC), polyvinylchloride (PVC), polypropylene (PP), fiberglass reinforced polyester, carbon steel, galvanized and stainless steel. Polypropylene is lipophilic and water repellent so the flow of the droplets to the surface is aided. Polymer plates though limit the operational temperature to 140°F. Oil weir and basin cover are made of carbon steel, stainless steel or fiberglass reinforced plastic (FRP) (Stewart and Arnold 2009).

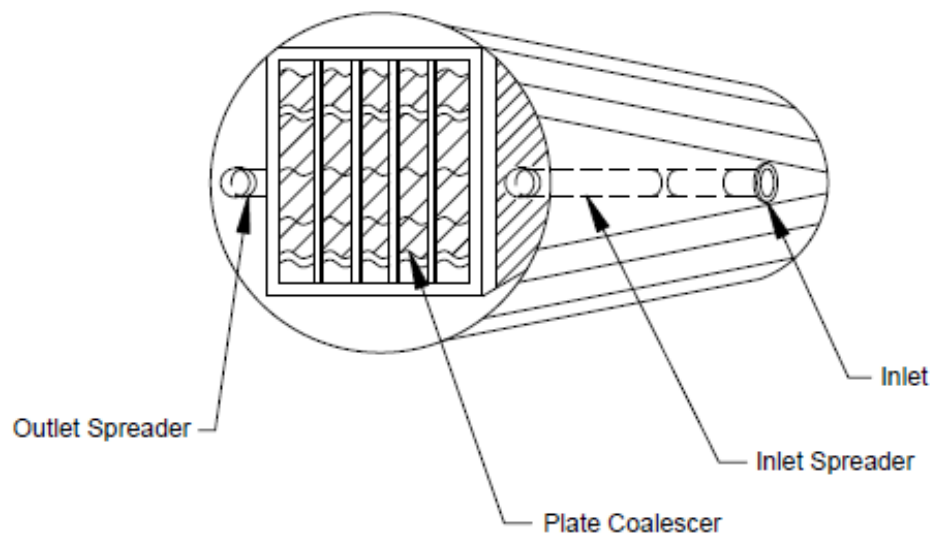
### *Cross flow Separators*

CPI has been modified in a configuration applicable to horizontal water flow and perpendicular to the plates as shown in Figure 46 and is preferred when a high pressure system is encountered. This modification enhances the sediment removal. Those devices can be introduced both in horizontal and vertical pressure vessels. Baffles are needed in smaller extend in horizontal vessels since the upper end of every plate moves the oil droplets directly to the oil zone while the lower end puts the sediments in the bottom of the vessel where no water flow occurs. Collectors and spreaders are required though since the pack is long and narrow so that the water flow is not stopped. Shear of oil droplets in the spreader may occur which is an undesired situation. Those devices can be installed both in atmospheric and vertical pressure vessels as shown in figures 47 and 48. Comparing CPI and cross flow separators, the fact that CPI separators are cheaper and they present higher oil removal efficiency should be mentioned. Cross flow separators though are preferable for use when a pressure vessel is required and for sand removal. Figure 49 shows a real life example of a cross flow plate pack. (Stewart and Arnold 2009)

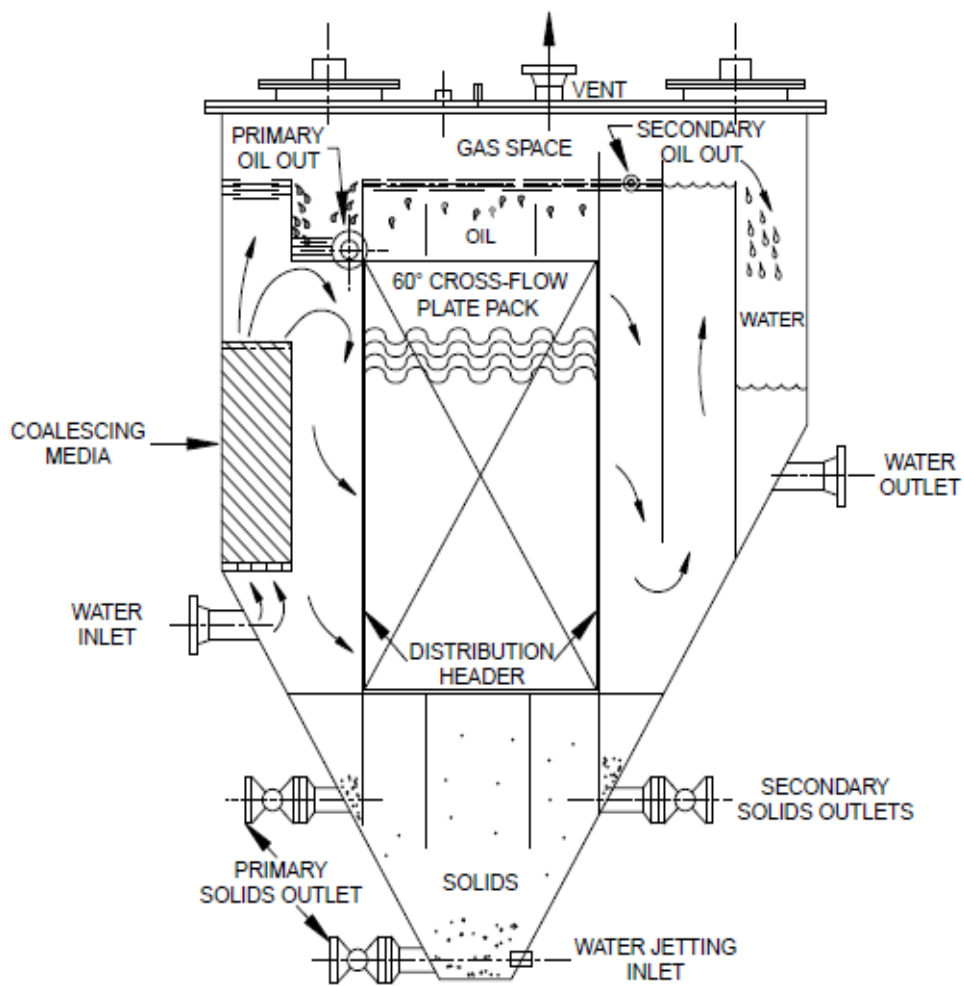
Practical limitations though exist in this case. Stoke's law is applicable for droplets of sizes 1 to 10  $\mu\text{m}$  while field experience shows that 30  $\mu\text{m}$  is the lower limit of droplets that can be removed due to pressure fluctuations and platform vibrations which tend to impede the rise of the droplets to the surface. (Juniel and Rawlins 2007)



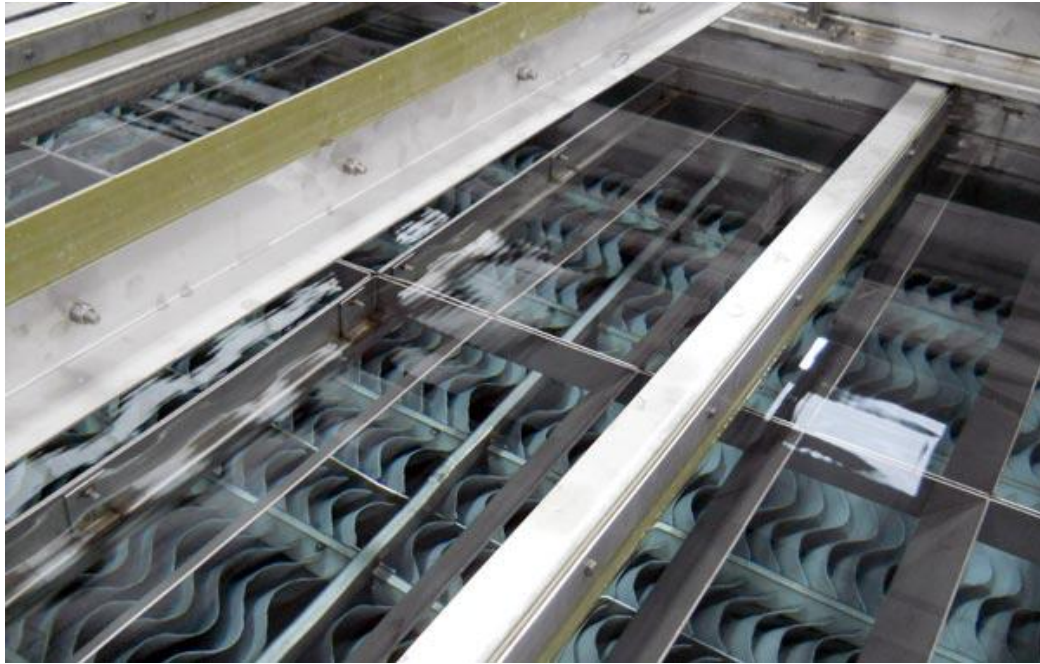
**Figure 46** - Flow pattern of cross flow plate pack (Stewart and Arnold 2009)



**Figure 47** - Cross flow device installed in a horizontal pressure vessel (Stewart and Arnold 2009)

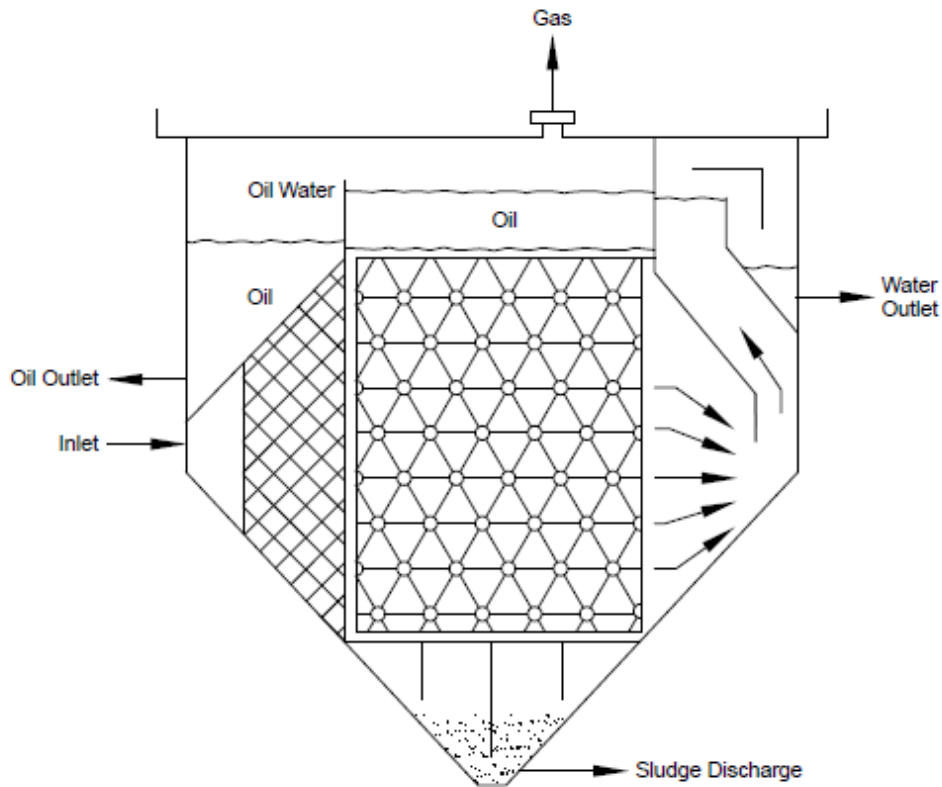


**Figure 48** - cross flow device installed in an atmospheric vessel (Stewart and Arnold 2009)



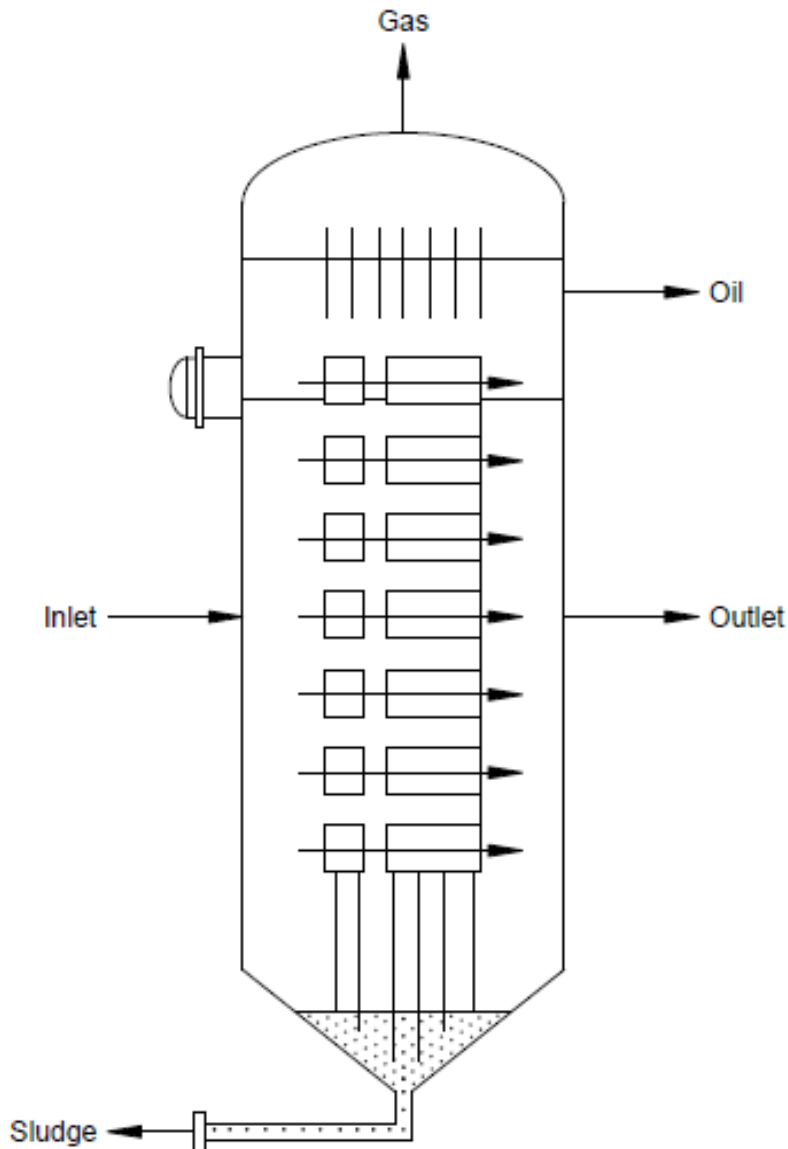
**Figure 49 - Cross flow plate pack** (Cross flow plate pack. Retrieved from: <http://frcsystems.com/pcl-dissolved-air-flotation-systems/>)

Cross flow separators can be updated for use of oil-water and sediment separation. This configuration proceeds with a two step treatment operation for the separation of oil and sediments from the water inflow. Cross flow is used instead of upflow or downflow. Both vertical and horizontal pressure vessels can be used as shown in Figures 50 and 51. Distributors and coalescers packs are used in both configurations to promote the spreading of the inlet flow to the full height and width of the vessel. Flow regime is turbulent which means that coalescing of oil droplets is favored. Inclined plates of hexagonal configuration receive the flow provoking a laminar flow regime. Those hexagonal plates push the oil droplets to the oil layer through the top of the pack to the oil layer and the sludge to the bottom of the separator (Stewart and Arnold 2009)



**Figure 50** - *Oil/water/sediment horizontal pressure vessel (Stewart and Arnold 2009)*

A 0.8 in span exists between the cross flow plates which have an inclination of 60° angle. In some configurations this space can be 0.46 in or 1.33 in. The hexagonal shape of the plates promote more coalescing space for the oil droplets. Those plates are made of polypropylene, polyvinyl chloride, stainless steel and carbon steel. The lipophilic character of polypropylene oil removal is enhanced but a limitation to the temperature is introduced which cannot be higher than 150F (55°C). Stainless and carbon steels on the other hand can be used in higher temperatures for effluents with high concentrations of aromatic hydrocarbons. The major advantage of this configuration compared to the rest of plate separators is it's ability to treat oil droplets of size down to 20µm. (Stewart and Arnold 2009)



**Figure 51** - Oil/water/sediment coalescing vertical pressure vessel (Stewart and Arnold 2009)

### *Performance considerations for Plate Separators.*

Flow direction is critical for the efficiency of plate separators. Oil removal is favored when downflow configuration is set and plates are installed on 45° angle. For this case solids content should be minimal. In case of big amounts of solid particles the upflow configuration is preferable. Plates should be put on 60° angle to limit erosion. In case that a pressure vessel is required for solids and oil removal, cross flow devices should be installed.

One of the main advantages of plate separators is that little maintenance is required. Plates can be removed easily to be treated separately. Moreover dimensions and

weight is limited compared to skim vessels which makes easier their installation. Inclined plates which are put in small distances is the main reason. Another advantage is that high concentrations of oil (up to 3000 mg/l) and solids can be treated with oil droplet removal size reaching 30  $\mu\text{m}$ . They are very efficient in removing sand particles of very small sizes. They are very safe since fire hazards and vapor losses are unlikely to occur since the vessels are totally enclosed. CPI is more efficient than cross flow separators. Their cost is very low compared to the rest of the devices used for water treatment and for their operation no power inlet is required

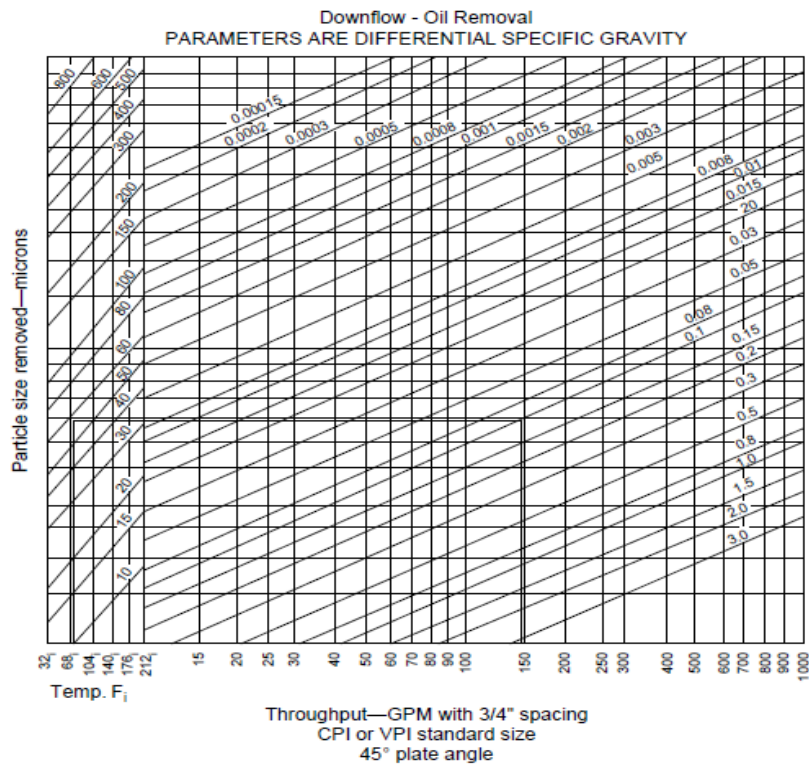
On the other hand one of their main disadvantages is that they have small efficiency when treating streams with slugs of oil and when treating large amounts of solids and emulsified streams.

Plate separators' use is required when steady water flow rate exists, size and weight are not constraints, the plates can be cleaned by specialized personnel, concentration of oil is high in the influent and it needs to be lowered to levels below 150 mg/l for a second stage treatment and solids are of small quantity in the waste stream and sand content less than 110 ppm

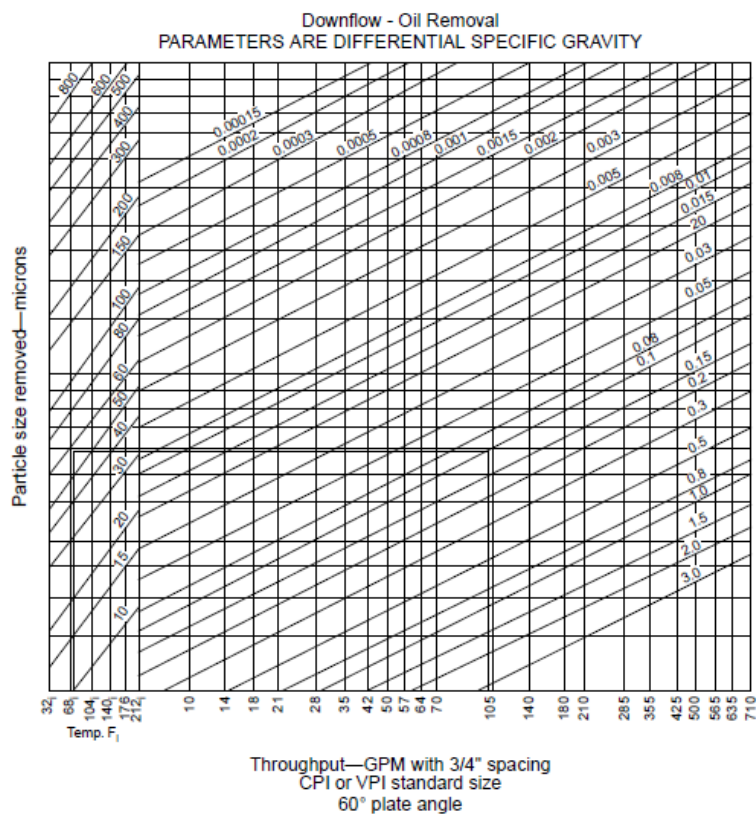
Plate separators' use should not be preferred when droplet sizes are smaller than 30  $\mu\text{m}$ , size and weight are primary considerations and solids removal is the primary goal of the separation (Stewart and Arnold 2009)

### *Selection Criteria for Plate Separators*

The performance of CPIs can be predicted using vendor-supplied nomographs. The correlation between temperature of the effluent, particle size, differential specific gravity of the oil and water and capacity for oil removal using the 45° angle for the plates (downflow) is shown in Figure 52 and for 60° angle plates (downflow) in Figure 53 (Stewart and Arnold 2009)



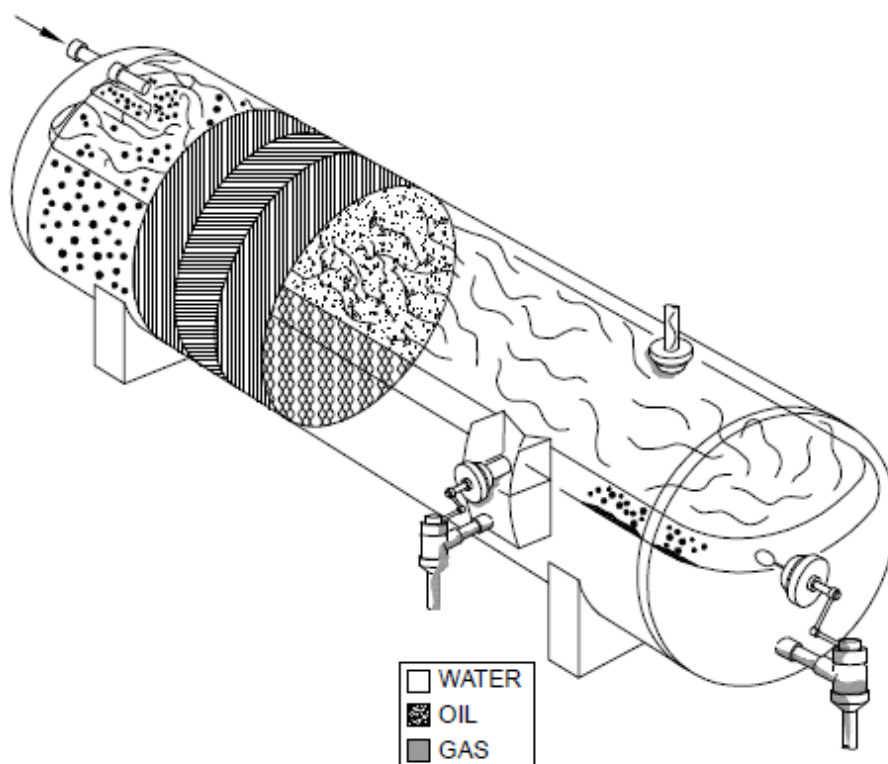
**Figure 52** - Nomograph for CPI with installed plates of 45° angle (downflow) (Stewart and Arnold 2009)



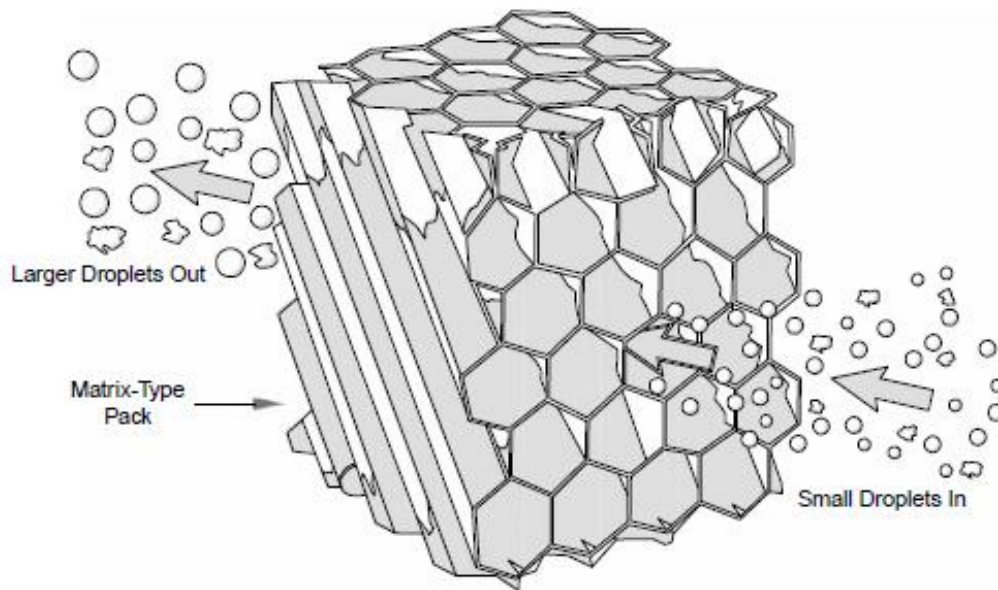
**Figure 53** - Nomograph for CPI with installed plates of 60° angle (downflow) (Stewart and Arnold 2009)

### *Skimmer coalescers*

Although skimmers are considered as a pre treatment stage vessels for the oil in water emulsion removal, particular modifications can enable their use as primary treatment stage vessels. Proposed configurations of those vessels include the installation of coalescing plates for horizontal skimmers or free water knockouts (FWKO) for the enhancement of the coalescence of small oil droplets which can escape the pre treatment. Accumulation of small oil droplets in oil wet surfaces which leads to the formation of bigger droplets is promoted by coalescers. Skimming of those droplets directly from the surface or secondary treatment via gravity application can be used for their removal. In order to avoid costs and save space the coalescing equipment can be installed in packs inside the gravity vessels. A schematic of this configuration is shown in Figure 54 for a FWKO. In order the plates to serve both as coalescing and gravity separation device, a lipophilic material should be used for their fabrication. In Figure 55 a cross section of a packing that serves as a coalescer can be observed. (Stewart and Arnold 2009)



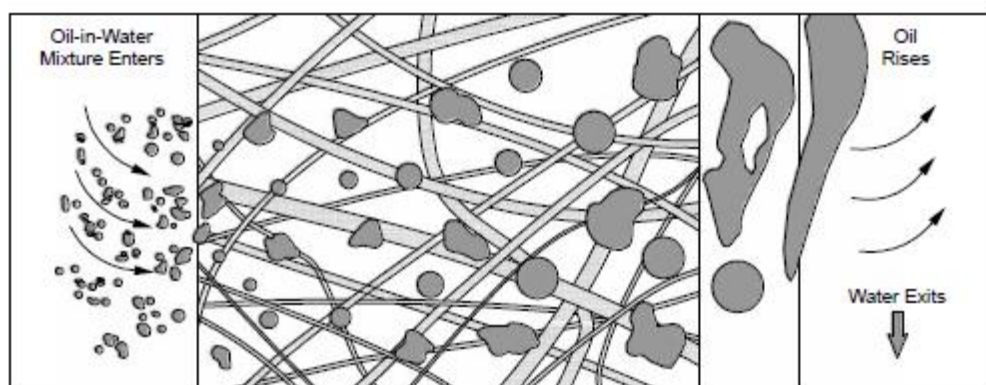
**Figure 54** - *Free water knockout with a coalescing plate pack configuration (Stewart and Arnold 2009)*



**Figure 55** - Packing of hexagonal plates serving as coalescer (Stewart and Arnold 2009)

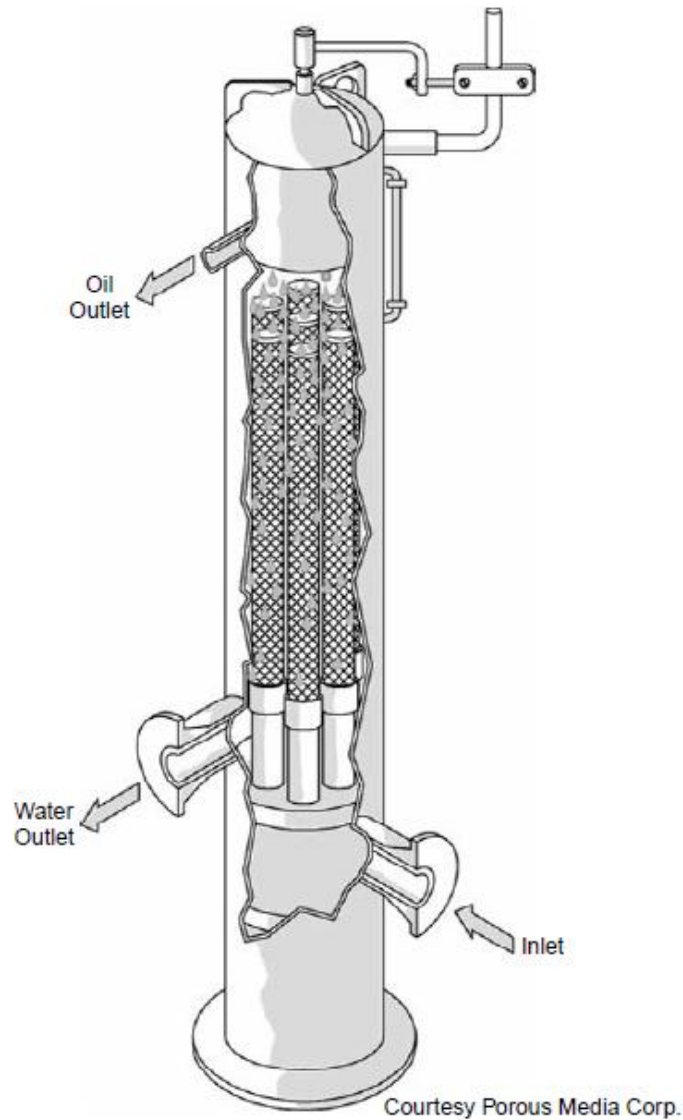
### *Matrix type*

Fiber packs can be also used to create a lipophilic surface. It's easier to work with those materials because of the large surface areas they can form and their easy fabrication. Flow has to go through fibers of lipophilic materials which are collected in packs. Oil droplets are captured by those fiber packs and then they coalesce as shown in Figure 56. and under the gravity forces rise to the oil layer and then are removed. Figure 57 shows a gravity separator with this exact configuration. (Stewart and Arnold 2009)



**Figure 56** - Oil coalescence in fiber packs (Stewart and Arnold 2009)

Lipophilic material can be introduced into loose media in a granular form to deep bed gravity settlers. Pack lengths can range from 2-9 ft. (Stewart and Arnold 2009)



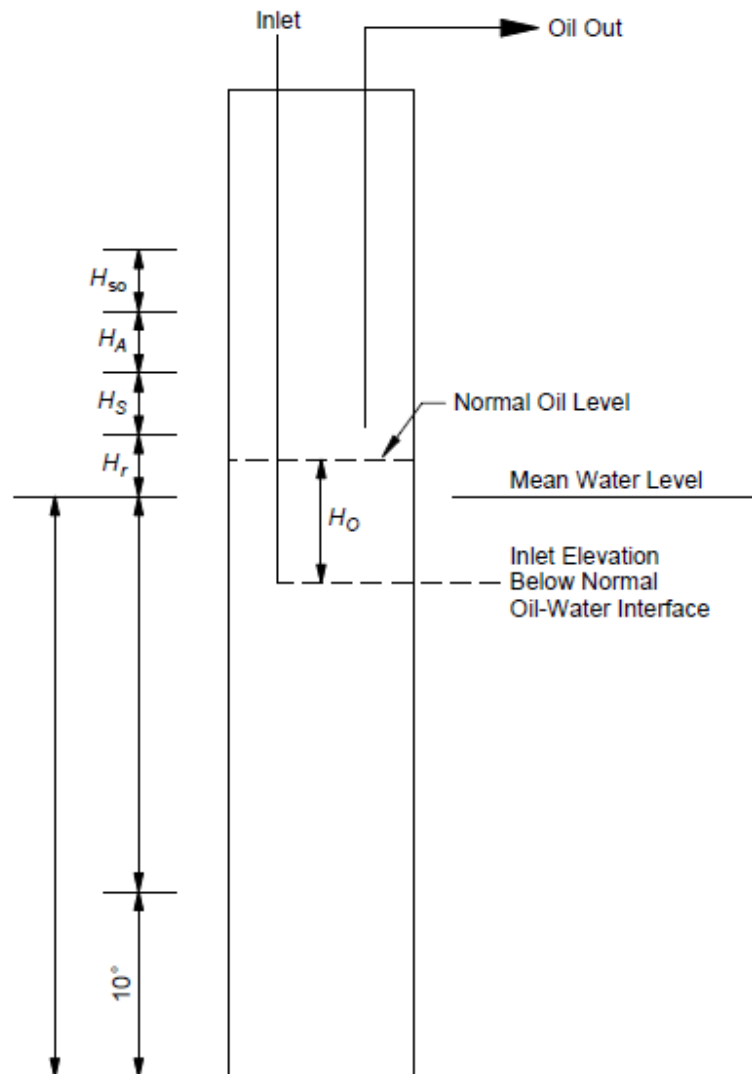
**Figure 57 - Matrix separator oil removal (Stewart and Arnold 2009)**

### *Performance Considerations*

Coalescers act as integral part in coalescing equipment in order to improve their performance. They are an important part of the vessel when small oil droplets are present in the incoming water flow and they should be used when low pressure separators, skimmers or plate separators have the ability to host them provided that coalescing section can be maintained and cleaned properly and oil droplets of size smaller than 50 $\mu\text{m}$  are to be treated. On the other hand they should not be used when droplet sizes are smaller than 10  $\mu\text{m}$  or higher than 100  $\mu\text{m}$  (Stewart and Arnold 2009)



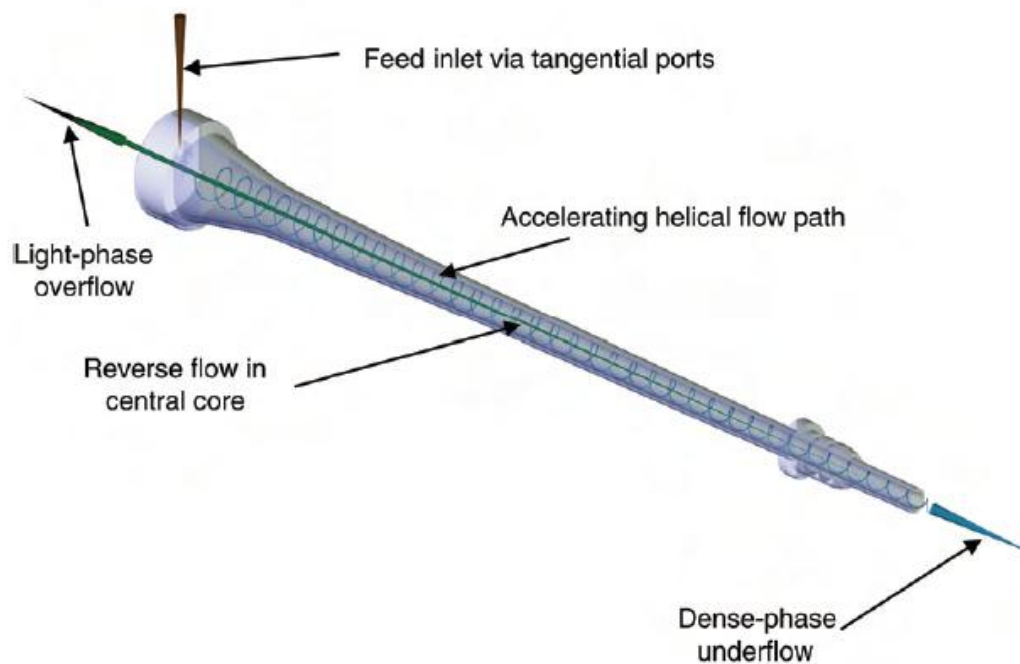
Although used for the -after treatment- discharge of water, disposal piles can be considered as a primary stage treatment since they are used as a final "trap" for hydrocarbons that may have escaped during treatment or due to equipment failure (Abdel Aal 2003). Disposal piles, a typical example of which is shown in Figure 59, are tubes of large diameter ranging between 24-48 inches starting from the platform and extending in the water are the disposal piles (Mastouri et al. 2010). Their size depends on the total flow of the water to be disposed. They are used for the discharge of the clean water.



**Figure 59** - Disposal pile length schematic (Stewart and Arnold 2009)

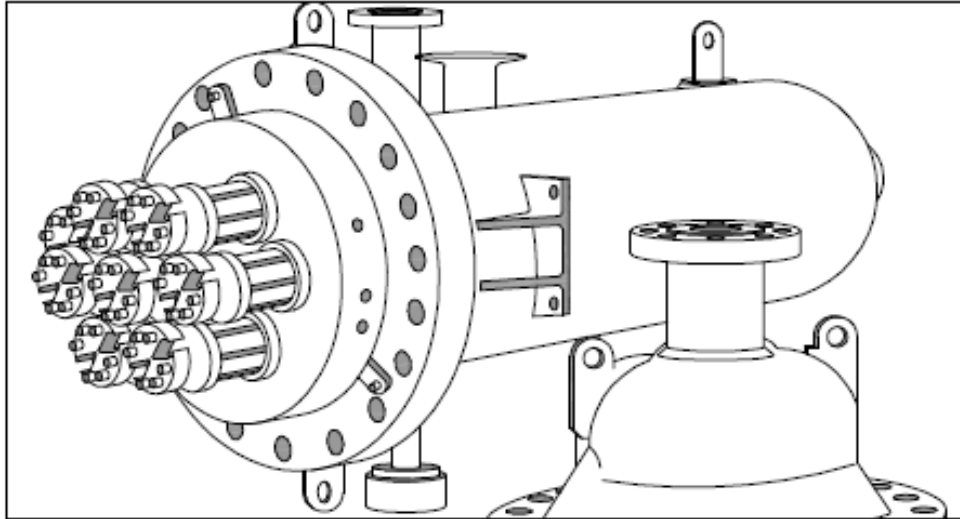
## Hydrocyclones

Often mentioned as "enhanced gravity separators" and utilizing centrifugal force, hydrocyclones or deoilers (Figure 60) are another vessel used for removal of oil droplets from water. They provide the highest throughput to size ratio of any water treating technology and are insensitive to motion or orientation (Juniel and Rawlins 2007). They are connected to an outer pressure retaining vessel and they consist of cylindrical swirl chamber, concentric reducing section, fine tapered section and cylindrical tail section. A typical multiliner vessel is shown on Figure 61. A nozzle inputs the oily water (Figure 62) and a high velocity vortex is created. Fluid acceleration is provoked in concentric reducing section and larger droplets are removed in fine tapered section while smaller ones are treated in the tail section. A small diameter reject port is used for the removal of oil while water moves downstream (Mastouri et al. 2010).

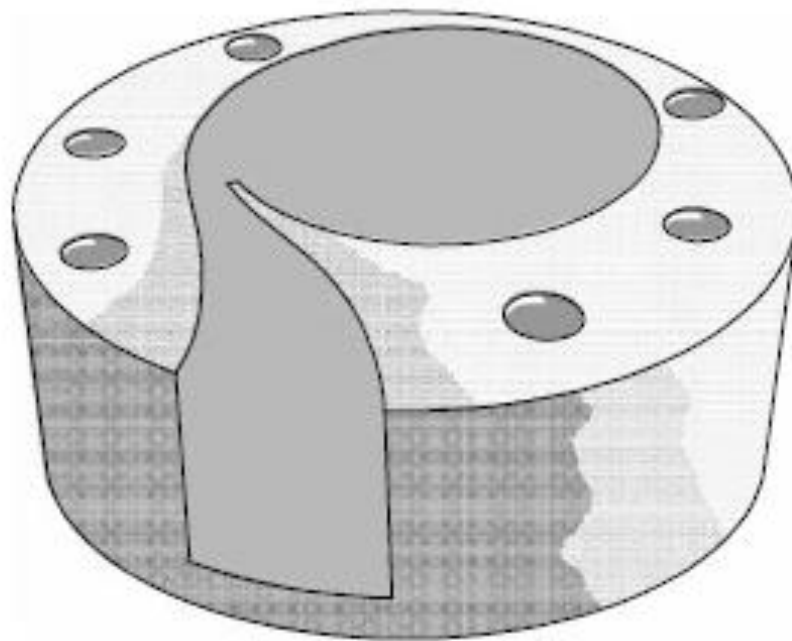


**Figure 60 - Hydrocyclone** (Juniel and Rawlins 2007)

Stokes' law governs the operation of a hydrocyclone. The size of a hydrocyclone is typically 35 to 60 mm and it is the actual size of the diameter of transition zone between concentric reducing and fine tapered sections. (Stewart and Arnold 2009)



**Figure 61 - Multiliner hydrocyclone**(Stewart and Arnold 2009)

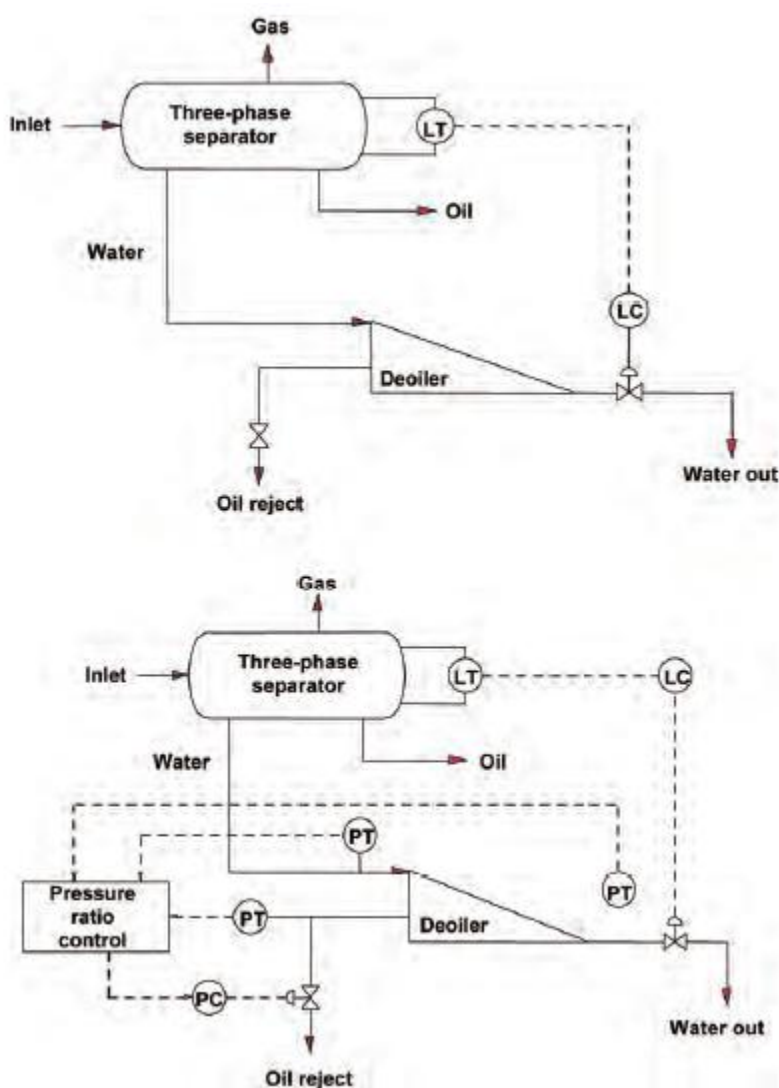


**Figure 62 - Inlet nozzle**(Stewart and Arnold 2009)

Hydrocyclones can have either horizontal or vertical configuration. More space is required for the horizontal configuration but its maintenance is easier and that's why it's mostly preferred. Usually pressures on level of 100 psi or higher are needed for its operation. Degassing vessels can be installed downstream for water treatment which provide short residence times. (Stewart and Arnold 2009)

For better results, hydrocyclones ideally must be installed as close as possible to the oily water outlet of the separators. This is due to the fact that hydrocyclones are pressure driven and locating them at the highest pressure location of the process since

oily water has not yet been exposed to droplet shearing pressure drops across level control valves. Their control system in this case is very simple since they use the standard interface level control system of the three phase separators as shown in Figure 63. A valve will control the flow rate through the hydrocyclone. Overflow can be controlled on the same principle with another valve which will operate parallel with the interface level control or by using simple pressure control systems known as the pressure ratio control system. Pumps can be used also to boost the pressure but their selection must be careful. They must be of closed impeller design, their efficiency must be at least on 70%, their maximum speed of 1750 rpm and the maximum pressure boost per 75 psi. (Juniel and Rawlins 2007).



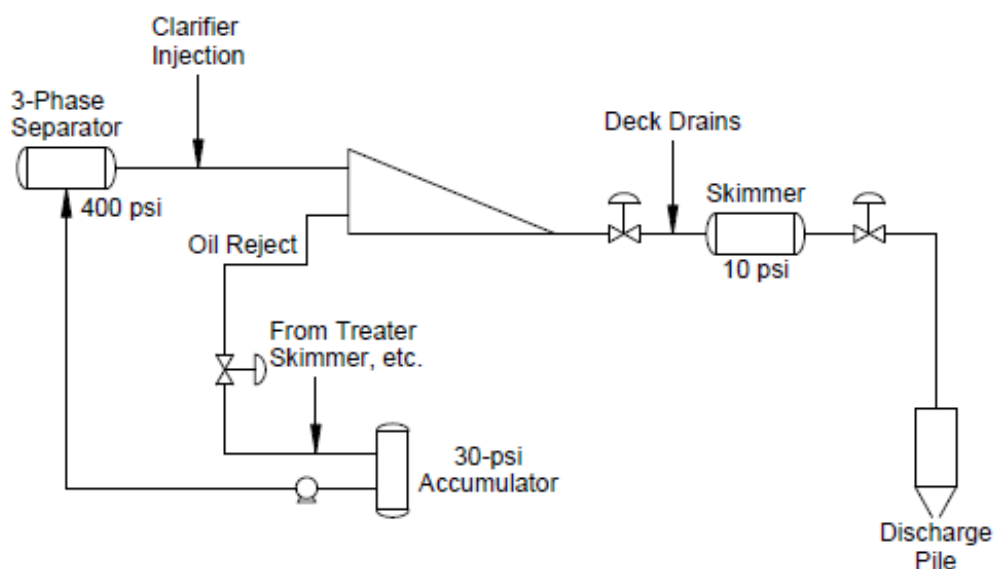
**Figure 63** - Hydrocyclone throughput control (top), Hydrocyclone pressure ratio control (bottom) (Juniel and Rawlins 2007)

## Static Hydrocyclones

Usually they are used as a primary treating device due to their high coalescence abilities. Downstream, a skim vessel should be installed for better treatment and a simple scheme for the installation is shown in Figure 64. In case of lower than 100 psi inlet pressure those vessels can use a low shear pump. Droplets with size less than 10-20  $\mu\text{m}$  cannot be treated sufficiently. Their performance is affected by the reject and pressure drop ratios. Reject ratio is the ratio of the reject fluid rate to the total fluid rate that enters the vessel with optimal values of 1%-3%. Below this value an inefficient oil removal will occur. Pressure difference ratio on the other hand is the difference between the pressure of inlet and outlet with optimal values ranging between 1.4-2. Oil droplet size, concentration of oil, difference in specific gravity and temperature (optimal value above 80F) are factors that affect efficiency of the separation also. A typical value of oil removal for hydrocyclones is 90%. (Stewart and Arnold al. 2009)

Their main advantages are that maintenance needs are low due to no existing parts and weight and space needs are limited. No sensitivity in motions exist which makes them suitable for offshore use and their capacity can be improved and their cost is low

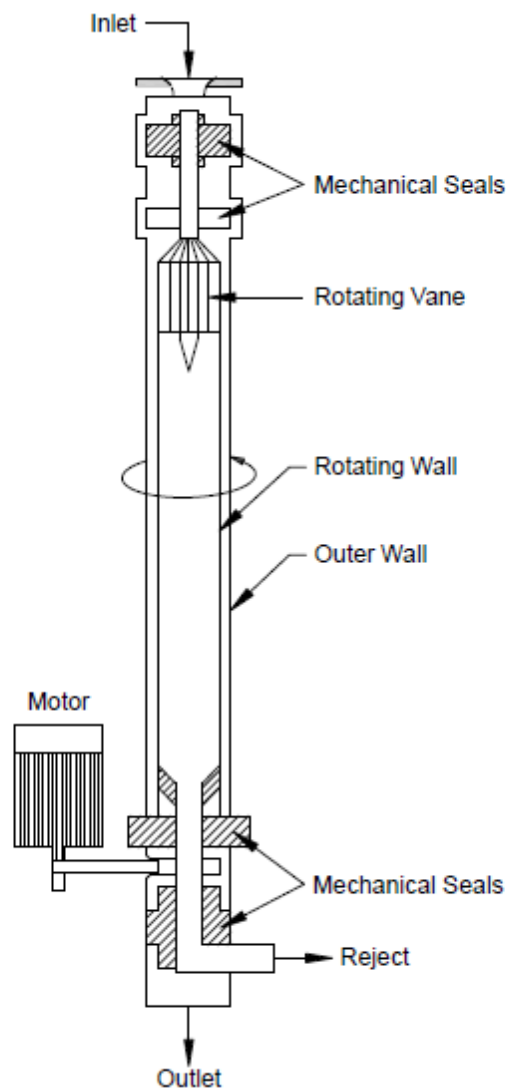
On the other hand their disadvantages are the need for pump installation in case of low inlet pressures and plugging of reject port due to sand or scale which can increase maintenance costs (Stewart and Arnold 2009)



**Figure 64** - Treatment scheme with hydrocyclone used as a primary treating vessel. (Stewart and Arnold 2009)

### *Dynamic Hydrocyclones*

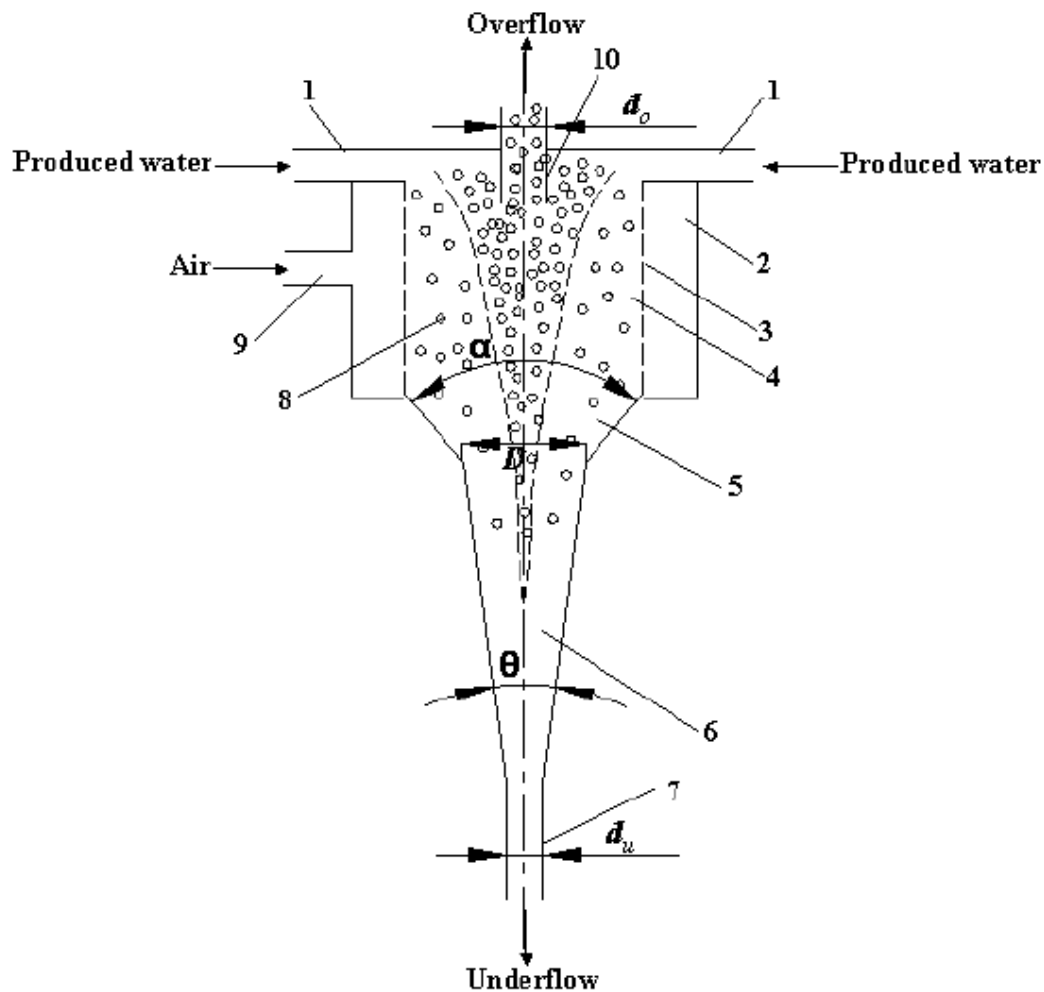
In this case an external motor is used for the operation of the vessel. Dynamic hydrocyclone's main parts include a rotating cylinder, axial inlet and outlet, reject nozzle and the external motor as shown in Figure 65. Due to the creation of the vortex from the cylinder and no need for high pressure drops, those vessels can operate at 50 psig and reject ratio is of secondary importance. Their performance is affected by reject flow which must be held constant in the inlet flow range and the rotational speed which should be between 1000 and 3000 rpm. Oil removal efficiency ranges between 50%-75% but those vessels are more capable of treating smaller oil droplets (down to 15  $\mu\text{m}$ ). (Stewart and Arnold 2009)



**Figure 65** - Dynamic hydrocyclone (Stewart and Arnold 2009)

### *Air Sparged Hydrocyclones (ASH)*

ASH hydrocyclones were invented by Miller in early 1980's and their concept is based on the assumption that the energy for the inertial collision of a droplet and a gas bubble will be increased by centrifuging. A swirl providing rotational motion generates this energy. The configuration of the vessel involves cylindrical geometry, two feed entries in the top, two concentric right vertical tubes, a buffer chamber header at the top and a froth pedestal at the bottom as shown in Figure 66. The air is sparged through inner porous tube. The generation of large number of air bubbles promotes the flotation of oil droplets. (Liu et al. 2005).

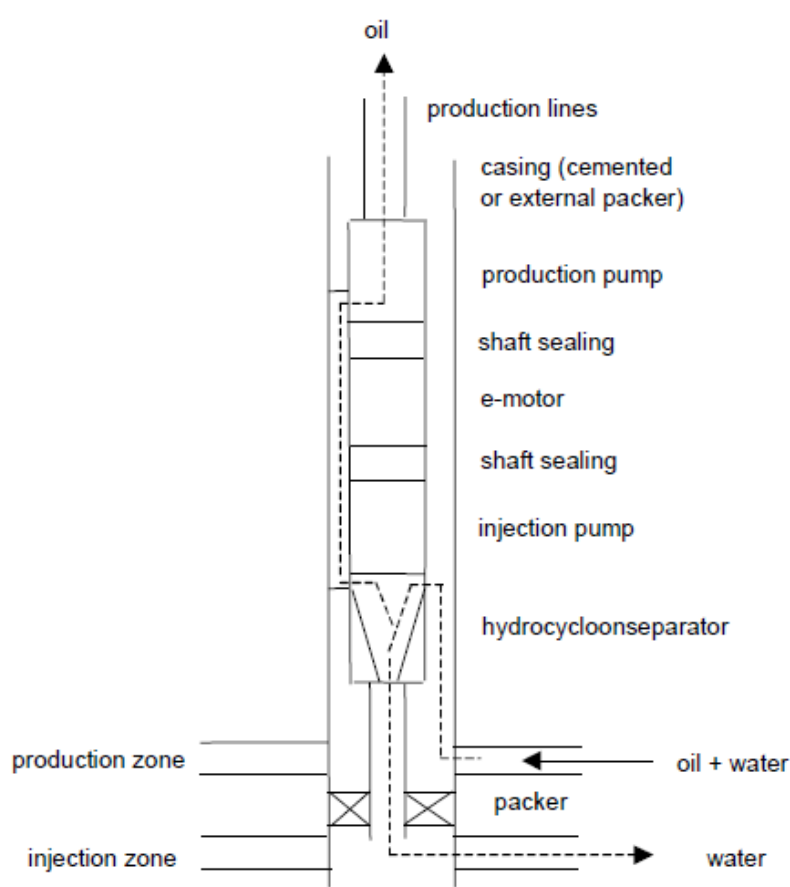


**Figure 66** - Air Sparged Hydrocyclone (ASH) schematic diagram. 1 - Overflow outlet, 2 - tangential inlet, 3 - air nipple, 4 - froth pedestal, 5 - vortex cavity, 6 - air chamber, 7 - porous tube, 8 - air bubble, 9 - vortex finder, 10 - buffer chamber (Liu et al. 2005)

### *DHS Technique for down hole oil-water separation*

DHS (Down Hole Separation) technique is used in the industry for the separation of the produced fluid down hole by the use of a hydrocyclone. The water that is

primarily separated from the fluid is injected back at underground zones and only the remaining oil-water mix is pumped to the surface leading to removal of dispersed hydrocarbons from water at least by 50%. This results in enhancement of oil production quantities and less use of chemicals. The schematic of the process is shown in Figure 67. The technique has some limitations since a primary requirement for its application is the existence of suitable water injection zones, API of oil higher than 20° and water cut higher than 50%. Production and injection zones should be isolated from each other. Their life span can reach 2 years and the chemical requirement is scale inhibitors and acid for the stimulation of injection zone. The technique is considered as promising but it is still under development and mostly used in offshore installations due to lack of capacity for water treatment equipment (OSPAR Commission 2013).

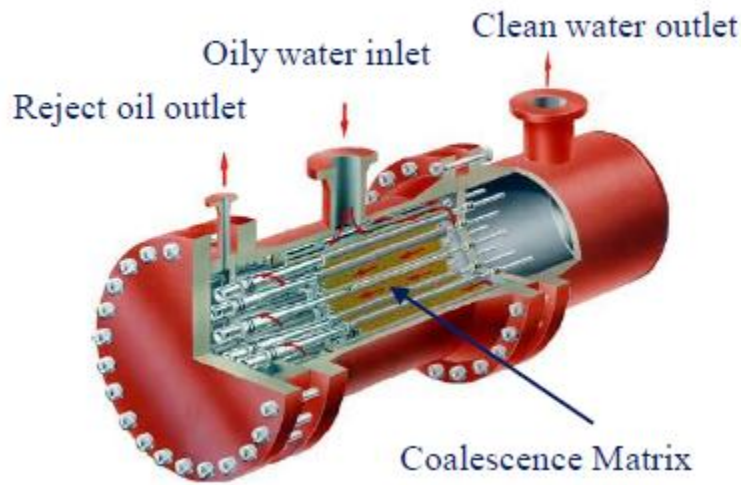


**Figure 67 - DHS operating scheme (OSPAR Commission 2013)**

### *Coalescence media for improvement of Hydrocyclone's efficiency*

Coalescing media in a cartridge assembly can be installed within the hydrocyclone or upstream of it for enhancement of the vessel's efficiency by reducing the oil in water concentration of the effluent by 80%. This is achieved due to the fact that such a coalescing medium will reduce the flow velocities. Its installation is low risk and cost

effective and its configuration within a hydrocyclone is shown in Figure 68. Typically those cartridges are manufactured by 316L or Duplex stainless steel (OSPAR Commission 2013).



**Figure 68** - Coalescing medium within a hydrocyclone (OSPAR Commission 2013)

### *Selection criteria*

Hydrocyclones should be preferred when particle size is in excess of 30  $\mu\text{m}$ , inlet pressure is at least 100 psig, space needs to be saved and motion exists in the platform. Also when solids and gas amounts are low, constant flow of inlet exists, maintenance cannot be applied easily and low power sources are present.

Hydrocyclones should not be preferred when tight emulsions of size lower than 20  $\mu\text{m}$  exist, inlet pressure is significantly lower than 100 psig, very low specific gravity difference exists between oil and water and large amounts of sand are produced. (Stewart and Arnold 2009)

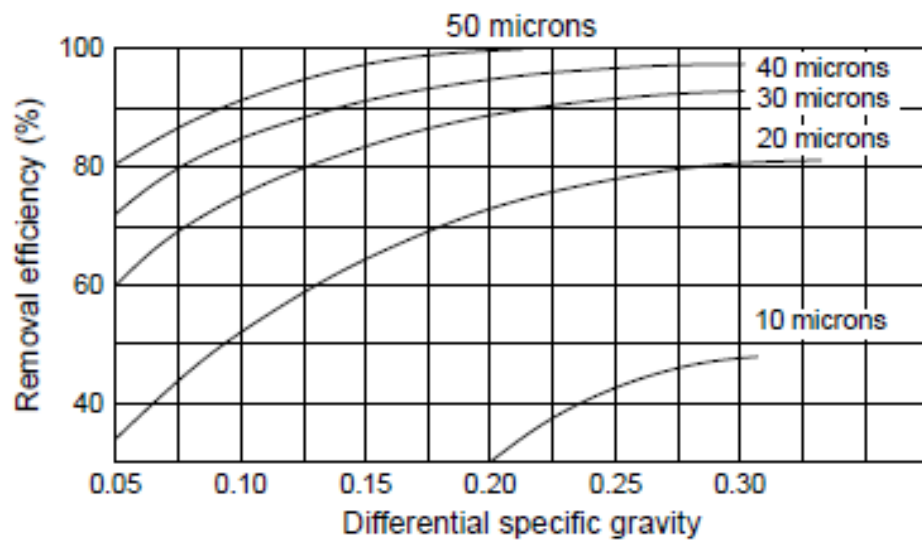
Equation 13 describes the efficiency calculation for hydrocyclones in terms of removing oil ability.  $C_i$  is defined as the dispersed oil concentration in inflow and  $C_o$  as the dispersed oil concentration in effluent. Figure 69 depicts the removal efficiency curves of a hydrocyclone and Figure 70 a typical control scheme. (Stewart and Arnold 2009)

$$E = \frac{(C_i - C_o)100}{C_i}$$

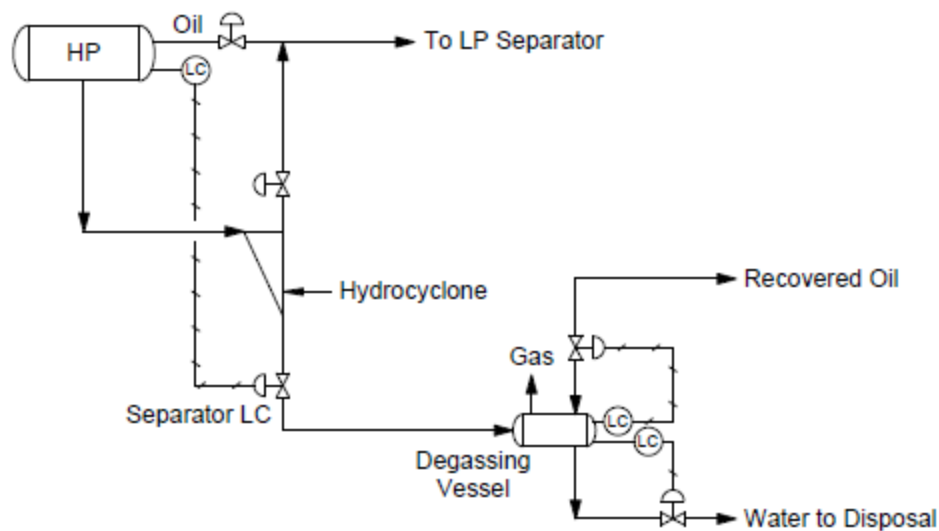
**Equation 13** - Hydrocyclones efficiency equation (Stewart and Arnold 2009)

Total flow rate and water cut in the feed are decisive factors for the separation efficiency of a hydrocyclone. Small flow rates provide higher efficiency for low water contents while for higher water contents, higher flow rates are demanded.

Hydrocyclones should be preferred for the treatment of simple emulsions rather than complex ones. Effective viscosity of the emulsion also affects the performance of a hydrocyclone since it is inversely proportional to its separation efficiency (Belaidi et al 2003).



**Figure 69** - Performance curves for hydrocyclones(Stewart and Arnold 2009)



**Figure 70** - control scheme for a hydrocyclone (Stewart and Arnold 2009)

## **Chapter 6 - Specialized Techniques and Equipment used for oil in water emulsion resolution and oil recovery - Secondary Treatment Stage**

After primary treatment of oil in water emulsions which aims in further removal of free oil which escaped pre treatment due to size distribution the chemical treatment takes place. Emulsion breakers are added to provoke destabilization of colloidal oil and then a second separation process begins. Air flotation vessels and Centrifuges are used also in the secondary treatment stage for the promotion of emulsion resolution.

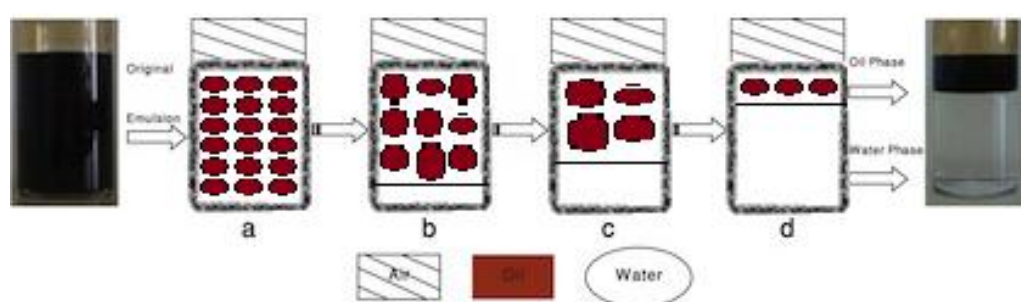
### **Chemicals**

Emulsion breaking technology has evolved a big chemistry chapter. In this work some of the most common chemicals used during the process of breaking oil in water emulsions will be presented. Apart from the separation of oil and water they provide protection for the equipment and improvement of the effluents quality. Usually chemicals are injected by pumps into the water stream and they are maintained in carbon or stainless steel tanks appropriate for their storage.

It is crucial to recognize the substances that are emulsified in the water during oil in water emulsion breaking. Oil and grease are commonly found in many process waters and groundwater. Oil that is found in contaminated water can be classified into free oil, mechanically emulsified oil, chemically stabilized emulsions, chemically emulsified or dissolved oil and oil wet solids. Free oil rises rapidly to the surface under calm conditions. Mechanically emulsified oil is present in form of droplets electrostatically stabilized without influence of surfactants ranging in size from microns to a few millimeters. Chemically stabilized emulsions are surface active agents provide enhanced stability due to interaction at the oil/water interface. Chemically emulsified or dissolved oil includes finely divided oil droplets (5 micron diameter), benzene and phenols. Oil-wet solids can be sediments, metal shavings or other solid matter where oil is adhered to. All petroleum products include a water-soluble fraction, the lighter the oil, the larger the soluble fraction. Gasoline releases MTBE (methyl tertiary butyl ether), organic lead, BTEXs, etc. Even heavy Bunker C has a small soluble fraction. Crude oil is a mixture of paraffinic, napthenic and aromatic hydrocarbons with sulfur, nitrogen and oxygen compounds on a small percentage. As a class, oils are non-ionized and non-conductive. Inorganics are not soluble in most oils (Alther 1997). ASP flooding process involves large quantities of alkali, surfactant and polymer chemicals which are produced to the surface along with the water. Surfactants are the main stabilizing factor of the emulsions since they reduce the oil-water interfacial tension and zeta potential of oil droplets. Demulsifiers are surface-active agents that counteract and neutralize the effect of those chemicals.

Solids present in the produced liquids such as iron sulfides, silts, clays, drilling mud etc. are making the demulsification process more difficult (Fakhru'l-Razi et al. 2009).

Various chemical agents are used to destabilize emulsions. Emulsion breakers must be capable of dispersing evenly throughout the emulsion, migrating to the inter-face quickly, and effectively countering the stabilizing effects of the emulsion. Mechanisms include balancing or reversing the interfacial surface tension on each side of the interfacial film, neutralizing the stabilizing electrical charges or precipitating the emulsifying agents as is done with the reactive cations  $H^+$ ,  $Al^{+3}$ ,  $Fe^{+3}$ , or  $Ca^{+2}$ . Acid, aluminum and ferric and calcium salts are the main commodity chemicals used for demulsification. The process of demulsification is shown in Figure 71.



**Figure 71** - Emulsion breaking stages after introduction of a demulsifier. (Modified from Kang et al. 2012)

Emulsion breakers can be commodity or specialty chemicals. In many cases the specialty chemicals will promote superior demulsification or be more cost-effective for oil-in-water demulsification. In water treatment, polymers can be used as primary coagulants, flocculants, filter aids or sludge conditioners (Allen 2008). As an example, polyquaternary amines have been used as an oil in water emulsion breaker in SAGD water treatment (Wang et al. 2005). Due to the negative charges on clay, cationic polymers are the most effective aid for filtration, followed by anionic and non-ionic polymers. Studies have suggested various water treating chemicals for oil in water emulsions and some typical examples are presented in Table 10. Commercial water treating chemicals, their use and their dosages are presented in Table 11 while Table 12 lists oil-in-water demulsification techniques, along with advantages and disadvantages (Goldblatt et al. 2014). Commercial demulsifiers are used to disrupt the oriented structure of the surfactant phase. These materials are not very soluble in either phase thus they concentrate at the interface. There they insert themselves between the surfactant molecules, increase the intermolecular distance, and weaken the binding forces constructed by the emulsifier. This results in separation. Chemical emulsion breakers provide the opposite charge to the emulsion. This will allow neutralizing the accumulated electrical charges on the interface of the emulsified

droplets. The dielectric characteristics of water and oil cause emulsified oil droplets to carry negative charges. Thus cationic demulsifiers are used primarily to destabilize o/w emulsions (Alther 1997).

Demulsifier	Studies
Diallyl dimethyl ammonium chloride	Hart et al. 1999, Ramesh et al. 1994 and 1997
Ampoteric acrylic acid (AA) copolymer	Braden 1996
Copolymer of polyglycol acrylate	Fock et al. 1986
Poly1-acryloyl-4-methyl piperazine	Fink 2003
Vinyl Phenol polymers	Fink 2012
Polydimethyl diallyl ammonium chloride	Hart 1995
Crosslinked oxalkylated polyalkylene polyamines	Fink 2012
Dithiocarbamates	Durham et al. 1989, Rivers 1992, Thompson 1987, 1989 and 1992
Sulfonated polystyrenes	Lundberg et al. 1988

**Table 10 - Typical examples of demulsifiers**

Commercial name	Polymers	Charge	Function in water treatment
Tramfloc 129	Poly(sodium acrylate)	anionic	Scale inhibitor and Reverse emulsion breaker
Spinomar NaSS	Poly (vinylsulfonic acid) potassium salt	anionic	Dispersant
Sokalan 25 CL Granular Sokalan PA 40	PAA (polyacrylic acid)	anionic	Anti-scaling additive
Baiyun BY-P18S	PDA (polydopamine)	Non-ionic	Antifouling and antimicrobial
Flocmiser 50 Magnaflow LT22 Golkem C5705 Magnaflow LT25 Golkem A170	PAM (polyacrylamide)	Non-ionic Cationic Anionic	Thickening agent, drag reduction agent, dewatering, flocculants
Percol 787	Quaternized AM/AETAC (acrylamide/ acryloxyethyltrimethylammonium chloride) copolymer	Cationic	Dewatering
Calgon Pol E-Z 2466	Acrylamide/cationic copolymer	Cationic	Flocculants
Calgon Catfloc L	DADMAC	Cationic	Coagulants

Calgon 250	(diallyldimethylammonium chloride) polymer	Cationic	Flocculants
	AM/METAMS (acrylamide/methacryloyloxyethyltrimethyl ammonium methosulfate) copolymer		
CPS Agefloc B-50	EPI-DMA (epichlorohydrin / dimethylamine) polymer	Cationic	Coagulants
Diatec 4400 A Clarifloc C-411	Quaternized Mannich polymer	Cationic	Dewatering and flocculants
Diatec 4400	Unquaternized Mannich polymer	Non-ionic	Dewatering
Stockhausen 611BC	AM/MAPTAC (acrylamide/methacrylamidopropyltrimethylammonium chloride) copolymer	Cationic	Dewatering
Polyquaternium-7 Tramfloc 734	DADMAC/AM (acrylamide-co-diallyldimethylammonium chloride) copolymer	Cationic	Flocculants
Pluronic	Polyoxyethylene and polypropylene co-polymers	Non-ionic	Demulsifiers
Superfloc C-500	Polyamines	Cationic	Coagulants, reverse emulsion breakers and corrosion inhibitors

**Table 11** - Commonly used commercial chemicals for oily water treatment (Modified from Wang 2016)

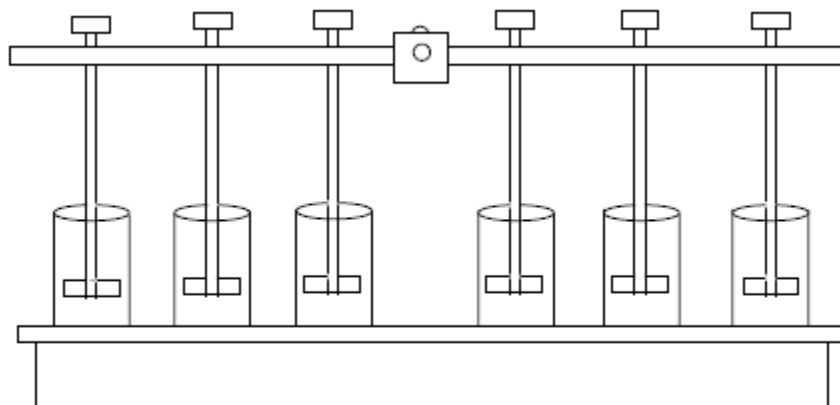
Technique	Method of Breaking	Advantages	Disadvantages
Simple Electrolyte Addition	Increases ionic strength which decreases emulsifier solubility and reduces charge repulsion	Simple and not expensive	Not effective for complex organic or solid agents
Metal Ions Addition	Changes emulsifier into insoluble metal salt if it's a simple soap	Simple and not expensive	Not effective for complex organic or solid agents
pH increase	Increasing pH will precipitate emulsifier if it's a simple soap	Simple and not expensive	It works only for simple soap emulsifiers, it can be corrosive and it can generate more complex agents
pH decrease	Decreasing pH will neutralize negative charges that stabilize emulsion	Simple and not expensive	corrosive
Inorganic Coagulants	Charge neutralization and adsorption of oil dispersed phase	Relatively not expensive	Relatively high sludge volume, corrosive and pH

Organic Polyelectrolytes	sensitive		
	Charge neutralization and bridging to increase contact and settling for displacement/destruction of the emulsifier	Low sludge volumes, multi-functional, pH tolerant, lower dosages needed than with inorganics, improved separation and more easily dewaterable sludge	Relatively high cost per pound for specialty chemicals

**Table 12 - Oil in water demulsification techniques (Goldblatt et al. 2014)**

### *Field bottle or Jar Test*

Certain rules must be followed for the choice of the most suitable available chemical for the oil in water emulsions' treatment. It is important that sufficient amount of the right chemical is added to the targeted emulsion. The most common technique for determination of the optimum dosage required is the Jar Test. Those tests can simulate full scale coagulation and flocculation processes. Different amounts of the same chemicals or the same amount of different chemicals are added in testing jars with oily wastewater samples of 100 ppm and are mixed for 1 min. Slower mixing of 30 rounds per minute is then applied and the floc is allowed to settle. The water that remains above the settle floc is an indication of each chemical's or dosage's efficiency. A typical configuration of the jar test is illustrated in Figure 72 (Spellman 2003).

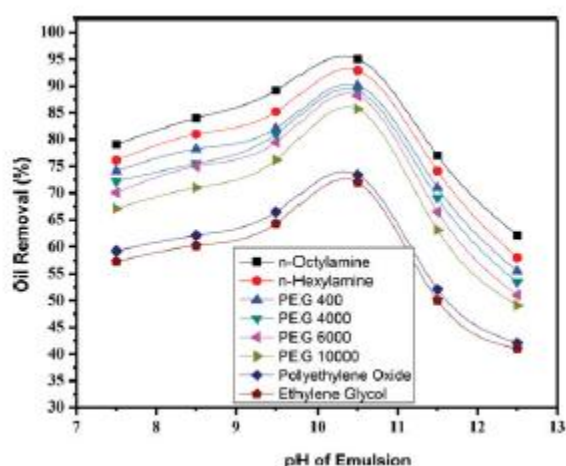


**Figure 72 - Jar test configuration of 6 testing jars (Spellman 2003)**

Also adequate heating must be provided so that optimum separation temperature is reached and the separation process is accelerated. It is critical that enough residence time is provided so that settling of demulsified water droplets is as efficient as possible. Lastly mixing of the chemical with the emulsion must be total (Liu et al. 2017).

### *Effect of pH on oil in water emulsion resolution*

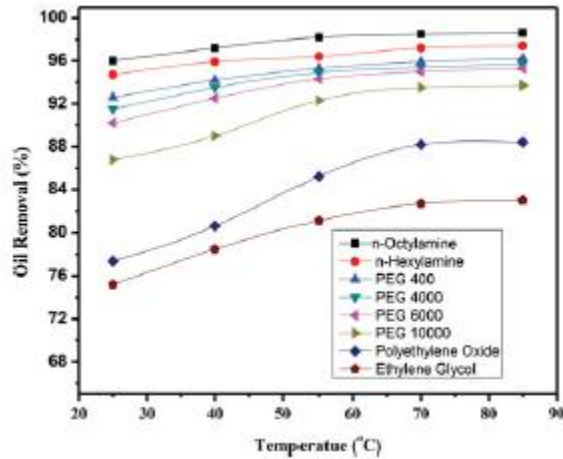
The type of demulsifiers used for emulsion resolution greatly affects the pH of the system which influences the flocculation process. The efficiency of different demulsifiers can vary for different pH values as shown in Figure 73 according to experiments carried out (Deng et al. 2005). Oil removal from oil in water emulsions is optimum for pH values of 10 to 11. Further raise of pH values above 12.5 decreases the efficiency of oil removal. A safe conclusion that can be extracted from Figure 73 is that emulsions are more stable in pH values above 12.5 and below 7.5. This phenomenon is due to the charging of asphaltene functional groups which leads to enhancement of surface activity of the oil water interface. (Poteau et al. 2005). Of course this is always dependent on the type of the crude oil and its unique characteristics (Rajak et al. 2016).



**Figure 73** - Effect of pH in the oil in water resolution process. Experiments carried out on stable conditions of temperature = 25°C, demulsifier dosage = 50 mg/l, initial oil concentration = 1000 mg/l and time = 60 min. (Rajak et al. 2016)

### *Temperature effect on oil in water emulsions resolution*

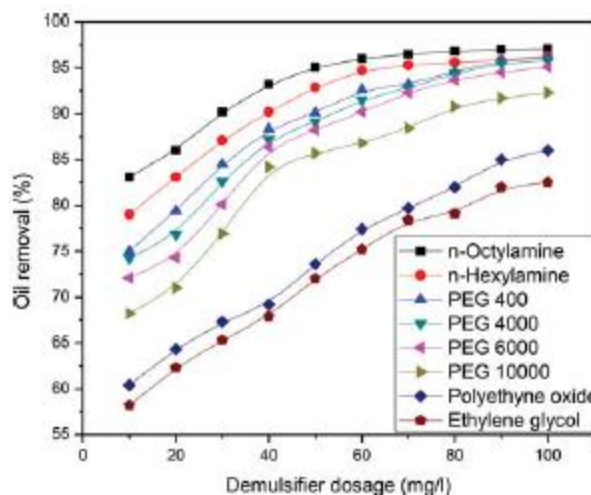
Studies (Rajak et al. 2016) have shown that the optimum temperature value for separation of oil in water emulsions is close to 70°C. Further raise of temperature has little or no effect in the oil removal efficiency as shown in Figure 74. Emulsions get destabilized in those temperatures due to Brownian motion and mass transfer across the interface. Demulsifier's molecules are transferred more rapidly to the interface at those temperatures. Simultaneously the interfacial viscosity of the continuous phase decreases and different densities and polarities of the two phases destabilize the emulsion leading to enhancement of the separation efficiency.



**Figure 74** - Effect of temperature in the oil in water resolution process. Experiments carried out on stable conditions of pH=10.5, demulsifier dosage = 60 mg/l, initial oil concentration = 1000 mg/l and time = 60 min. (Rajak et al. 2016)

### Demulsifier dosage effect on oil in water emulsion resolution

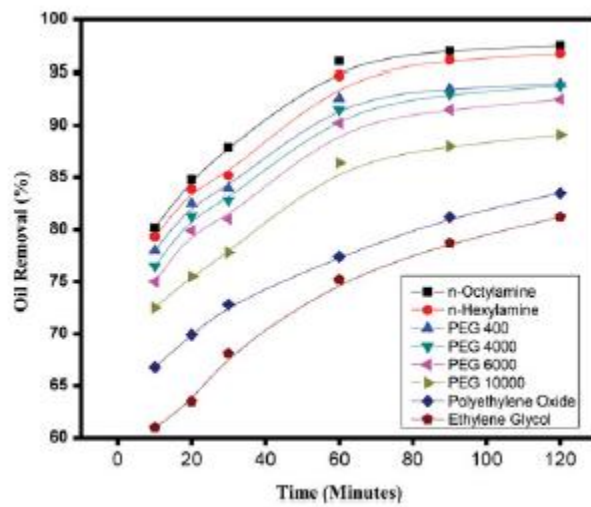
Selected dosages for any type of demulsifier must be precise both for the enhancement of separation efficiency and economic reasons. Experiments (Rajak et al. 2016) have shown that separation efficiency increases proportionally with demulsifier dosage increase. Optimum dosages vary for different demulsifiers. Neutralization of emulsion stabilizing factors lead to a plateau of efficiency rate as can be observed in Figure 75. Further increase of dosages have only a marginal effect.



**Figure 75** - Effect of demulsifier's dosage in the oil in water resolution process. Experiments carried out on stable conditions of pH=10.5, temperature = 25°C, initial oil concentration = 1000 mg/l and time = 60 min. (Rajak et al. 2016)

### *Settling time effect on oil in water emulsion resolution with the use of different demulsifiers*

Settling time provided to the emulsion after the introduction of the demulsifier is a critical factor for the resolution efficiency. Flocculation and coalescence processes require a minimum retention time for proper separation. Studies (Rajak et al. 2016) have shown that oil separation efficiency is enhanced with increase of retention time provided and reaches its top values on 60 minutes time span as shown in Figure 76. After this time value, efficiency remains almost constant due to the fact that the dynamic equilibrium of molecular motion at the interface is reached.



**Figure 76** - Effect of retention time in the oil in water resolution process for different demulsifiers. Experiments carried out on stable conditions of pH=10.5, temperature = 25°C, initial oil concentration = 1000 mg/l and demulsifier's dosage = 60 mg/l. (Rajak et al. 2016)

### *Separation Index*

Separation Index has been developed for the characterization of emulsions which is critical for the proper selection of demulsifiers. Efficiency of different demulsifiers for a certain emulsion can be evaluated by the fraction of clean water phase that is produced after its application in a regular bottle test as described by studies (Kokal 2006). For the calculation of the emulsion Separation Index, Equation 14 has been proposed. In this Equation,  $w$  is the water separation at a given demulsifier concentration as percentage of basic sediment and water after a certain time interval and  $w_{fn}$  is the time span between the readings of the water content in minutes (Fink 2012).

$$I = \frac{\sum w}{w_f n} \times 100$$

where:

$w$  = the water separation for given demulsifier concentration as the percentage of basic sediment and water after a time interval

$w, n$  = the number of readings of water content

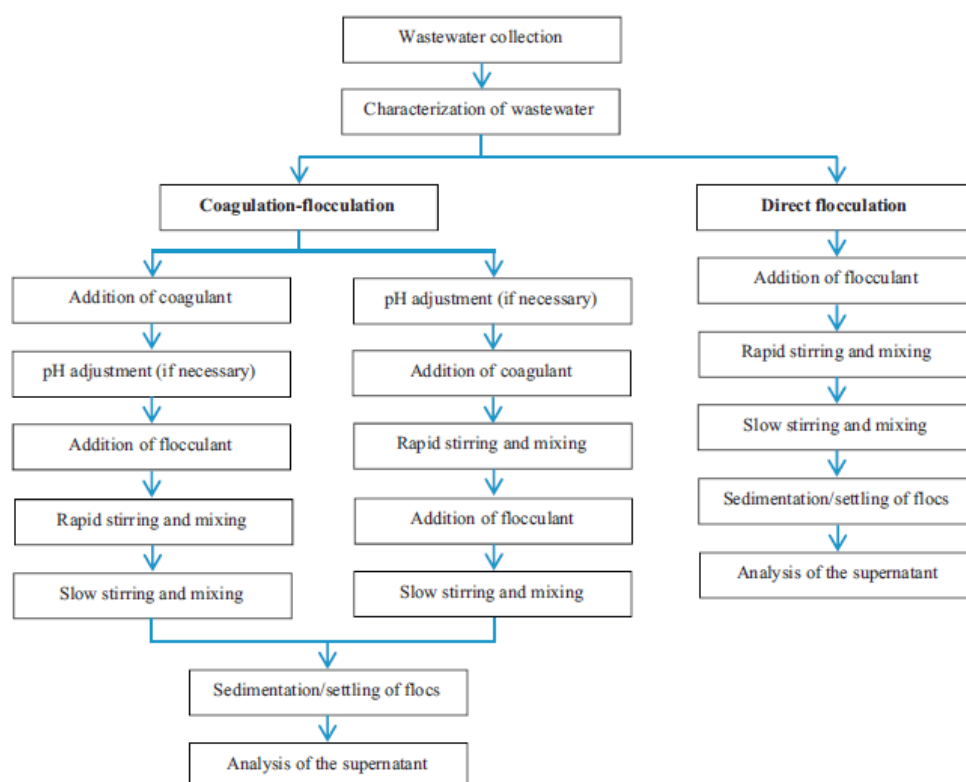
**Equation 14 - Separation Index (Fick 2012)**

This index has been used to correlate factors such as temperature, shear, asphaltene content, watercut, demulsifier dosage and differences in crude oil types with emulsion breaking efficiency. Under continuous supervision of the characteristics of the produced emulsions this index can help in diagnosis and solution of emulsion related problems such as optimization of the dosage of demulsifier and adding of other chemicals (Kokal et al. 2000).

### *Flocculation and emulsion resolution*

Flocculation theory is based in the principle that its force on oil droplets and particles should overcome the charge repulsion between oil and water. Charge interaction of the external phase is the main mechanism used for the oil in water emulsion breaking process. The main target of the whole process is the breaking of the ion bond between oil and water. By addition of surface active compounds called demulsifiers, the film of oil and water formed in their interface is weakened. In order to promote coalescence of two oil droplets their charge must be counterbalanced by the addition of a flocculant. Acids have been proved to be efficient emulsion breakers since the whole process has been proved to be more effective for pH values of 3 or lower (Wang et al. 2004).

Coagulation-Flocculation or direct flocculation can be applied for the treatment of emulsions. Cationic inorganic metal salts are firstly introduced as coagulants and then ionic or non-ionic polymers are introduced as flocculants in case of the first method (Chong 2012). During direct flocculation medium charge density with high molecular weight cationic polymers is used and this method is more usually applied in oil industry (Lee et al. 2014). A schematic of both methods procedures is shown in Figure 77. Flocculants are working together with gravity settlers and similar mechanical equipment creating a floc where the oil droplets are absorbed. This floc will be later returned to the crude oil production. Lately injection of flocculants upstream of the separators after demulsifier introduction has shown improved performance. The most common flocculants in the oil industry are high valent metal salts, cationic polymers, anionic polymers, nonionic polymers, amphoteric polymers and dithiocarbamates. Surfactants can be used to enhance the process also (Kelland 2014).



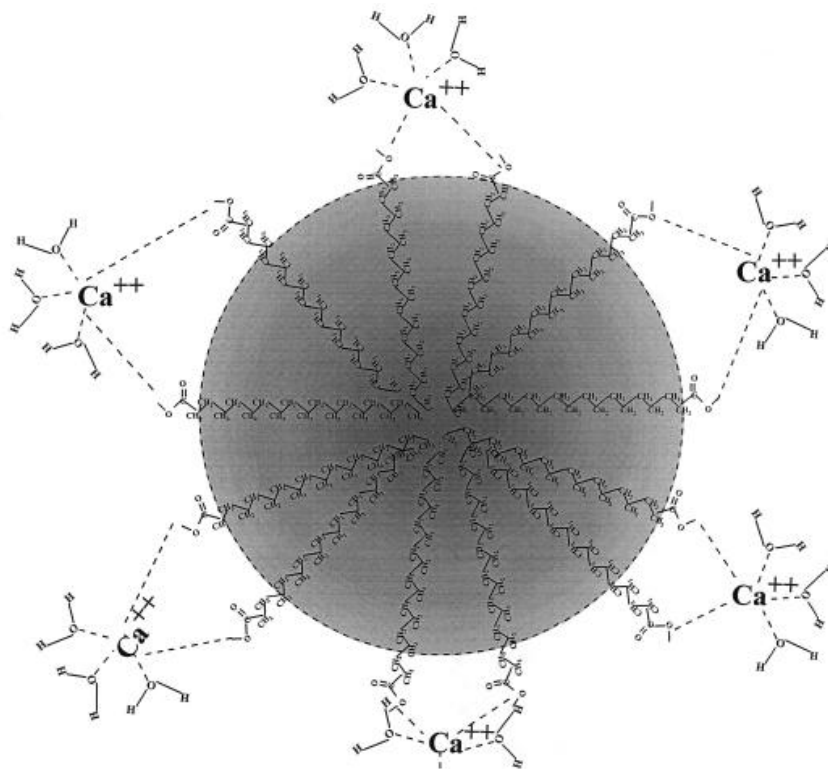
**Figure 77** - Coagulation-flocculation and direct flocculation procedures (Lee et al. 2014)

Oil in water emulsion treatment requires heat for the reduction of viscosity which leads to weakening of the interfacial film between oil and water.

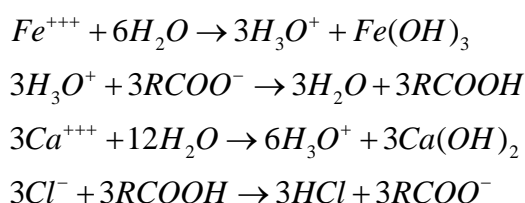
In general demulsifiers should contain solvents, surface active ingredients and flocculants. Benzene, toluene, xylene, short chain alcohols and heavy aromatic naphta can be use as solvents and carriers for the demulsifier. Some of those solvents can affect the solubility of emulsifiers contained in the treated effluent. Surface active ingredients are the ones who affect the hydrophilic-lipophilic balance (HLB) which was analyzed in a previous chapter. HLB values can vary from 0 to 20 with low values corresponding to hydrophilic surfactants while higher one to lipophilic surfactants. In case of oil in water emulsions HLB value is expected to be high, thus a surface active ingredient with low HLB is required for their treatment. Flocculants will promote coalescence by means of flocculation of oil droplets. (Sjoblom 2001)

Salts who aim in the change of conductivity of the external phase can also provoke a destabilization of the oil and consequently the resolution of the emulsion. Valance metallic salts such as zinc chloride, ferric chloride, stannic chloride and aluminum chloride have been used for further destabilization. Hydroxyl by-products which appear as voluminous gels are formed from the use of those salts and they can cause problems due to high toxicity of the metallic salts both for environmental reasons and for catalysts. For those reasons metallic salts have been widely avoided lately and organic salts with low toxicity have replaced them. (Becker 1997) Neutrality in the surface between oil and water phases is maintained by the ionic character of oil phase and the cationic character of water phase. Stability is provided by this mechanism as

discussed previously in an example of commonly occurring calcium cations which is shown in Figure 78. In case of metal salts introduction, the anionic phase will be protonated. Moreover in cases where salts like ferric chloride ones are introduced, an exchange of hydroxyl anions and chloride anions will take place and a pair of hydronium cation - hydroxyl anion will be formed. The actual reactions are shown in Figure 79.



**Figure 78** - Commonly occurring calcium cations in a calcium stearate emulsion (Becker 1997)



**Figure 79** - Ferric chloride salts introduction to an emulsion governing reactions (J.R. Becker 1997)

In the end the surface of the emulsion is ionically charged. Every ferric cation gives four metal hydroxides which form metal hydroxide flocks highly hydrated and enlarge the disposal problem. The emulsion will be resolved as an oil fatty acid in this case due to the exchange of protons between  $RCOO^-$  which is in equilibrium and the water.

## Flocculants

Flocculants are used for the facilitation of agglomeration and the creation of larger flocs during the emulsion resolution process. The creation of clumps is the primary target of flocculants' use. They need to be added slowly into the treated water and mixed with caution.

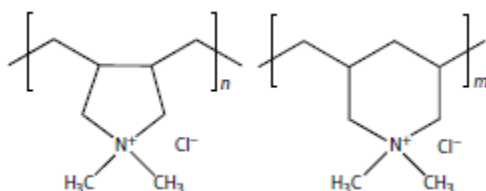
### Cationic polymers

Incorporation of quaternary nitrogen atoms produces the cationic polymers used mainly in oil industry. Diallyldimethylammonium chloride (DADMAC polymers) and Acrylamide or acrylate based cationic polymers are the most commonly ones used. An example of diallyldimethylammonium polymer is shown in Figure 80 and an example of acrylamide or acrylate based cationic polymer is shown in Figure 81. Their common characteristic is their high molecular weight (>1000000 for DADMAC and up to 3000000 for Acrylamide) (Kelland 2014).

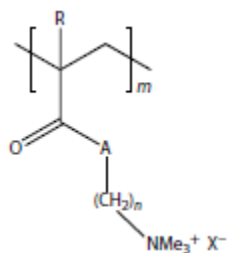
A commercial example of such a flocculant is Poly-DADMAC by CHEMTEX. It should be diluted to the concentration of 0.5%-0.05% based on solid content. It is adaptable to pH values between 0.5 and 1.4. The dosage is based on the turbidity and the concentration of the water. The most economical dosage is based on the trial. The dosing spot and the mixing velocity should be carefully decided to guarantee that the chemical can be mixed evenly with the other chemicals in the water and the flocs are not broken. Ideally it should be dosed continuously (Retrieved from: <http://www.chemtexlimited.com/coagulant.html#poly-dadmac>).

Studies (Hart et al. 1995 and 1996) has proved Acryloxyethyltrimethyl ammonium chloride as an efficient oil in water emulsion breaker under a wide variety of conditions.

Other cationic polymers used are polyalkyleneimines, polyalkanolamines, polyvinylammonium chlorides, polyallylammonium chlorides, branched polyvinyl imidazoline acid salts, cationic polysaccharides and condensed tannins (Kelland 2014)



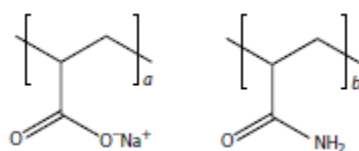
**Figure 80 - DADMAC polymer structure example (Kelland 2014)**



**Figure 81** - Acrylamide or acrylate based cationic polymers' monomeric structure example (Kelland 2014)

### Anionic polymers

In case that positive charges are present in the oil droplets anionic polymers are used after acidizing operations or primary treatment with cationic flocculants, for the acceleration of floc formation process. Mostly they are salts of high molecular weight acrylic polymers as shown in Figure 82. (Kelland 2014)



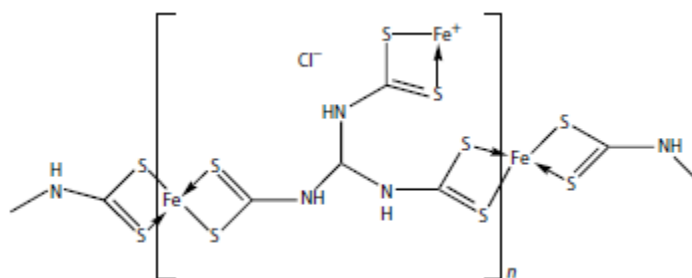
**Figure 82** - Sodium acrylate/acrylamide copolymer as an example of anionic polymers used in oil industry (Kelland 2014)

### Amphoteric polymers

This category is comprised of polymers both of anionic and cationic functional groups. Although they have seen little use in the industry they have a promising potential due to the properties of both cationic and anionic functional groups (Dao et al. 2016)

### Dithiocarbamates

Pseudocationic polymeric flocculants commonly known as DTCs are a class of chemicals produced by the reaction between polymeric or oligomeric primary or secondary amines with CS<sub>2</sub> and base in aqueous or alcoholic solution. They have good environmental properties since they are biodegradable and less toxic than cationic polymers. An example of a DTC is shown in Figure 83. (Kelland 2014)



**Figure 83** - Example of DTC structure (Kelland 2014)

### *Highly valent metal salts*

Iron, zinc and aluminium salts are the most common ones used in this case. This category of salts can be added to polymer flocculants to enhance their performance due to their high positive charge density. Corrosion and formation of sludge can be their use's undesired side-effects but they are considered as highly effective (Kelland 2014). Insoluble hydroxides are formed when those salts are introduced in the water. The formation of such hydroxides provides charges for the neutralization of the colloidal particles, leading to flocs formation. The major drawback of their use is that this kind of salts are sensitive to pH and alkalinity changes. Thus the formed flocs can be easily re-dispersed (Ogden 1998).

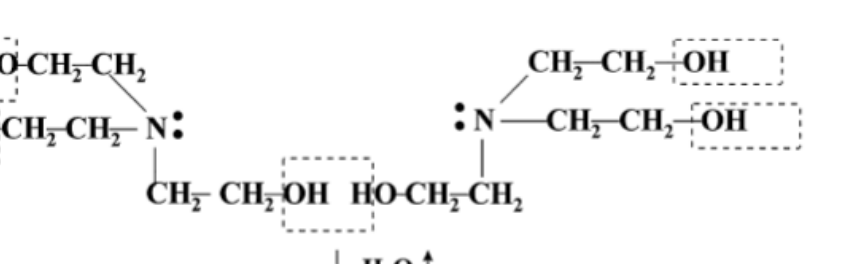
### *Organic polysalt emulsion breakers*

Organic polysalts have to be chosen carefully so that a possible problem during the refining process of the oil will not occur. Polyamines are mostly preferred for this job. Maximum possible number of amines in those chemicals are wanted so that charge to mass ratio is favorable for the breaking of the emulsions. Addition of ethylene and propylene oxides to ammonia results into ethanolamines and propanolamines which are much more effective (Becker 1997).

### *Idealized organic polysalts*

A chemical structure which would present the maximum possible charge to mass ratio and with the propriate solubility is desirable. The product of condensation of triethanolamine is a case. Some derivative salts of the reaction of removal of water from hydroxyethyl groups of triethanolamine forming an ether is shown in Figure 84. The product should be brought as close as possible to gel stage so that emulsion breaking is more efficient. As mentioned before charge to mass ratio is of high importance accompanied by the borderline external phase solubility or dispersibility. Figure 85 shows some of the products of this reaction that can be used in emulsion

**Triethanolamine**



**Networked Poly-Triethanolamine** + **RCl** → **Poly-Salt**

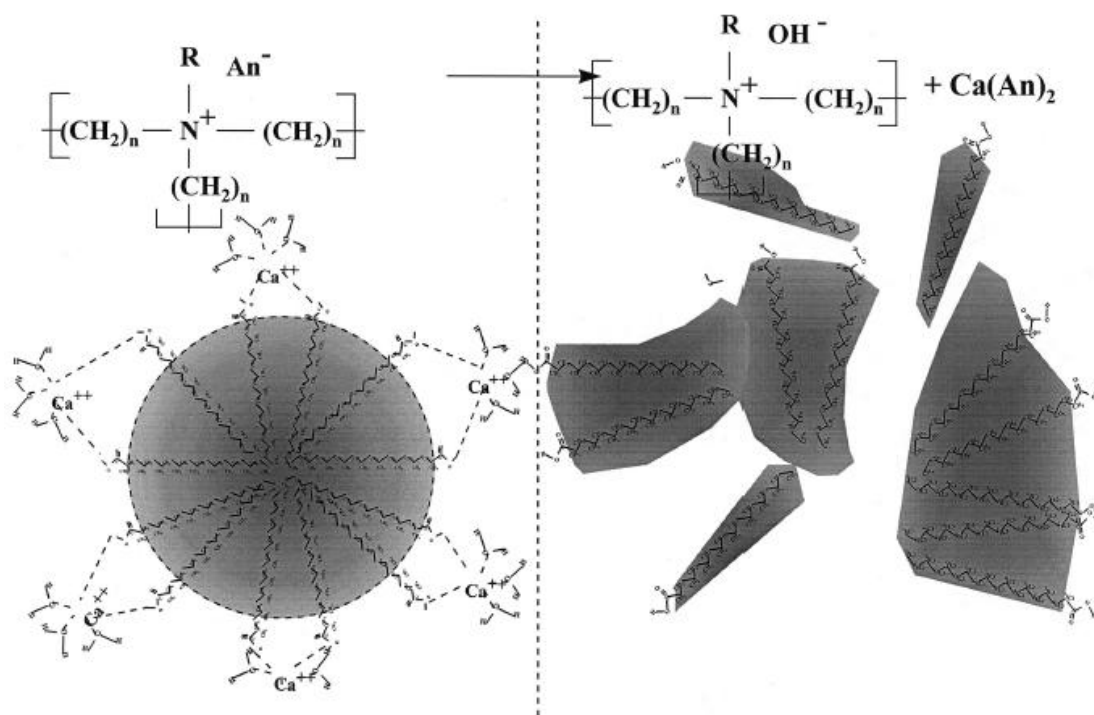
**R = H, CH<sub>3</sub>, Other Electrophiles**

$$\begin{array}{c}
 \begin{array}{c} \text{CH}_3 \text{ An}^- \\ | \\ \left[ (\text{CH}_2)_n \text{N}^+ - (\text{CH}_2)_n \right] \\ | \\ (\text{CH}_2)_n \\ | \\ \left[ \right] \end{array} \\
 \\
 \begin{array}{c} \left[ \begin{array}{c} \text{O} \\ | \\ \text{CHCH}_3 \\ | \\ \text{CH}_2 \text{ An}^- \end{array} \right] \\ | \\ \left[ (\text{CH}_2)_n \text{N}^+ - (\text{CH}_2)_n - \text{CH}_3 \right] \\ | \\ (\text{CH}_2)_n \\ | \\ \left[ \right] \end{array} \\
 \\
 \begin{array}{c} n = 2 \\ R = \text{CH}_3 \\ \text{An}^- = \text{Cl}^- \end{array}
 \end{array}$$

**Figure 85 - Oil in water emulsion breakers (Becker 1997)**

### Polyamine and quaternium salts

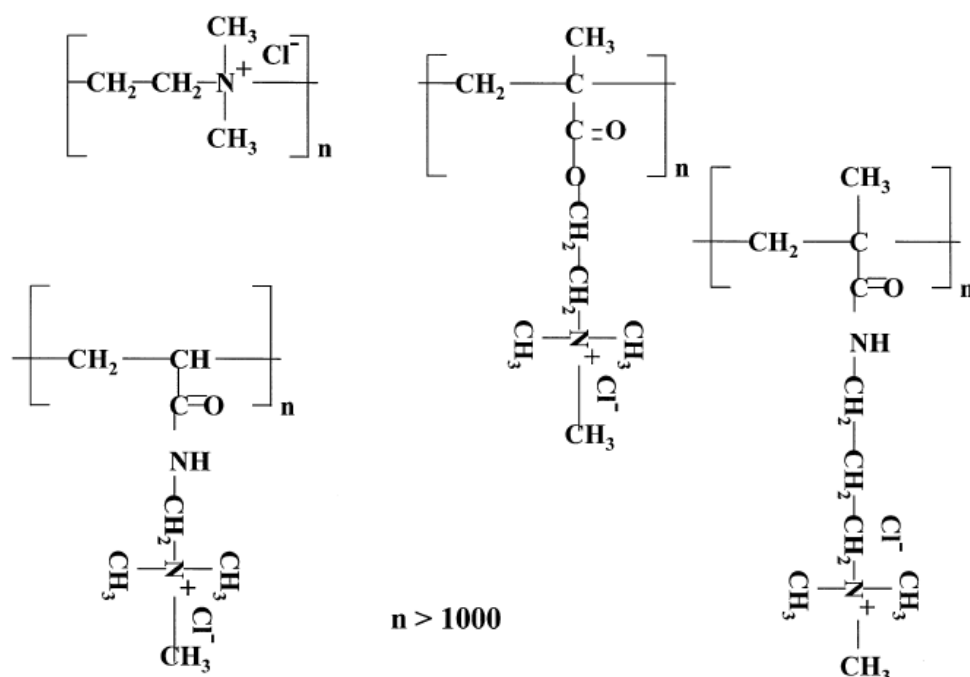
Another category of salts used for the destabilization of emulsions are the polyamine and quaternium salts. Protonation of the carboxylate anions of the bipolar surface without the formation of hydroxyl flocks due to the absence of trivalent metallic cations is the mechanism that governs this process. Solubility of the polyamine salts and quaternaries is not affected despite the addition of a hydroxyl anion in their structures. In case of bivalent metal salts though, the solubility of the metal hydroxyl is very low in the water phase but its effectiveness in emulsion breaking is lower also. As a result, greater density of charges is required to reside within the metal or polyquaternium salts so that emulsion neutralizing is more efficient. Partially cross-linked trifunctional counterparts are more effective emulsion breakers due to the fact that they contribute greater charge to solute displacement than the linear molecules which have a tendency of extension in the water phase, producing a diffuse charge locus. In any case small amounts of emulsifiers can cause very stable emulsions and small amounts of de-emulsifiers can destabilize them as shown in Figure 86 (Becker 1997).



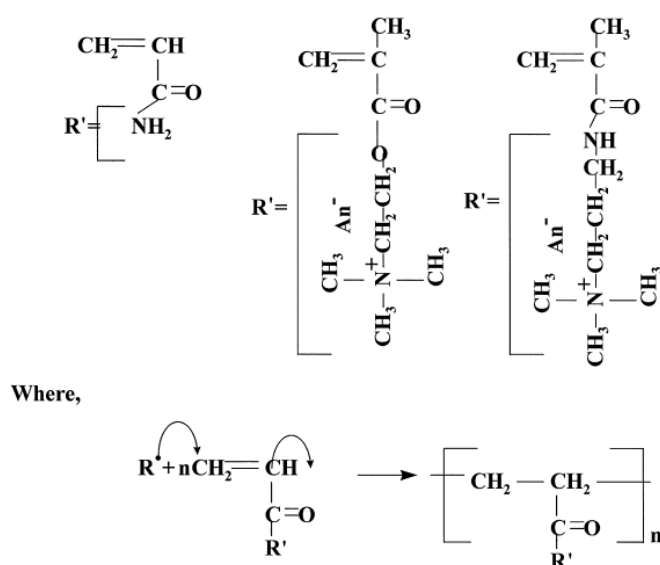
**Figure 86** - Stabilization (left) and destabilization (right) of emulsions general scheme (Becker 1997)

Linear bifunctional polyamine salts are not sufficiently active emulsion resolution chemicals in many cases. For high molecular weight linear polyamine salts, flocculation can be caused to the oil phase, making much easier the skimming and flotation processes (Becker 1997). During synthesis of this kind of salts amino-

methylated-polyacrylamide, poly-dimethyl-amino-ethylacrylate, poly-dimethyl-amino-propyl-methacrylamide, poly-ethylene-imine and others can be introduced to raise the molecular weight and thus produce a more effective flocculation process. Different methods have been tried to produce as higher molecular weight as possible. Polymerization of the reactive monomers of the internal phase of an oil external emulsion is one of the most common techniques and some products of it is shown in Figure 87. A large variety of copolymer structures exist in countless combinations, thus in Figure 87 homo-polymer sections are shown. Figure 88 shows some of the monomers that can be used for this process.



**Figure 87** - Linear polyamine salts of high molecular weight (Becker 1997)



**Figure 88** - Typical polymerizable monomers used in emulsion resolution (J.R. Becker 1997)

## *Coagulating agents*

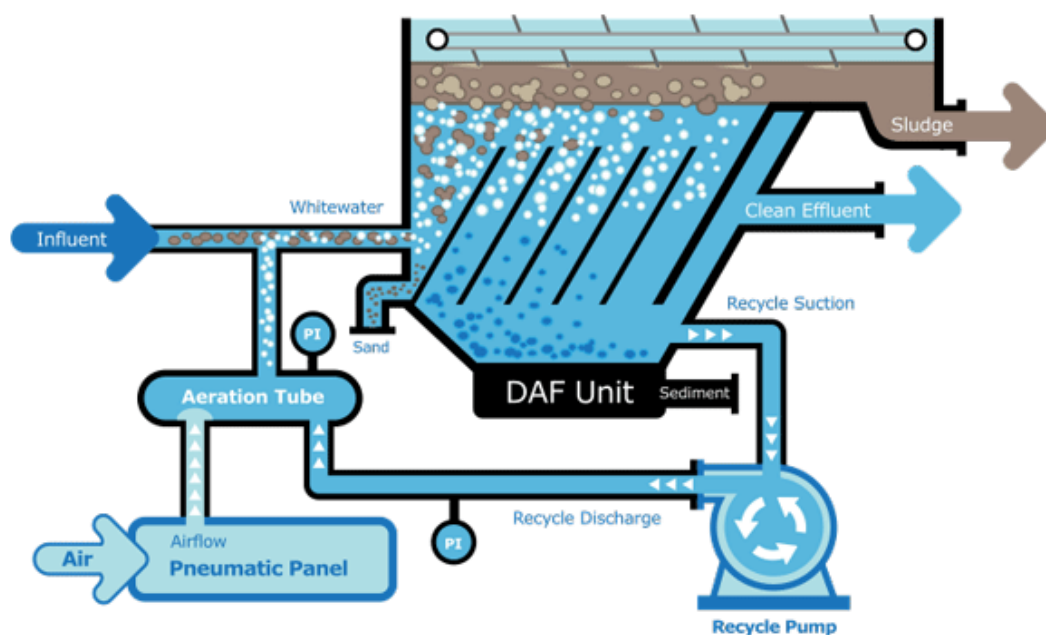
Suspended and colloidal wastes are removed by the introduction of those chemicals. They neutralize the repulsive forces that are caused by electrical charges, enhancing the coagulation process creating flocs. The most common inorganic coagulants used in oil in water emulsion breaking are Alum-Aluminum sulfate ( $\text{Al}_2(\text{SO}_4)_3$ ), ferric sulfate ( $\text{Fe}_2(\text{SO}_4)_3$ ), ferric chloride ( $\text{FeCl}_3$ ) and sodium aluminate ( $\text{Na}_2\text{Al}_2\text{O}_4$ ) (Cheremisinoff 2002). Other coagulants for oily water treatment include hot lime, FMA, Spillsorb and calcite and ferric ions (Duraismy et al. 2013). After introduction of coagulating agents in the treated oil in water flow, rapid mixture should occur for the dispersion of coagulants throughout the liquid.

## *Strategic approach for the use of chemical demulsifiers for oil in water emulsion breaking and chemical introduction limitations*

The process of chemical treatment of oil in water emulsions is highly susceptible to influent quality and it is more suitable for large volumes of treated stream (e.g.  $>1135 \text{ m}^3/\text{day}$ ). Optimal application of any chemical demulsifier requires close control and skilled operators. Costs can be high depending on the stream characteristics and large volumes of sludge can be produced. Corrosion problems can occur in the equipment if the choice of the chemical is not the proper one (Igwe et al. 2013). Almost 99% of oil in water emulsions contain anionic or non ionic surfactants. After neutralization of Zeta potential of oil droplets, pH adjustment is needed. This can be achieved by the introduction of metal salts such as aluminium, iron or calcium chlorides in cases where pH is higher than 9. When pH is in the range of 5 to 9 no introduction of chemical for pH adjustment is needed in most of the cases. In case that new adjustment at pH values in the range of 3 to 4 is needed, sulfuric acid must be added. Reaction time of 5 minutes should be given and then sodium hydroxide must be added to bring the pH in values around 7.5. Sufficient time should be given for the rise or fall of the flocs and introduction of cationic polymers should take place for the improvement of settling. A more expensive solution to this is the introduction of Tannin or polyaluminium chloride instead of other metal salts, which require no pH adjustment. Next step involves the introduction of cationic polymers for the neutralization of charges to promote the coalescence of the oil droplets. Once the repulsive forces of the double layer are overcome, small amounts of anionic polymers must be added to cause flocculation and creaming. All those steps need to be carefully designed by special trained personnel for the enhancement of separation with minimum cost possible (Alther 1997).

## Flotation units

The only water treating equipment that doesn't depend on gravity for the separation process is the flotation unit which can be used as shown in Figure 90 within the treatment configuration scheme. Mainly the method of dissolved air flotation (DAF) or dissolved gas flotation (DGF) and the method of induced or dispersed air flotation (IAF) or induced gas flotation (IGF) are used. The mechanism used for the separation in those vessels include gas bubbles introduction to the water phase which attach on the oil droplets or solids and rise together in the liquid interface as oil foam. This foam is later removed and gathered for more processing. Specific gravity of the combined oil-gas droplet is drastically lower than this of the oil droplet alone. This accelerates the rising motion of the combined droplet to the interface according to Stokes' law causing an acceleration to the oil-water separation itself. Efficiency of the vessels can be improved by the addition of coagulants, polyelectrolytes or demulsifiers.



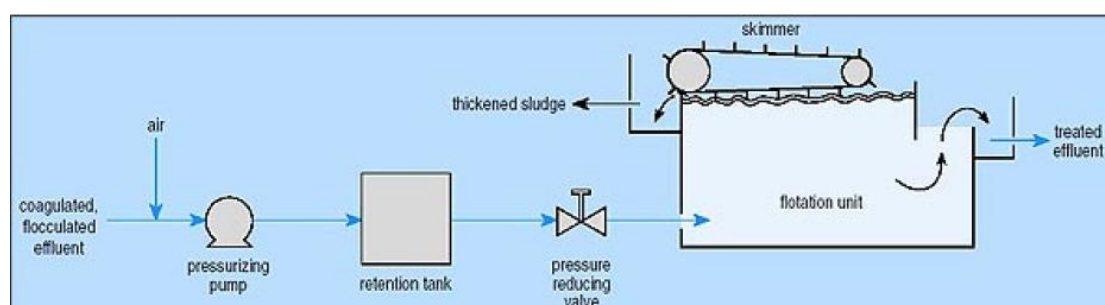
**Figure 89** - DAF unit scheme (DAF. Retrieved from: <http://frsystems.com/pcl-dissolved-air-flotation-systems/>)

Bubbles of 30 to 120  $\mu\text{m}$  are produced by the use of saturated with air pressurized water in DAF method. Coagulated oil and solids then will float due to the incorporation of the bubbles to the floc. On IAF method, larger bubbles (up to 1000  $\mu\text{m}$ ) are produced since mechanical agitation is used for entrainment of air into treated water. Those bubbles also attach to the flocs and come to the surface. DAF method is more widely used in USA. Total, partial and recycle pressurization flow sheets are used for this method. Recycle pressurization is used in almost 80% of the treatment systems. DAF system usually includes a flotation vessel, recycle hardware and rapid mix and flocculation devices as shown in Figure 89 (Stewart and Arnold 2009). IAF

system follows the same principles with the difference that the treated waste goes through a static mixer and is designed to operate at higher loadings than DAF. IAF though focuses on adherence of impurities to the surface. IAF systems are designed for space saving and demand lower installation costs. On Table 13 a comparison between the two systems is illustrated.

DAF or DGF	IAF or IGF
Air saturation equipment is required for the dissolution of air in water	High energy consuming mechanical mixing of air in water
Flotation of impurities	Separation is caused by surface interaction between bubbles and impurities
Bubble size 30-120 $\mu$ m and slow rise rate	Bubble size up to 1000 $\mu$ m and fast rise rate
Particles rise slower though lower loading rates and longer detention time	Short detention time due to rapid kinetics
Reduced floc achievement due to low turbulence and longer detention	Increased floc achievement due to high energy and shear
Focused on coagulation and flocculation	Focused on air- water interface reactions
More solids and oil in skimmed float	Less solids and oil in collected froth

**Table 13 - DAF and IAF systems comparison (Stewart and Arnold 2009)**



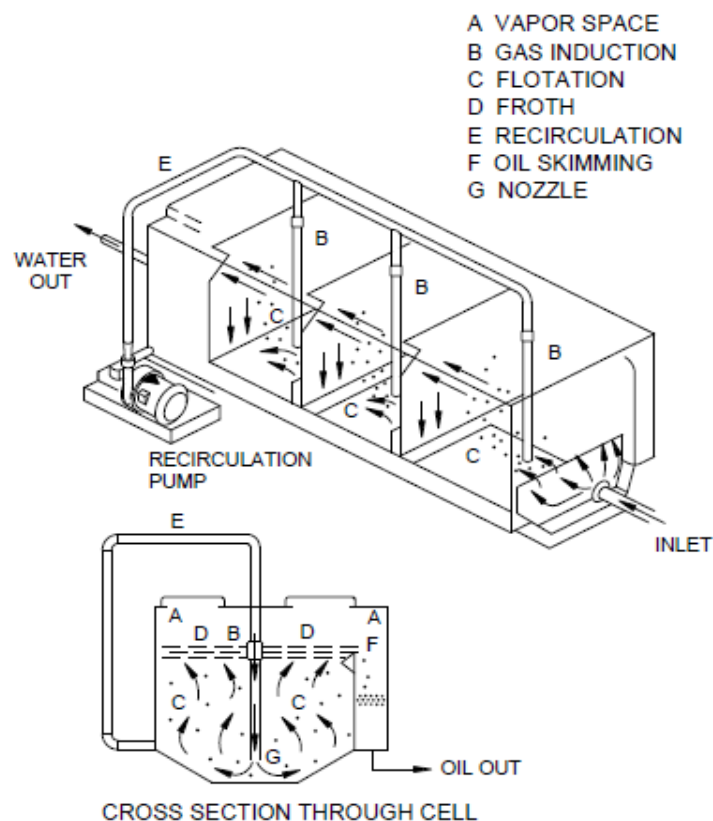
**Figure 90 - Flotation unit (Drewes et al. 2009)**

Temperature plays a key role in their efficiency since high temperatures demand higher pressures for the dissolution of gas into water. Thus low operational temperatures are preferable. Two different main categories of flotation units exist, the dispersed gas units or the induced gas flotation units (IGF) and the dissolved gas flotation units (DGF) (Drewes et al. 2009). Over the last 15 years another category of flotation units has been introduced in the industry, the compact flotation units (CFU) (Daigle et al. 2012). Their use is wide and they can achieve up to 93% oil removal (ALL Consulting 2003).

## Flotation

During flotation, water phase is enriched in gas bubbles which adhere to the oil droplets. This causes an increase to the buoyancy of the oil droplets and causes a faster motion to the surface of water. Due to the gas, a foam layer is formed in the

surface in which the oil droplets get trapped and then removed. This process is used mainly for oil droplets of size smaller than 10 microns and high levels of 90%+ oil removal can be achieved. A gas flotation vessel is shown in Figure 91. Water enters the recirculation header and then is guided to eductors. During the flow, water is enriched in gas bubbles through a nozzle. Then flotation is caused due to bubbles in the chamber and foam is formed in the froth which in the end of the process is removed by a mechanical device. (Stewart and Arnold 2009)



**Figure 91 - Gas flotation unit (Stewart and Arnold 2009)**

A qualitative model is developed based on liberal assumptions to predict the efficiency of such a vessel. This model is developed in order to understand the effects of various parameters in the vessel's efficiency and that's why units are not listed. Three different equations need to be combined to get the result. Equations 15a, 15b and 15c.

$$E = \frac{C_i - C_o}{C_i}$$

$$E = \frac{K}{Q_w + K}$$

$$K = \frac{6\pi K_p r^2 h q_g}{q_w d_b}$$

where:

$E$  = efficiency per cell

$C_i$  = inlet oil concentration

$C_o$  = outlet oil concentration

$Q_w$  = liquid flow rate

$K_p$  = mass transfer coefficient

$r$  = radius of mixing zone

$h$  = height of mixing zone

$q_g$  = gas flow rate,  $q_w$  = liquid flow through the mixing zone

$d_b$  = diameter of gas bubble.

**Equations 15 a,b,c** - Qualitative model for the efficiency of a gas flotation vessel (Stewart and Arnold 2009)

This model is based also on physical observations. The efficiency of the vessel is independent of the oil concentration or the droplet size. It is dependent though on the gas flow rate. If the gas flow rate is high, efficiency increases and on the contrary in case of an increased water flow rate, efficiency decreases. Of course the design details of the vessel need to be taken into account before proceeding with the aforementioned model. Gas flotation units normally include multiple cells in series. In case of multiple cells in the flotation unit, the overall efficiency is calculated by Equation 16 where  $n$  is the number of cells. (Stewart and Arnold 2009)

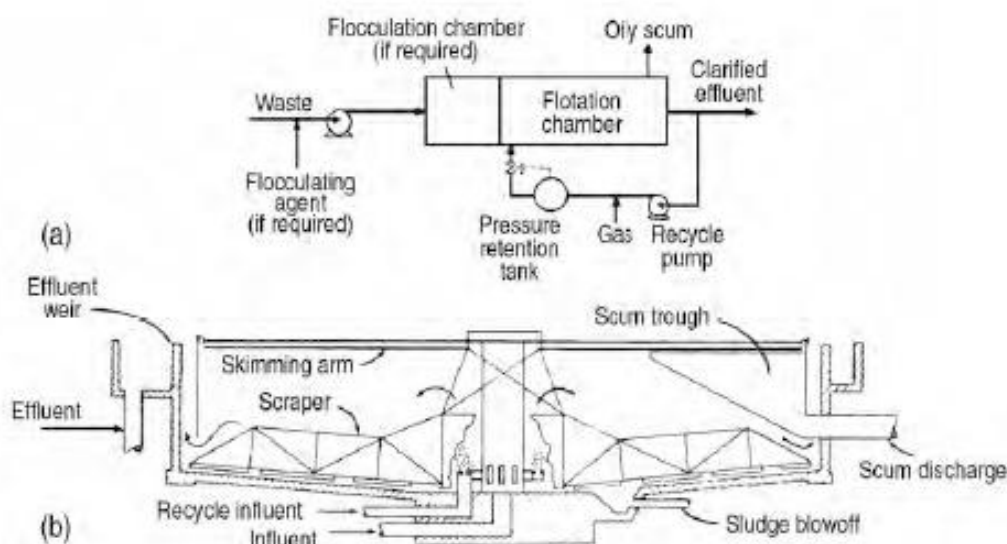
$$E_t = 1 - (1 - E)^n$$

**Equation 16** - Overall efficiency equation for multiple cells (Stewart and Arnold 2009)

Most designers keep a minimum of at least 50% efficiency for each separate cell. In a typical flotation unit of 5 cells, if 50% is the minimum efficiency level for each cell then the total efficiency of the vessel will be in a minimum level of 97%. This is a costly configuration though and most of the vessels have 3 or 4 cells. The minimum water retention time for each cell is 1 minute so that the gas bubbles have sufficient time to rise to the surface of the liquid. (Stewart and Arnold 2009)

### *Dissolved Gas Units (DGF) or Dissolved Air Units (DAF)*

In those vessels, a 20% to 50% of the water to be treated is saturated with natural gas by high pressure vessels. Higher pressure will introduce higher amounts of natural gas in the water. Bubbles in this case will be of size between 10-100  $\mu\text{m}$ . Most units offer 20 to 40 psig (140 to 280 kPa) contact pressure. Following the saturation process, a procedure of injection of the saturated water to the flotation tank. Small diameter gas bubbles will come in contact with oil droplets and the oily water solution will be broken since the commingled droplet will reach the interface. The whole procedure is graphically expressed in Figure 92. Nevertheless this type of vessel hasn't enjoyed much of success in the oil fields. They enjoyed success in refinery operations due to the need of big space for their operation. Fresh air can be used as a gas induce in this case since the water effluent is already oxygenated. In case that water is treated to be re-used for injection processes, natural gas should be used because of the possibility of explosions due to oxygen. This requires special installation and equipment (Abdel-Aal et al. 2003)

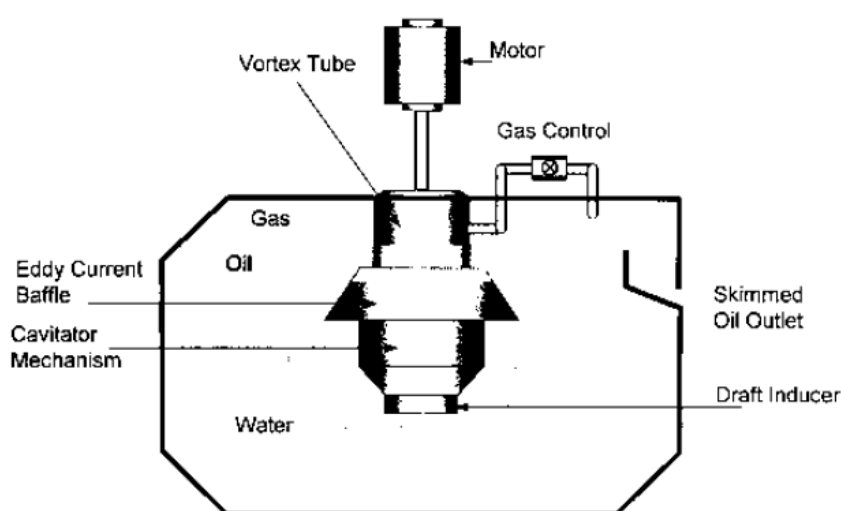


**Figure 92** - Dissolved gas flotation unit schematic (Juniel and Rawlins 2007)

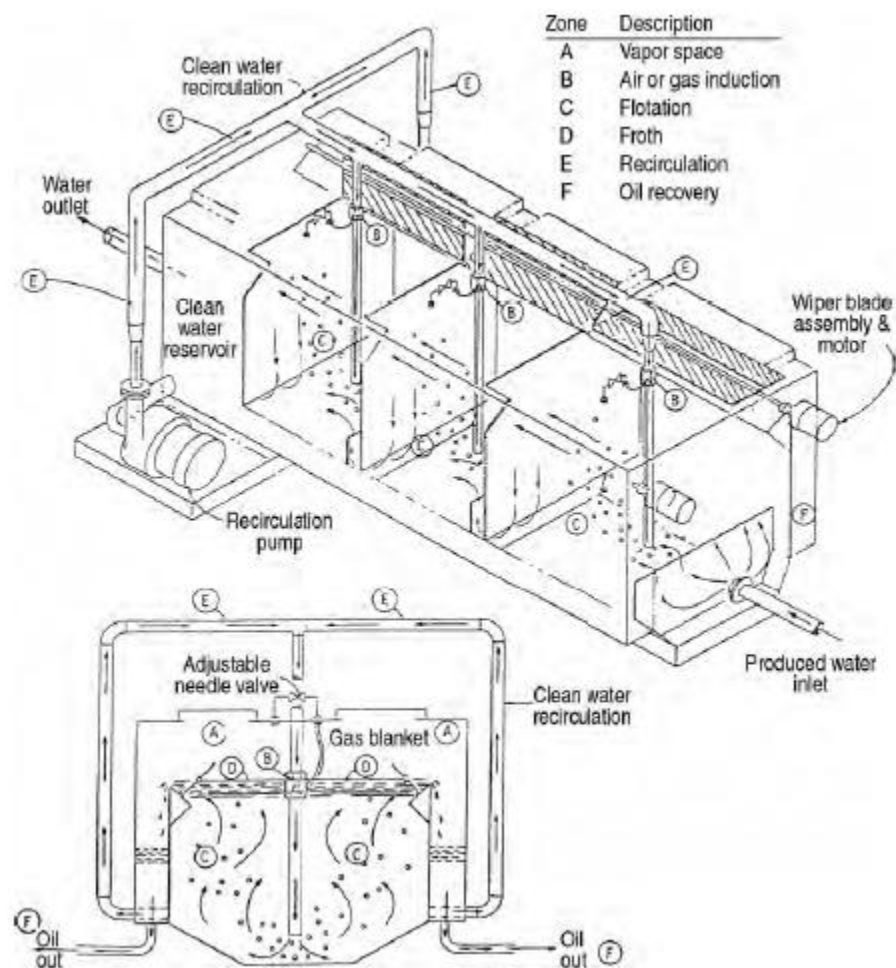
The average amount of water that can be treated range between 0.2-0.5 scf/barrel and flow rates between 2 and 4 gpm/ft<sup>2</sup>. Retention times of 10-40 minutes are needed and height should be between 6 and 9 ft. They are mostly used in chemical plant operations while they are avoided for producing operations due to large size, no existence of vapor recovery units for the recycling of gas in most production facilities and scale caused from the produced water in the devices. (Stewart and Arnold 2009)

### *Induced or Dispersed Gas Units (IGF) or Induced Air Units (IAF)*

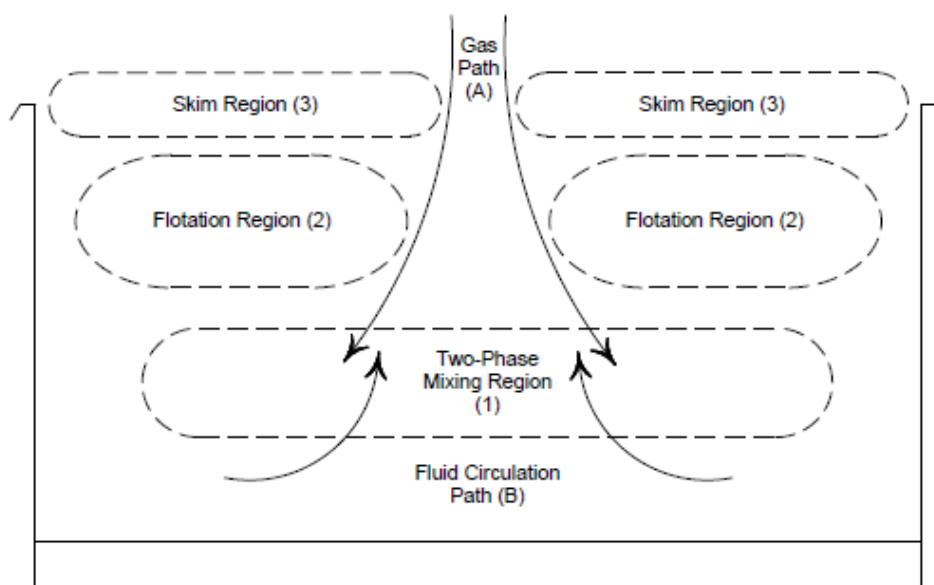
Those vessels use hydraulic inductor devices or vortex set up by mechanical rotors for the dispersion of gas bubbles in the water. Many different configurations have been proposed. Figure 93 shows a typical configuration of the vessel proposed by Petrolite Corporation (Abdel Aal et al. 2003). In this case gas bubbles are created, introduced and dispersed into the bulk of the water to be treated by inducing a mechanically created vortex. A rotor powered by an electric motor created a vacuum within the vortex tube forcing the gas to withdraw into the vortex and disperse into the water. Froth created by gas bubbles carrying the oil droplets moves to the surface where it is collected in recovery channels for removal (Abdel Aal et al. 2003). Figure 94 shows a vessel using a different approach. In this case an inductor device is used. A portion of the treated water is recycled back to the unit under the operation of a pump. Flow through a venturi causes a pressure reduction in the water which sucks gas from the vapor space at the top of the unit. Gas is released through a nozzle near the bottom and carries the oil droplets to the surface as it rises (Abdel Aal et al. 2003). Figure 95 shows the drive mechanism of the generation of bubbles in water, the mixing region where droplets collide with bubbles, the flotation region where they gather in the top of the water zone and the skimming mechanism. Mostly they contain three to five separate cells, with a retention time of 1 minute and the bulk water moves from one cell to another through underflow baffles. The design of the rotor and internal baffles is critical for the unit's efficiency due to high gas induction rate, small diameter gas bubble and relatively large mixing zone needed. 50% of the oil in each cell can successfully be removed which leads in an overall efficiency of 90% for the whole cell line. In case of motion sensitive installations though this number is lower (Juniel and Rawlins 2007).



**Figure 93** - Typical configuration of a dispersed gas unit with inductor device as proposed by Petrolite Corporation (Abdel Aal et al. 2003).

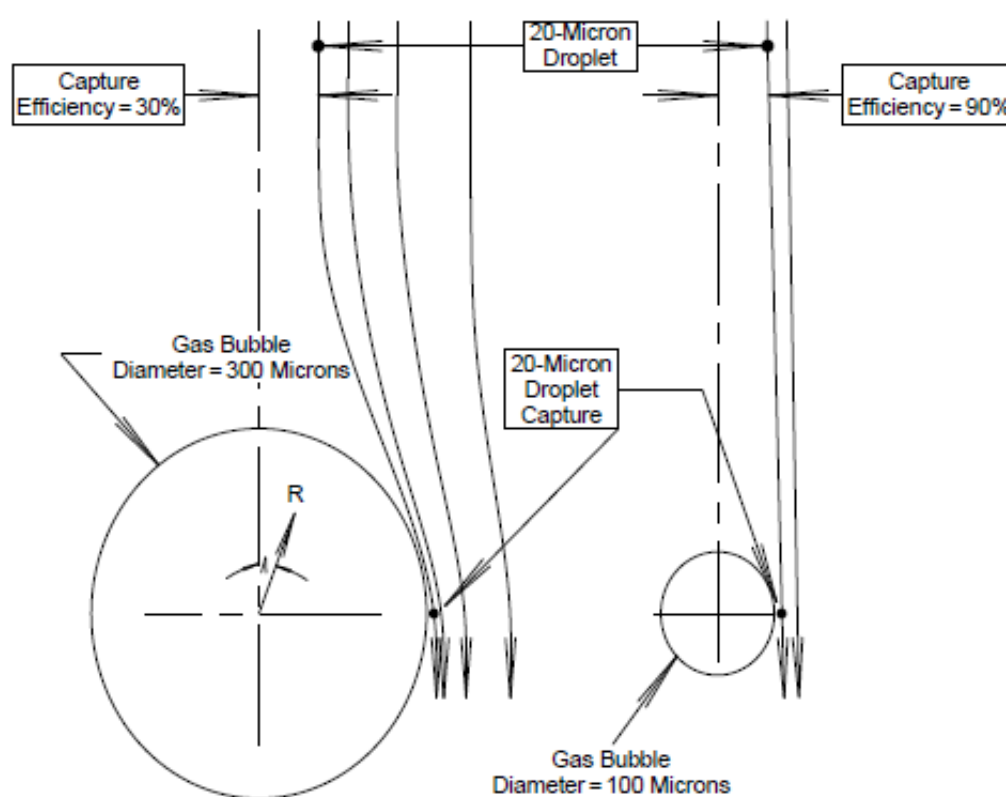


**Figure 94** - Typical configuration of a dispersed gas unit with inductor device (Juniel and Rawlins 2007).



**Figure 95** - Dispersed gas flotation unit mechanisms sequence. (Stewart and Arnold 2009)

Chemicals such as polyelectrolytes can be introduced for the enhancement of bubble-oil attachment and in cases needed bubble-solid attachment. Their amount in the water should be between 1 and 10 ppm. Their ability to enhance the intermolecular forces between bubbles and droplets and their tendency to migrate to the bubble surface is the main reason why they are used. De-emulsifiers should also be added in 20 to 50 ppm range. Turbulence is another factor that affects positively the contact of bubbles and droplets. High turbulence is favored close to bubble generators. Efficiency of the vessel is enhanced when small gas bubbles are formed. Salinities above 3% permit a stable size of bubbles. Despite this the separation can be improved due to dissolved solids which can create conditions for smaller bubble sizes. The effect of the bubble size is shown in Figure 96. Flotation has no effect on oil droplets smaller than 2  $\mu\text{m}$ . (Stewart and Arnold 2009)



**Figure 96** - Gas bubble size effect on oil droplet rate (Stewart and Arnold 2009)

Small oil droplets are not favorable to high bubble concentration. For the oil recovery to be improved, shear stresses provoked by choking or pumping of the water should be avoided. Oil removal is improved as gas-water ratio increases as shown in Table 14 which is created by field tests.

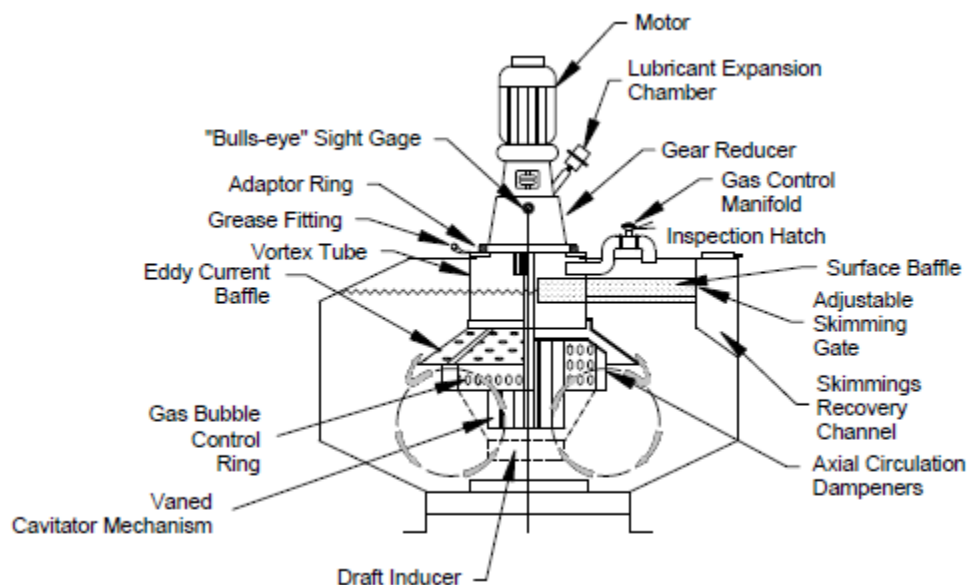
Water cells	Cumulative Gas-Water ration, ft <sup>3</sup> /bbl	PPM oil in treated water
Inlet water	0	225
1	9	96
2	18	50
3	27	20
4	34	14
Discharge cell	35	14

**Table 14 - Gas concentration effect on oil recovery (Stewart and Arnold 2009)**

Mixing of bubbles into the water should be avoided and that can be succeed if the rising velocity of the bubbles is higher than turbulent and downflow water velocities. Foam that is formed in the surface is skimmed by a combination of weirs and paddles. Those weirs should be always adjusted to the right height for the effective removal of the foam.

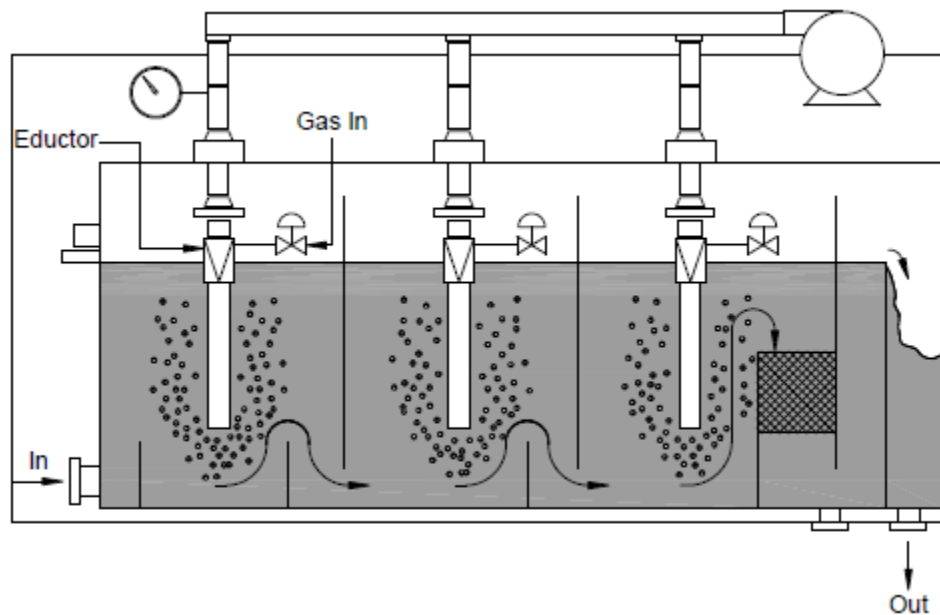
### *Hydraulic induced units*

Gas bubbles are introduced in the effluent into the low pressure zones of venture tubes in those vessels. Hydraulic induced units (Figure 97) operate under a configuration that sends the clean water to recirculation header and through this to venturi eductors. Water is enriched in gas that exists in the vapor space and is introduced through nozzles. Bubble rise causes the formation of froth which is later skimmed from a mechanical device. Configurations of one, three (Figure 98) or four cells are available for those units. Their gas/water ratio demand is less than 10ft<sup>3</sup>/bbl and the power needed for their operation is much less than mechanical rotor units.

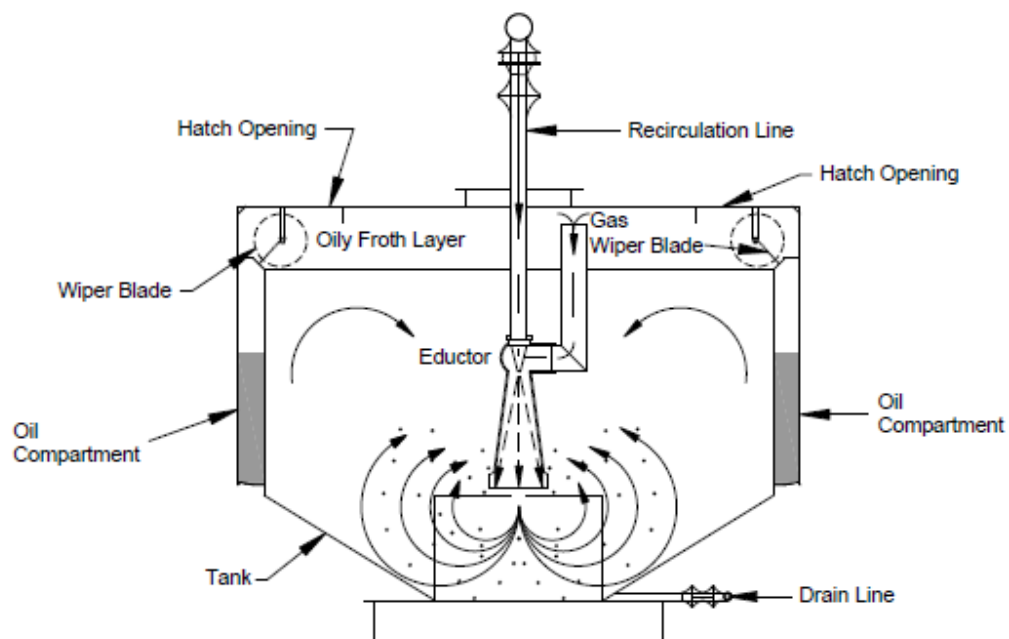


**Figure 97 - Hydraulic Induced Gas Unit (Stewart and Arnold 2009)**

Those units have a much simpler design and ability to operate above atmospheric pressure. Paddles and distributors are replaced by Venturi educators whose design can vary depending on the manufacturer. On Figure 99 a typical Venturi educator is presented. The water recycle rate is around 50%. Nevertheless efficiency of different stages tend to be lower than in mechanical rotor units due to the fact that bubble size and distribution cannot be controlled easily. (Stewart and Arnold 2009)



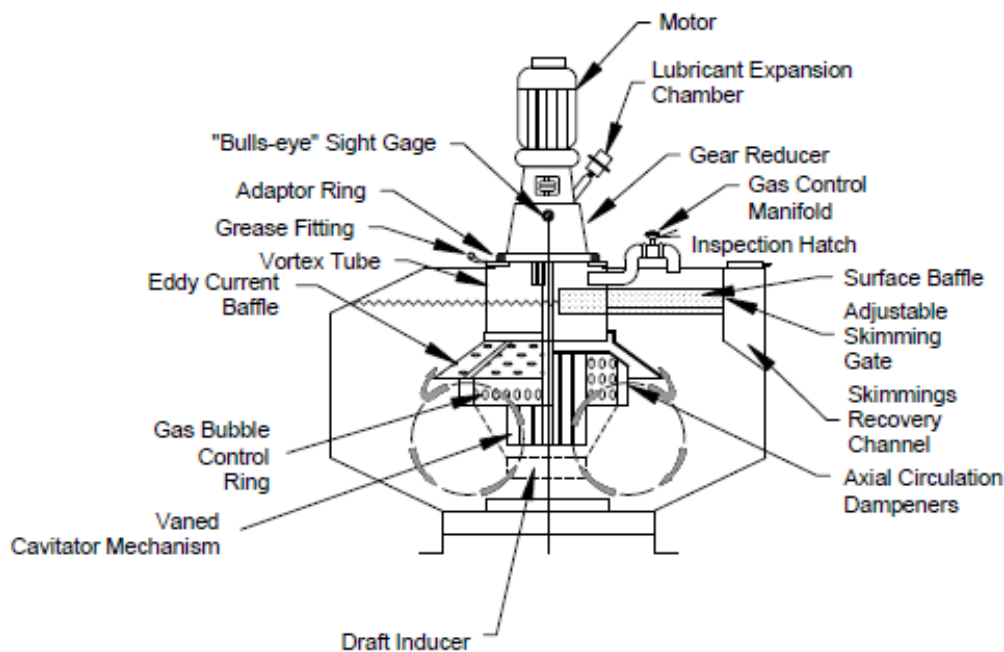
**Figure 98 - Hydraulic Induced Gas Unit with a configuration of three cells (Stewart and Arnold 2009)**



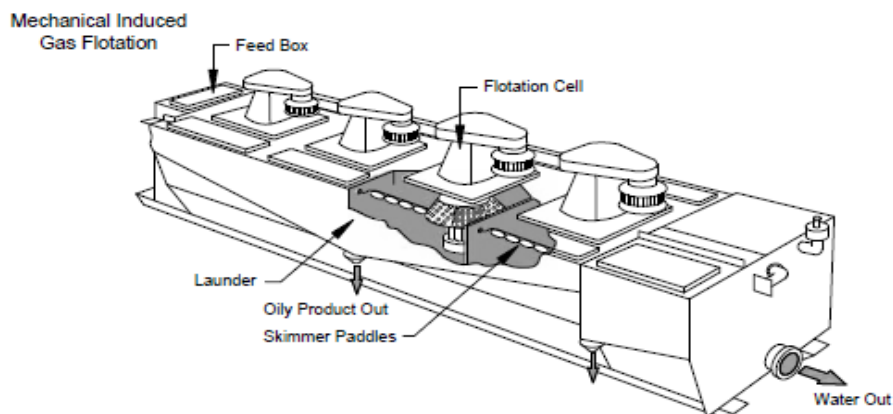
**Figure 99 - Hydraulic inductor (Stewart and Arnold 2009)**

## *Mechanical Induced Units*

Entrainment of gas in a vortex generated by a stirred paddle is used in this vessel (Figure 100). Vortex and vacuum is created in the vortex tube and with this process gas is introduced in the water. Flow path is shown in the figure and a baffle is used for the removal of the froth. Three or four (Figure 101) cells configurations exist for this vessel. Underflow baffles promote the movement of the effluent from one cell to another. Their complex design demands intense maintenance and mostly they operate on atmospheric pressures. (Stewart and Arnold 2009)



**Figure 100** - Mechanical induced unit within a dispersed gas flotation unit (Stewart and Arnold 2009)



**Figure 101** - Mechanical Induced Unit with four cells configuration (Stewart and Arnold 2009)

## *Other Configurations*

Different configurations have been proposed. Flow patterns and number of cells are the main variables for each one. Previously mentioned characteristics of each vessel should be used from the designers to propose the scheme that will provide the highest possible efficiency.

One of the proposed configurations is a combination of dissolved gas flotation system and CPIs. CPI injects recycled portion of the water into the stream. This action though can cause turbulence under specific conditions and neutralize the effect of CPI so this configuration is not recommended. (Stewart and Arnold 2009)

Another configuration is the Sparger design. Through a complexed design, gas is introduced in the water from external high pressure source and bubbles are formed through the porous medium nozzles. The size of the bubbles depend on the pores size. Pores should be on the same size as the smallest droplets of oil. Small sizes of droplets and bubbles require retention times of 10 minutes. Multiple spargers can be used for smaller bubbles and greater flow rates to promote gas mixing with produced water. A major drawback is that porous media experience high maintenance costs due to plugging. (Stewart and Arnold 2009)

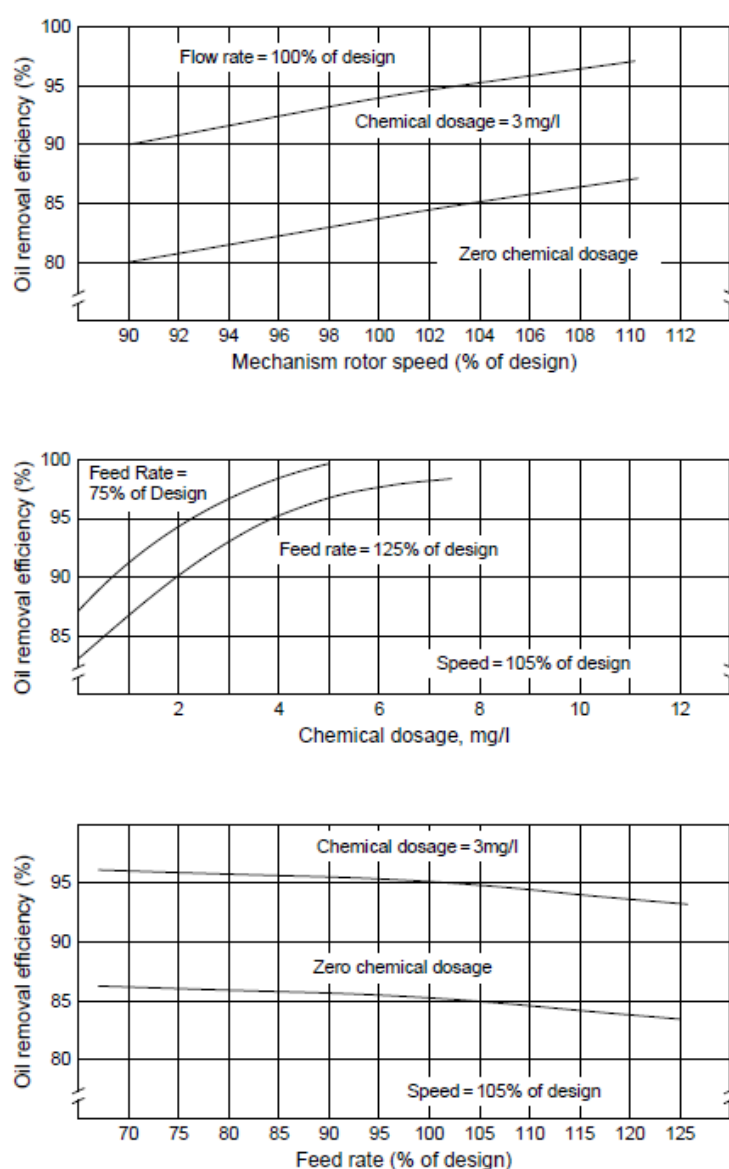
## *Performance Considerations*

Enhanced performance needs to be achieved. In order to accomplish this goal special care needs to be taken for specific factors. Level condition of the cells must be maintained throughout their use. Weirs can be affected by any level change and liquid surges can occur. Level of the liquids must be controlled for effective weir operation. Flow should not promote the dispersion of oil droplets due to the fact that separation will become more difficult. Extra oxygen from atmospheric air should not be permitted to enter the unit due to its corrosion promotion abilities. Hatches should be closed. A suitable chemical treatment program should be applied for successful flotation. Dosages should be exact and units always checked for any corrosion or deterioration provoked by the chemicals. Furthermore pH should always be under monitor due to the fact that acid gases induced for gas flotation can cause an increase which may result in scaling.

Field tests have shown that oil droplets of 10-20  $\mu\text{m}$  size and higher are completely removed and there is some effect on sizes 2-5  $\mu\text{m}$ . Oil removal efficiency absolutely depends on the chemical treatment program as shown in Figure 102. Mechanical units should be preferred for treatment of concentrations between 50 - 150 mg/l while hydraulic units should be preferred for treatment of concentrations above 500 mg/l. Flow rates of 70 - 120% of the initial estimated ones during the designing of the units, should be maintained for high efficiency. Separation efficiency depends on the

concentration of the influent while 140°F is the optimal water treatment temperature for separation at normal pH values.

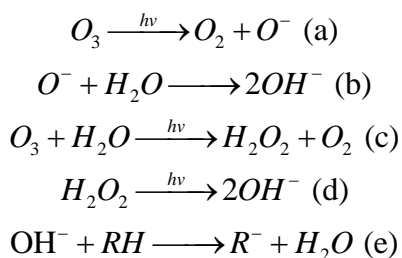
Under these considerations gas flotation units should be used when oil concentrations for the inlet are 250-500 mg/l, effluent discharge requirements are 25-50 mg/l, power cost budget is low or moderate and heavy oils are encountered. Gas Flotation units should not be used on the contrary when the installation is not stable (floating production facilities), a water stream composed from waters with different characteristics is to be treated and the concentration of oil in the treated water needs to be very low (Stewart and Arnold 2009)



**Figure 102 - Chemical treatment program effects on efficiency of mechanical induced flotation units. (Stewart and Arnold 2009)**

## Advanced Oxidation Process

The main strategy of this chemical process is the degradation of organic species through the hydroxyl radical ( $\text{OH}^\cdot$ ) which leads to formation of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and inorganic salts. The best available technique in the industry currently is the UV/ $\text{O}_3$  process which takes place according to the chemical reactions shown by Equations 17 a,b,c,d and e.

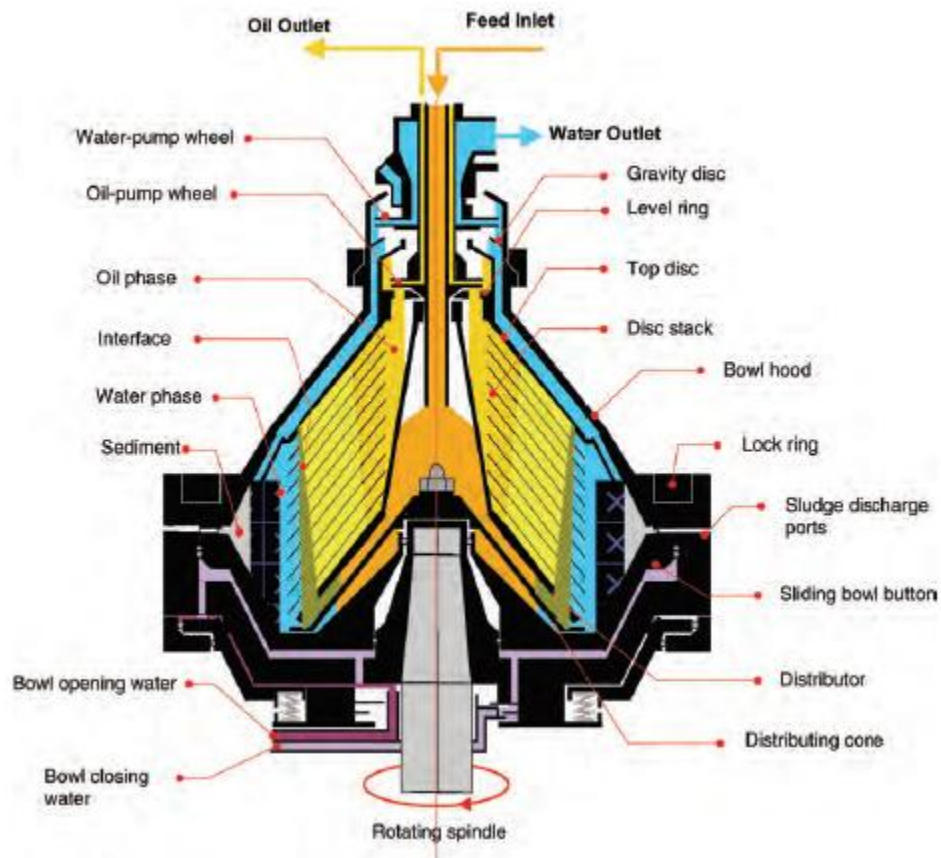


**Equations 17 a,b,c,d and e** - Chemical reactions governing the advanced oxidation process (OSPAR Commission 2013)

Once this reaction is complete, the radical  $\text{R}^\cdot$  will cause chain reactions until the complete mineralization of the organic molecule. Following the injection of ozone in form of airstream in the water, the liquid should pass through ultraviolet radiation. This technique's efficiency in oil in water emulsion resolution reaches 50% (OSPAR Commission 2013).

## Centrifuges

Disc stack centrifuges can be used also for the emulsion breaking and they are in use the last 30 years. They are preferred for the removal of very small droplets where coalescence is not easy. Their main parts are frame, drive motor, transmission, separator bowl and inlet/outlet arrangements as shown in Figure 103. A feed pipe introduces the water into the rotating bowl where separation takes place and up to 6000 g-forces can be encountered. The bowl provides a settling distance of 0.5 mm for the droplets and the annular channels can be used as parallel separation vessels. Oil flows towards the center of the bowl while water and sediments flows against the underside of the disc. With those vessels droplets of 1-2  $\mu\text{m}$  can be removed. (Juniel and Rawlins 2007).



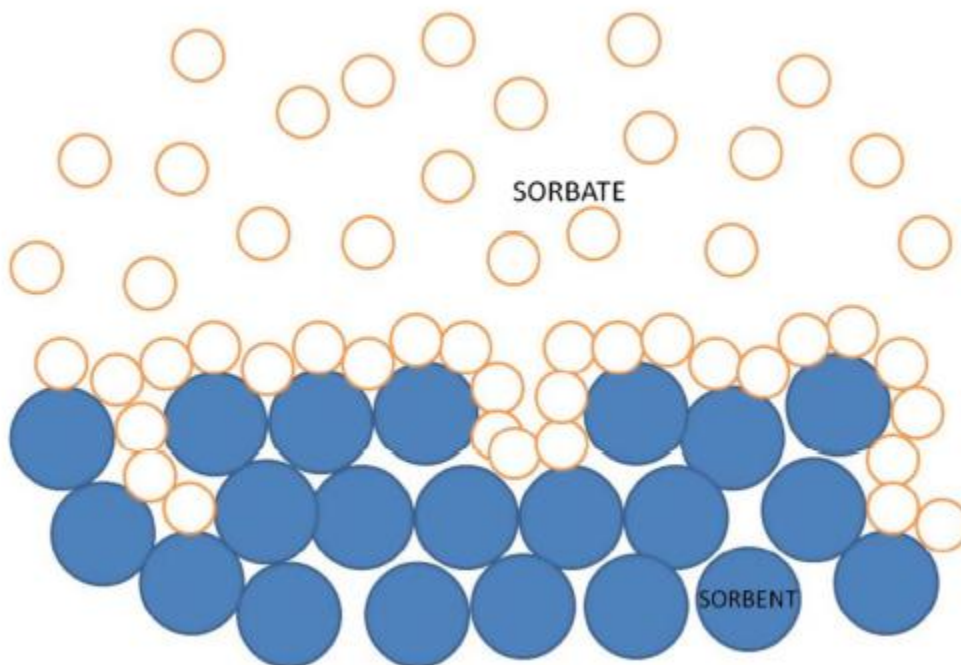
**Figure 103** - Disc stack centrifuge schematic (Juniel and Rawlins 2007).

## Chapter 7 - Specialized Techniques and Equipment used for oil in water emulsion resolution and oil recovery - Tertiary Treatment and Advanced Treatment stages

Tertiary and Advanced treatment stages are the most important stages of oil in water emulsion treatment for the compliance with water discharge regulations. Scientific research is focused mainly on those stages lately and further presentation of the latest trends on their evolution will take place in a following chapter.

### Filters - Tertiary Treatment stage

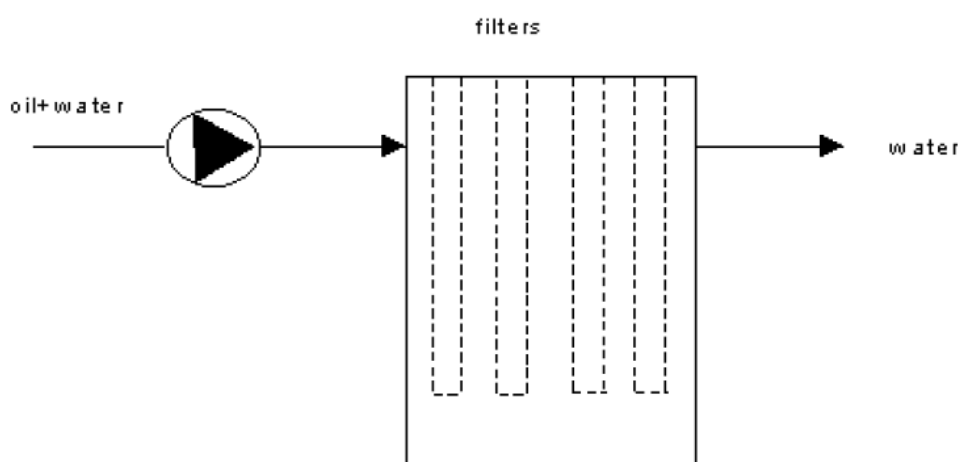
Low processing cost and simple process design makes adsorption an effective technique for oil in water emulsion treatment. The attraction between the sorbent and the sorbate drives the process and forces the accumulation of sorbate molecules on the sorbent surface without penetrating it (Figure 104). The three stages of oil adsorption are diffusion of oil molecules in the surface of the sorbent, entrapment of the oil molecules in the sorbent structure due to capillary action and their agglomeration in the porous structure of the sorbent (Sabir 2015).



**Figure 104** - General mechanism of adsorption process. Sorbate molecules are accumulating on the sorbent's surface without penetrating it. (Sabir 2015)

Filters are categorized to synthetic and naturals. Synthetic filters usually are composed of polypropylene, polyester and polyamide. Natural filters are mostly

related to wool-based materials, kenaf and activated carbon. Many compounds can be used for the removal of dispersed oil from contaminated water through filtration techniques. Adsorbents are classified in two categories depending on their ability to regenerate or not (Gimmerman 2006). Adsorption filters are applied for the treatment of aliphatic hydrocarbons but in most cases they cannot be regenerated since chemical adsorption of the contaminants has occurred. Oil in water emulsion removal efficiency can reach 95% through this process (OSPAR Commission 2013). The process diagram through which filtration of oily wastewater for emulsion treatment is illustrated in Figure 105. Activated carbon, organoclay, copolymers, zeolite and resins are industrially used for the adsorption of dissolved solids. Carbon surfaces have the ability of adhering organic compounds of produced water. Activated carbon removes soluble BTEX (benzene, toluene, ethylbenzene and xylenes). Organoclay removes insoluble free hydrocarbons which form the emulsions of oil in water. Copolymers based on methylmethacrylate (MMA) and divinylbenzene (DVB) reduce oil content in water by 85%. Zeolites are used as ion-exchange resins that adsorb dissolved organic matter in water. Adsorber's efficiency depends highly on temperature, pH, suspended oil, organic metal complex, salinity and dissolved organics and chemicals (Fakhru'l-Razi et al. 2009).



**Figure 105** - Process diagram for filtration of oily wastewater (OSPAR Commission 2013)

### *Bentonite based powders*

A mix of Bentonite with aluminum salts, polymers and other additives is proposed (Alther 1997) for emulsion breaking. This method requires pH values in the range of 7 to 9.5 and is mostly used in case of lack of sophisticated equipment. This method has the advantage of not requiring lab tests prior to its application and oftenly it doesn't require more than one step to completion. Excellent removal of metals and

organics is achieved with very low treatment costs. A modification of this method can be used for wastewaters with small quantities of oil. Bentonite is modified with quaternary amines for this purpose. The organoclay is used either as a powder in batch treatment systems to remove oil and other organics or it is used as a granule for flow through systems at a particle size of 8 x 30 mesh. The organoclay is blended with anthracite to prevent early plugging of interstitial pores in the adsorber vessel. Montmorillonite which is the main clay constituent in bentonite exchanges nitrogen ions with quaternary amines replacing sodium, potassium and calcium. By the addition of this organically modified clay in the water, the amine chain is oriented perpendicular to the clay surface since montmorillonites have the shape of a rectangular platelet. Thus the hydrophobic end of the quaternary amine with the halide attached to it (chlorine, bromine, etc.) stays undissolved in the water. During the contact of an oil droplet with this part of the quaternary chain, it will enter, dissolve and partition into the oil droplet in case that the oil is mechanically or poorly emulsified by a surfactant. A solid/liquid emulsion is formed in this way where the hydrophilic end is "dissolved" into the clay instead of water. The quaternary chain is wetted by the oil or vice versa. This method is used as final treatment for emulsions that have escaped the separation equipment and they contain small amounts of oil (Alther 1997).

### *Activated carbon*

Activated carbon has been introduced successfully in oil industry as effective surfactant remover. Its primary industrial use was the removal of alkyl benzyl sulfonate (ABS) and linear ABS. Non-ionic surfactants tend to adsorb well onto carbon especially on alkaline environments. A general rule governing the application of this method is that the higher the molecular weight and polarizability and the lower the solubility the higher is the sorption caused. Activated carbon rates are higher for pH rates of 7.5 to 9. Presence of aromatic rings and halides encourages high sorption rates (Alther 1997). Commercially, activated carbon can be found in granular or powder form and there are various grades of activated carbon available depending upon mesh size, iodine content, acid volume etc (Retrieved from: <http://www.chemtexlimited.com/raw-water-treatment-chemicals.html#activated-carbon>). The granular activated carbon (GAC) adsorption technique involves the contact of treated water with the carbon media in a fixed bed column. The oil droplets and the rest of organics are adsorbed on the surface of the carbon after water's inlet into a carbon container. The carbon demands reactivation after its use (Orszulik 2008).

### *Walnut Shell Filters*

One of the most common materials and techniques used in oil in water emulsion separation processes is walnut shell filters. Walnut shell filters (Figure 106) are used

for the removal of residual dispersed hydrocarbons from the produced water. Mechanical agitation or walnut shell recirculation in the backwash cycles are used in this case. Chemicals are not needed due to the effective oil removal. Waste volume is of 1% of the total throughput which makes walnut shell filters appropriate for offshore installations due to space limitations. A disadvantage is that in low temperatures, crude oil is difficult to be removed, thus chemicals or heating is demanded for the cleaning of the filters between the operational cycles. (Juniel and Rawlins 2007).



**Figure 106 - Industrial Walnut shell filters (Juniel and Rawlins 2007)**

## **Membranes - Advanced Treatment stage**

The use of membrane technology for the treatment of oily water has been applied recently in the oil industry (Munirasu et al. 2016). Membrane filtration systems are categorized in micro filtration (MF), ultra filtration (UF), nano filtration (NF) and reverse osmosis (RO). It can be observed by the magnitude of each one they are applied in different droplet size distributions. The categories that are applicable in oil industry for the removal of oil in water emulsions are MF, UF and NF since they have been used for decades due to their economical and environmental friendly feasibilities. In particular NF membranes are the most efficient in oil removal from water, its recycle and reuse in oil and gas industry. RO membranes provide better separation results but their cost is much higher than the NF ones and their use in the oil industry is limited. Industrial examples of usage of RO membranes as final treatment stage are Chennai Petroleum Company Limited, San Ardo in California and

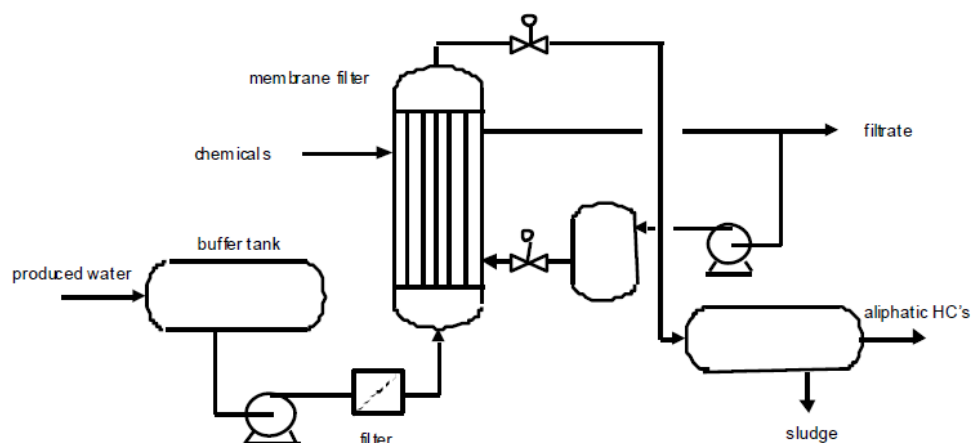
Wellinton oilfield in Colorado (Munirasu et al. 2016). In some cases though, experimental studies proposed the combination of all of membrane categories with mechanical equipment for oil in water removal efficiency reaching 99% (Ebrahimi et al. 2009) and 99.5% (Ebrahimi et al. 2010). Forward Osmosis (FO) membranes have also been proposed recently (Zhang et al. 2014) with efficiency of oil in water removal reaching 99.9% but they are still on experimental level. Polymers such as cellulose, nylon, PTFE or ceramics are used as base for their manufacturing (Drewes et al. 2009).

Polymeric membranes are relative inexpensive. They are made from materials such as cellulose, nylon, PTFE, polyacrylonitrile and polyvinylidene. Integrity testing is needed to ensure that there is no damage in the membrane and its operation is proper. Testing can be conducted by pressurized air which is applied into the membrane at pressure lower than the one which would bypass the membrane and measurement of the pressure decay. Their life is estimated typically in 7 years (Drewes et al. 2009).

Ceramic membranes are popular over the last years due to their mechanical, thermal and chemical stability. Zirconia membranes in particular have been proved more efficient in separation of oil and water and less fouling than polymeric ones although more expensive (Ashaghi et al. 2007).

Various configurations such as hollow fibre, tubular or spiral membranes are in use. Despite the fact that membrane technology in some cases has reached an effluent oil concentration of 5 ppm, it is notable that they are not widely used in heavy duty industrial applications of emulsion breaking so far (Mastouri 2010).

Aliphatic hydrocarbons are the primary target of membrane filtration techniques. A standard process of membrane filtration involves the low pressure flow of water through the membrane medium. Cross flow techniques and turbulent flow along the membrane surface are not permitting filter cake build up. The trapped in the pores of the membrane oil droplets are removed by the use of cleaning chemicals while the main part of separated from water hydrocarbons is directed into settling tanks. Emulsion removal efficiency ranges between 70-90% and a schematic of the membrane filtration process is illustrated in Figure 107 (OSPAR Commission 2013).



**Figure 107 - Membrane filtration process schematic (OSPAR Commission 2013)**

## Biodemulsifiers - Advanced Treatment stage

Research on biodemulsifiers or microbial demulsifiers has commenced since 1980s. Studies (Kosaric 1989) have proposed microbial cell surfaces for the formation of demulsifying agents. Biodemulsifiers are a potential alternative to chemical demulsifiers due to their low toxicity, facile biodegradability and exclusive properties. They can be recycled and reused without reduce in their performance rates and they can be effective under extreme conditions. The demulsification mechanism in this case involve the adsorption of biodemulsifiers at the oil water interface and the displacement of emulsifiers which leads to destabilization of the emulsion. The main target of development for biodemulsifiers used in oil in water emulsion treatment is the increase of cell concentration (Zolfaghari et al. 2016). Cells of bacteria *Nocardia amaraebacteria*, *Corynebacterium petrophilium* and *Rhodococcuse aurantiacus* harvested at stationary phases of growth have proved efficient for oil in water emulsion breaking. The demulsifying capability of those microbial cell surfaces is not affected by heating or other chemical treatments except alkaline methanolysis (Fink 2012). Biodemulsifiers are categorized into cellular and extracellular metabolic demulsifiers. *Nocardia*, *Corynebacterium*, *Micrococcus*, *Rhodococcus*, *Ochrabactrum anthropi* and *Alicalignes* are examples of cellular biodemulsifiers while Acetoin, Fengycin, fatty acids and carbohydrates are examples of extracellular metabolic demulsifiers (Zolfaghari et al. 2016). A study (Coutinho et al. 2013) proposed *Pseudomonas aeruginosa* MSJ for the treatment of oil in water emulsions with efficiency reaching 99.7% while another study (Park et al. 2000) proposed *Streptomyces* with a demulsification efficiency of 95%. *Bacillus mojavensis* (XH1) was proposed (Hou et al. 2014) also with 35.5% demulsifying ratio.

## Chapter 8 - Patented, commercially available and experimental equipment and chemicals for oil in water emulsion treatment

Technological and scientific advances suggest new ways for oil in water emulsion treatment. Some of them are gradually introduced in the industry while others are still on experimental or theoretical level. An attempt of listing and describing the most recent trends in oil in water emulsion treatment is made in this chapter of the present work. A list of some of these trends is presented in Table 15.

Technology	Influent oil (mg/l)	Effluent oil (mg/l)
Vortoil hydrocyclone (35 mm)	43	11
Vortoil hydrocyclone (60 mm)	408	16
Colman - Thew hydrocyclone	100	12
Rotary hydrocyclone	100	15
Disk stack centrifuge	<1000	5
Crossflow microfiltration	28-583	5
High gradient magnetic separation	190-240	23
Electrolytic treatment	1000-2000	3-11

**Table 15** - Performance of some of the most modern techniques for oil in water emulsion treatment (Orszulik 2008)

A general idea about the equipment used in the industry was given on previous chapters. Companies design their own equipment depending on the requirements of operation for each case and introducing their own designing details and patents. A few industrial commercially available examples of equipment will be presented below. Table 16 summarizes some of the major equipment vendors for water treatment. Individual researching groups propose their own treatment scheme for oil in water emulsion treatment and certain examples will be also demonstrated.

Equipment - Method	Vendor
Hydrocyclone	Cameron
	Siemens
	Veolia
	FL Smith
	EnerScope
Centrifuge	EVTN
	Alpha
	Laval
Filtration	Cameron
	New Logic
	Siemens

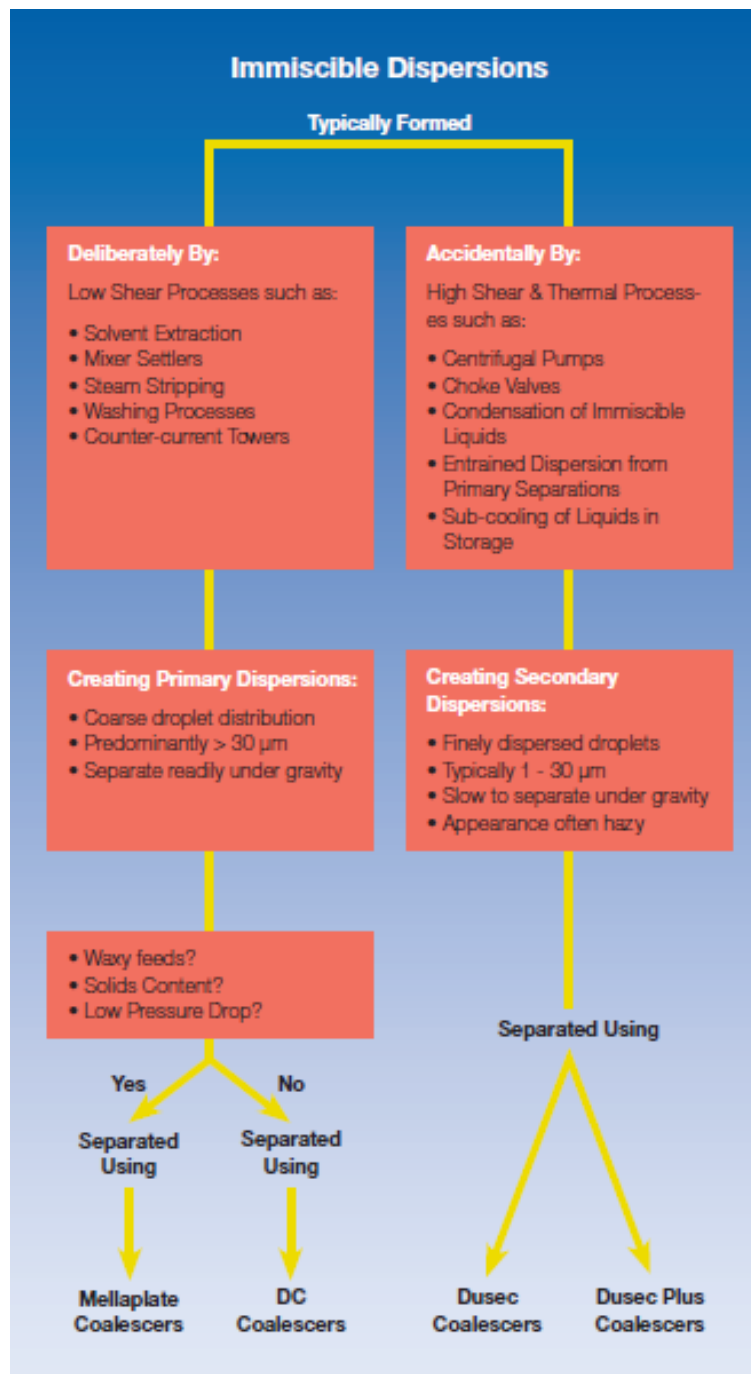
Coalescence	Veolia
	Ecodyne
	ACS Industries Inc
Flotation	Siemens
	Veolia
	ProSep Technologies
Combined processes	Enviro-Tech
	Siemens
	Veolia
Adsorption	IDI
	MI-Swaco
	ProSep Technologies
Oxidation	Cameron
	Siemens
	Veolia
Solvent extraction	CETCO
	MyClex
	Ecosphere Technologies
	VWS MPP Systems B.V.
	Veolia
	Ecodyne

**Table 16 - Equipment Vendors (Daigle 2012)**


## Industrial Patents for Coalescers

Sulzer company proposes various configurations of coalescing equipment for the enhancement of oil in water emulsion breaking. Figure 108 shows a typical scheme for the vessels used for each case.

Mellaplate coalescers have a configuration of parallel plates that are arranged in the axial direction of the vessel. Plates' angle can be 45° or 60° and the spacing can be of the order of 15 to 100 mm and the sheets are made of structured corrugated metal or plastic sheets. Separation efficiency is improved on the principle that the oil and water phases are disengage continuously along the plates. Flow stability is improved and the risk of droplets repentrainment is reduced. This vessel is proposed for systems with high risk of fouling and increased plate angles. In case of phase inversion efficiency is maintained on high levels and it's suitable for cases where gaseous phase exist. Mellaplate coalescers are applicable to primary dispersion cases and they can operate at separation fluxes up to 100m<sup>3</sup>/m<sup>2</sup>/h. Figure 109 shows 4 different Mellaplate coalescers models and their distinctive characteristics. On Figures 110 and 111 an actual model of Sulzer Mellaplate W is presented and its arrangement within a separator with a simultaneous addition Mellaplate M wave and foam breaker (Retrieved from <http://www.sulzer.com>).



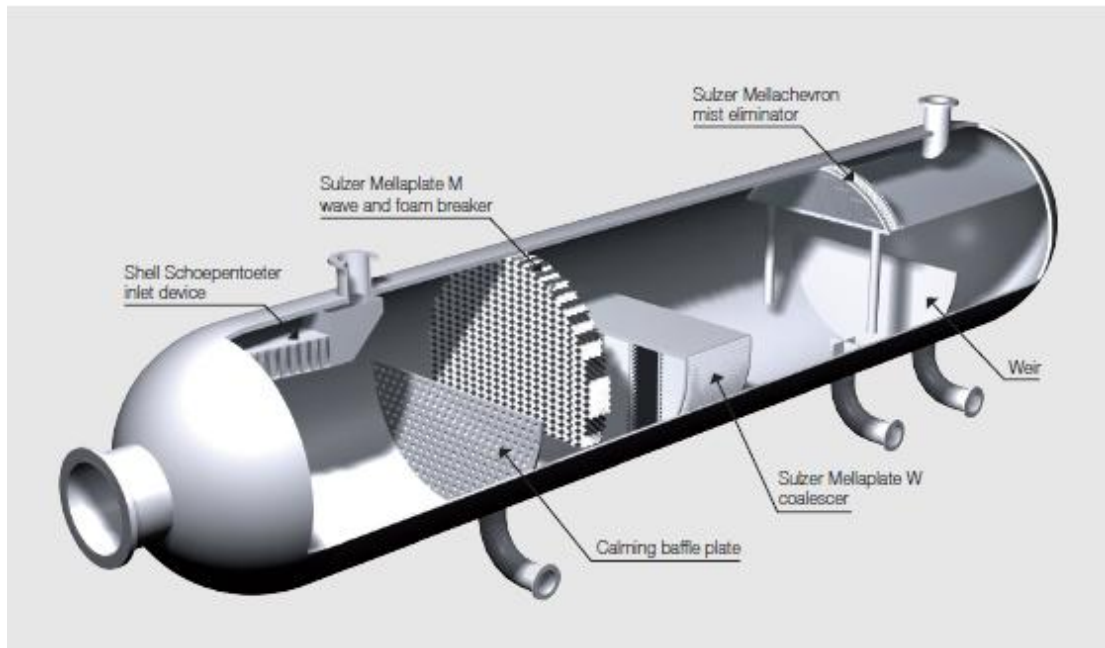
**Figure 108** - Overview of Sulzer coalescer types and the cases each one is applicable  
(Retrieved from <http://www.sulzer.com>).

Sulzer Mellaplate coalescers are available in four different types:	Mellaplate W	Mellaplate MG	Mellaplate M	Mellaplate N
				
	Flat parallel plates	Structured corrugated flat plates	Structured corrugated metal sheets	Structured corrugated plastic sheets
	Relative Capacity <sup>1)</sup>	1	1.5	1.5
	Typical droplet cut-off size	$\geq 50 \mu\text{m}$	$\geq 100 \mu\text{m}$	$\geq 50 \mu\text{m}$
	Pressure drop	Negligible	0.5 – 4 mbar	1 – 10 mbar
	Solids Handling	High fouling resistance	Good to high fouling resistance	Moderate to good fouling resistance
Remarks			Also used as wave and foam breaker elements	More suited for de-oiling due to the plastic surface

**Figure 109 - Sulzer Mellaplate Coalescers** (Retrieved from <http://www.sulzer.com>).

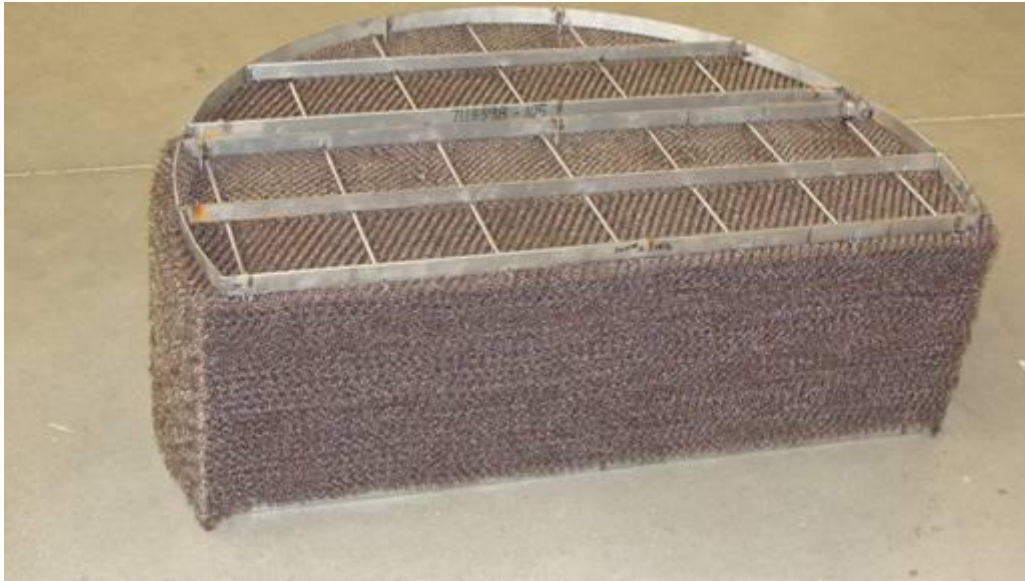


**Figure 110 - Sulzer Mellaplate W** (Retrieved from <http://www.sulzer.com>).



**Figure 111** - Sulzer Mellaplate M and W models within a three-phase separator (Retrieved from <http://www.sulzer.com>).

Sulzer DC Coalescers (Figure 112) provide significantly lower settling times for droplets of size down to 30 microns. Metal and plastic is used due to their difference in surface energy to enhance the droplet coalescence as shown in Figure 113. Both filaments are knitted together to form the mesh. Steel or alloy C22, C276, 400, 625 or 800 is used for the metallic part while PP, FEP, ETFE, PTFE or glass fibers are used for the plastic one. This configuration provides large cost savings in pressure vessels since efficiency is maintained on high levels even with phase inversion. Fluxes of  $120 \text{ m}^3/\text{m}^2/\text{h}$  can be achieved. As shown in Table 17, this configuration is proved better than single medium alternatives. DC coalescers can be installed both vertically and horizontally in vessels but they are sensitive to the presence of solids bigger than 50 microns which can cause excessive blockage (Retrieved from <http://www.sulzer.com>).

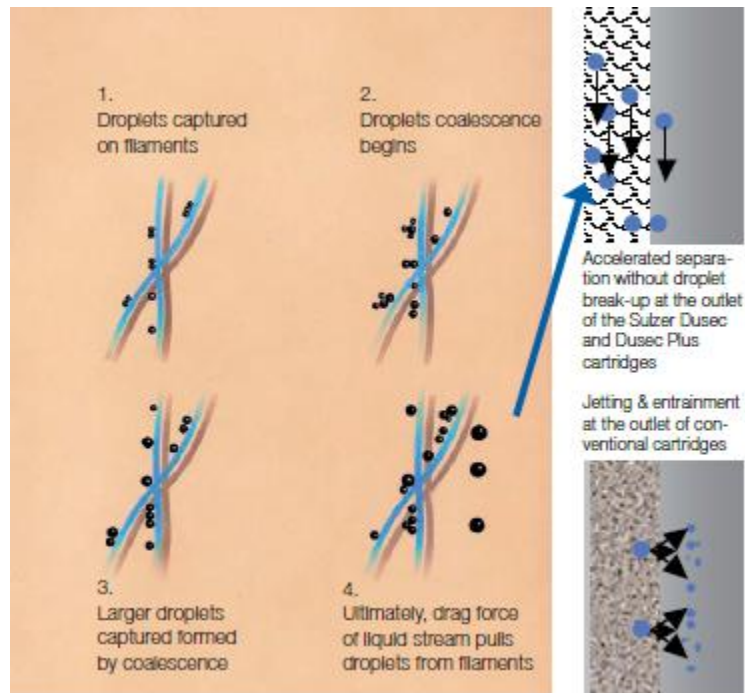


**Figure 112 - Sulzer DC Coalescer** (Retrieved from <http://www.sulzer.com>).

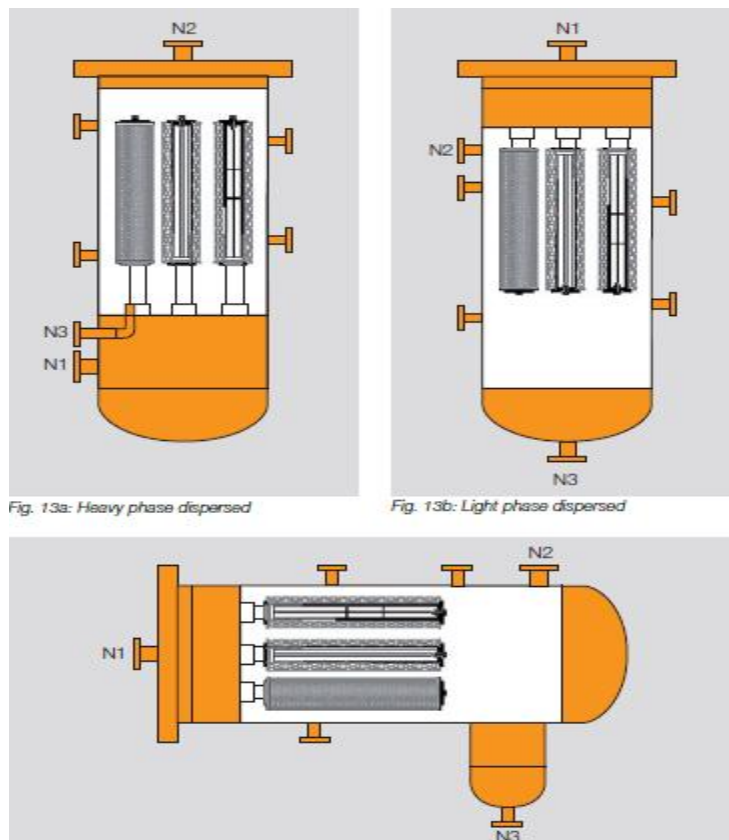
Packing	Dispersed phase	Relative Flux
Stainless Steel	Kerosene	0.1
	Water	1
Polypropylene	Kerosene	1.1
	Water	0.05
Sulzer DC Coalescer Stainless Steel and Polypropylene	Kerosene	1.45
	Water	1.45

**Table 17 - Comparison of fluxes between single media coalescers and Sulzer DC Coalescers** (Retrieved from <http://www.sulzer.com>).

Sulzer Dusec and Dusec Plus use cartridge configuration (Figure 115). Radial flow of the liquid is taking place outwards from the center. A selection of fiber materials and their surface properties combined with optimized layer compositions ensure the enhanced efficiency in oil in water emulsions which can reach 10 ppm entrainment of free droplets. Drop sizes treated are in the range of 1 to 30 microns. The working principle of Dusec Cartridge Coalescers is shown in Figure 113. Flow resistance encountered by the liquid improves the coalescing process. Adhesive forces cause interception of oil droplets onto the fiber surfaces at selective points where clusters form. Under viscous drag forces, droplets after a certain size separate from the fiber and undergo through a repeating process of coalescence. Due to higher packing densities, the vessel's size is reduced drastically which makes it ideal for offshore use and leads to capital cost reduction. They can be available for both horizontal and vertical configurations as shown in Figure 114 and they can be used both in highly aggressive chemical environments and high temperatures (Retrieved from <http://www.sulzer.com>).



**Figure 113** - Droplet coalescence principle in a Sulzer Dusec and Dusec Plus Coalescers (Retrieved from <http://www.sulzer.com>).



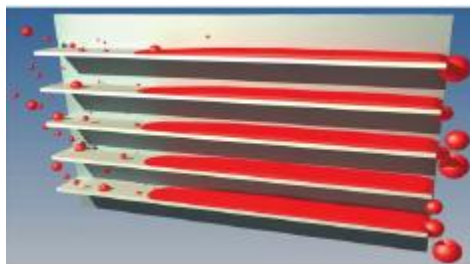
**Figure 114** - Vertical and Horizontal configurations of Sulzer Dusec and Dusec plus coalescers within a separator. N1 is the feed, N2 is the light phase outlet and N3 is the Heavy phase outlet (Retrieved from <http://www.sulzer.com>).



**Figure 115** - *Sulzer Dusec coalescer (Retrieved from <http://www.sulzer.com>).*

## Coalescing Pump

Coalescence company has introduced the CLSR-series coalescing pump. It is a centrifugal pump containing a rotating bundle which collects small oil droplets and promotes their coalescence into bigger ones. The bundle contains tubes of mm size range where coalescence occurs as shown in Figure 116. Trials have shown that droplets down to 1 micron can be treated and that 90% reduction of droplets for sizes smaller than 10 microns can be achieved with the use of this vessel. It is simple to operate since it's a centrifugal pump technology which requires no usage of absorbers and chemicals. Its operational window is large since it can operate under varying conditions and it is applicable for all separators. Its size and cost is small and its high tolerance in motion makes it ideal for offshore installations while its maintenance requirement is minimal (Daigle and Cox 2012).



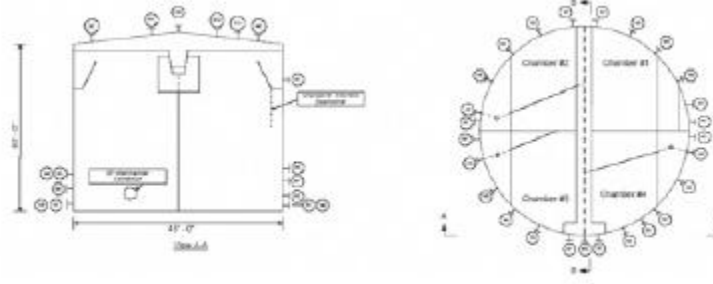
**Figure 116** - *Coalescence of droplets inside CLSR-series coalescing pump tubes (Daigle and Cox 2012)*

## Industrial Patents for Skim tanks - Induced Gas Flotation (IGF) within Skim tanks

Introduction of gas bubbles in the fluid stream has been developed for a more enhanced approach in the oil in water emulsion separation. Sparging tubes and eductors are used to cause oil floating in the surface where it can be skimmed off. IGF design involves a multistage approach, with vessels divided into separated chamber for the reduction of short-circuiting effect. Gas introduction is happening in each chamber separately causing a progressive removal of oil in each stage and an enhancement of the overall performance of the vessel. Low retention times though in such vessels make difficult the handling of any upsets in upstream processes. To confront this issue, GLR solutions proposed a configuration which was combining the skim tank and induced gas flotation technologies, resulting to a multi chambered Skim tank. An industry example of this system is shown in Figure 117. In this system a pump or a pressure vessel design can be used to inject gas bubbles of 30  $\mu\text{m}$  size to aid oil in water separation. Oil droplets rising in the surface are manually skimmed off. ENI has planned to install an automated skimming operation based on a timed cycle. Automated skimming operations will require less supervision and they will ensure that oil within the tank will be maintained on adequate levels to prevent transfer in the clean water line. Designs with four chambers are adopted lately by ENI for the improvement of oil removal capability and buffering capacity. A typical example of a four chamber design is shown in Figure 118 (Rodriguez et al. 2006)



**Figure 117** - Industrial installation of skim tanks (ENI tanks T04 and T05) (Rodriguez et al. 2006)

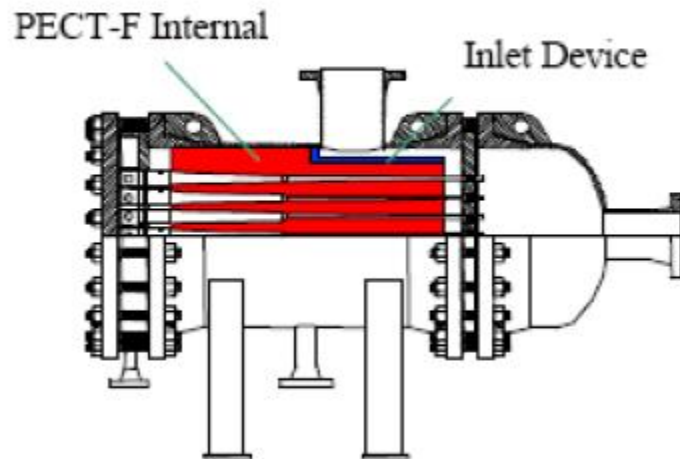


**Figure 118 - Typical four chamber API Tank Design (Rodriguez et al. 2006)**

## Industrial Patents for Hydrocyclones

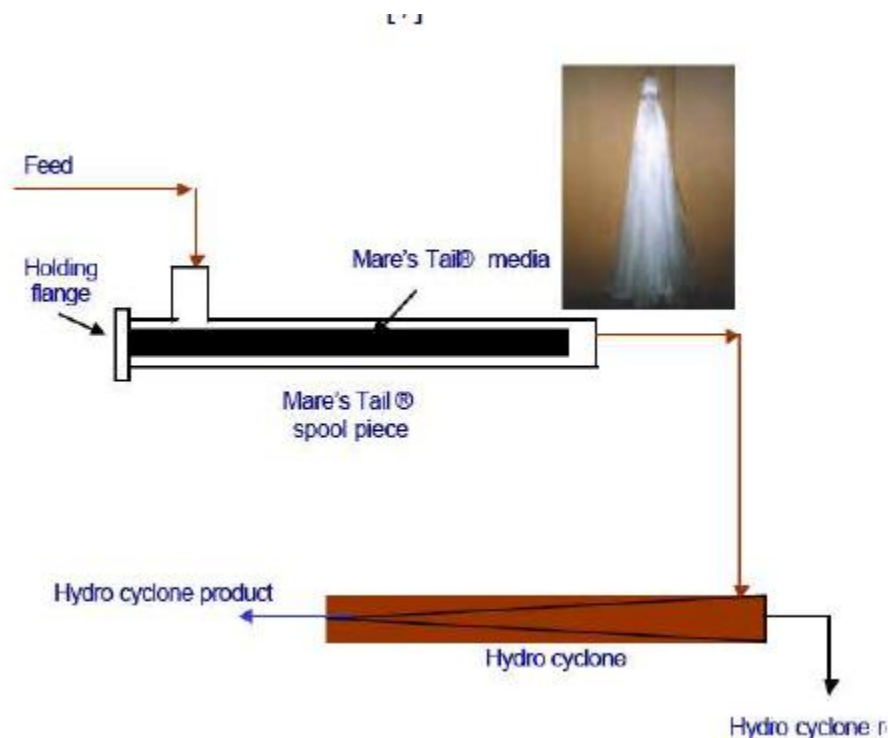
Pre-coalescers are a category of equipment that has been industrially evolved over the last decades. As pre-coalescers are referred vessels used upstream of gravity type or centrifugal separation technologies. Their operation principle is based on increasing of oil droplet sizes so that removal of oil is easier in downstream processes. Mostly packed polyethylene strands which provide large surface areas are used in those vessels. Oil droplets are attracted in those strands and after a process of coalescence they form bigger droplets which return to the stream due to the fact that they are too large to be held by the strands. This kind of equipment doesn't brake emulsions itself but it enhances the efficiency of downstream vessels such as hydrocyclones (OSPAR Commission 2013). Most widely used pre-coalescing systems are PECT-F by Cyclotech Company and Mare's tail (Tulloch 2003).

Cyclotech Company developed the Performance Enhancing Coalescence Technology (PECT-F). It is a coalescing concept based on fibers to improve the performance of Hydrocyclone deoiling systems. PECT-F is installed in the inlet of a hydrocyclone in a cartridge configuration. Conventional Hydrocyclones provide up to 20 seconds of retention time which is an adequate time for PECT-F to achieve a partial oil droplets coalescence and form oil droplets of sufficient size for their complete removal by a hydrocyclone. This technology is cost effective since it reduces the amount of chemicals used for coalescence in hydrocyclones. Figure 119 depicts a hydrocyclone equipped with PECT-F technology.



**Figure 119** - PECT-F pre-coalescing technology in a hydrocyclone (Sinkler et al. 1999)

Mare's tail is another pre-coalescing device used upstream of hydrocyclones to enhance separation. It is consisted of oleophilic polypropylene fibers inside a cartridge. The principle is the same as in PECT-F technology but in this case the retention time needed to achieve sufficient coalescence is 2 seconds. The principle of operation of Mare's Tail is shown in Figure 120 and its name is due to the fact that fibers bundle look like a horse tail (Tulloch 2003)



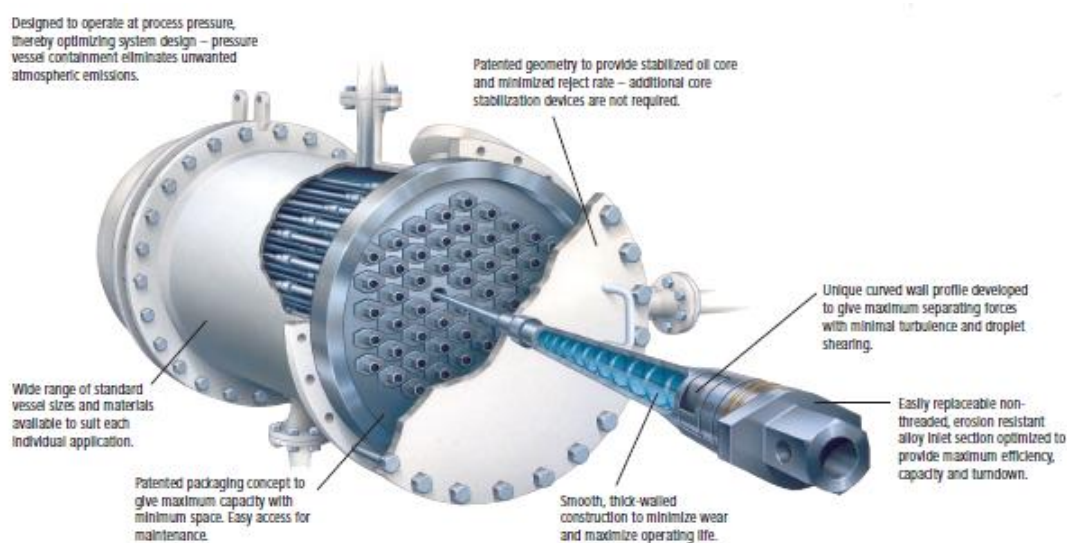
**Figure 120** - Mare's tail principle of operation (Knudsen et al. 2004)

An industrial commercial Hydrocyclone example is the PROSPIN hydrocyclone by PROSEP company (Figure 121). It's small dimension and high emulsion breaking efficiency makes it ideal for offshore installations. It's removal efficiency ranges between 85 and 95% when oil droplets of size range higher than 12 microns are to be treated (*Retrieved from [www.prosep.com](http://www.prosep.com)*).



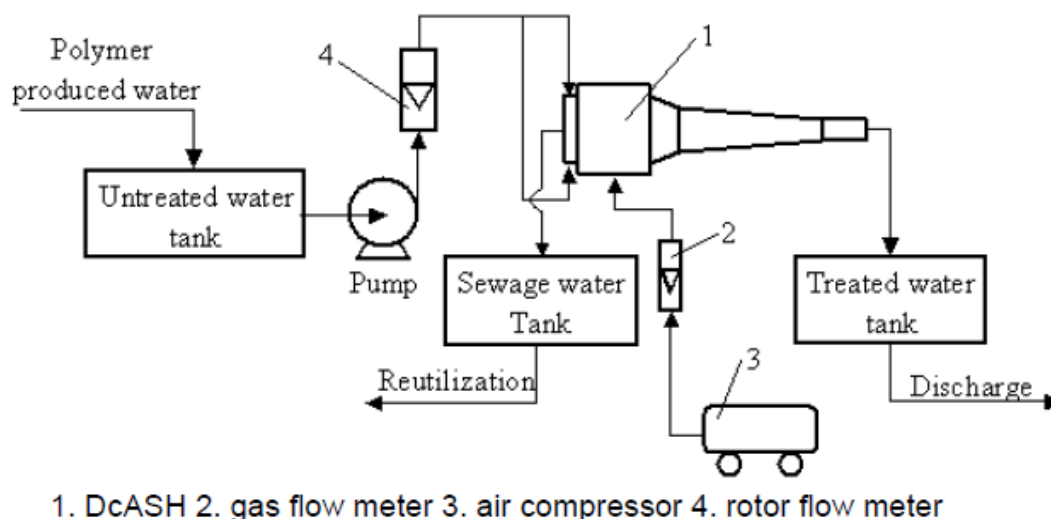
**Figure 121** - PROSPIN hydrocyclone (*Retrieved from [www.prosep.com](http://www.prosep.com)*)

Another commercial hydrocyclone system used in the industry by operators such as Shell, ESSO Balder FPV and BP Schlehallion FPSO is VORTOIL Deoiling Hydrocyclones by CAMERON. Concentrations of oil in water down to 2% can be treated with this system achieving high separation capacity. Wear resistant materials used in this vessel such as tungsten carbide make this vessel appropriate for sand separation also. VORTOIL hydrocyclone has small package footprint and low weight and its ramped geometry maximizes flow and minimizes erosion. It doesn't experience motion problems which makes it ideal for offshore applications while its required maintenance is minimum. Figure 122 shows the exact innovative operational scheme for VORTOIL hydrocyclone (*Retrieved from [www.cameron.slb.com](http://www.cameron.slb.com)*).



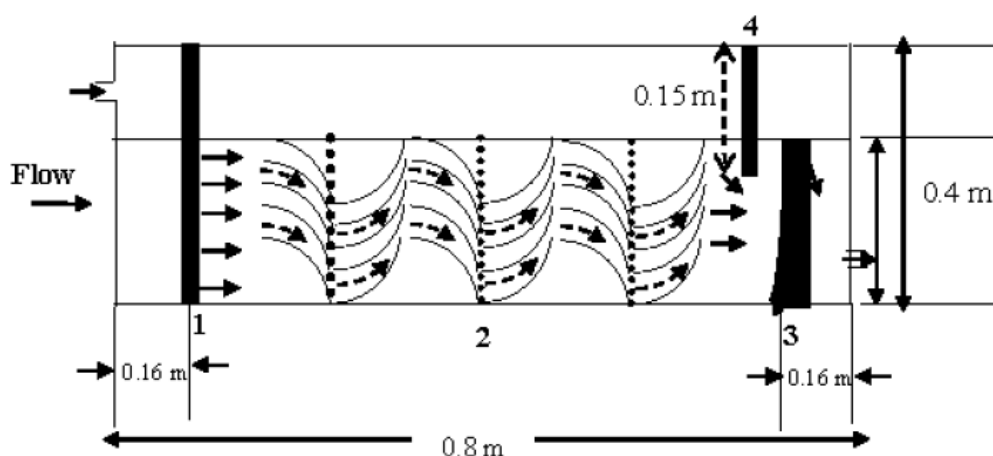
**Figure 122** - Operational scheme of VORTOIL hydrocyclone (*Retrieved from [www.cameron.slb.com](http://www.cameron.slb.com)*).

An experimental patent of hydrocyclone was proposed (Liu et al. 2005) for the treatment of produced water from polymer flooding processes. A double cone air sparged hydrocyclone (DcASH) was designed for this purpose and its configuration is illustrated in Figure 123. DcASH advantage when compared to conventional ASH hydrocyclones are that it can achieve efficiency of 90%.



**Figure 123 - DcASH (Liu et al. 2005)**

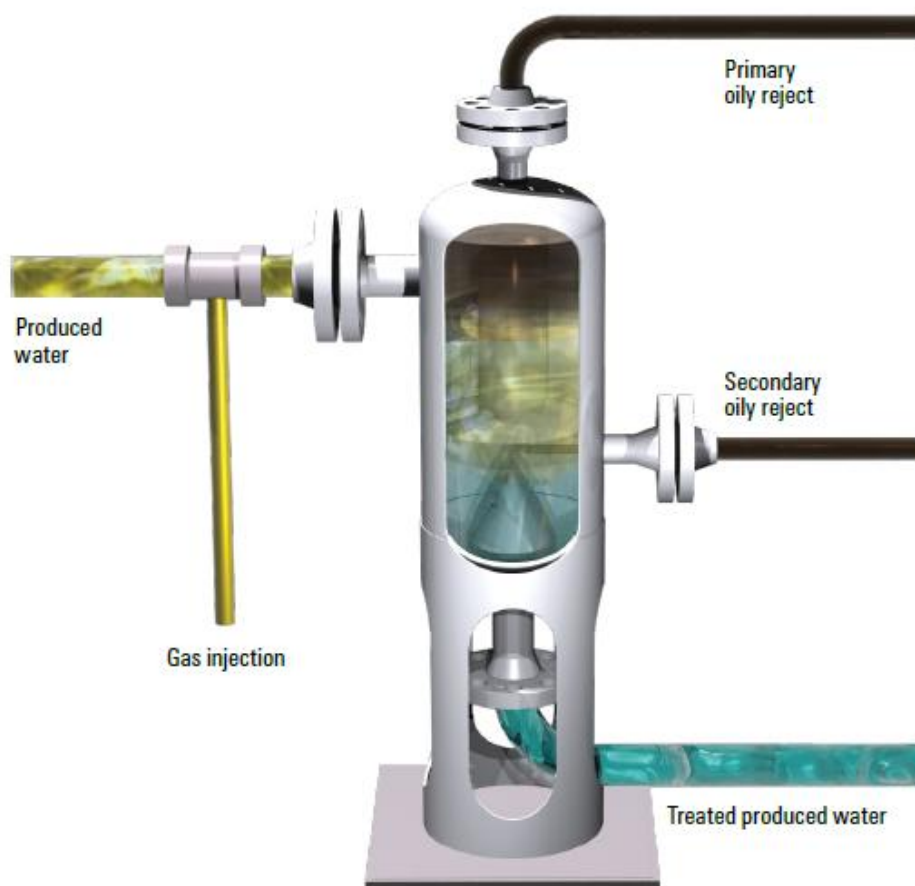
An experimental configuration of a bench scale prototype oil-water separator with series of inclined parallel arc coalescence plates (IPACP) was proposed (Almarouf et al. 2015) as illustrated in Figure 124. The idea is based on a rectangular settling basin equipped with multiple parallel arc coalescence plates of different angles. Oil droplets of higher than  $10\mu\text{m}$  diameter are removed through the proposed scheme which is more efficient in treatment of waters containing high levels of oil relative to dilute systems. The maximum removal efficiency achieved was 96.2%.



**Figure 124 - Proposed separation vessel configuration. (1-Vertical Slot Baffle, 2-Plate Pack, 3-Effluent Weir, 4-Oil Retention Baffle) (Almarouf et al. 2015)**

## Industrial Patents for Flotation Units

EPCON dual compact flotation unit (CFU) by M-I EPCON AS, a fully owned subsidiary of M-I SWACO - Schlumberger, is a vessel which is used for three phase separation (water/oil/gas) and has been proved efficient in oil in water emulsion breaking. The system is simple and it achieves optimal oil in water removal with 27% better separation rates than conventional technologies and 75% greater removal efficiency. The separation is promoted by gas flotation due to residual gas in water, added gas or both. Oil droplets are coalescing and separation from water is promoted. The operation scheme is shown in Figure 125. It's footprint is at least 50% smaller than other flotation units and it's operating life is long enough (Retrieved from <http://www.slb.com>).



**Figure 125 - EPCON dual CFU** (Retrieved from <http://www.slb.com>).

Technology for compact flotation units is proposed by different vendors and another industrial compact flotation unit is VORSEP by Siemens shown in Figure 126 installed in an offshore rig. VORSEP uses the patented Brise pump system for the creation of micro fine gas bubbles which are mixed into a dual sided impeller. Bubble sizes can be adjusted depending on the water characteristics. Turbulent flow in oil rigs resulting from motions can be confronted by the head-in-head arrangement of

Siemens which reduces turbulence and water carried with removed oil, maximizing the efficiency of separation (Retrieved from <http://www.energy.siemens.com>)



**Figure 126** - VORSEP installed in an oil rig (Retrieved from <http://www.energy.siemens.com>)

CAMERON proposed another compact flotation unit the TST CFU (Figure 127). This vessel is available as single or multiple stages vessel and it is designed to handle inlet oil concentrations over 1000 mg/l. Up to 4 stages can exist within one vessel configuration and their number is dependent on the inlet fluid conditions while retention time for each one can be reduced down to 20 seconds. Multiple separation stages within one vessel provide space saving which is critical for offshore installations. Special internals such as static mixture, riser pipe, distribution arms and guide vans have been developed for the mixing of oil and gas and their removal from water. Both induced and dissolved gas flotation is used in this system and its efficiency ranges between 90 and 98% (Retrieved from [www.cameron.slb.com](http://www.cameron.slb.com)).



**Figure 127** - TST Compact Flotation Unit (Retrieved from [www.cameron.slb.com](http://www.cameron.slb.com)).

Gas flotation is considered as a very effective method for removing hydrocarbons from water. Its efficiency can be raised by increasing the amount of gas that is introduced into the treated fluid. That means that the bigger is the amount of bubbles in the treated fluid, the better separation of oil in water emulsions will occur. Another decisive factor for flotation efficiency is the coalescence of the oil droplets. This can be enhanced by the introduction of coagulants. Table 18 summarizes some of the most important commercially available patented flotation equipment and its special attributes

Manufacturer	Model Name	Technology	Additional Remarks
UNICEL Vertical IGF	Unicel	Vertical Induced Gas Flotation	<ul style="list-style-type: none"> <li>- Capacity: 160 m<sup>3</sup> d<sup>-1</sup> to 25,400 m<sup>3</sup> d<sup>-1</sup></li> <li>- Effluent Oil Concentration: 5-10 mg L<sup>-1</sup></li> <li>- Use of baffled central rise for better contact and radial dispersion of oil-solid flocs</li> </ul>
EPCON Dual Multistage Compact Flotation Unit Technology,	Epcon DualCFU	Centrifugal Force and Flotation	<ul style="list-style-type: none"> <li>- Capacity: 72 m<sup>3</sup> d<sup>-1</sup> to 24,000 m<sup>3</sup> d<sup>-1</sup> Single stage</li> <li>- Effluent Oil Concentration: &lt;10 mg L<sup>-1</sup></li> <li>- Internal design</li> </ul>

Schlumberger			enhancement to reuse the previously lost excess gas for better oil water separation efficiency
	Siemens	Quadricell	Mechanical Induced Gas Flotation - Capacity: Up to 5000 mg L <sup>-1</sup> - Effluent Oil Concentration: <5 mg L <sup>-1</sup> - The Quadricell separator uses four cells in series for maximum liquid/air contact
	Siemens	Spinsep Vertical	Vertical column Induced (Eductor), Dissolved Gas (Brise) Pump or sparger - Capacity: 654 m <sup>3</sup> d <sup>-1</sup> to 15,808 m <sup>3</sup> d <sup>-1</sup> - Coalescing device(SPIRALSEP) at the pipe inlet; -90° inlet angle to create circular motion for better agglomeration; Packing scrub for oil droplet coalescence
	Siemens	Veirsep Horizontal	Horizontal configuration with Induced (Eductor), Dissolved Gas (Brise) Pump or sparger - Capacity: 164 m <sup>3</sup> d <sup>-1</sup> to 23,984 m <sup>3</sup> d <sup>-1</sup> - Coalescing device (SPIRALSEP) at the pipe inlet - Multi cell flotation chamber; - Pressurized and atmospheric configuration is possible
	Siemens	Hydrocell Hydraulic IAF	Horizontal Hydraulic (educator) induced air flotation -Capacity:556 m <sup>3</sup> d <sup>-1</sup> to 15,900 m <sup>3</sup> d <sup>-1</sup> - Patented educator induce and disperse gas bubbles
	Technologies	AutoFlot-Mechanical	Horizontal Mechanical Induced air flotation - Capacity: 1248 m <sup>3</sup> d <sup>-1</sup> to 27,264 m <sup>3</sup> d <sup>-1</sup> - Reduces free oil and solids by 90-95% with maximum inlet concentrations of 200 mg L <sup>-1</sup> of free oil and less than 100 mg L <sup>-1</sup> of total suspended solids
	Exterran	Revolift VS Flotation	Induced gas flotation systems - Capacity: 795 m <sup>3</sup> d <sup>-1</sup> to 4372 m <sup>3</sup> d <sup>-1</sup> (possible to reach 23,848 m <sup>3</sup> d <sup>-1</sup> with

Cameron	other configuration);		- Effluent water quality targets of $< 20 \text{ mg L}^{-1}$
	TST CFU		- Multi-chambered design
	Vertical Multi-stage separation with dissolved or induced gas flotation		<ul style="list-style-type: none"> <li>- Capacity from <math>120 \text{ m}^3 \text{ d}^{-1}</math> to <math>16,800 \text{ m}^3 \text{ d}^{-1}</math></li> <li>- Design consists of special internals that includes static mixture, riser pipe, distribution arms and guide vanes</li> <li>- Capable of handling in oil content (<math>1000 \text{ mg L}^{-1}</math>) and can achieve below <math>10 \text{ mg L}^{-1}</math> Oil in Water through multiple stages</li> </ul>

**Table 18** - Commercial gas flotation equipment used for oil in water emulsion treatment (Saththasivam et al. 2016)

An experimental study (Thoma et al. 1999) described a Dissolved Air Precipitation (DAP) process through bubble generation by dissolved air precipitation for use in solvent sublation bubble columns. This process can be described as a non foaming adsorptive bubble separation. Air is precipitated into water and forms bubbles of 60-100 mm diameter through a valve. Results of the experiment shown removal of dissolved octane of 95%, micro-dispersed decane of 75% and dissolved ethylbenzene of 40%.

## Industrial Patents for filtering technology

An industrial commercial example of media filter is PROSHELL nutshell media filter by PROSEP. Pecan/walnut media used in this filter eliminates the need for backwash water, scouring and surfactants. It's oil in water removal efficiency reaches 95% while it can reach 98% with the proper chemical demulsifying program, removing droplets larger than 3 microns (Retrieved from [www.prosep.com](http://www.prosep.com)).

Another proposed filtering system is Woolspill (Figure 128) by HYDRO-CARBON Filtration and Separation Company. It's an oil adsorption system which is composed of a natural wool product with the ability to adsorb up to 36 times its own weight in oil. Woolspill utilizes the natural affinity of wool for oil adsorption and it is effective for all hydrocarbons, particularly for highly viscosity oils. It is biodegradable and it is considered as one of the best adsorbents commercially available. Its adsorption mechanism is based in the fact that wool fibers have an oleophilic outer cuticle which tends to be covered in natural greases and a hydrophilic central structure. It is about

the size of a pea known as knop and it consisted of up to 300 fibers which form a spherical shape. Fibers are of 30-38 microns in diameter. It is available in the market in form of loose granulated product or as a continuous non woven material. A commercial filter has been developed by the company for the total remove of petroleum hydrocarbons and suspended solids from water in cases where traditional separation vessels fail (Retrieved from <http://www.hydro-carbon.nl>) .



**Figure 128 - Woolspill** ((Retrieved from <http://www.hydro-carbon.nl>)).

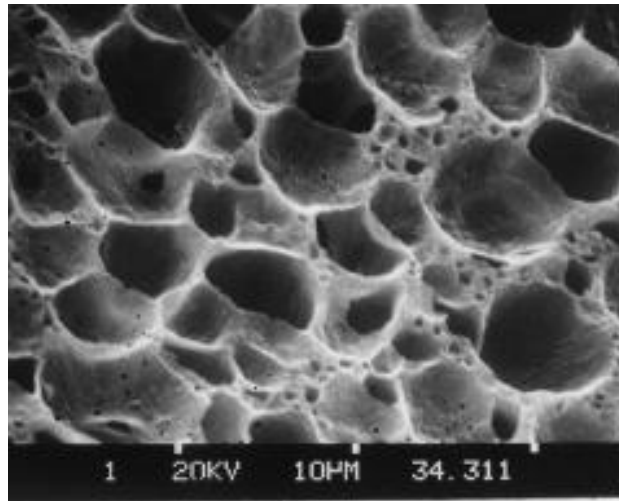
Biological aerated filters (BAF) are bio-filters that use permeable media for the facilitation of biochemical oxidation and removal of emulsions from water stream. Their filtering media have a 4 inch diameter for the prevention of clogging of pore spaces and it is effective for water streams with chloride levels below 6600 mg/l. It's oil removal efficiency can reach 80%. BAF systems have a long lifespan, they do not require chemical addition, they are cheap but they require solids disposal for accumulated sludge (Igunnu and Chen 2012).

AMIAD filtration systems has introduced EBS filters in the market. Their main advantage is that they are fully automatic with an electric self-cleaning mechanism. They can treat oil droplets of size down to 10 microns. An EBS filter is shown in Figure 129 (Retrieved from [www.amiad.com](http://www.amiad.com)).

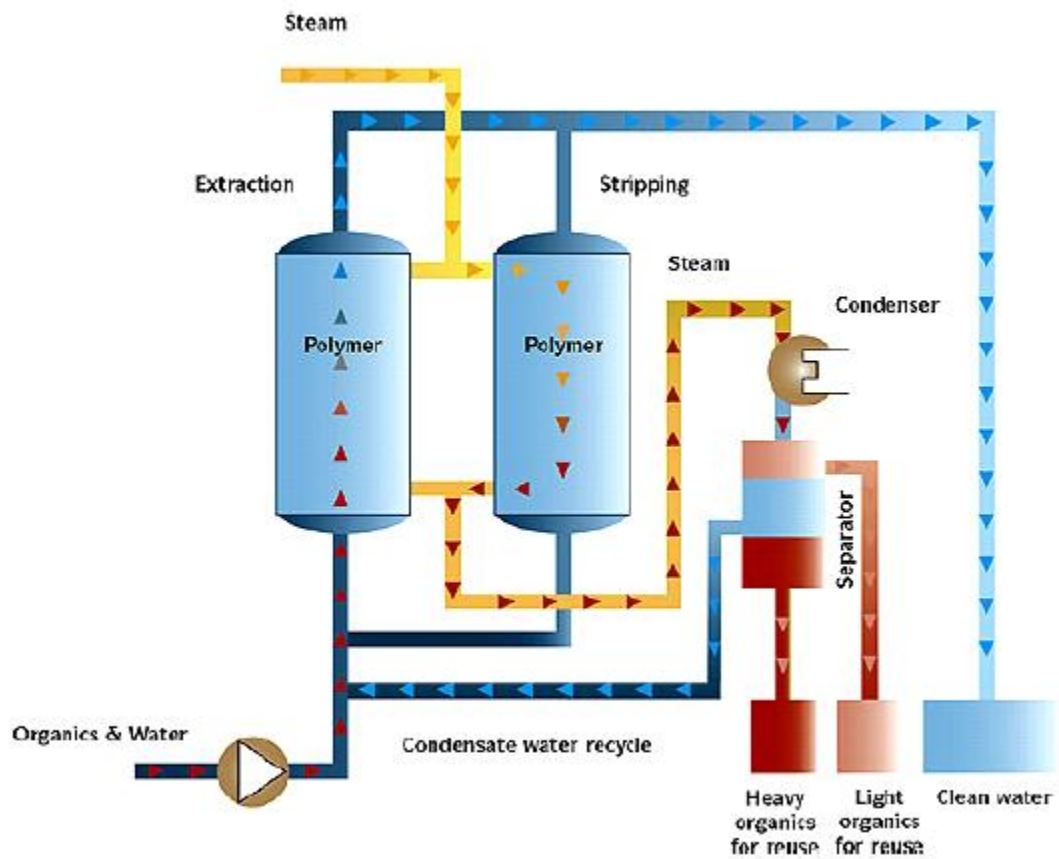


**Figure 129 - EBS Filter** (Retrieved from [www.amiad.com](http://www.amiad.com))

Macro Porous Polymer Extraction (MPPE) technique has shown a 99% reduction of dispersed hydrocarbons in water, promoting the breaking of oil in water emulsions (Meijer 2007). MPPE is a liquid-liquid extraction technology which internal structure of the macro porous polymer is shown in Figure 130 and an industrial unit of it is shown in Figure 132. The principle of usage of this technology is shown in Figure 131 and it's based on a flow of the emulsified water stream through a column packed with MPPE particles. Extraction liquid included in the polymer beads are breaking the emulsions by removing the hydrocarbon components. Aliphatics, aromatics, polyaromatics and chlorinated hydrocarbons can be removed with efficiency of 99.9% (Meijer 2007). Major users of this technology both onshore and offshore are Total, Shell, Exxon, Statoil, Offshore South China Sea, Woodside Pluto, Inpex Ichthys FPSO, and BP.



**Figure 130** - *Internal structure of a MPPE (Meijer 2007)*



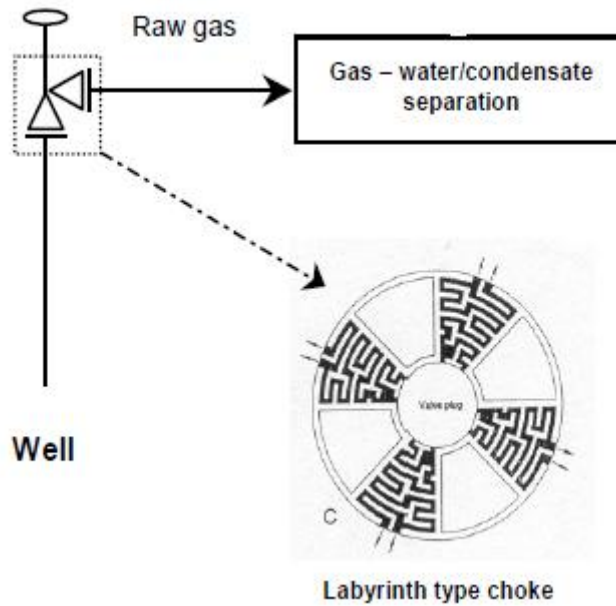
**Figure 131** - *Principle of MPPE process (Meijer 2007)*



**Figure 132 - MPPE industrial unit (Meijer 2007)**

### **Labyrinth type choke valve**

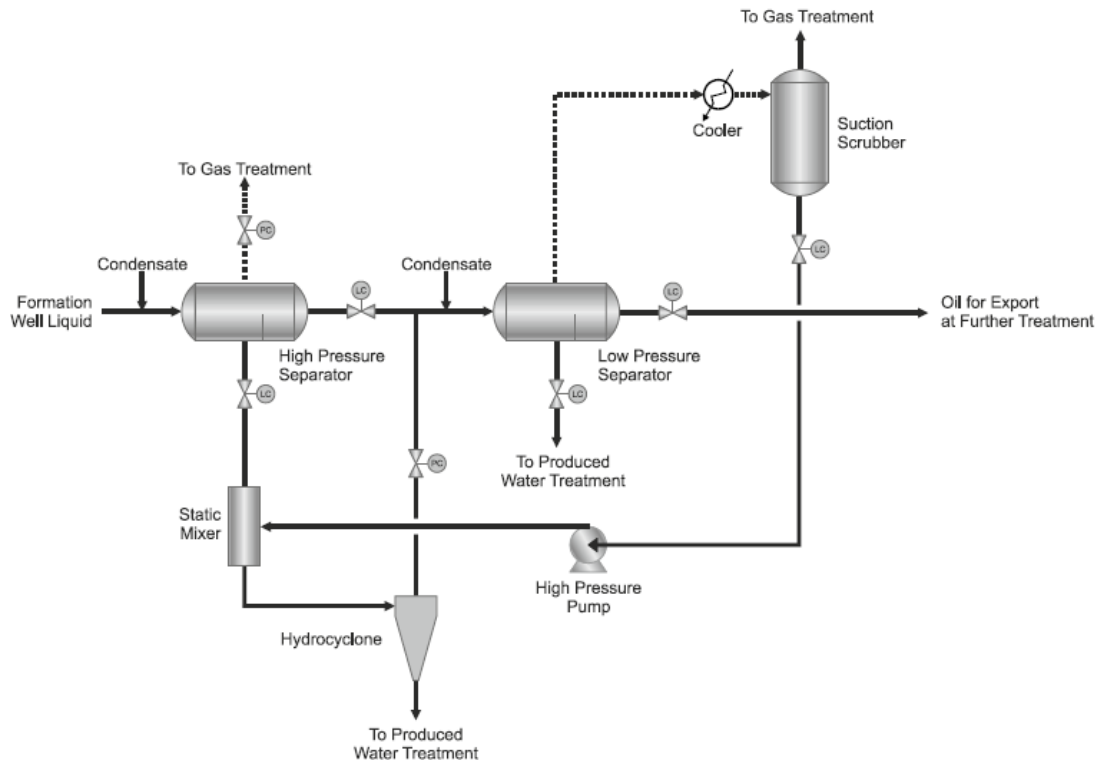
Originally designed to minimize the sound produced by valves, this kind of equipment proved to be efficient in minimizing the shear rates leading to maximization of oil droplets' size and subsequent simplification of the separation process. Figure 133 illustrates its position in the treating scheme. It is preferred for stream stripping technique which will be discussed later on. Gas is pressurized through friction and its speed is subsonic instead of sonic as in conventional chokes (OSPAR Commission 2013).



**Figure 133** - *Labyrinth type choke (OSPAR Commission 2013)*

## The CTour process

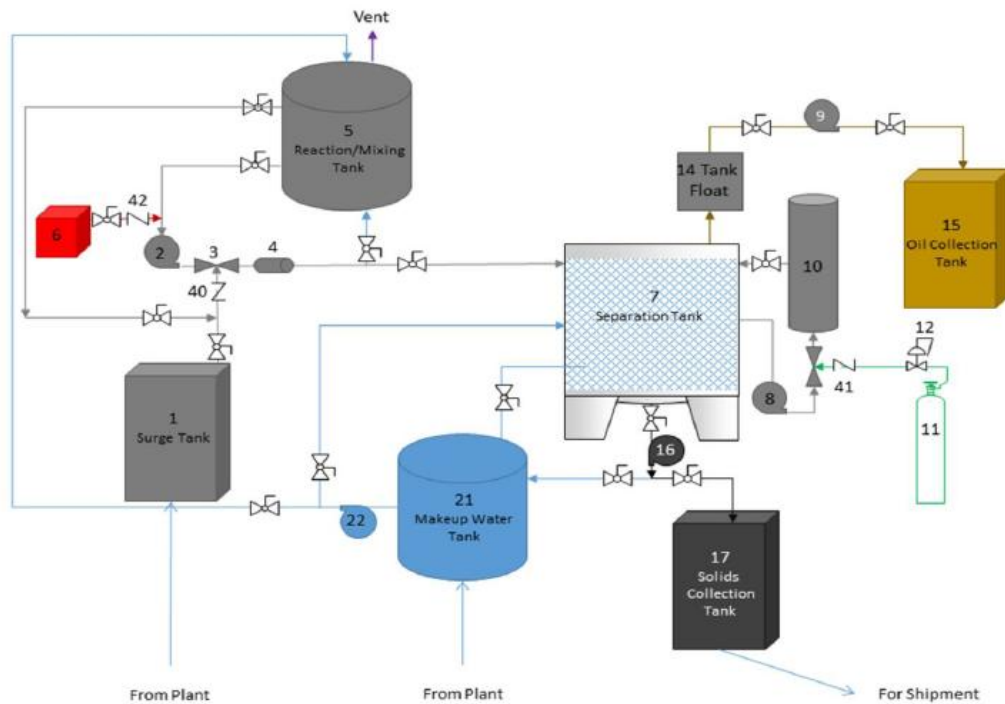
CTour is a process that uses condensates to remove oil in water. After the use of all ordinary measures for the removal of oil from water, condensate is added as an extraction agent. Oil that is dissolved in the water turns into droplets under the presence of the condensate and the mix of condensate/oil is completely removed by a hydrocyclone. A sketch of the typical process is shown in Figure 134. This process was developed at the RF-Rogaland Research Institute and at Norsk Hydro Research Center in Norway with the participation of Statoil, Norsk Hydro, BP, Shell, Philips, Elf, KPS and RF. For the successful operation of the CTour process a condensate of sufficient volume must be collected which will remain liquid at the operating pressure and temperature. It must be injected in 0.3-2% (volume/volume) ratio, in the water, upstream to the treatment equipment. Sufficient mixing and dispersion of the condensate must take place and retention time adequate enough (3-5 minutes) should be provided so that oil droplets are formed. Those oil droplets should be removed then and recycled back to the hydrocarbon recovery system (Voldum et al. 2008).



**Figure 134 - Typical CTour process operation sketch (OSPAR Commission 2013)**

## SEAIR inc Oil Sludge Treatment Process

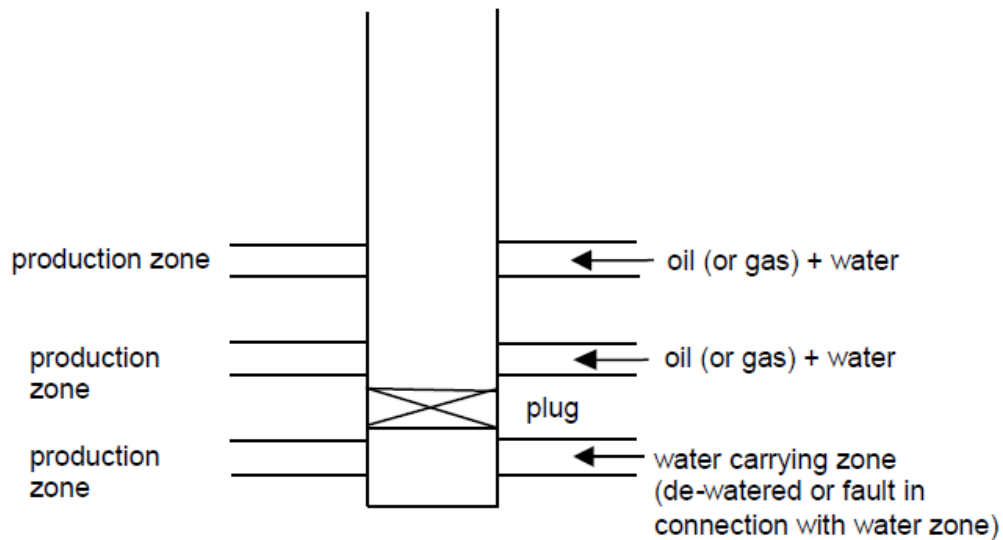
SEAIR inc has introduced a scheme for oil sludge treatment (Figure 135) which involves oil in water emulsion breaking by diffusing gasses into liquids with lower costs. Process fluid enters the SEAIR diffusion chamber where gas is introduced. Sludge is added to water together with proprietary chemical. Then the liquid flows into SWEET (Superior Water Emulsion Effacing Treatment) vessel where microbubbles attach to the dispersed oil droplets leading to separation of sludge into clean saleable oil, water for disposal and solids. To achieve this the mixture should be allowed to settle over a period of 30 to 90 minutes. A float system will then draw clean oil and pump it to an oil collection tank while the solids will be pumped off the bottom transfer line. Nitrogen will be injected if further oil separation is needed. Through this process sludge volume is reduced by 80% and 20% of its initial volume is recovered as saleable oil which in economical terms is translated into total annual value of 485,000\$ for volumes of 5 m<sup>3</sup>/day (Retrieved from [www.seairinc.com](http://www.seairinc.com)).



**Figure 135 - SWEET oil sludge treatment scheme** (Retrieved from [www.seairinc.com](http://www.seairinc.com)).

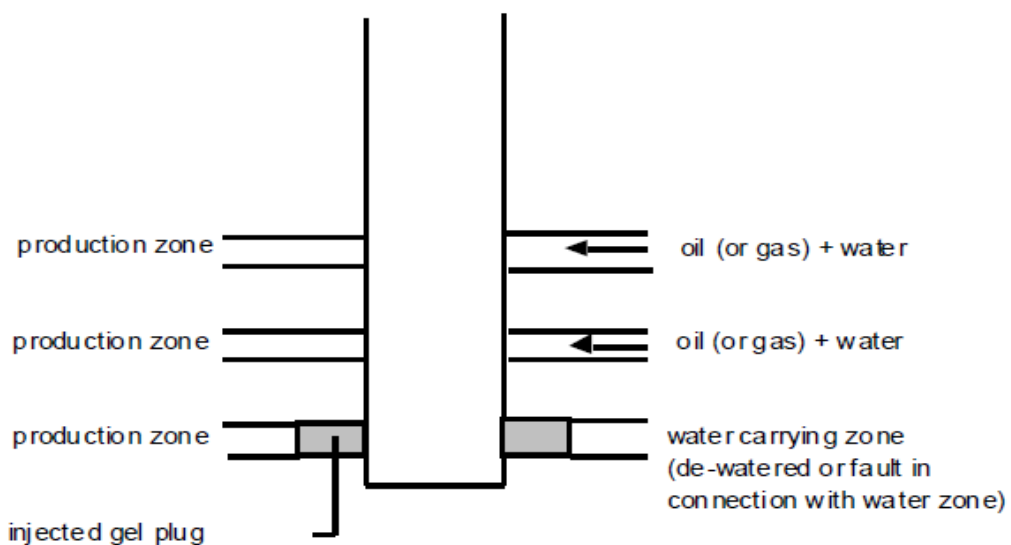
## Mechanical and chemical water shut-off techniques

A technique for the minimization of produced oil in water emulsions is the mechanical water shut-off which is applied when water breakthrough occurs. Figure 136 illustrates its operation principles. Production zones with high watercut percentages are sealed by plugs, cementing placement of expansion pipes or pack off in possible combination with chemical shut off. Dispersed oil in the surface produced water can be reduced by 50-75% with the use of this technique and it is used for multi-layer reservoirs. Its application is rare in horizontal wells due to difficulties related to the orientation of the well and increased cost. The chemical use is reduced leading to reduce of costs for breaking of oil in water emulsions (OSPAR Commission 2013).



**Figure 136 - Mechanical water shut off operating scheme (OSPAR Commission 2013)**

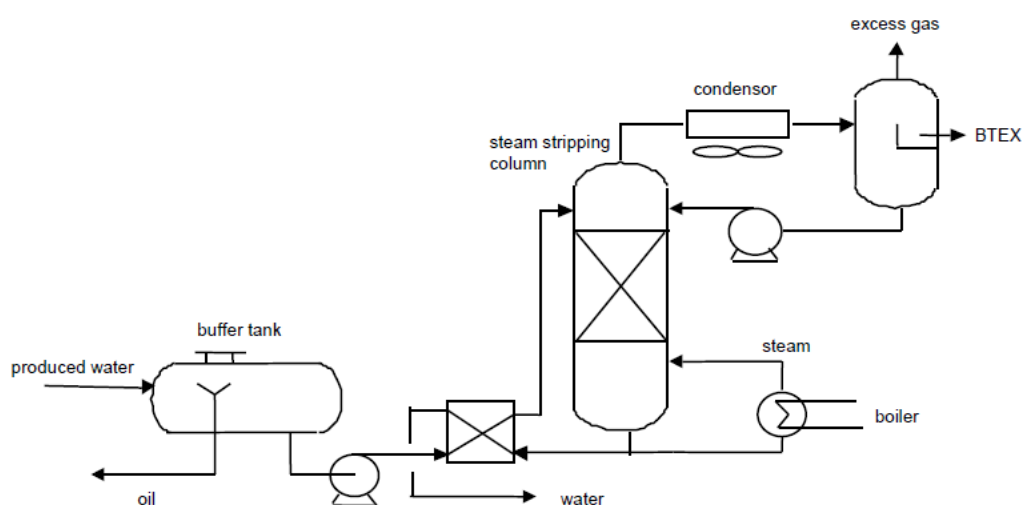
Chemical water shut off is based on the same strategy of minimizing oil in water emulsions in the surface produced water. Figure 137 illustrates its operation principles. Special polymers such as cross-linkers which form a water-blocking gel are used. Chemical water shut off advantage over mechanical is that the full diameter of the well remains available for repairs and that the chance of bad sealing is less while its disadvantage is that this gel cannot be removed in case of production reduction. Dispersed oil is reduced by 50%. This technique's limitation is that it's not applicable if reservoir temperature exceeds 150°C but contrary to the mechanical water shut off, it can be applied easier in horizontal wells (OSPAR Commission 2013).



**Figure 137 - Chemical water shut off operating scheme (OSPAR Commission 2013)**

## Steam stripping technique

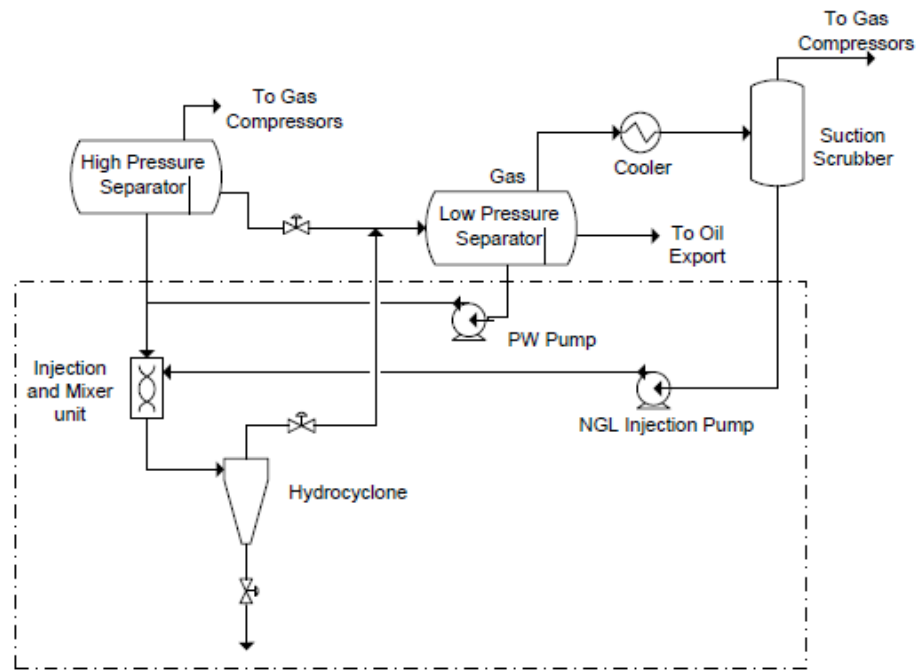
Hydrocarbon removal from water in offshore installations by means of steam stripping is common in the industry. Water flows into a packed column where steam is applied. Steam of high hydrocarbon content condenses the hydrocarbons that are dissolved or dispersed in the water leading to oil in water emulsion breaking and easy extraction from the aqueous phase. Figure 138 illustrates the process diagram of steam stripping. Dispersed oil can be reduced by 97%. Buffer tank which ensures constant flow and skimming of oil needs to be installed. A major drawback of this technique is that energy consumption levels are high (OSPAR Commission 2013).



**Figure 138** - Steam stripping process diagram (OSPAR Commission 2013)

## Condensate induced extraction technique

This technique is based on injection of condensate into the water stream for oil in water emulsion resolution. The condensate coalesces with the dispersed oil droplets into larger ones. Those large oil droplets have low density and can be efficiently separated by other deoiling devices such as hydrocyclones. This technique has been implemented successfully in Statfjord B and C, Ekofisk 2/4J, Snorre A, Aagsgard A and Troll C platforms and a typical schematic is shown in Figure 139 (OSPAR Commission 2013).



**Figure 139** - Typical condensate induced extraction technique within an oil in water emulsion treatment system (OSPAR Commission 2013)

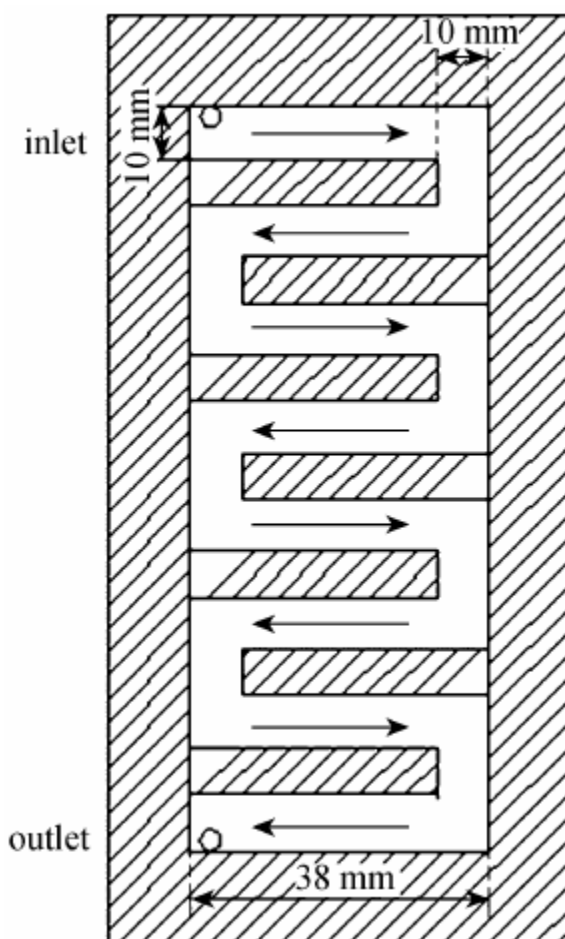
## Membranes for oil in water emulsion treatment

Microfiltration techniques have evolved lately as an alternative for the treatment of oil in water emulsions, especially in offshore fields due to lack of space which is required for bigger installations like hydrocyclones. Tangential flow microfiltration for the separation of solids from produced liquids has been applied for decades (Wan 2014). Microfiltration membrane technology has become very popular for oil in water treatment over the last years since it can be more economically viable than other methods proposed, their use demands lower energy and it involves no moving parts of equipment.

Crossflow membrane microfiltration (CFMF) and ultrafiltration (CFUF) are suggested in various studies (Scott et al. 2000, Van der Waal and Racz 1989, Lopez 1995, Koltuniewicz et al. 1995, Hlavacek 1995 and Hu and Scott 1997) to treat oil in water emulsions. Polytetrafluoroethylene Hydrophobic Membranes (PTFE) are a notable subcategory of the membranes used for oil in water emulsion treatment. However in this kind of treatment, optimization of the proposed processes is required. To achieve this, increasing temperature, pressure and flow are needed for the proportional increase of the permeate flux. Moderate temperatures and pressures in combination with the maximum possible flow rate is recommended for the best results (Sadrzadeh et al. 2008).

Novel felt-metal supported PVA composite hydrophilic membranes using cross flow ultrafiltration have been proposed (Wang et al. 2012). The experimental process in

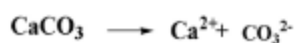
this case involved a confined space apparatus which formed a thin channel of flow between two parallel plastic plates (Figure 140). Oil droplets were attached in the plate's surfaces and coalesce. Polypropylene plates were found to have the best efficiency in this case.



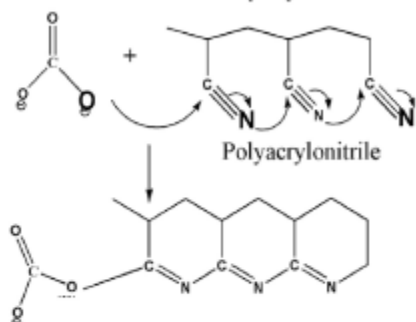
**Figure 140** - Shape of the flow channel (Wang et al.2012)

Polyacrylonitrile (PAN) based ultrafiltration membranes are proposed (Melbiah et al. 2017) in a recent study for oil in water emulsion treatment. Those membranes are based in blending of amphiphilic Pluronic F127 copolymer and inorganic calcium carbonate ( $\text{CaCO}_3$ ) nanoparticles by a nonsolvent induced phase inversion process. The proposed mechanism is shown in Figure 141. Calcium carbonate increased the efficiency of the membrane since its ions interact effectively with water through hydrogen bonding of electrostatic attraction leading to enhancement of hydrophilicity, which coupled with the large number of pores of the membrane lead to excellent antifouling properties. The addition of Pluronic F127 improved the antifouling properties of the membrane. The PAN/PF127/ $\text{CaCO}_3$  membrane was found efficient for oil in water emulsion treatment with droplet sizes lower than 10 microns.

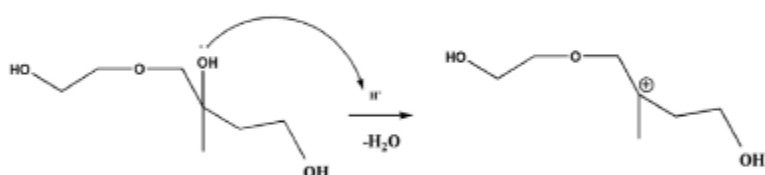
i) Generation of carbonate anion :



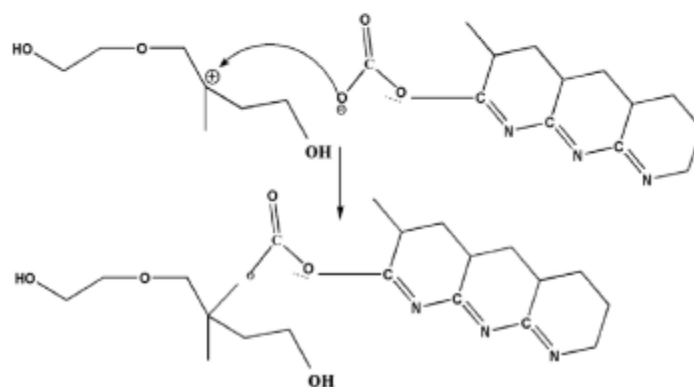
ii) Attack of carbonate anion on Polyacrylonitrile :



iii) Generation of 3<sup>o</sup> Carbocation from Pluronic Acid :



iv) Attack of cation to the carbonate ion :

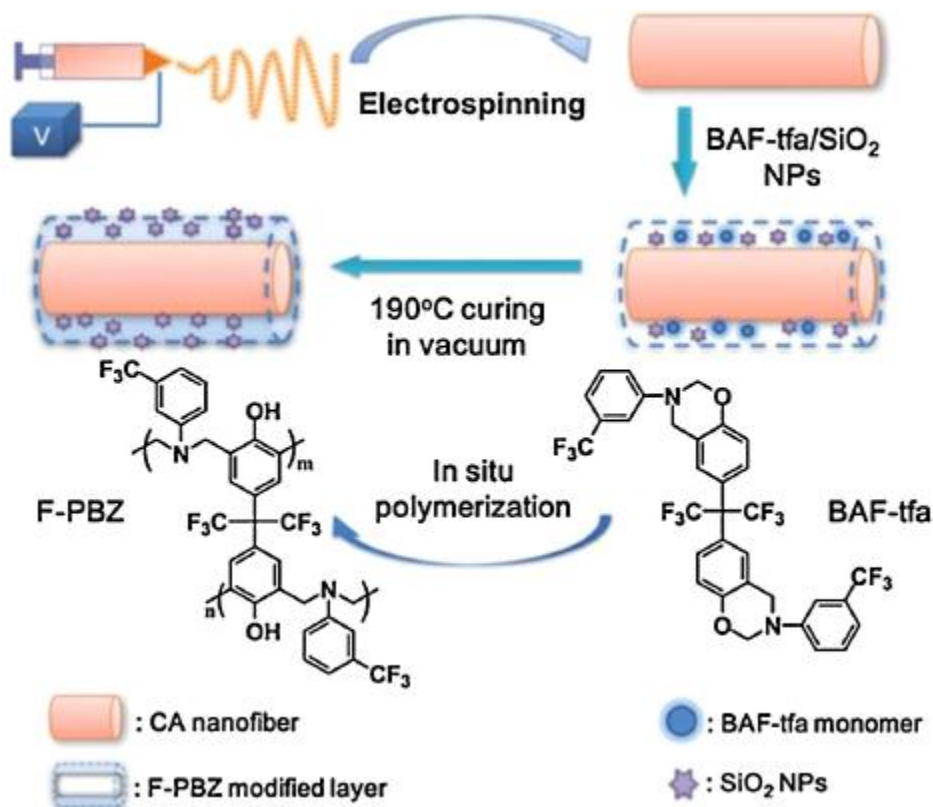


**Figure 141** - Proposed chemical mechanism for Pluronic 127 and  $\text{CaCO}_3$ , PAN membrane (Melbiah et al. 2017)

In another study (Liu et al. 2016) stainless steel meshes (SSMs) and polyvinylidene fluoride (PVDF) membranes were coated with polyaniline nanofibers in a one step dilute polymerization process at low temperatures. Those membranes were found efficient in oil in water emulsion separation, suggesting that nanostructured conductive polymers of high nitrogen content are proper materials for the fabrication of oil in water emulsion separation membranes.

Different types of nanofibrous sorbents have been developed in the industry due to ability of those materials to drive the oil in the voids between the fibers and their multipores leading to enhanced oil-water separation. Hydrophobic oleophilic polymer, composite and carbon nanofibers are the three main categories of nanofibrous sorbents. Their high separation efficiency makes them ideal for construction of nanofibrous membranes for oily wastewater treatment. In a recent study (Wang 2015)

the efficiency of electrospun nanofibrous materials was investigated. In the aforementioned study, nanofibrous membranes with electrospun nanofibers and an in situ polymerized fluorinated polybenzoxazine (F-PBZ) functional layer that incorporated  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$  are proposed. Both of them have shown good antifouling properties and efficient oil in water emulsion separation. The in-situ process of polymerization for the synthesis of F-PBZ/ $\text{SiO}_2$  nanofibrous membrane is illustrated in Figure 142.

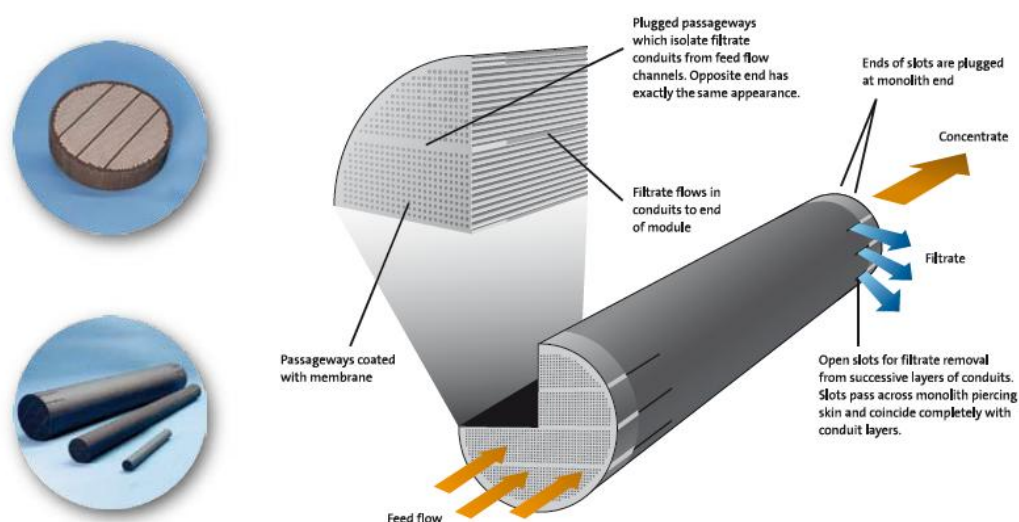


**Figure 142** - Schematic showing the in-situ polymerization approach to the synthesis of F-PBZ/ $\text{SiO}_2$  NPs-modified CA nanofibrous membranes (Wang et al. 2015)

In another study (Lee et al. 2013) electrospun polystyrene nanofiber membrane with superhydrophobicity and superoleophilicity for selective separation of water and low viscous oil was proposed as highly efficient in removal of diesel from water. A study (Liao et al. 2014) proposed membrane of  $\text{CaCO}_3$  mineralized PAA-grafted PP which achieved an oil in water emulsion removal efficiency of >99%. A membrane of  $\text{SiO}_2$  NPs-SNM is proposed in another study (Yang et al. 2014) as highly efficient oil in water emulsion remover. PVA/PAN composite membranes are also proposed (Wang et al. 2010) as highly efficient oil in water emulsion treating membranes since an efficiency of 99.5% in emulsion removal was achieved. A Janus nanofiber polyacrylonitrile (PAN) membrane with a single-side hydrophobic carbon nanotube network for oil in water emulsion separation was also proposed (Jiang 2017) and its separation efficiency was 99.7%.

VEOLIA has introduced in the market the CeraMem membrane technology for both microfiltration and ultrafiltration applications related to oil in water emulsion removal

from water. The design of CeraMem allows the utilization of large diameter monolith membranes, reducing the footprint of installed equipment. Separation is promoted by very high packing density in a single membrane module. Its cleaning and regeneration is easy and Figure 143 shows the key features of it (Retrieved from [www.veolia.com](http://www.veolia.com)).



**Figure 143 - CeraMem** (Retrieved from [www.veolia.com](http://www.veolia.com))

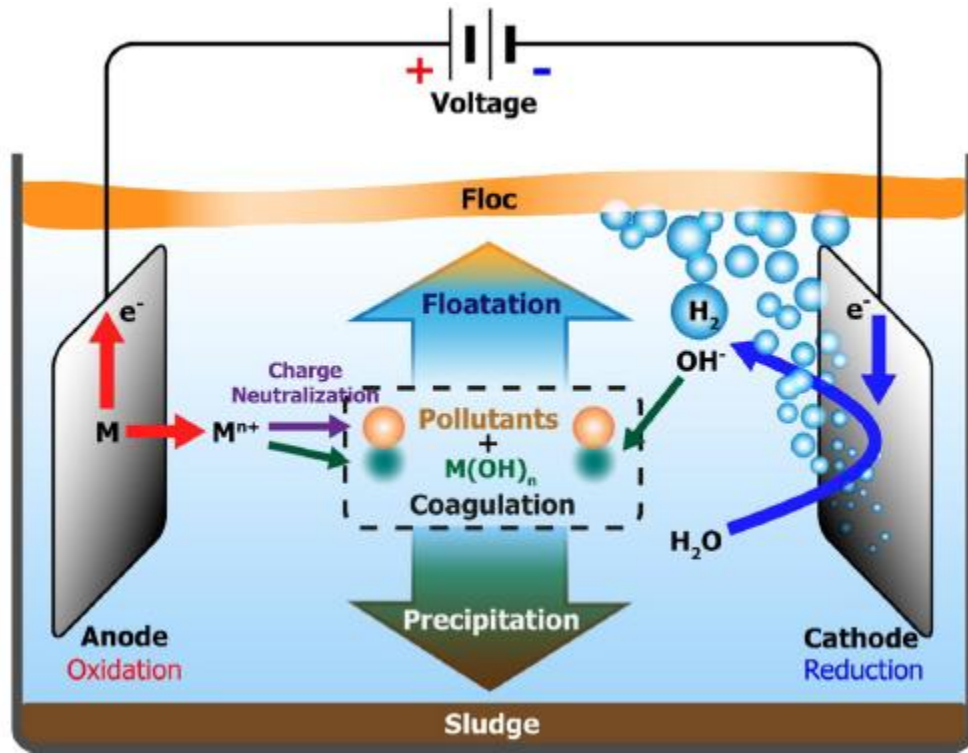
A study (Xiang et al. 2015) proposed a superoleophobic PVDF membrane by polydopamine for oil in water emulsion breaking. A conventional polyvinylidene fluoride membrane was modified with dopamine and produced good results of separation of oil in water emulsions for oil concentrations below 80 ppm. The particular membrane was proved fouling resistant and able to recover flux.

Sponges prepared by facile dip coating in stearic acid solution and heat treatment were proposed (Wang et al. 2017) for treatment of oil in water emulsions. Oil droplets are separated effectively from water via a vacuum system by sponges that can sorb 17.4-41.6 times their own weight for more than 100 cycles. The process is described as simple and low-cost and it is important to highlight its oil-recovery ability through simple squeezing of the sponges.

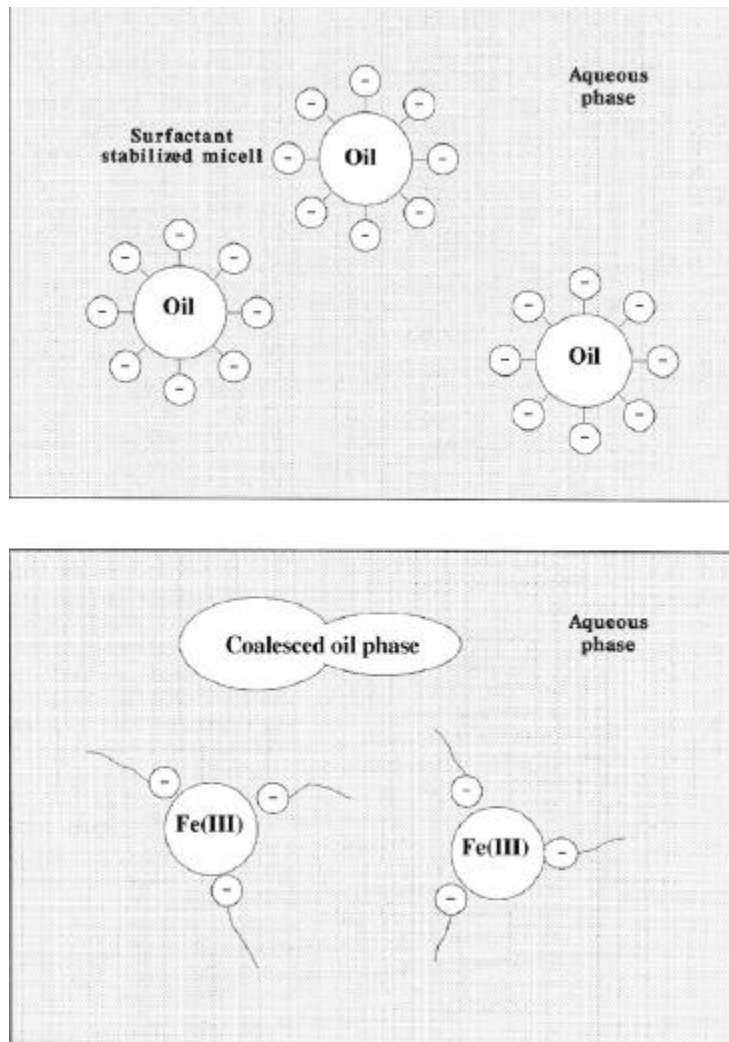
## Electrochemistry in oil in water emulsion treatment

Electrocoagulation is another experimental method which is proposed in studies (Ma 2006, Younker et al. 2011, Karhu et al. 2012, Abdel-Aziz et al. 2016 and An et al. 2016) for oil in water emulsion breaking although electrical demulsification has seldom been applied for destabilization of oil in water emulsions (Zolfaghari et al. 2016). Electrocoagulation occurs when a direct electric current passing through electrolyte, produces dissolution of metal cations at the anode and hydroxyl ions and hydrogen gas at the cathode as illustrated at Figure 144. The cations that can be  $\text{Al}^{3+}$ ,

$\text{Fe}^{2+}$  etc are destabilizing oil in water droplets by neutralizing their charge as illustrated in Figure 145, leading to resolution of emulsions. Monomeric and polymeric hydroxide products, acting as coagulants, are produced also (An et al. 2016).



**Figure 144** - Mechanism of electrocoagulation (An et al. 2016)



**Figure 145-** *Stabilization of an oil in water emulsion under surfactant (top), destabilization and coalescence of oil droplets by cations (bottom) (Yang 2007)*

An experimental process of electrocoagulation is proposed in a study (Abdel-Aziz et al. 2016). The idea is based in a horizontal coiled aluminum cylinder which acts as an anode and a horizontal aluminum disc at the bottom of the cell which acts as a cathode. Anode outer surface permits electrocoagulation while inner surface acts as a temperature control panel. Depending on the current density, electrolyte conductivity, initial pH of the electrolyte and oil concentration the percentage of oil removal can reach 99.72%. Better separation occurs for higher current density, pH in the range of 3-8 and high electrolyte concentration while it is affected negatively by increased initial oil concentrations. It can be considered as a cheap solution of oil in water emulsion treatment compared to this of chemical coagulation since it can be set up by cheap scrap iron and aluminum. Another study (Karhu et al. 2012) proposed also aluminum or stainless steel as anodes for the treatment of oil in water emulsions and concluded that it is a cost effective treatment method. A study (Ma 2006) proposed the use of double anodes with active metal, graphite and iron as cathode for the reduction of COD by 90% within a 6 minute time span through production of  $\text{Mn}^{2+}$  which promoted coagulation of organic pollutants. An experimental study (Younker

et al. 2016) achieved a removal rate of 56% for electrical coagulation. However, high voltages can cause re-emulsification and the efficiency of electric coalescence of oil in water emulsions depends on type and concentration of their chemical constituents and the water content. A study (Ichikawa et al. 2004) proposed that the increase of electrolyte or the decrease of the ionic surfactant concentrations enhances the chemical demulsification. This study also proposed that the denser is the emulsion the faster the demulsification process.

### **TwinZapp technique**

TwinZapp is a combination of electrical oxidation and filtration. The configuration of the system involves electrical oxidation cells with multiple metal electrodes and the application of a direct current voltage. The release of radicals such as oxygen and hydroxyl destabilize the surface-active components and create free oil layer which is then collected by filtration medium with an oil in water emulsion breaking efficiency higher than 90% (OSPAR Commission 2013).

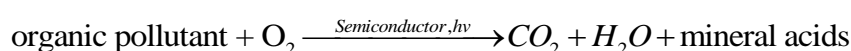
### **Microwave irradiation treatment of oil in water emulsions**

This technique was first proposed (Wolf 1986) as a superior heating technique over the conventional heating schemes. Demulsification through microwave treatment occurs due to two basic phenomena. Firstly the temperature of the water phase increases due to reduction of viscosity and the drainage of the interfacial film. Heating doesn't depend on conductivity and is faster. Secondly, molar rotation takes place under microwave radiation. Due to charging of droplets, the distribution of ions in the interfacial regions is affected. Accumulation of ions of opposite charge to the droplets is taking place and the emulsion collapses due to neutralization of Zeta potential. This technology can be considered as emerging and promising due to the fact that it is cheap and highly efficient and is minimizing the use of chemical demulsifiers (Martinez-Palou et al. 2013). Microwave power and time are the two main factors that affect the optimization of this technique. Overheating of oil in water emulsion systems is typical over the attempt of enhancing the separation through this technique and it should be avoided (Zolfaghari et al. 2016). The introduction of salt in the oil in water emulsions has been proposed by various studies (Martinez-Palou et al. 2013 and Kuo and Lee 2010) for enhancement of separation.

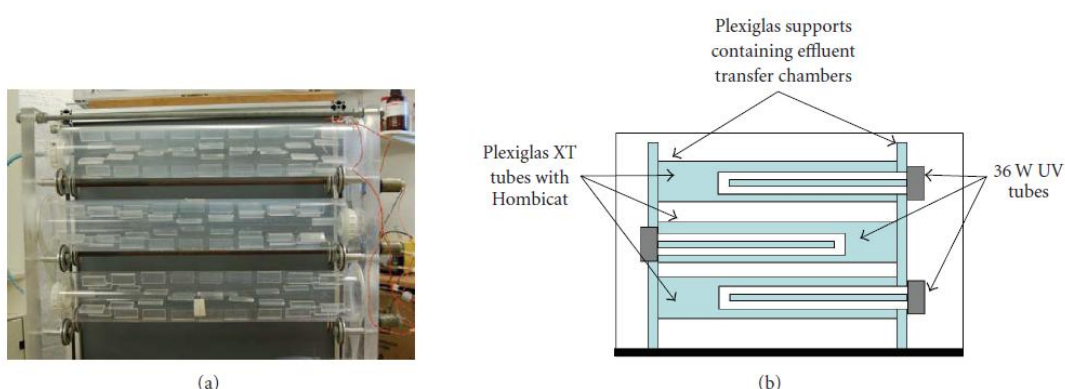
### **Photocatalytic methods for oil in water emulsion treatment**

The general chemical process through which organic pollutants are removed from water is described in Equation 18. Studies (Bessa et al. 2001, Li et al. 2006 b & 2007, Adams et al. 2008 and Wang et al. 2016) proposed different processes for photocatalytic treatment. In two of those studies (Li et al. 2006 & 2007), the method

of photoelectrocatalysis is proposed as much more effective than the photocatalytic methods since its COD removal efficiency of produced water was much higher for photoelectrocatalysis method. A process using a drum reactor of titanium substrate with a single pass continuous flow system for water treatment was proposed (Adams et al. 2008), which resulted in reduce of hydrocarbons content in water by 90% within 10 minutes. UV sunlamp tubes were used in this case for the irradiation of the reactor drums. A configuration of this reactor is shown in Figure 146. An experimental study (Wang et al. 2016) proposed an effective photocatalytic demulsification process through alteration of the electrical balance of oil in water emulsions after introducing surface-charged  $\text{TiO}_2$  particles. The main target of the proposed process was the discharging and destruction of the interfacial film which was achieved with high efficiency results.



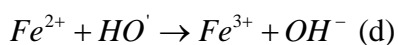
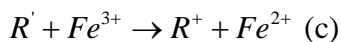
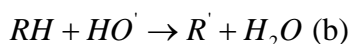
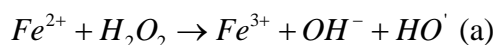
**Equation 18** - Governing chemical process equation for the removal of pollutants from water through photocatalytic methods (Fakhru'l-Razi et al. 2009)



**Figure 146** - (a) Photocatalytic reactor drum setup and (b) drum reactor configuration in UV box (Adams et al. 2008)

## The Fenton process

Fenton process is considered the most simple advanced oxidation process. It is named Fenton after the researcher which proposed the process for the first time with the usage of maleic acid oxidation. The process sequence involves oxidation, neutralization, flocculation and sedimentation. The removal of organics takes place during oxidation and coagulation which are caused by OH radicals and ferric hydroxo complexes. The degradation mechanism of the process is illustrated by Equations 19 a,b,c,d and its advantages and disadvantages are illustrated at Table 19 (Nidheesh and Gandhimathi 2012).

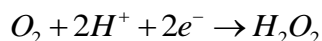


**Equation 19** - Degradation mechanism of Fenton reaction (Nidheesh and Gandhimathi 2012)

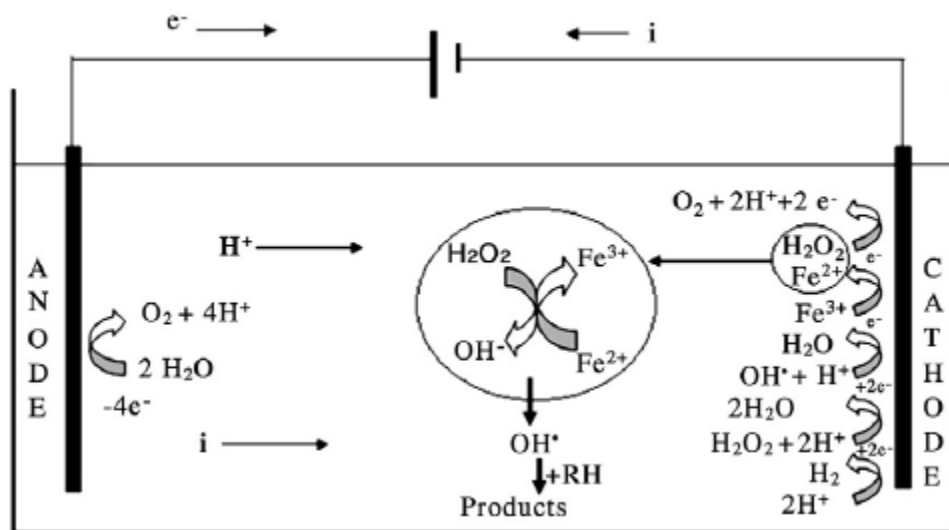
Advantages	Disadvantages
No energy input is needed for the activation of hydrogen peroxide	Consumption of ferrous ions is faster than their regeneration
Inexpensive	Sludge of Fe ions demands expensive treatment
Easy to operate	pH range limitation 2-3
Easy to maintain	Phosphate anions and intermediate oxidation products may deactivate iron ions
Short reaction time	Water is additionally polluted by homogenous catalyst and it cannot be retained during the process
No mass transfer limitation due to homogenous catalytic nature	
No catalyst in energy form	

**Table 19** - List of advantages and disadvantages of Fenton processes (Nidheesh and Gandhimathi 2012)

Based on the described reaction chemistry, eco-friendly electrochemical oxidation processes (EAOPs) such as E-Fenton have been evolved. Usually they use two different configurations. Reagents are added to the reactor and inert electrodes of high catalytic activity are used as anodes in the first case. The second configuration involves the addition of hydrogen peroxide only while  $Fe^{2+}$  is provided by the iron anodes. Equation 20 describes the continuous supply of  $H_2O_2$  to the contaminated solution during E-Fenton process which is the main advantage of the process over the conventional Fenton process. The typical E-Fenton process is shown in Figure 147 (Nidheesh and Gandhimathi 2012).



**Equation 20** - E-Fenton process governing chemical reaction (Nidheesh and Gandhimathi 2012)



**Figure 147** - Chemical reaction mechanism of E-Fenton process (Nidheesh and Gandhimathi 2012)

The method is applicable to petrochemical industry since it can effectively treat the wastewater flows and remove more than 50% of COD (Nidheesh and Gandhimathi 2012)

## Ultrasound application technique for oil in water emulsion treatment

A study (Heping et al. 2016) proposed the application of ultrasound field for oil in water emulsion resolution. High frequency ultrasound was found to improve the separation rates since oil droplets were coalescing towards the direction of the acoustic propagation. The best separation rates were achieved within 2 and 10 MHz sound frequency span.

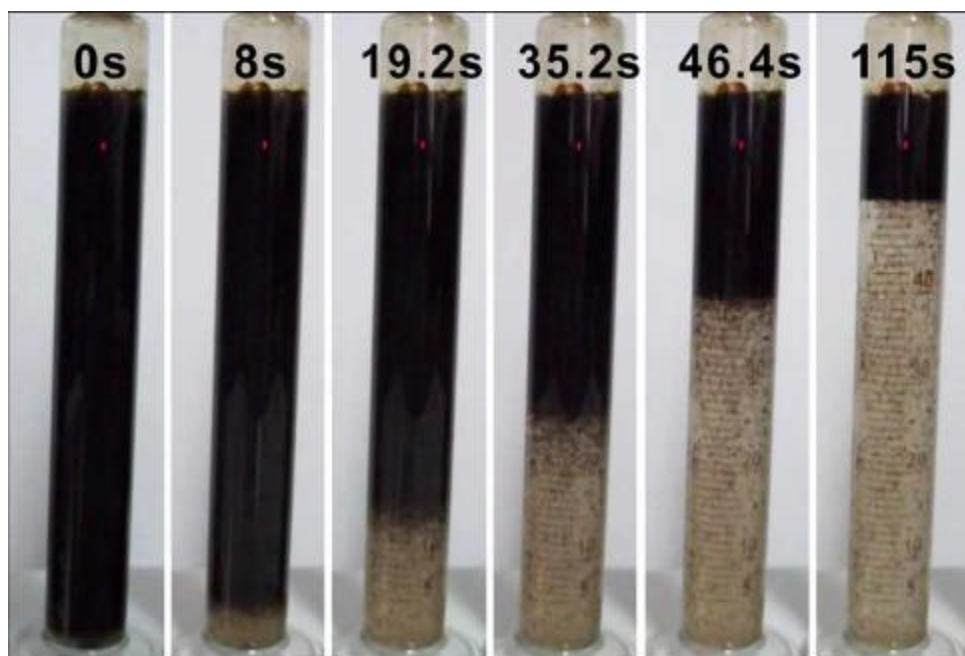
## Specialized materials for oil in water emulsion treatment

### Osorb

Osorb is a material characterized as hydrophobic glass which can be used in temperatures up to 210°C and pH up to 10 which has shown a high efficiency of adsorbing hydrocarbons. It is developed by ABS materials as a swellable organophilic material that can extract hydrocarbons from oil field waters. More specifically it can absorb 8 times its own weight by swelling 8 times its original size. It can be regenerated over 100 times by thermal treating or rinsing (Edmiston et al. 2011)

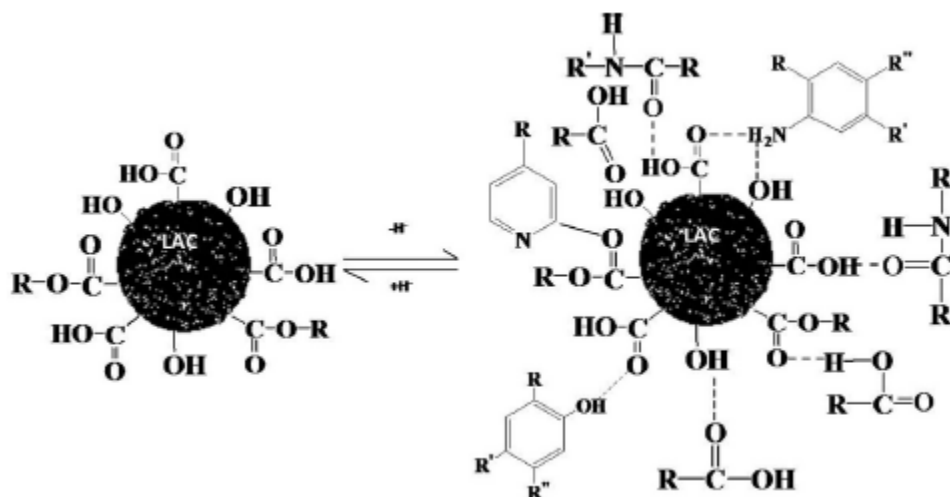
### *Graphene Oxide Nanosheets*

Usage of amphiphilic graphene oxide nanosheets were proposed (Liu et al. 2015) as an efficient technique for demulsification of oil in water emulsions. It is a well promising technique which shows great prospect for the treatment of crude oil in water emulsions at ambient conditions. Graphene oxide nanosheets can succeed demulsification efficiency over 99.9% for crude oil emulsions in water while they can be used for demulsification of extra heavy oil emulsions in water also. Their efficiency is attributed to the strong adsorption with the molecules of asphaltenes and resins due to  $\pi$ - $\pi$  and  $n$ - $\pi$  interactions. This technique was found to be highly pH dependent due to amphiphilicity of the graphene oxide. Figure 148 depicts the fast evolution of separation process by the use of graphene oxide nanosheets.



**Figure 148** - Evolution of the separation process using graphene oxide nanosheets (Liu et al. 2015)

Lignite activated coke (LAC) is proposed as an alternative to activated carbon for the adsorption of organics from water (Tong et al. 2016). Its ability of adsorbing organic compounds containing carboxyl and phenolic hydroxyl groups is governed by hydrogen bonding (Figure 149) and the functional carboxylic, phenolic and lactonic functional groups on LAC's surface.



**Figure 149** - *Hydrogen bonding between LAC and various organic pollutants (Tong et al. 2016)*

Apart from specialized materials for direct treatment of oil in water emulsions, it is critical to point out the importance of the materials used for the fabrication of flow lines and pipelines. This is due to corrosive agents such as  $\text{H}_2\text{S}$  and  $\text{CO}_2$  that exist in the produced water and need to be treated by corrosion inhibitors which can cause very stable oil in water emulsions in combination with high pressure. It is proposed (OSPAR Commission 2013) that for low pressure lines synthetic materials such as GRE/GRP should be used while for high pressure lines duplex steel or Inconel coating is used to minimize the use of those chemicals.

### Experimental and newly introduced industrial demulsifiers

Chemical demulsifiers are a state of art subject for the breaking of oil in water emulsions. Chemical treatment is the fastest and most widely used method or emulsion breaking (Hao et al. 2016). The most common categories of demulsifiers were described in a previous chapter. Optimization of the separation process can be achieved with combination of known demulsifiers or the introduction of new ones. Steric interactions or structural barriers and electrostatic repulsion are responsible for the stabilization of oil in water emulsions (Tadros 1983). The efficiency of demulsifier is dependent on its adsorption at the oil-water or droplet surface. The best demulsifiers are those that rapidly displace preformed rigid films and leave a mobile film in its place (Rajak et al. 2016). A list of coagulants proposed by various studies is shown in Table 20.

Coagulant type	Optimal dosage (mg L <sup>-1</sup> )	Optimal pH	Influent concentration	Removal Efficiency
Aluminium sulphate	100	8	1630	99.3%
Ferric Sulphate	120	7	1630	99.94%
Ferric Chloride	500-700	8.41 ± 0.15	169.7 ± 17	73 ± 5%
Alum	600-800	6.93 ± 0.2	169.7 ± 17	78.59 ± 0.8%
Ferrous Sulphate	700-1000	8.9 ± 0.2	169.7 ± 17	72 ± 4.2%
Aluminium sulphate	50	4	500	93%
Ferric Chloride	100	6	500	>95%
Alum	800-1400	8-10	-	99% COD removal

**Table 20** - Newly introduced coagulants (Saththasivam et al. 2016)

A critical parameter for emulsion breaking is the adjustment of its pH value which is succeed usually by addition of chemicals like sulfuric acid, ferric or aluminium salts, lime or polyelectrolytes. As flocculants polymers characterized by high molecular weight are used to promote aggregation of colloids. Coagulants such as ferric or aluminium salts on the other hand, are used to overcome the electrostatic barriers between particles and bubbles. For every pH value of a wastewater containing emulsions there is an optimum value for the concentration of the chemical additives. A combination of coagulation and dissolved air flotation proposed (Zouboulis and Avranas 1999) showed promising results in the destabilization of the oil in water emulsion systems. Cationic coagulant ferric chloride was introduced to promote the agglomeration of individual dropets. Flotation was enhanced by the introduction of anionic collector sodium oleate. This chemical conditioning of the system resulted in 95% effectiveness of oil removal from the treated effluent.

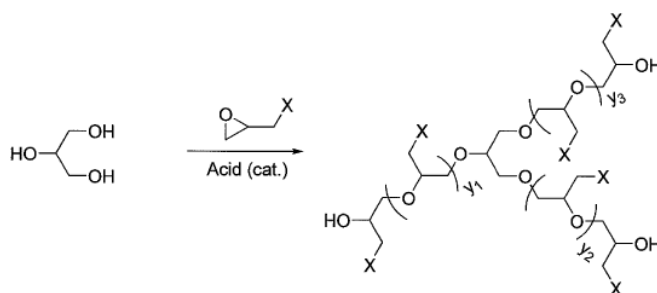
Another study (Tong et al. 2013) proposed a mix of calcium chloride (CaCl<sub>2</sub>), poly(dimethylamine-co-epichlorohydrin)(P-DcE) and cationic polyacrylamine (CPAM) for the demulsification of super heavy oil wastewater. Its removal efficiency was high for mineral oil droplets (98.04%) and it is proposed as an environmental friendly and cost effective chemical emulsion breaker.

Chitosan and its hydrophobically modified derivatives were examined (Bratskaya et al. 2006) as oil in water emulsion breakers. Complete phase separation for the proposed derivatives was achieved only for pH values higher than 7.5 for surfactant-

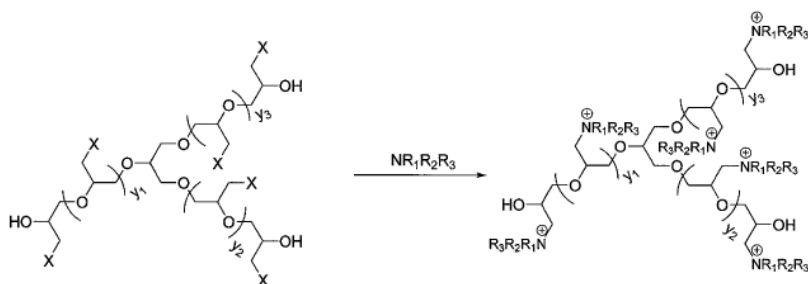
free emulsions. For emulsions affected by surfactants the efficiency was nearly independent of pH on range 4 to 9.

Experimental studies (Yang et al. 2002) examined the PET fiber's potential as a filter medium for produced water. PET fiber surface was grafted by groups of COOH, =NH and -OH changing the fiber from oleophilic to hydrophilic. The efficiency results of this PET modification were comparable to walnut shell filter medium. PET fiber's effluent quality reached 3.302 micron of oil droplets while for the same conditions of separation, walnut filter escaping oil droplets' size was 10.74 microns. Surface modification method was applied in another experimental study also (Liu et al. 2007) where PET fibre was modified by sulphonate ramification. The hydrophilic fibre ball obtained could adsorb oil of high concentration and was proved ideal for ASP produced water treatment. Ideal pore distribution enhances the treatment efficiency and treatment load ability.

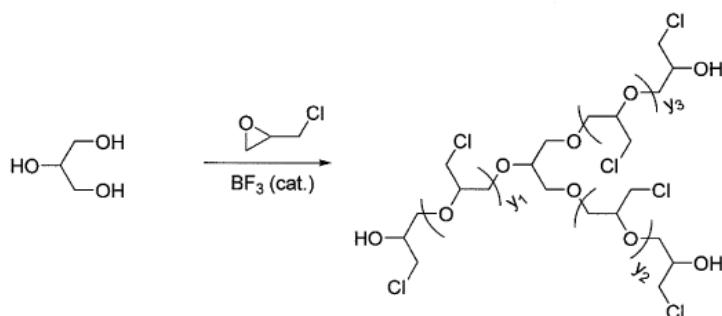
A patent (Tekavec and Faust 2014) claims the invention of an efficient oil in water emulsion breaker comprised of one or more polyepihalohydrins. A second proposal is the substitution of one or more of the polyepihalohydrins by a polyelectrolyte in any combination. This invention is cost effective since it allows the use of less epihalohydrin due to the high molecular weight glycerol initiator. Figure 150 shows the general structure of polyepihalohydrin compounds where X can be chloride, bromide, iodide, trifluoromethylsulfonate, toluenesulfonate, methylsulfonate or any combinations of the above, where y<sub>1</sub>, y<sub>2</sub> and y<sub>3</sub> values can range from 1 to 20. Figure 151 shows quaternized and branched polyepihalohydrins where R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> can be alkyl, aryl or hydrogen and y<sub>1</sub>, y<sub>2</sub> and y<sub>3</sub> values can range from 1 to 20. Figure 152 shows the embodiment for synthesis of branched polyepichlorohydrin where y<sub>1</sub>, y<sub>2</sub> and y<sub>3</sub> values can range from 1 to 20. Figure 153 shows the embodiment for the quaternization of branched polyepichlorohydrin y<sub>1</sub>, y<sub>2</sub> and y<sub>3</sub> values can range from 1 to 20



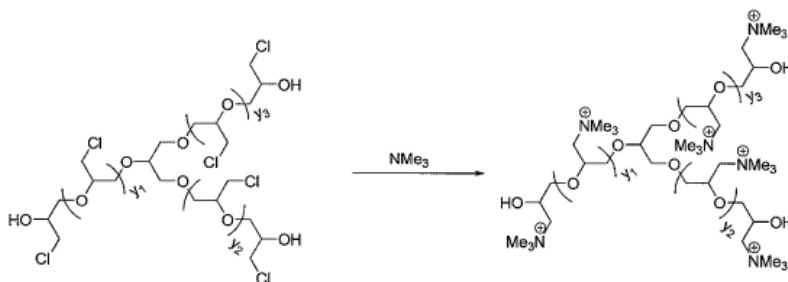
**Figure 150** - General structure of polyepihalohydrin compounds (Tekavec and Faust 2014)



**Figure 151** - Quaternized and branched polyepihalohydrins (Tekavec and Faust 2014)



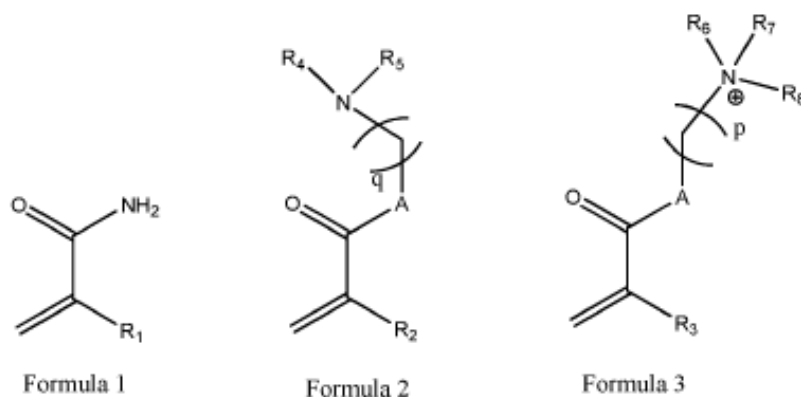
**Figure 152** - Embodiment for synthesis of branched polyepichlorohydrin (Tekavec and Faust 2014)



**Figure 153** - embodiment for the quaternization of branched polyepichlorohydrin (Tekavec and Faust 2014)

Another patent for oil in water emulsion breaker (de Hernandez et al. 2016) involved copolymers derived from the monomers illustrated in Figure 154.  $R_1, R_2$  and  $R_3$  can be hydrogen or alkyl while  $R_4, R_5, R_6, R_7$  and  $R_8$  are independently alkyl. A can be -NH- or O- and p and q can take values from 1 to 6. The copolymer's average molecular weight ranges between 20,000 and 2,000,000 Daltons, it can be branched, hyperbranched, comb, dendrimer or star polymer and preferably it should be prepared in aqueous solution. Based on the volume of the produced water the breaker should be applied in amounts ranging from 10 to 250 ppm. The monomers from formulas 1,2

and 3 should be mixed with a monomer inhibitor chelator such as ethylenediaminetetraacetate (EDTA) and a chain transfer agent such as sodium hypophosphite.



**Figure 154** - Monomers for synthesis of oil in water emulsion breaker (De Hernandez et al. 2016)

Monomers of formula 1 can be acrylamide, methacrylamide or a combination of two.

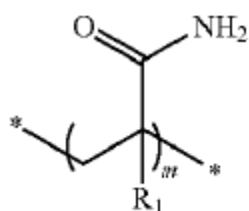
Monomers of formula 2 can be dimethylaminopropyl methacrylamide (DMAPMA), dimethylaminopropyl acrylamide, dimethylaminoethyl methacrylate, dimethylaminopropyl methacrylate, dimethylaminoethyl acrylate, dimethylaminopropyl acrylate, N,N, dimethyl(metha)acrylamide, N,N-methylene bisacrylamide, polyamidoamines, polyethylene imines or a combination of those.

Monomers of formula 3 can be [3-(methacryloylamino)propyl]trimethyl ammonium chloride (MAPTAC), [3-(acryloylamino)propyl]trimethyl ammonium chloride (APTAC), 2-acryloyloxyethyltrimethyl ammonium chloride (AETAC), 2-methacryloyloxyethyltrimethyl ammonium chloride (METAC), diallyldimethyl ammonium chloride (DADMAC), acryloyloxyethyldimethylbenzyl ammonium chloride (AEDBAC), methacryloyloxyethyldimethylbenzyl ammonium chloride (MEDBAC) or a combination of those with the most efficient formulation being [3-(methacryloylamino)propyl]trimethyl ammonium chloride (MAPTAC), [3-(acryloylamino)propyl]trimethyl ammonium chloride (APTAC), diallyldimethyl ammonium chloride (DADMAC) or their combination (De Hernandez et al. 2016).

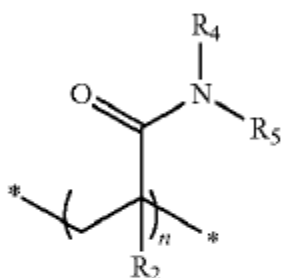
A patented oil in water emulsion breaking process (Little et al. 2016), proposes the utilization of a polyquaternary ammonium salt containing polyamine intermediate with a difunctional alkylating agent or a crosslinking agent. The proposed salt comprises the product reaction of a poly(triethanolamine) with an alkylating agent which can be a C<sub>1</sub>-C<sub>12</sub> alkyl halide, a C<sub>1</sub>-C<sub>12</sub> haloalkanol, a halo-substituted ammonium salt, an aryl halide, an alkaryl halide, an alkylene oxide under acidic conditions or a combination of them. The efficacy of this process depends on water

drop, water and interface properties and oil dryness. The preferable molecular weight of the polyquaternary ammonium salt should be between 2,000 and 20,000 Daltons and its effective amount for treatment ranges between 2 and 75 ppm. It can be used in compilation with a flocculant for enhancement of resolution results.

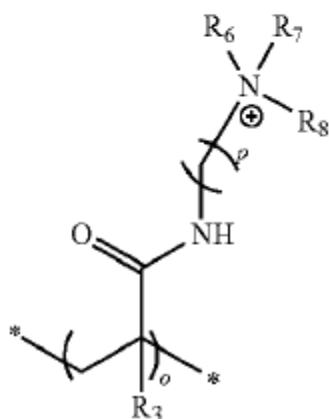
Another oil in water emulsion breaker proposed (Squicciarini 2016) involves an emulsion breaker composed of a terpolymer made of monomers of Figure 155.  $R_1, R_2$  and  $R_3$  can be hydrogen or alkyl,  $R_4, R_5, R_6, R_7$  and  $R_8$  can be alkyl,  $p$  can have values from 1 to 6 and  $m, n$  and  $o$  are integers. The molecular weight of the terpolymer can range between 20,000 and 20,000,000 Daltons. Monomers can have the formulation of Figure 156 also with the same principles applying.



Formula 1

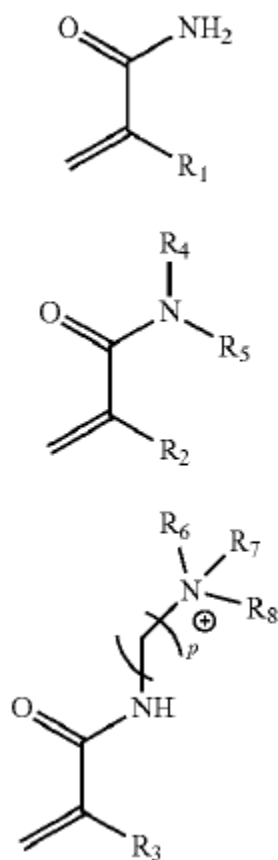


Formula 2



Formula 3

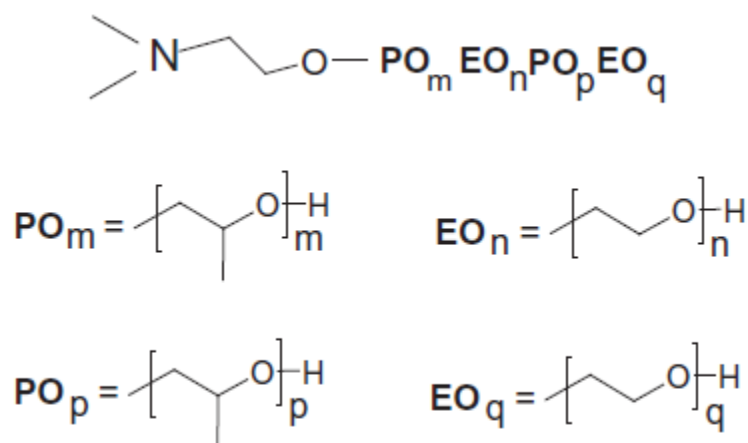
**Figure 155** - Monomers for the composition of the proposed oil in water emulsion breaker (Squicciarini 2016)



**Figure 156** - Alternative formulation of monomers of Figure 155 for the composition of oil in water emulsion breaker (Squicciarini 2016)

Experiments carried out (Rajak et al. 2016) shown that noctylamine, n-hexylamine and polyethylene glycol-400 are very efficient demulsifiers. Best results were obtained at pH values around 10.5, retention time of 60 minutes, temperature of 70°C and dosages of 60-80 mg/L.

A block polyether was designed (Duan et al. 2016) based on the hydrophilic-lipophilic deviation concept for the recovery of oil from wastewater. A specific copolymer of ethylene oxide (EO) and propylene oxide (PO), the DMEA-mnpq is proposed for this purpose and its structure is illustrated in Figure 157. Through the addition of the proposed chemical, the coalescence of oil droplets is promoted. Furthermore the oil can be recovered much more easier than in the cationic polymers' treatment schemes.

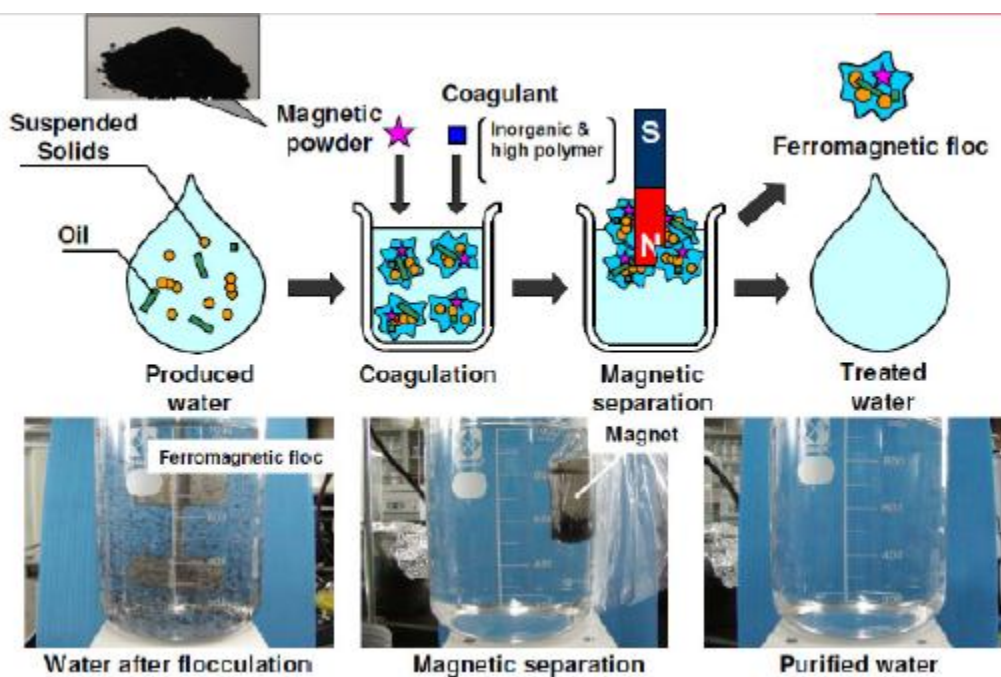


**Figure 157 - DMEA-mnpq structure** (Duan et al. 2016)

Very stable oil in water emulsions can be formed during surfactant/polymer and alkaline/surfactant/polymer processes for enhanced oil recovery (Li et al. 2006 a). The addition of cationic surfactants as proposed (Hirasaki et al. 2010) can accelerate the separation of this type of emulsions. In particular C8TAB (n-octyltrimethylammonium bromide) or any other industrially available cationic surfactant can cause significant coalescence which leads to emulsion breaking. The cationic surfactant's quantity demand is reduced in case of simultaneous non ionic demulsifier resin introduction. In the same study amphoteric surfactants like cocobetaine gave similar results to those of cationic surfactants.

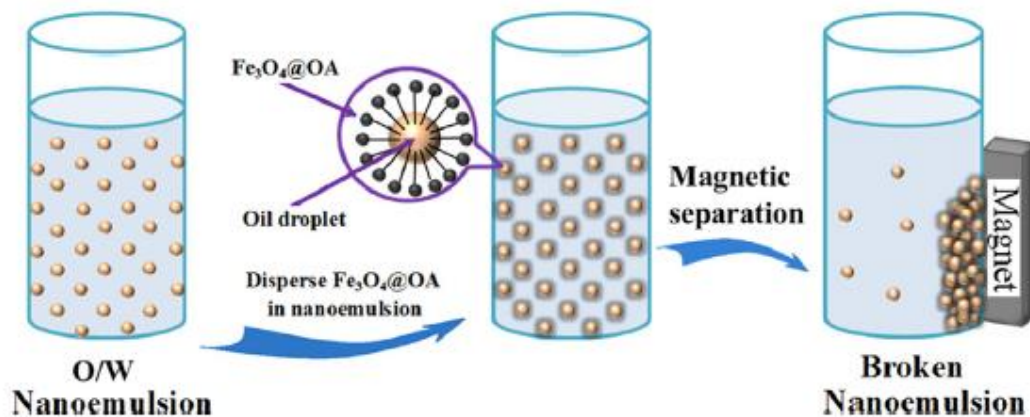
Cationic surfactants can be formed also by the alteration of cation and anion combinations in ionic liquids. Thus ionic liquids constitute a whole new chapter in the demulsifiers technology (Hirasaki et al. 2010, Guzman-Lucero et al. 2010, Lemos et al. 2010, Silva et al. 2013 and Flores et al. 2014). Halogenide ionic liquids containing imidazolium or ammonium cations have been reported to be efficient emulsion breakers (Li 2016). Same applies for non-halogenide ionic liquids with fluorinated anions such as  $\text{BF}_4^-$ ,  $\text{PF}_6^-$  and  $\text{NTf}_2^-$ . In cases where microwave radiation was applied for acceleration of the heating process the results of emulsion breaking were even better since a reduction in the viscosity was caused. Certain study (Li 2016) shown that halogenide ionic liquids with hydrophobic cations were very successful in oil in water emulsion breaking. Especially for equimolar amounts of ionic liquid to surfactant, complete demulsification was observed.

Magnetic flocculation removal is called the process of breaking oil in water emulsions by the addition of a mix of magnetic powder and high polymer based coagulants. Magnetic skimmers are used in this case for the removal of the coagulated extractants (Daigle et al. 2012). The basic principle of this technique is shown in Figure 158.



**Figure 158 - Magnetic flocculation technique (Daigle et al. 2012)**

Magnetic demulsifiers were examined and proposed in various studies (Peng et al. 2012, Lemos et al. 2012, Calcagnile et al. 2012, Liang et al. 2014, Li et al. 2014, Liang et al. 2015, Lu et al. 2016 & 2017a&b, Duan 2017 and Liu et al. 2017). In most cases  $\text{Fe}_3\text{O}_4$  is used as a magnetic substrate due to its low cytotoxicity. It is accumulating at the oil-water interfaces imparting its magnetic properties on the dispersed droplets (Peng et al. 2012, Liang et al. 2015) causing coalescence under an external magnetic field. Surfactants or polymers are needed for the improvement of its interfacial activity and dispersibility according to aforementioned studies. Magnetic amphiphilic composites were developed (Lemos et al. 2012) for the separation of biodiesel in water emulsion. Polyether polyol demulsifier was developed (Li et al. 2014) based on the same principle for oil in water emulsion breaking. Oleic acid coated magnetite nanoparticles (Liang et al. 2015) were proposed for the treatment of oil in water nanoemulsions reaching an emulsion breaking efficiency of 97%. Figure 159 is showing the basic principle of separation for the magnetic demulsifiers applied in this particular case of nanoemulsions.



**Figure 159** - Basic principle of the coalescence of oil droplets with the use of magnetic demulsifiers for nanoemulsions breaking. (Liang et al. 2015)

Magnetic iron oxide nanoparticles (MIO) were developed (Lu et al. 2016) with coprecipitation method, coating with silica, modification with  $\gamma$ -methacryloxypropyl triisopropoxidesilane (MPS) and attachment of Poly(N-isopropylacrylamide) (PNIPAM) molecular chains on the surfaces of MIOs, for the treatment of oil in water emulsions. High demulsification efficiency of MIOs under the application of magnetic field was observed for low temperatures. Their regeneration ability through rinsing with hot water was 7 cycles while there was no pH sensitivity. MIOs are proposed as promising materials for the treatment of oily wastewaters due to their low cost and environmental friendly character.

Coating of  $\text{Fe}_3\text{O}_4$  with silica for the attachment of (3-aminopropyl)triethoxysilane (APTES) was proposed for enhancement of the magnetic nanoparticles oil in water emulsion breaking (Lu et al. 2017a). Their regeneration ability was 9 cycles. Under acidic and neutral conditions those magnetic nanoparticles were found to be highly efficient in oil in water emulsion breaking. The proposed mechanism of oil in water emulsion breaking of this study is illustrated in Figure 160 and it is explained by the fact that under acidic conditions the electrostatic repulsion governs the accumulation of MNPs onto oil droplets while under neutral conditions the governing mechanism is the interfacial activity. For base pH values, electrostatic repulsion was reducing the MNPs efficiency.



**Figure 160** - Interaction mechanism between APTES coated magnetic nanoparticles for the resolution of oil in water emulsions (Lu et al. 2017a)

Magnetic nanoparticles - chitosan grafted were developed (Lu et al. 2017b) for the treatment of oil in water emulsions. Solvothermal method was used, coating with aminopropyl-functionalized silica (AFPS) and attachment of chitosan molecular chains. Under both acidic and neutral conditions AFPS-coated magnetic nanoparticles proved as efficient demulsifiers due to electrostatic attraction. Chitosan grafting improved the efficiency under alkaline conditions due to hydrophobic interaction which overcame the force of electrostatic repulsion. Their regeneration ability was 7 cycles and their easy synthesis process and environmental friendly character makes them potent for efficient treatment of oil in water emulsions.

Core-shell magnetic thermosensitive composite nanoparticles were synthesized with graft method for oil in water emulsion treatment (Duan et al. 2017). Polyoxyalkylated N,N-dimethylethanolamine was attached into magnetite nanoparticles creating the M-DMEA which under magnetic external field application reached 92.3% efficiency of oil in water emulsion removal. It can be recycled for 3 times and it is considered as promising demulsification material for oil in water emulsion treatment.

Recyclable magnetic graphene oxide (Liu et al. 2017) was found to be a rapid, high efficiency and reusable solution for demulsification of crude oil in water emulsions. Demulsification efficiency of the process proposed reached 99.98% due to the fact that small oil flocules, in presence of magnetic graphene oxide, can be eliminated by an external magnetic field. In this case the economic cost of the demulsification process can be significantly reduced due to the fact that magnetic graphene oxide can be reused for 6-7 times. Furthermore graphene oxide efficiency on separating oil in water emulsions under the presence of cetyltrimethylammonium bromide (CTAB)

which is a common surfactant present in petroleum industry was investigated in a study (Fang et al. 2016) and the result was a complete resolution of the oil in water emulsion.

Use of organoclays was proposed (Alther 2001) for oil in water emulsion treatment. Introduction of surfactants such as quaternary amines in clays proved to form the so-called organoclays which can remove 30 to 50% of their weight in oil from water. Blending of organoclays with other filter media such as anthracite coal is demanded to prevent swelling and blinding of the filter vessel. According to Alther experiments organoclay is 7 times more efficient than Granular Activated Carbon (GAC) which is mainly used as filter in oily wastewater treatment while hydrochloric acid proved more efficient as an emulsion breaker than sulfuric acid in the same study.

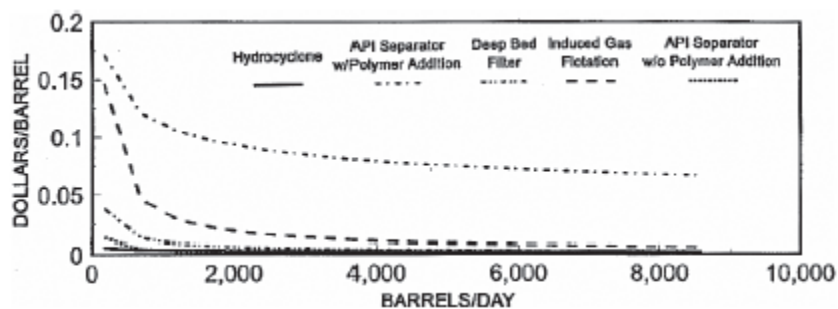
Attapulgite, a natural clay was proposed (Al Haddabi et al. 2015) for the removal of dissolved organic carbon (DOC) from oily wastewater as a potential low cost adsorbent. Increase of temperature and dosage of attapulgite in oily wastewater proved to reduce significantly the DOC. Adsorption ability was slightly dependent on pH values while attapulgite powder showed better removal efficiency than granular attapulgite.

Studies (Zhou et al. 2000) proposed FMA chemical as a good coagulant and de-oiler. It is an inorganic mixed metal polynuclear polymer. Oil removal efficiency can range between 92 and 97%.

## Chapter 9 - Economics

Treatment of emulsions can contribute a large part of profit to the companies and it is mandatory for them in case of oil in water emulsions so that they can comply with laws and regulations of each state and avoid penalties. Prevention of the formation of emulsions is one way to minimize the cost for their treatment but if this is not feasible, a compilation of low cost and high efficiency should be made for their treatment. Of course the minimization of water quantity produced together with oil is the primary goal that aids this cause.

Once water is produced and emulsions are formed, appropriate treatment methods and equipment should be used. Equipment should be of smallest possible size and be chosen according to its potential for future development, lease expansion and water production that can increase. Figure 161 shows the cost performance of the deoiling technology for the treatment of oil in water emulsions. For the creation of the curves presented in Figure 161 typical values of 5 mg/l of oil and gas concentration in effluents of gas flotation or API separator units, 98% removal efficiency for deep bed filtration and 80% efficiency for hydrocyclones were assumed. Chemicals raise the cost of the treatment as it is obvious (Orszulik 2008).



**Figure 161** - Cost of deoiling technologies for the treatment of emulsions (Orszulik 2008)

Chemical treatment should be planned carefully also. Appropriate chemical demulsifiers should be chosen and used in exact doses. The stage of their introduction to the oil/water bulk, the means of their mixing with emulsions and the temperature are of high importance due to the fact that they are not recoverable. Chemicals should also be compatible with the treating equipment so that corrosion and other problems that can affect the treatment process are avoided.

Equipment should be used at its optimum rate of efficiency under proper supervision of experienced personnel. Testing and record keeping are playing a key role to this. Records for temperatures, pressures, power consumption, chemical usage and performance on a daily basis are important for decisions concerning the modification or replacement of the equipment. Preventive maintenance also should take place in order to avoid serious damages which can provoke costly shut down of parts of the equipment for a long time.

Figure 162 represents all the costs mentioned before and always companies should find the appropriate operation plan to keep a balance between cost-effective solutions and states' environmental restrictions. (Petrowiki.org/Economics\_of\_treating\_emulsions)

TABLE 3.6—COSTS OF EMULSION TREATING		
Equipment Investment Costs		
<u>Material</u>	<u>Labor To Install Equipment</u>	<u>Other Expenses</u>
<ul style="list-style-type: none"> <li>• Treating equipment and facilities</li> <li>• Auxiliary equipment, controls, and accessories</li> </ul>	<ul style="list-style-type: none"> <li>• Company labor</li> <li>• Contract labor</li> </ul>	<ul style="list-style-type: none"> <li>• Surface rights</li> <li>• Special services</li> <li>• Other</li> </ul>
Operating Costs		
<u>Material</u>	<u>Labor</u>	<u>Other Expenses</u>
<ul style="list-style-type: none"> <li>• Chemicals</li> <li>• Chemical injection equipment</li> <li>• Diluents and solvents</li> <li>• Testing apparatus</li> <li>• Depreciation allowances</li> <li>• Other</li> </ul>	<ul style="list-style-type: none"> <li>• Supervisory</li> <li>• Operator or pumper</li> <li>• Steaming or cleaning crew</li> <li>• Company crew</li> <li>• Contract</li> <li>• Other</li> </ul>	<ul style="list-style-type: none"> <li>• Equipment rental</li> <li>• Fuel (gas or liquid)</li> <li>• Electricity</li> <li>• Transportation</li> <li>• Laboratory expenses</li> <li>• Other</li> </ul>
Maintenance Costs		
<u>Material</u>	<u>Labor</u>	<u>Other Expenses</u>
<ul style="list-style-type: none"> <li>• Maintenance</li> <li>• Replacements and additions</li> <li>• Repairs</li> </ul>	<ul style="list-style-type: none"> <li>• Supervisory</li> <li>• Pumper or operator</li> <li>• Mechanic</li> <li>• Painting</li> <li>• Company crew</li> <li>• Contract</li> <li>• Other</li> </ul>	<ul style="list-style-type: none"> <li>• Equipment rental</li> <li>• Transportation</li> <li>• Other</li> </ul>
Overall System Performance		
<ul style="list-style-type: none"> <li>• Volume of oil treated</li> <li>• Water content of treated oil</li> <li>• Volume of water produced</li> <li>• Volume of water treated</li> <li>• Volume of oil salvaged from water treatment</li> <li>• Remarks or observations</li> </ul>		

**Figure 162 - Emulsion treatment costs** (Petrowiki.org /Economics\_of\_treating\_emulsions)

Tertiary and Advanced treatment as mentioned before are the most critical stages of oil in water emulsion treatment. The continuous search for new technologies to improve those two stages of emulsion treatment is due to enhancement of separation efficiency, minimization of discharge impacts in the environment and minimization of costs. It is crucial to realize that cost is a major characteristic which plays role in the industrial application of experimentally proposed techniques. Ionic liquids have experimentally been studied in the past for oil in water emulsion resolution for example but their high cost makes their in-field application not viable. Table 21 summarizes the costs of the best available techniques for those stages of separation.

Method	Cost
Activated Carbon Systems	Moderate
Air stripping techniques	Low capital and operating costs (average of 0.1\$/1,000 gal plus 1.5\$/kgal if activated carbon is used in combination)
Membrane filtration	Low operating costs
Chemical oxidation	Moderate operating costs
Biological Treatment with Biodemulsifiers	Moderate capital costs and low operating costs

**Table 21** - *Best available tertiary and advanced stage treatment of oil in water emulsions costs (Igwe et al. 2013)*

## CONCLUSIONS

The main target of this work was to provide a deep understanding of the equipment and processes used in the industry for enhanced oil recovery techniques applied on oil in water emulsions.

The oil in water emulsion resolution problem is a part of two major issues for the industry. Enhanced oil recovery and produced water management. Companies on the one hand have to comply with legislation issues regarding the quality of the discharged water and its' final hydrocarbon content which is directly connected to oil in water emulsion resolution. Failure to meet the standards of discharge means large penalties and fines. On the other hand emulsion resolution is critical for the oil recovery since large quantities of oil can be produced during separation of dispersed oil in water

An extensive description of the mechanisms driving the oil in water emulsion formation and resolution was attempted. It is critical for any engineer who will design a treatment scheme to realize the physicochemical principles on which oil in water emulsions' reactions are based. Various techniques for characterization, monitoring and simulation of treatment for the oil in water emulsions were presented also since in order to create an efficient treatment scheme, it is of high importance for the engineers to know specific attributes of the liquids to be treated.

An attempt of categorization of the equipment and processes used for oil in water emulsion treatment into 5 stages was made. Pre-treatment, primary treatment, secondary treatment, tertiary treatment and advanced treatment. The categorization was attempted following the rule of the minimum possible diameter of oil droplet that can be treated from each vessel. On pre-treatment stage, vessels such as conventional separators, skimmer tanks, disposal piles and skim piles with approximate minimum drop size removal of 100 microns were presented. On Primary separation stage, the approximate minimum drop size removal reaches 50 microns for vessels such as coalescer separators and hydrocyclones. Secondary separation stage which involves the use of flotation units, centrifuges and chemicals deals with sizes down to 10 microns while Tertiary separation, which involves filters and Advanced separation stages, which involves the use of membranes and biodemulsifiers, reach minimum drop size removal of 1 micron.

Industry have developed various commercially available products which can combine the technology of vessels mentioned before and can be applied for different cases. The present work tried to list some of the most important commercially available vessels, techniques and chemicals available in the market. Also, experimental solutions for oil in water emulsion resolution were presented. The tendency of researchers is to focus on environmental friendly and cost effective techniques for oil in water emulsion

resolution such as membranes which have presented high efficiencies of oil in water emulsion resolution and magnetic demulsifiers which are still on experimental level, presenting high separation efficiency though.

A final remark of this thesis is that various treatment schemes can be applied and there is not a unique formula for every stream. Engineers have to use the best available technology in combination with the most cost effective solution for the maximum efficiency of oil recovery results.

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