

Produced Water Treatment



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1 Introduction

Produced water treatment is essential to achieve environmental compliance for overboard, inshore and land disposal. This module reviews the components contained within produced water and the options for treatment. Sand is often produced with produced water and sand management techniques are presented.

Produced water can consist of formation water (water naturally occurring through the geological process) and injection water that has been injected to provide reservoir support and enhance production.

As production history advances the ratio of formation water to injection water in the produced fluids will change. Often the amount of water produced increases as the field production ages and towards the end of field life production composition can be as high as 95% v/v water.

Treatment of the water will be necessary and the plant may also be required to handle other water sources – drains and ballast water. Once again the Chemical Engineer has to address the life of field issues to ensure that the design can accommodate changing demands.

Historically the reported amount of dispersed oil discharged in the UKCS has been:

- 2005 4,900 tonnes of dispersed oil discharged with an average concentration of 20 mg/l.
- 2007 3,000 tonnes of dispersed oil discharged with an average concentration of 15 mg/l.

This reduction was primarily due to produced water reinjection (PWRI) back into the reservoir hence no overboard disposal.

2 Disposal Regulations

For the NE Atlantic, OSPAR (Oslo and Paris Commission) regulates offshore discharges through national authorities. In the UK, DECC - Department of Energy and Climate Change, issues oil discharge permits. Historic OSPAR limit was an average of 40 mg/l of dispersed oil (not dissolved). In 2006 new tighter regulation requires an average of 30 mg/l (dispersed oil) and an overall reduction of 15% in mass of oil discharged with PW compared to 2000. With rising Produced Water (PW) volumes as UK fields mature this is a significant constraint. DECC (UK) issues annual licences limiting the amount of oil that can be discharged by an installation.

Chemical use (e.g. demulsifiers, corrosion inhibitors) is controlled by permits based on marine environmental risk assessment.

Radioactive discharges controlled by permit by the Scottish Environment Protection Agency (SEPA) in Scotland and EA in England.

For comparison worldwide produced water effluent oil concentration limitations are:

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

Australia 30 mg/l

Thailand 50 mg/l

USA 29 mg/l offshore water

Onshore disposal of produced water is usually around 5 mg/l.

3 Produced Water Constituents

Produced water contains a number of substances, in addition to hydrocarbons, that affect the manner in which the water is handled. The composition and concentration of substances may vary between fields and even between different production zones within a single field. The terminology used for concentration is milligrams per litre (mg/l), which is mass per volume ratio and is approximately equal to parts per million (ppm).

The constituents are;

Dissolved solids - salts

Dispersed oil – mostly aliphatics and heavy aromatics

Dissolved oil – mostly light aromatics

Polar hydrocarbons – organic acids, glycols, methanol

Polycyclic aromatic hydrocarbons (PAHs) – naphthalenes

Chemicals – corrosion inhibitor, scale inhibitor, demulsifier etc

Solids – scale, formation solids, corrosion and erosion products

Heavy metals: e.g. Pb, Cr, Hg, Zn

Low level radioactivity (NORM naturally occurring radioactive material)

3.1 Dissolved Solids

Produced waters contain dissolved solids, but the amount varies typically from less than 100 to over 300,000 mg/l, depending on the geographical location as well as the age and type of reservoir. In general, water produced with gas is condensed water vapour with few dissolved solids, hence it is fresh with a very low salinity. Aquifer water produced with gas or oil will

be much higher in dissolved solids. Produced water from hot reservoirs tends to have higher total dissolved solids (TDS) concentrations while cooler reservoirs tend to have lower levels of TDS.

Dissolved solids are inorganic constituents that are predominantly sodium (Na^+) cations and chloride (Cl^-) anions. Other common cations are calcium (Ca^{2+}), magnesium (Mg^{2+}), and iron (Fe^{2+}), while barium (Ba^{2+}), potassium (K^+), strontium (Sr^+), aluminum (Al^{3+}), and lithium (Li^+) are encountered less frequently.

Anions present are bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), and Sulphate (SO_4^{2-}).

All produced water treating facilities should have water analysis data for each major reservoir and for the combined produced water stream. Especially important are constituents that could precipitate to form scales.

3.2 Precipitated Solids (Scales)

3.2.1 Calcium Carbonate (CaCO_3)

Calcium carbonate (CaCO_3) precipitate can be formed by mixing two dissimilar waters, however the usual cause is the reduction in pressure and release of dissolved carbon dioxide from the produced water. This increases the produced water's pH, which reduces the solubility of CaCO_3 and leads to scale precipitate. Temperature effects are equally important since CaCO_3 is less soluble at higher temperatures and will form a deposit in heat exchangers, heaters, and treaters. Its solubility is approximately 1000 mg/l at 60 °F (15 °C) and diminishes to 230 mg/l as temperature is increased to 200 °F (93 °C).

3.2.2 Calcium Sulphate (CaSO_4)

Calcium Sulphate (CaSO_4) is one of several sulphate scales, it is also called gypsum. Like CaCO_3 , it can form either as a result of mixing dissimilar waters or naturally as a result of changes in temperature and pressure as the water travels from the subsurface to the surface treating facility. CaSO_4 solubility is at its maximum level of 2150 mg/l at approximately 100 °F (38 °C) and diminishes to 2000 mg/l as it cools to 60 °F (15 °C). The solubility of CaSO_4 also declines with increasing temperature above 100 F with its solubility reducing to 1600 mg/l at 200 °F (93 °C). CaSO_4 also increases in solubility as the salinity of the produced water increases.

3.2.3 Iron Sulphide (FeS_2)

Iron Sulphide (FeS_2) is a product of corrosion usually caused by waters containing dissolved hydrogen sulphide coming into contact with equipment fabricated from carbon steel or iron

materials. Mixing water containing iron cations (Fe^{2+}) with another water containing Hydrogen Sulphide will also result in a FeS_2 precipitate.

3.2.4 Barium and Strontium Sulphate (BaSO_4 and SrSO_4)

Barium and Strontium Sulphate (BaSO_4 and SrSO_4) are much less soluble than Calcium Sulphate, but they are not as common in produced waters. BaSO_4 solubility is quite low, having a value of approximately 3 mg/l over the range from 100 (15 °C) to 200 °F (93 °C). SrSO_4 solubility is 129 mg/l at 77 °F (25 °C) and diminishes to 68 mg/l as the solution temperature increases to 257 °F (125 °C). If a produced water stream containing appreciable quantities of barium or strontium ions is mixed with Sulphate-rich water (e.g. sea water), barium and/or strontium scaling can be expected. These waters are incompatible due to this scaling characteristic and mixing should be carefully analysed as these scales are particularly difficult to manage.

3.2.5 Scale Management

Hydrochloric acid can be used to dissolve calcium carbonate and iron sulphide scales. However, iron sulphide reacts with hydrochloric acid and produces hydrogen sulphide, a highly toxic gas having the odour of rotten eggs. Due to the high toxicity of hydrogen sulphide, safety provisions need to be implemented.

Calcium sulphate is not soluble in hydrochloric acid, but chemicals are available that will convert it to an acid-soluble form that can then be removed by the acid. This process is slow, however, because a two-step process must be repeated to strip the scale layer by layer. Thus, the removal of calcium sulphate is more difficult than the removal of calcium carbonate. Dissolving barium or strontium sulphate is extremely difficult. These hard scales can be removed by mechanical means which is a time-consuming process. Mechanical removal of scale can create a disposal problem for the resulting waste material and could also result in contamination by naturally occurring radioactive materials (NORM).

Scale-inhibiting chemicals are available to retard or prevent all types of scale. They mostly function by enveloping a newly precipitated crystal, thereby retarding growth.



3.3 Sand and Other Suspended Solids

In addition to scale particles, produced water often contains other suspended solids. These include formation sand and clays, stimulation (fracturing) proppant, or miscellaneous corrosion products. The amount of suspended solids is generally small unless the well is producing from an unconsolidated formation, in which case large volumes of sand can be produced. Produced sand is often oil wet and its disposal is a problem. The presence of sand will also lead to more erosion.

Small amounts of solids in produced water may or may not create problems in water treating depending on the particle and its relative attraction to the dispersed oil. If the physical characteristics and electronic charge of such solids result in an attraction to the dispersed oil droplets, the solid particles can attach to the dispersed oil droplets to stabilize emulsions, thereby preventing coalescence and separation of the oil phase. The combined specific gravity of the resulting oil/solid droplet can be approximately equal to that of the produced water, and gravity separation becomes difficult if not impossible.

3.4 Dissolved Gases

The gases found in produced water include methane, ethane, propane, butane, hydrogen sulphide, and carbon dioxide. In the reservoir the water will be saturated with these gases at relatively high pressures. As the produced water flows up the wells, most of these gases flash to the vapour phase and are removed in the separation train. The pressures and temperatures at which the produced water is separated from the oil and gas streams will impact the amount and composition of dissolved gas that will be contained in the produced water stream feeding the water treating facilities. The higher the separation pressure, the higher the quantity of dissolved gases.

If hydrogen Sulphide is present in the produced reservoir fluid hydrogen sulphide will likewise be present in the produced water stream. Hydrogen sulphide is corrosive, can cause iron sulphide scaling, and is extremely toxic if inhaled. Additionally, iron sulphide (the corrosion product of hydrogen sulphide) presents a potential fire hazard since it is prone to auto-ignition (pyrophoric) when exposed to air.

If carbon dioxide is present in the produced reservoir fluid, it too will be present in the produced water. This will lower the pH making the water more corrosive, the change in pH can also result in CaCO_3 scaling.

3.5 Oil in Water Emulsions – Dispersed Oil

Most emulsions encountered in the oil field are water droplets in an oil continuous phase and are called “normal emulsions.” The water is dispersed in the form of very small droplets

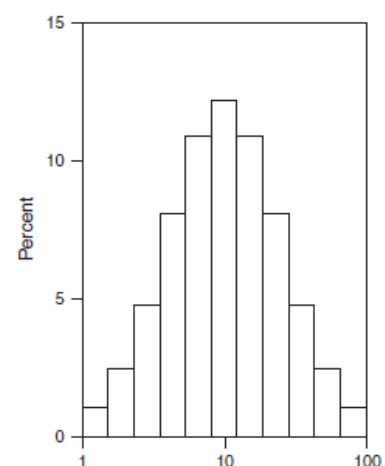
typically ranging between 100 and 400 micron in diameter. Oil droplets in a water continuous phase are known as “reverse emulsions” and can occur in produced water treating operations. If the emulsion is unstable, the oil droplets will coalesce when they come in contact with each other and form larger droplets, thus breaking the emulsion.

As covered in the Separation module a stable emulsion is a suspension of two immiscible liquids in the presence of a stabilizer or emulsifying agent that acts to maintain an interfacial film between the phases. Chemicals, heat, settling time, and electrostatics are used to alter and remove the film and cause emulsion breakdown.

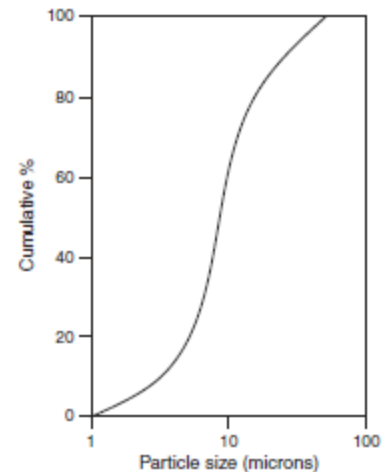
Emulsion breakers for water-in-oil emulsions, also known as destabilizers or demulsifiers, are oil-soluble and are added to the total well stream ahead of the process equipment. Being oil-soluble, the emulsion breaker is carried with the crude. Thus, if the emulsion is not broken in the first-stage separator, the chemical has additional time to act in the subsequent separators. Oil-in-water emulsions can be broken by “reverse emulsion breakers,” which are special destabilizers or demulsifiers. These are similar to the conventional emulsion breakers except that they are water-soluble. Reverse emulsion breakers are generally injected into the water stream after the first oil–water separation vessel. Typical concentrations are in the 5-15-ppm range, and over-treating should be avoided because these chemicals can stabilize an emulsion. Oil droplets will coalesce to yield an oily film that can be separated from the produced water using gravity settling devices such as skim vessels, coalescers, and plate separators. However, small droplets require excessive residence times, so flotation cells or acceleration enhanced methods such as hydrocyclones and centrifuges are used. Equipment selection is based on the inlet oil’s droplet diameter and concentration.

For equipment that operates on the principle of Stokes’ law the diameter of the oil droplet has a major effect on the separation and removal of the oil droplet from the water. The capability of a given de-oiling device or system to remove and recover dispersed oil decreases as the droplet size decreases. Oil droplet size distribution is a fundamental characteristic of produced water and must be considered in designing and sizing treating systems to meet regulatory standards for effluent water compliance.

A typical histogram of an oil droplet distribution. The histogram divides the particle counts into discrete size ranges along the horizontal axis. The height of the vertical bars corresponds to the volume percentage of oil droplets in each range.



For the design of a new field the droplet diameter is uncertain and equipment is generally designed using historical comparisons with similar systems. Also, the dispersed oil droplet size distribution may vary from point to point in a produced water system, and from one system to another. The size distribution is affected by interfacial tension, turbulence, temperature, system shearing (pumping, pressure drop across valves and pipe fittings). The droplet size distributions should be measured in the field when troubleshooting and/or upgrading systems, whenever possible.



3.6 Dissolved Oil

Dissolved oil is all hydrocarbons and other organic compounds that have some solubility in produced water. The source of the produced water affects the quantity of the dissolved oil present. Produced water derived from gas/condensate production typically exhibits higher levels of dissolved oil. In addition, process water condensed from glycol regeneration vapour recovery systems contains aromatics including benzene, toluene, ethyl benzene, and xylenes (BTEX) that are partially soluble in produced water.

Gravitational-type separation equipment will not remove dissolved oil. Other technologies such as bio-treatment, adsorption filtration, solvent extraction, and membranes, are currently being evaluated by the industry for removing dissolved oil.

Water chemistry and hydrocarbon solubility are also related to toxicity. Dissolved saturated paraffinic (aliphatic) petroleum hydrocarbons have low solubilities in water and have not demonstrated significant toxicity.

Aromatics, such as benzene, toluene, ethyl benzene, and xylene, are more soluble and much more toxic.

3.7 Naturally Occurring Radioactive Material - NORM

NORM can be transported to the surface in produced water and can be found in production wastes, equipment, and solids at production facilities. Because of concern over human exposure to environmental radiation, oil-field NORM have received regulatory attention and managing waste has become a significant cost factor for the industry.

Oil field NORM results from the presence of uranium and thorium in hydrocarbon bearing formations. Many oil and gas bearing formations contain shales that have higher than average

concentrations of uranium and thorium. These elements occur in chemical forms that are not water-soluble under reservoir conditions (U238 and Th232). U238 and Th232 decay into different isotopes of radium (Ra236 and Ra228). These radium isotopes further decay into the radioactive radon (Rn232). Both radium and radon are soluble in formation water under reservoir conditions and can be transported to the surface along with oil, gas, and produced water. Once produced water leaves the reservoir, decreases in temperature and pressure can lead to the precipitation of NORM scale and particulates in production equipment, where it can accumulate as hard scales, sludge, or tank bottoms. Radon in produced fluids partitions into the gas phase during primary separation and enters the gas processing stream. Radon's boiling point is between that of ethane and propane, and radon is concentrated in the natural gas liquids fraction (this is generally a problem only in a gas plant fractionation section). Accumulated NORM containing solids are periodically cleaned out of vessels during maintenance and must be disposed of recognising the hazard posed.

3.8 Bacteria

Most produced waters contain bacteria but generally in small amounts. The type and number of bacteria are important when selecting a biocide program. All bacteria have many strains, and some will be immune to a specific bactericide. Thus, continued testing and periodic change of chemicals may be needed.

The types of bacteria are:

Aerobic bacteria - they require oxygen and are present in large quantities when seawater or surface water is used for waterflood injection. Chlorine, usually from a hypochlorite generator, is used for control.

Anaerobic bacteria, grow in the absence of oxygen. One strain is the sulphate reducing bacteria (SRB) that excrete sulphide ions that form hydrogen sulphide. The associated corrosion of equipment, safety hazard from H₂S, particle plugging, potential H₂S souring of a water-flood zone, and unsightly aesthetics of iron sulphide as well as sulphide smell cause these bacteria to be a major problem. A rigorous, permanent biocide program using commercial bactericides, or a chemical (glutaraldehyde, formaldehyde, or acrolein), is needed.

Facultative bacteria, grow in an aerobic or anaerobic environment. Their presence can create conditions aiding the growth of sulphate reducing bacteria (SRB). Specialized chemical selection is needed for control.

3.9 Produced Water Properties and Composition Ranges

Heavy metal	Minimum value (mg/l)	Maximum value (mg/l)
Calcium	13	25 800
Sodium	132	97 000
Potassium	24	4300
Magnesium	8	6000
Iron	<0.1	100
Aluminium	310	410
Boron	5	95
Barium	1.3	650
Cadmium	<0.005	0.2
Copper	<0.02	1.5
Chromium	0.02	1.1
Lithium	3	50
Manganese	<0.004	175
Lead	0.002	8.8
Strontium	0.02	1000
Titanium	<0.01	0.7
Zinc	0.01	35
Arsenic	<0.005	0.3
Mercury	<0.005	0.3
Silver	<0.001	0.15
Beryllium	<0.001	0.004

Parameter	Minimum value	Maximum value
Density (kg/m ³)	1014	1140
Conductivity (μS/cm)	4200	58 600
Surface tension (dyn/cm)	43	78
pH	4.3	10
TOC (mg/l)	0	1500
TSS (mg/l)	1.2	1000
Total oil (IR; mg/l)	2	565
Volatile (BTX; mg/l)	0.39	35
Base/neutrals (mg/l)	—	< 140
Chloride (mg/l)	80	200 000
Bicarbonate (mg/l)	77	3990
Sulphate (mg/l)	<2	1650
Ammoniacal nitrogen (mg/l)	10	300
Sulphite (mg/l)	—	10
Total polar (mg/L)	9.7	600
Higher acids (mg/l)	<1	63
Phenol (mg/l)	0.009	23
Volatile fatty acids (mg/l)	2	4900

Fakhru'l-Razi A, Pendashteh A, Abdullah LC, et al. Review of technologie sfor oil and gas produced water treatment. J Hazard Mater2009;170:530–51.

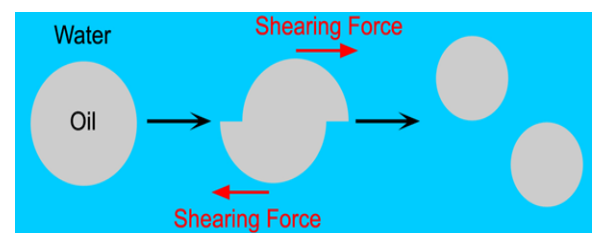
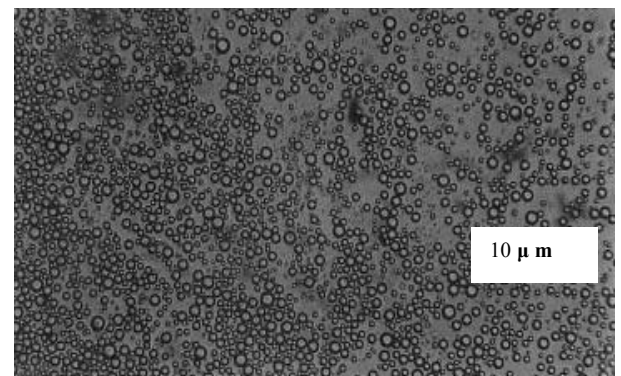
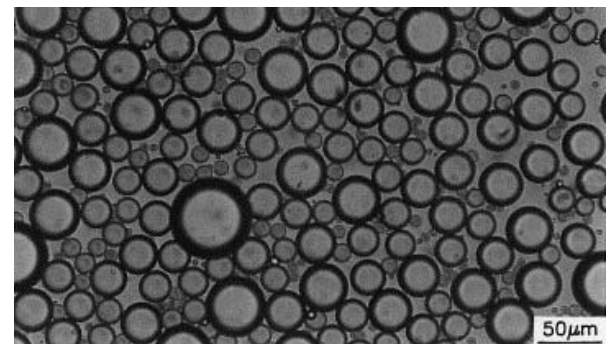
4 Oil Water Dispersion and Coalescence

4.1 Dispersion

Although an emulsion, the term dispersion is frequently used for produced water. Dispersion refers to the process of a discontinuous phase (oil) being split into small droplets and distributed throughout a continuous phase (water). This dispersion process occurs when energy is input to the system in a short period of time. This energy input overcomes the natural tendency of two immiscible fluids to minimize the contacting surface area between the two fluids.

The dispersion process is diametrically opposed by coalescence, which is the process in which small droplets collide and combine into larger droplets. As the oil and water mixture flows through the process plant, these two processes are simultaneously occurring. A droplet of oil splits into smaller droplets when the kinetic energy of its motion is larger than the difference in surface energy between the single droplet and the two smaller droplets formed from it. While this process is occurring, the motion of the smaller oil droplets causes coalescence to occur. Therefore, it should be possible to define statistically a maximum droplet size for a given energy input per unit mass and time at which the rate of coalescence equals the rate of dispersion.

One proposed relationship for the maximum particle size that can exist at equilibrium was proposed by Hinze as follows:



$$d_{\max} = 432 \left(\frac{t_r}{\Delta P} \right)^{2/5} \left(\frac{\sigma}{\rho_w} \right)^{3/5}, \quad (3.2)$$

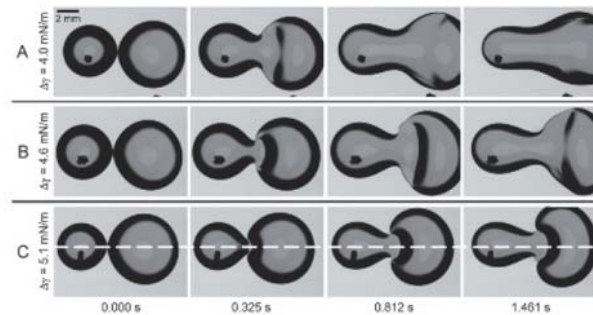
where

d_{\max} = diameter of droplet above whose size only 5% of the oil volume is contained, μm ,
 σ = surface tension, dyn/cm ,
 ρ_w = density, g/cm^3 ,
 ΔP = pressure drop, psi ,
 t_r = retention time, min .

It can be seen that the greater the pressure drop and, thus, the shear forces that the fluid experiences in a given period of time while flowing through the treating system, the smaller the maximum oil droplet diameter will be. That is, large pressure drops that occur in small distances through chokes, orifices, throttling valves, etc., result in smaller droplets. In practice such equations are of limited applicability as a result of the complexity of fluid flow and surface chemistry interactions.

4.2 Coalescence

The process of coalescence in water treating systems is more time dependent than the process of dispersion. In a dispersion of two immiscible liquids, immediate coalescence seldom occurs when two droplets collide. If the droplet pair is exposed to turbulent pressure



fluctuations, and the kinetic energy of the oscillations induced in the droplet pair is larger than the energy of adhesion between them, the contact will be broken before coalescence is completed. If there is no energy input, then the frequency of droplet collision, which is necessary to initiate coalescence, will be low, and coalescence will occur at a very low pace. The following empirical expression has been proposed;

$$t = \frac{\pi}{6} \left(\frac{d^j - (d_o)^j}{\phi K_s} \right), \quad (7-1)$$

where

d_o = initial droplet size, microns,

d = final droplet size, microns,

ϕ = volume fraction of the dispersed phase,

K_s = empirical parameter for the particular system,

j = an empirical parameter that is always larger than 3 and dependent on the probability that the droplets will “bounce” apart before coalescence occurs,

t = time required to grow a droplet of size d , min.

Again such expressions are of limited use due the very complex nature of the colloid chemistry.

5 Oil Water Treatment

The three techniques that are used in the design of common produced water treating equipment are ;

- Gravity separation
- Coalescence
- Flotation.

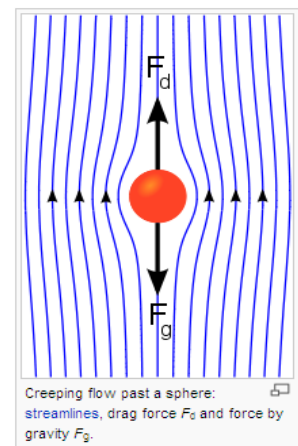
The most commonly used water treating equipment depends on the forces of gravity to separate the oil droplets from the water continuous phase. The oil droplets, being lighter than the volume of water they displace, have a buoyant force exerted upon them. This is resisted by a drag force caused by their vertical movement through the water. When the two forces are equal, a constant velocity is reached.

Like oil, gas, water separation Stokes Law is applicable. Several conclusions can be drawn from this simple equation:

$$v_{settle} = \frac{d^2 \cdot (\rho_w - \rho_o)}{18 \cdot \mu} \cdot g$$

It is clear that;

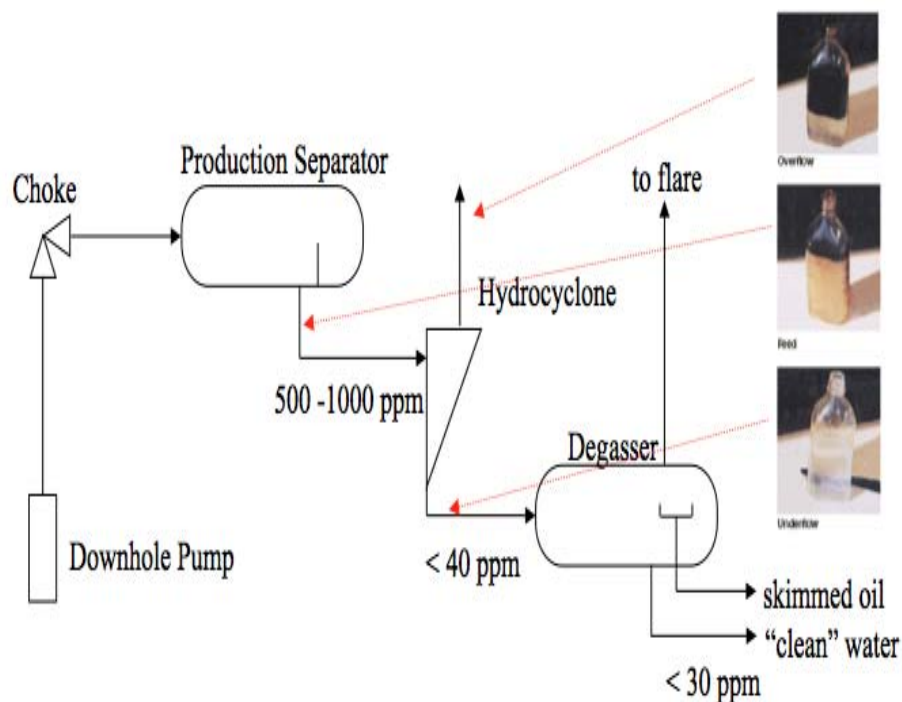
1. The larger the size of an oil droplet, the larger the square of its diameter and, thus, the greater its vertical velocity will be. That is, the bigger the droplet size, the less time it will take for the droplet to rise to a collection surface and thus the easier it will be to treat the water.



2. The greater the difference in density between the oil droplet and the water phase, the greater the vertical velocity will be. That is, the lighter the crude, the easier it will be to treat the water.
3. The higher the temperature, the lower the viscosity of the water and, thus, the greater the vertical velocity will be. That is, it is easier to treat the water at high temperatures than at low temperatures.
4. If g is increased separation will be improved.

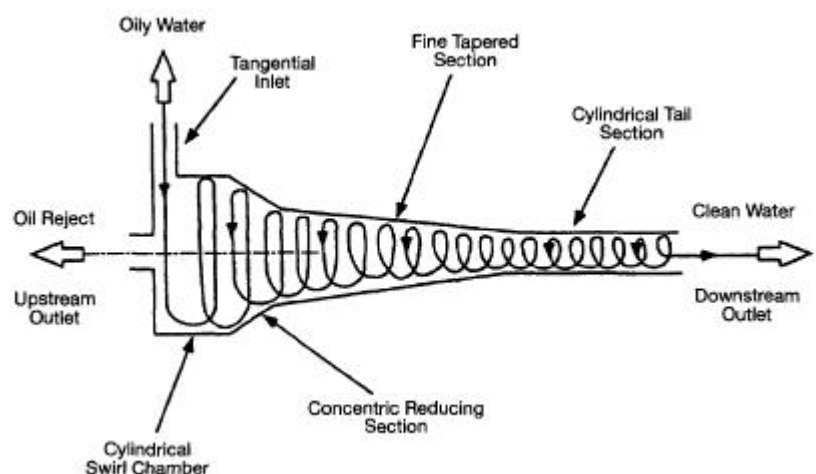
5.1 Typical UKCS Produced Water Treatment System

A typical system is shown in the following figure. Here water from a three phase separator is routed to a hydrocyclone then to a degassing vessel. Often with the aid of reverse demulsifiers this arrangement will in most cases deliver oil in water below the required disposal specification of 30 mg/l.



5.2 Hydrocyclones

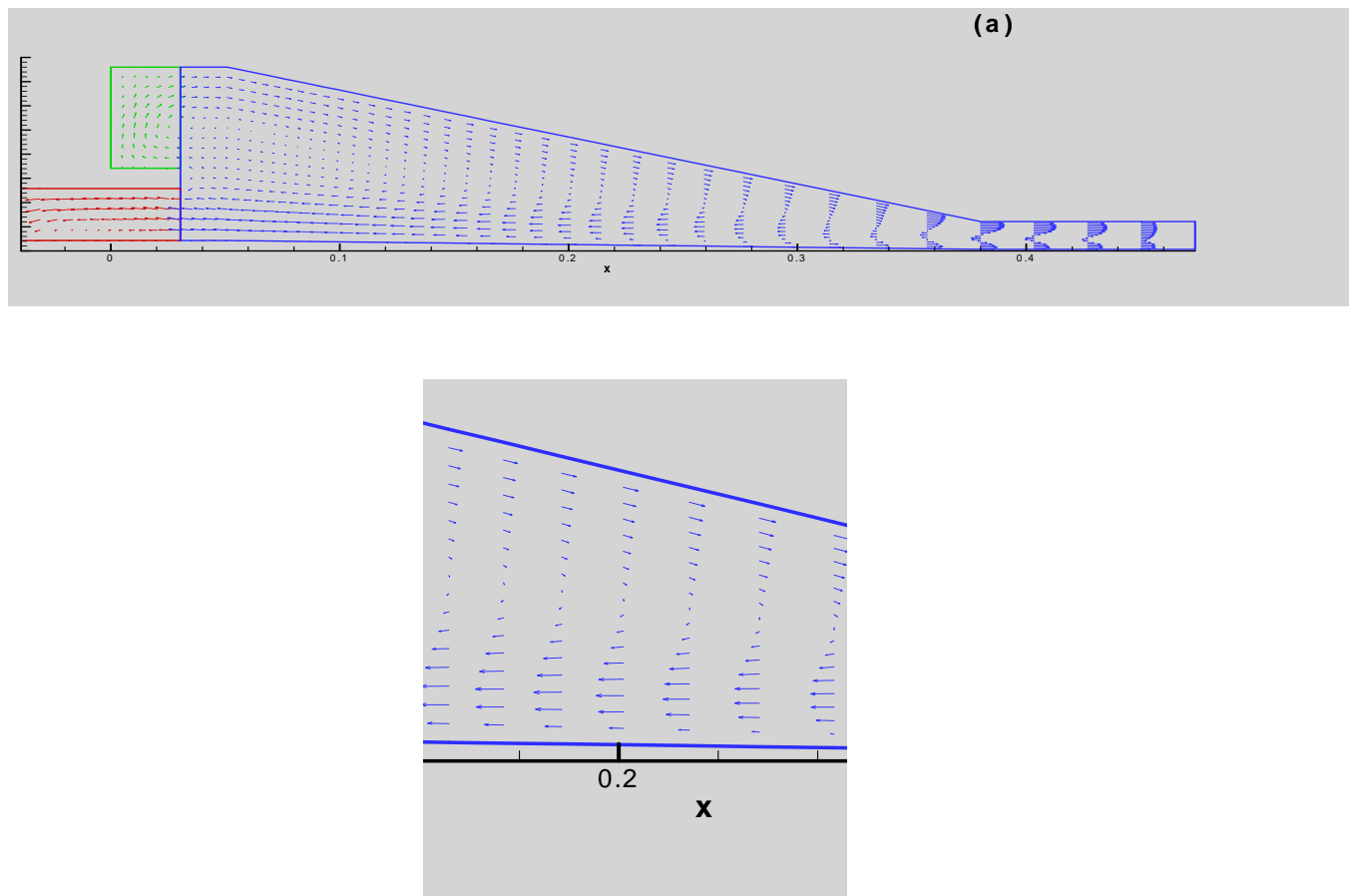
Hydrocyclone separators, sometimes called enhanced gravity separators, use centrifugal force to remove oil droplets from oily water. As shown, the static hydrocyclone



separator consist of the following four sections: a cylindrical swirl chamber, a concentric reducing section, a fine tapered section, and a cylindrical tail section. Oily water enters the cylindrical swirl chamber through a tangential inlet, creating a high-velocity vortex with a reverse-flowing central core. The fluid accelerates as it flows through the concentric reducing section and the fine tapered section. The fluid then continues at a constant rate through the cylindrical tail section. Larger oil droplets are separated out from the fluid in the fine tapered section, while smaller droplets are removed in the tail section. Centripetal forces cause the lighter-density droplets to move toward the low pressure central core, where axial reverse flow occurs. The oil is removed through a small-diameter reject port located in the head of the hydrocyclone separator. Clean water is removed through the downstream outlet.

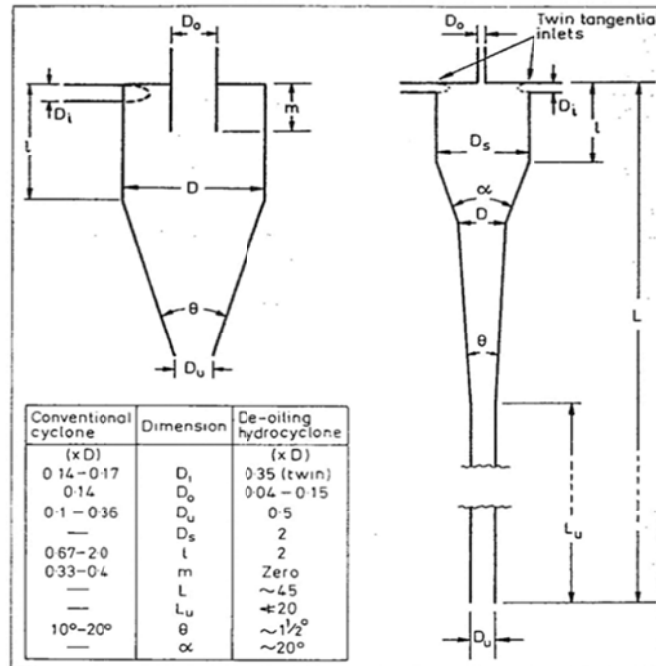
5.3 Hydrocyclone Design

Design of Hydrocyclones is proprietary to specialist companies, the Chemical Engineer would approach relevant companies for a design against a specification. Much use of CFD is made for design and velocity profiles in a half section are shown. Note the flow reversal at the rotating core.



5.3.1 Hydrocyclone Geometry

There are two distinct geometries used



The squat left hand unit is a Bradley type – used mainly for solids removal. The elongated arrangement is a Thew Type, developed at Southampton University, and is used for oil removal from water – liquid/liquid.

Typical dimensions of a Thew type are as follows;

$$D_i = 15\text{mm}$$

$$D_s = 50\text{mm}$$

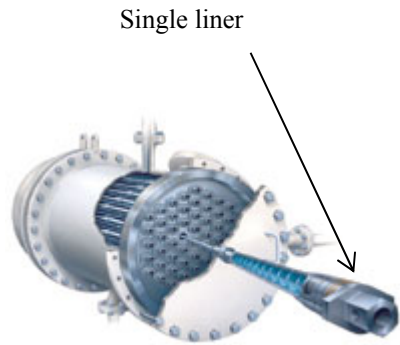
$$D_i = 15\text{mm}$$

$$D_o = 15\text{mm}$$

$$D_u = 5\text{mm}$$

$$L = 450\text{mm}$$

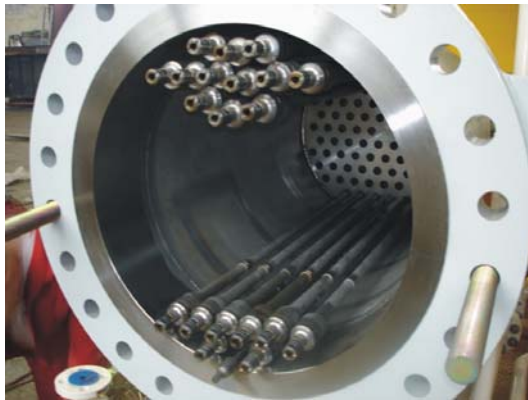
Suppliers provide units with $D_s = 25, 50$ and 75mm Rate is accounted for by providing more or less Hydrocyclones. The hydrocyclone units are often termed liners and are arranged as shown.



Source: Vortoil



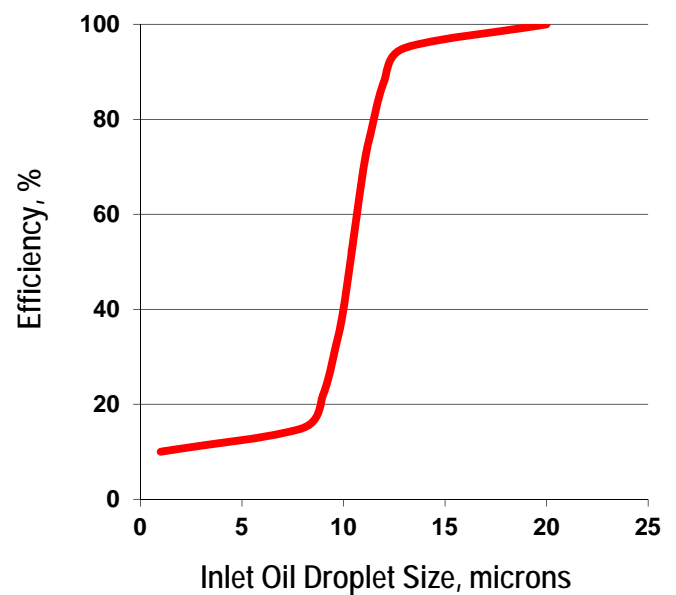
Source: NATCO



Droplet Removal Efficiency

A typical droplet removal is shown. As can be seen there is a critical droplet size of 10-15 microns where the efficiency of removal significantly reduces.

Pressure drop and velocity are also key to effective performance. Typically, as flow rate increases, the efficiency of separation increases and then levels out over the unit's operating range. Further increases in flow will eventually cause the efficiency to drop sharply.



A certain minimum flow rate is necessary to set up the vortex motion and to establish centrifugal separation forces that grow in intensity as the flow rate increases and improve the separation efficiency. A point will be reached for a given set of conditions, however, beyond which further increases in flow rate will cause performance deterioration. This is caused principally by the following.

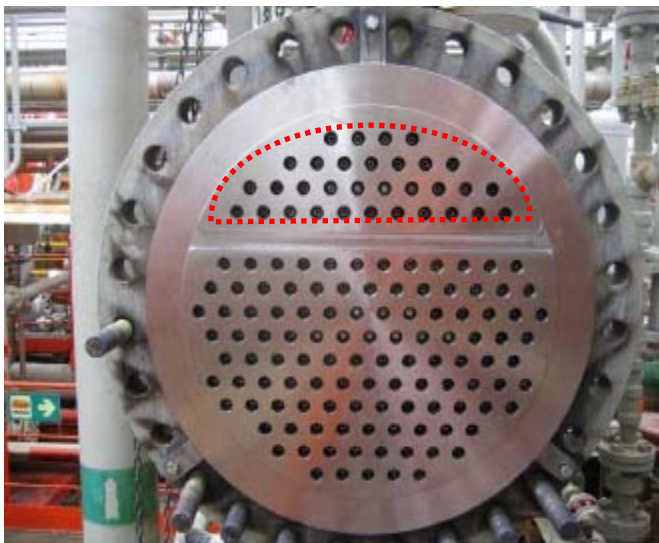
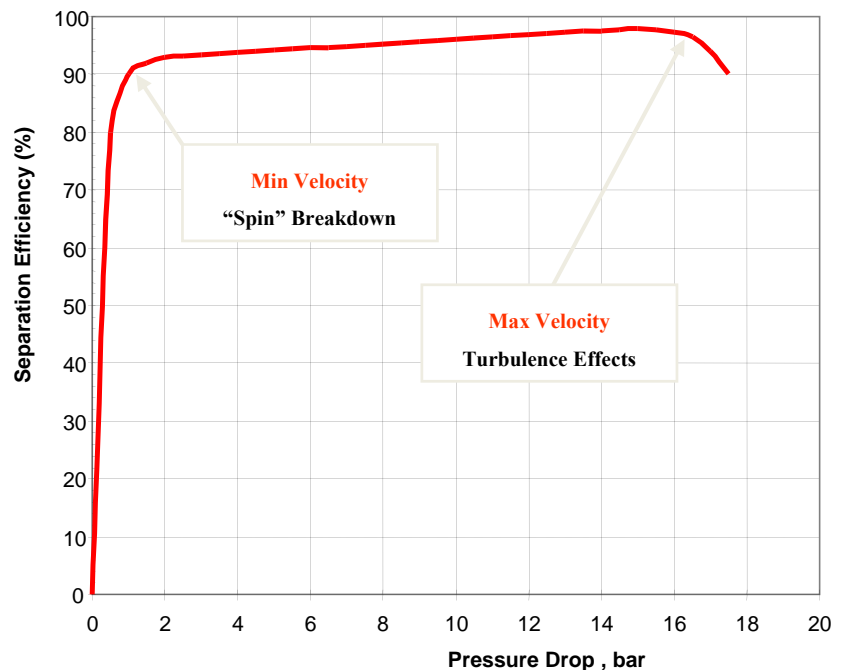
1. At very high flow rates, shearing of the oil droplets can occur, creating smaller droplets that are harder to separate.

2. As flow rate increases, the core pressure approaches atmospheric pressure, thereby reducing the available pressure to drive the reject stream. This inhibits the reject flow rate and results in little and eventually no separation.

This effect means that operation at reduced rates can pose a problem. In this instance an option is to isolate some liners thereby increasing the velocity in the operational liners.

This can be done by the use of

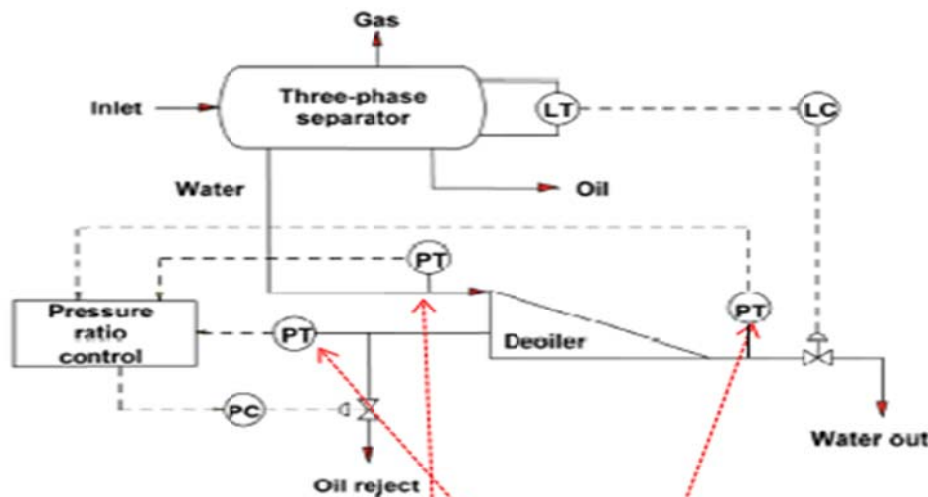
blanking plates manipulated by external valves as shown. Some designs offer the ability to individually isolate liners.



Note that the minimum pressure drop is around 2 bar. For a three phase separator operating at less than 2 bar, effective operation may require a boost pump. Such pumps are designed to be low shear to reduce droplet size reduction as the fluid passes through the pump.

5.3.2 Hydrocyclone Control

Hydrocyclone press control is critical for effective oil removal. The pressure difference ratio (PDR) is key and must be maintained above 1.6. PDR is defined as follows.

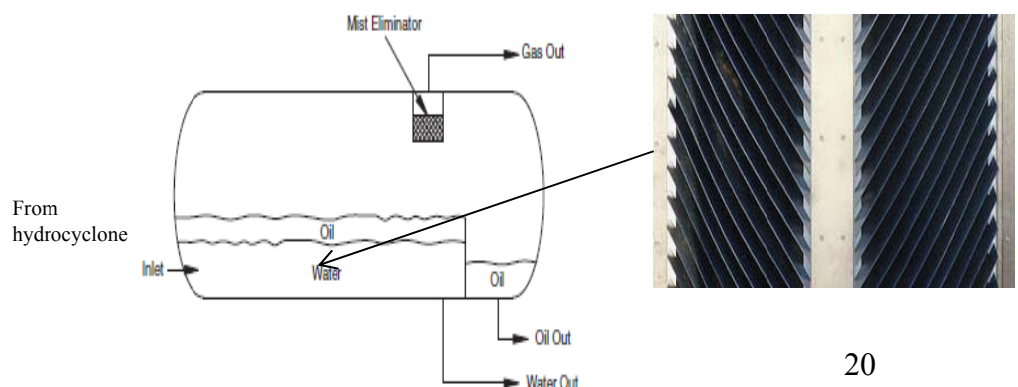


$$PDR = \frac{P_{in} - P_{or}}{P_{in} - P_{wo}} > 1.6$$

6 Degasser – Produced Water Flash Drum

Downstream of the Hydrocyclones a flash drum is used to provide a final polishing stage to further reduce oil in water and also to liberate any dissolved gases in the water. This drum normally operates 0.1- 0.2 bar above atmospheric pressure with evolved gases being sent to the low pressure flare system. The principles are the same as those discussed in the three phase separator module. Like the previous three phase separators the drum will incorporate a variety of internal features;

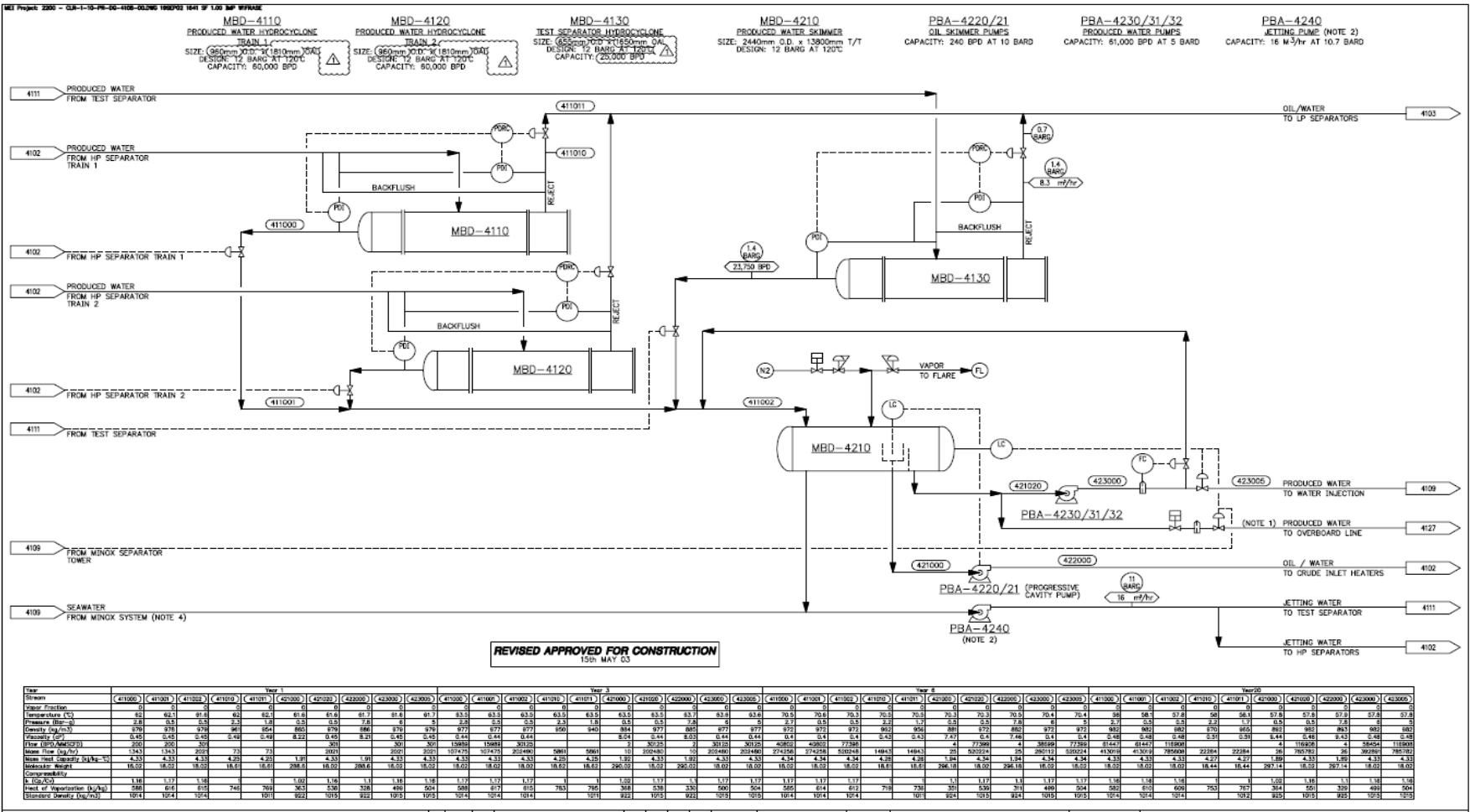
- Inlet devices
- Gas flotation internals



Schematic of a horizontal skimmer vessel.

- Distribution and calming baffles
- Liquid/liquid coalescers
- Oil skimming devices
- Liquid outlet distributors

A typical Produced Water PFD follows

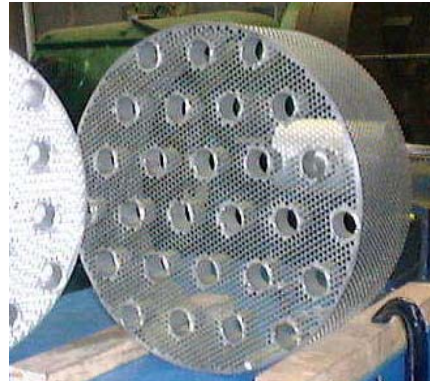
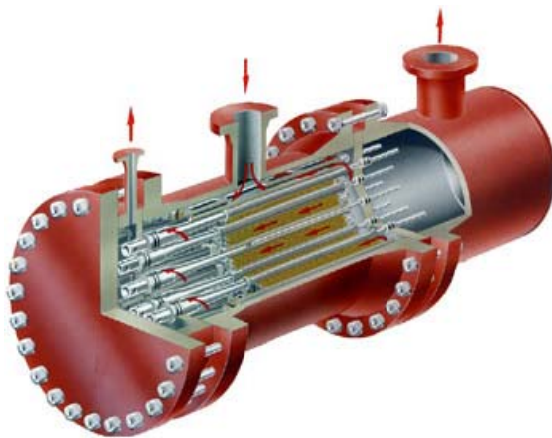


7 Oil Water Separation Enhancements

As discussed previously, if oil coalescence can be promoted separation efficiency will improve. Methods available for coalescence are;

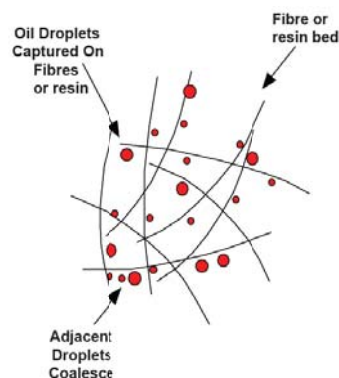
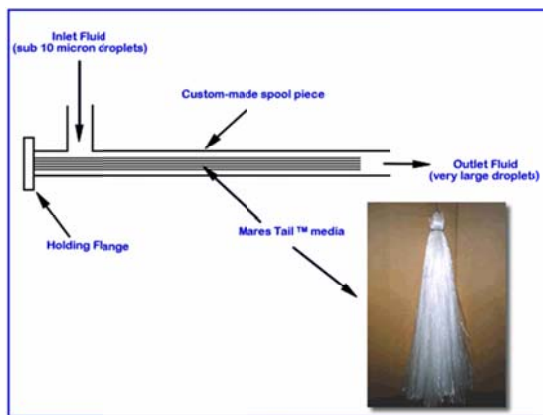
7.1 PECT-F

Proprietary coalescing device which is inserted into the shell of the hydrocyclone bank. As the oily water flows through the external matrix oil droplets coalesce.



7.2 Mares Tail

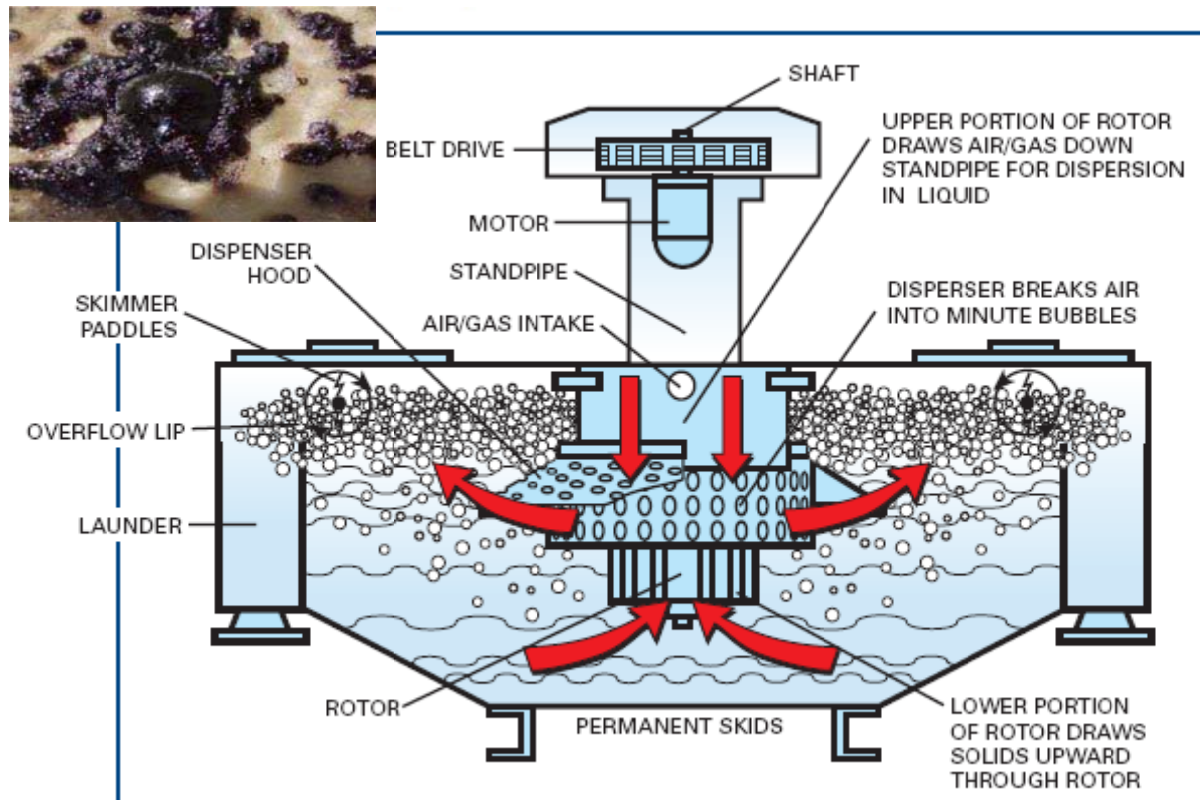
The descriptive name is an oleophilic material inserted into upstream pipework. Oil coalescence is promoted in the material strands.



8 Gas Flotation Units - Depurator

Oil separation is achieved by oil adhering to rising gas bubbles. A depurator is used which provides multiple cells, typically four where the following takes place;

- 1: Aeration. Each cell is equipped with a motor-driven, self-aerating rotor mechanism. The spinning rotor acts as a pump, forcing fluid through a disperser and creating a vacuum in the standpipe. The vacuum pulls gas into the standpipe and thoroughly mixes it with the fluid.
- 2: Flotation. The gas/fluid mixture traveling through the disperser creates a mixing force that causes the gas to form minute bubbles. Oil droplets and suspended solids attach to the bubbles as they rise to the surface.
- 3: Removal. The oil and suspended solids gather in a dense froth at the surface, where they are removed from the cell via launders.



Depurators can be very large and are now not favoured for offshore installations as hydrocyclones are much more compact and insensitive to motion.

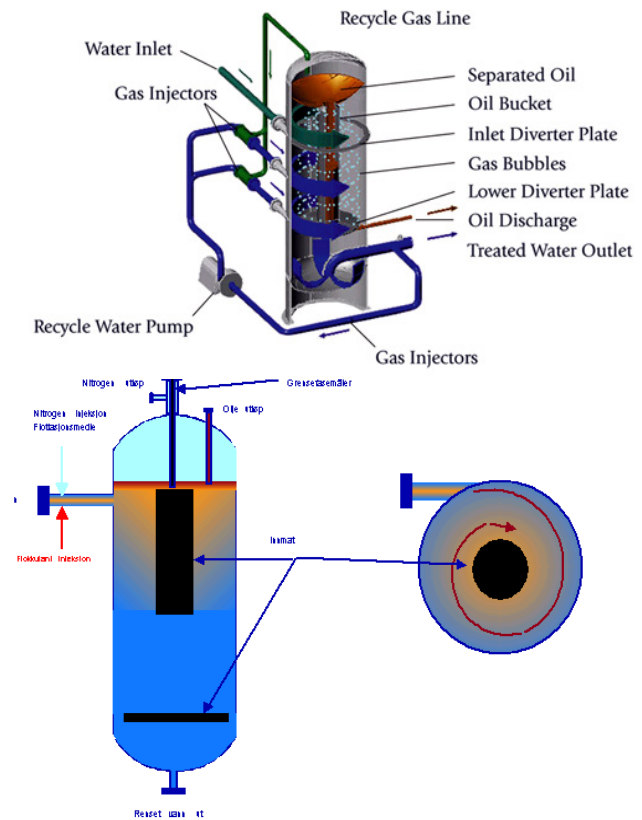


8.1 Compact Gas Flotation

Some suppliers are now offering a more compact form of Depurator. The produced water enters a vessel in a horizontal, tangential direction. A gas flotation effect is induced by the release of dissolved gas in the produced water. Oil droplets agglomerate and coalesce, facilitating separation from the water. Residence time is typically 30 seconds.

Manufacturers claim outlet concentration of 5 mg/l.

The action of the liberated gas also allows for removal of dissolved aromatic components by a stripping action – polycyclic aromatics (PAH) and benzene, toluene, ethylbenzene and xylene (BTEX).



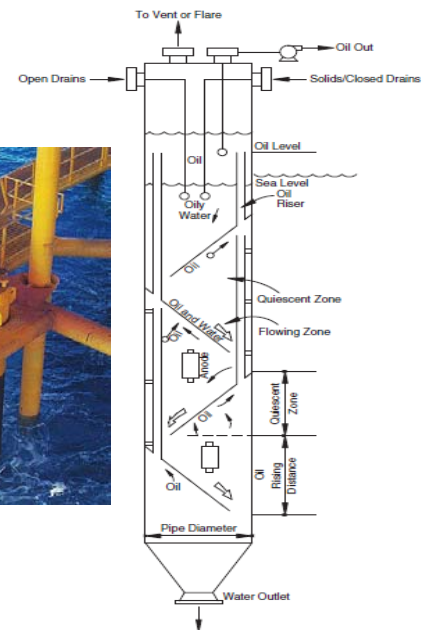
Treatment Levels

A summary of typical treatment levels is shown.

Method	Equipment	Approximate Droplet Size Removed (μm)
Gravity Separation	Degasser	100 - 150
	Skim Pile	
Plate Coalescence	Parallel Plate Interceptors	30 - 50
Gas Flotation	Depurators Flotation Units	20 – 40
Enhanced Gravity	Hydrocyclones	20 – 40
	Centrifuges	2 – 10
Osmosis	Membranes	1

9 Skim Piles/Caissons

Skim piles are gravity water-treating devices used offshore – often for deck drainage. Oil in water flows through a series of baffle plates. Large droplets migrate to the underside of the baffle plates then to an oil collection system. Field experience indicates a typical residence time of 20 minutes is required.



10 Produced Water Reinjection (PWRI)

This is the preferred disposal method for new projects by some Operators. PWRI is encouraged by DECC (Department of Energy and Climate Change). Note that it does not necessarily avoid the need to have good OIW (oil in water) as disposal to sea is required when PWRI is not available. PWRI can supplement Sea Water (SW) injection for pressure support. It may also be reinjected into a separate aquifer. When produced water is mixed with sea water care must be taken with chemical compatibility to prevent scaling and precipitation. Filtration and management of solids/sand can be a key issue. Note that pumping power demand can increase combustion emissions – hence trading off oil to sea with CO₂ to the atmosphere.

11 Produced Water Future Legislation

The UK has moved to a risk based assessment for produced water disposal. This will introduce toxicity testing moving the focus from dispersed oil to both dispersed and dissolved components. To treat dissolved components may require additional processing and processing plant. A key focus will PAHs and related cyclic and heterocyclic compounds, alkyl phenols and metals because of their assumed contribution to the ecological effects of produced water. Potentially harmful substances are listed below.

Substance group	Substances
Metals	arsenic, cadmium, chromium, copper, mercury, lead, nickel and zinc, iron and barium
The monoaromatic hydrocarbons (BTEX)	benzene, toluene, ethylbenzene and xylene
Dispersed oil:	C7-C40 aliphatic hydrocarbons
16 US-EPA Polycyclic Aromatic Hydrocarbons (PAHs)	naphthalene, acenaphthene, acenaphthylene fluorene, anthracene, phenanthrene, fluoranthene, pyrene, benz(a)anthracene, chrysene dibenzo(a)anthracene, benzo (g,h,i)perylene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3,-cd)pyrene
Other PAHs	C1-naphthalenes, C2-naphthalenes, C3-naphthalenes, C1-phenanthrenes, C2-phenanthrenes, C3-phenanthrenes, dibenzothiophene, C1-dibenzothiophenes, C2-dibenzothiophenes, C3-dibenzothiophenes
Phenol/alkylphenols	phenol, C1-alkylphenols, C2-alkylphenols, C3-alkylphenols, C4-alkylphenols, C5-alkylphenols, C6-alkylphenols, C7-alkylphenols, C8-alkylphenols and C9-alkylphenols
Organic acids	formic acid, acetic acid, propionic acid, butyric acid, valeric acid, isobutyric acid and isovaleric acid and naphthenic acids.

Potential treatment techniques for dissolved component management are;

11.1 Adsorption

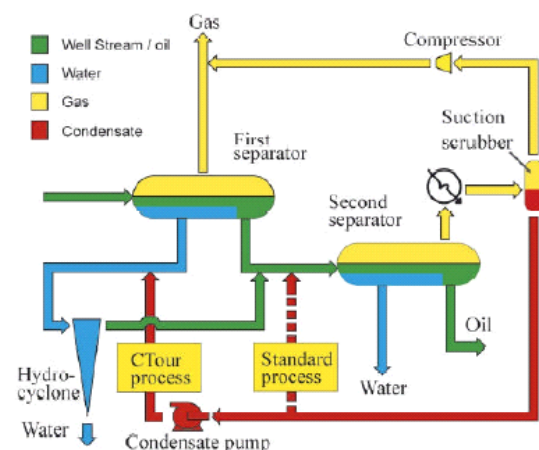
Produced water flows through a solid bed of adsorbent material. Several proprietary units offered by a number of suppliers. Mostly the beds are non-regenerable media based on starch or clay but regenerable options are now being marketed. Clearly if disposal is frequent the operating costs – OPEX - can be very high.



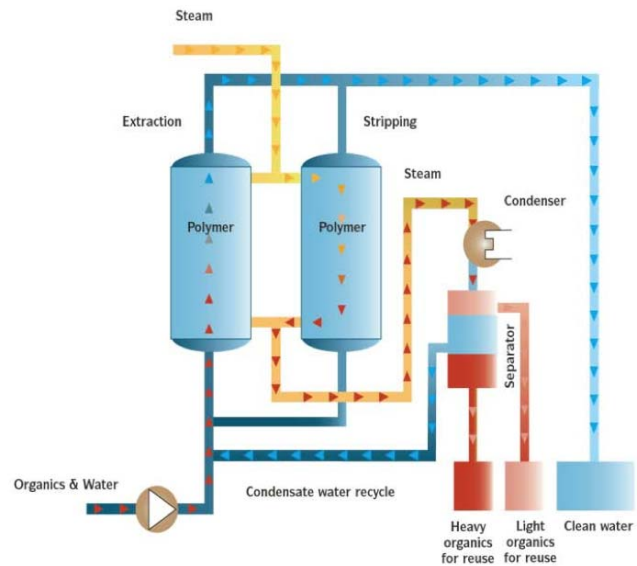
11.2 Extraction

Produced water it is brought into a contact with a hydrocarbon solvent and dissolved organics move to the hydrocarbon phase. Two proprietary packages are marketed are C-Tour and MPPE.

CTour uses a natural gas condensate.



MPPE uses a bed containing the extraction fluid which is periodically regenerated using steam and the oil/organics are recovered as shown.



11.3 Ultra Violet – Ozone Treatment

Advanced oxidation process using UV and ozone to create hydroxyl radicals OH^\cdot which react with hydrocarbons to convert to water and CO_2 . The process manages dissolved and dispersed hydrocarbons. There have been encouraging trials onshore at Flotta and offshore on Judy and Montrose.

11.4 Membranes

Membranes can be considered simplistically as filtration at a molecular. A range of processes are offered termed;

Reverse Osmosis

Nanofiltration

Ultrafiltration

Microfiltration

The target sizes are shown;

Size, μm	Ionic		Molecular		Macromolecular		Microparticle		Macroparticle	
	0.0001		0.01		0.1		1.0		100	
Approx. Mol. Weight	100 200		1,000 10,000		100,000 500,000					
Relative Size of Materials	Soluble Salts		Viruses				Bacteria			
					Latex/Emulsions					
	Metal Ions		Humic Acids				Clays		Cysts	
									Silt	
			Dissolved Organics				Algae		Sand	
Separation Process	Reverse Osmosis		Nanofiltration		Ultrafiltration		Microfiltration		Conventional Filtration	

11.4.1 Shell Corrib Produced Water Treatment

Corrib represents state of the art in produced water treatment. The plant achieves less than 0.3 mg/l hydrocarbons. For the Produced Water Treatment the following process steps have been installed.

1. Tilted Plate Separator (TPS) for removal of suspended solids and free oil.
2. Ultra filtration (UF) for removal of emulsified oil and certain organics
3. Nano filtration (NF) for the removal of the majority of heavy and other metals.
4. Carbon filtration for the removal of soluble organics.
5. Ion Exchange for the removal of residual heavy metals.



The separated solids from the TPS, concentrate from the NF, cleaning waste from the UF and NF, activated carbon backwash water and regenerate waste from the ion exchange columns are diverted to a balance tank, from which they are pumped into a reaction/flocculation tank. Chemicals are used to raise the pH, precipitate, coagulate and flocculate the metals in solution (including mercury). This produces a flocculated mass, which is dewatered on a filter press, producing a filter cake, which will contain the metals for separate disposal. The filtrate is recycled back to the Produced Water, TPS feed tank.

12 Production Chemicals

On a typical oil processing installation a range of chemicals can be used, these will generally partition into the hydrocarbon or aqueous phase depending on their chemistry. Their presence can affect the efficiency of water treatment. A summary follows.

Demulsifier - a blend of surfactants added to the produced fluids to enhance the separation of crude oil and water and optimise the quality of both the crude oil and the water. Demulsifier can be very specific for particular types of oils and waters. Chemical treatment companies can generally modify the blends such that a very good water quality is achieved without the need for further deoilers. If a demulsifier is dosed in too high concentrations (overtreating), stable oil-in-water emulsions in the separated water can be created.

Deoiler (Reverse Emulsion Breakers) - a chemical (also blend of surfactants) which is added to the separated water with the aim of promoting the coalescence (and subsequent removal) of finely dispersed oil droplets in the water. No general rule-of-thumb can be applied for the selection of treating chemicals to address a particular produced water quality problem. Testing by experienced staff using appropriate techniques is required to select and optimise any treatment. Different types of water clarifiers can possibly be applied.

Coagulants - neutralise the charges surrounding oil droplets and thereby promote coalescence. Coagulants are therefore often ions with a high charge.

Flocculants - are often polymeric products which can form bridges between droplets and thereby form large stable flocs which are easier to separate.

Scale inhibitors - prevent the formation of scales (e.g. calcium carbonate, calcium sulphate, barium sulphate and strontium sulphate) by attaching itself to the crystal surface and thereby preventing/modifying crystal growth.

Corrosion inhibitors - fall into two categories: passivating and protecting film formers.

Corrosion inhibitors generally enhance the creation of stable emulsions and thus from a water cleaning point of view they should be avoided if possible.

Biocides - are used to kill existing and/or prevent future bacteria growth. Bacteria normally originate from intervention (e.g. drilling fluid / brine contamination, seawater injection, etc.) but can also be naturally present in the reservoir.

Paraffin, hydrate and asphaltene inhibitors - these inhibitors are generally a form of aromatic hydrocarbon solvent that could be slightly soluble in water.

13 Sand Management

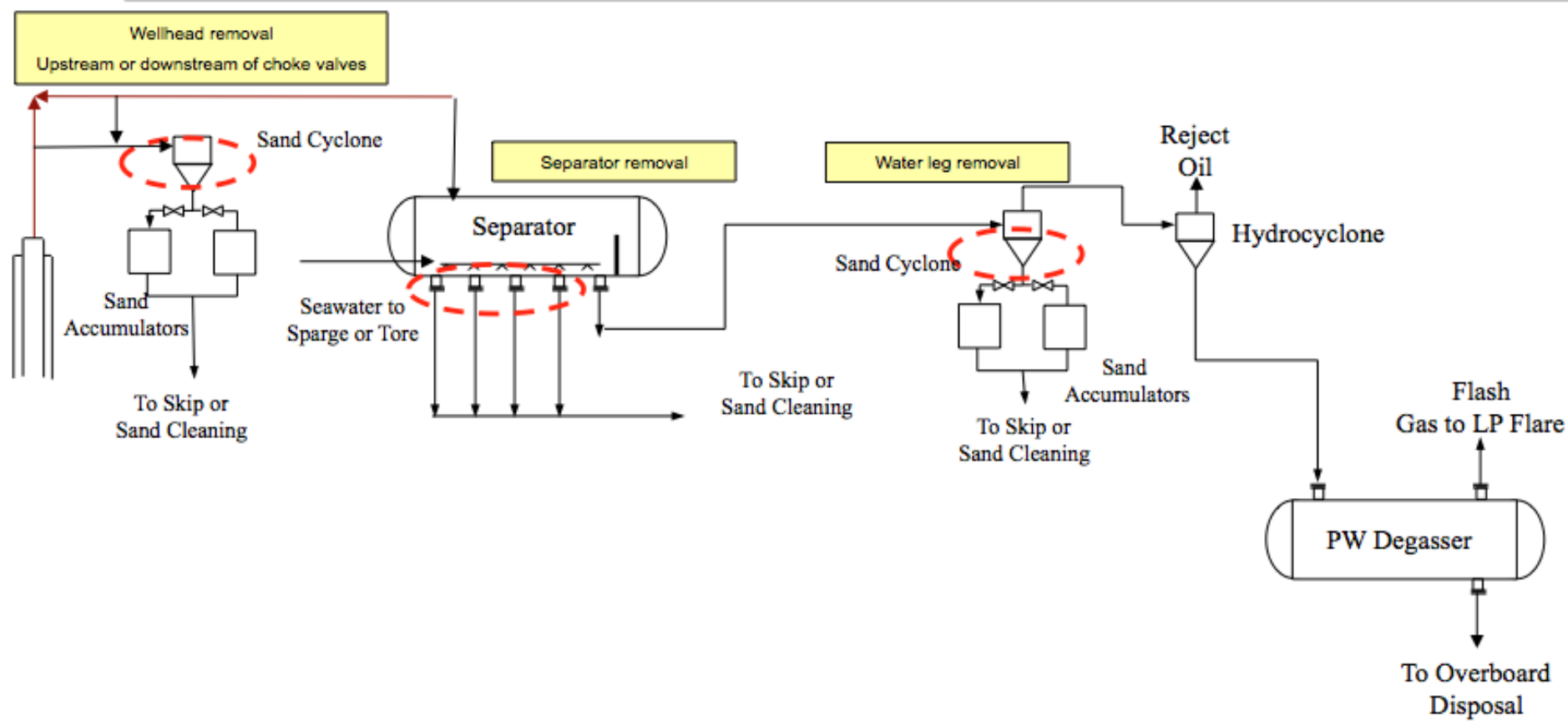
Many installations have to handle sand and due to its density it will generally move with the water phase. Sand can prove very problematic for process plant. Consequential erosion and potential loss of containment is a serious concern. At present there are no specific regulatory limits for the concentration of oil on sand/scale or total weight of oil on sand/scale that may be discharged from offshore installations. DECC expects the principles of Best Available Technology (BAT) to be applied when determining what methods for treatment and discharge of oil on sand and scale are to be employed. Discharge is covered by an OPPC permit (Oil Pollution Prevention and Control).

- Permitted levels of oil discharged with sand are based on historic performance
- Sand must be cleaned of oil
- Samples of sand must be taken for analysis
- Wash water to be routed via produced water treatment facilities or hazardous drains
- Chemicals discharged as a result of the operation must be reported to DECC

If exemption is not applied for then the sand must be put in a safe container and sent onshore for disposal.

13.1 Sand Removal

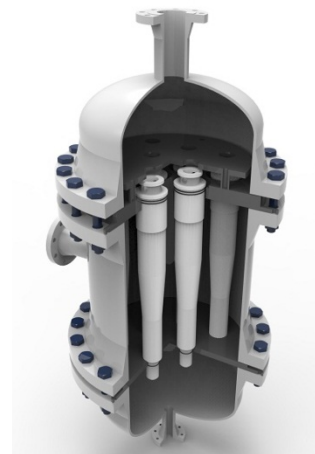
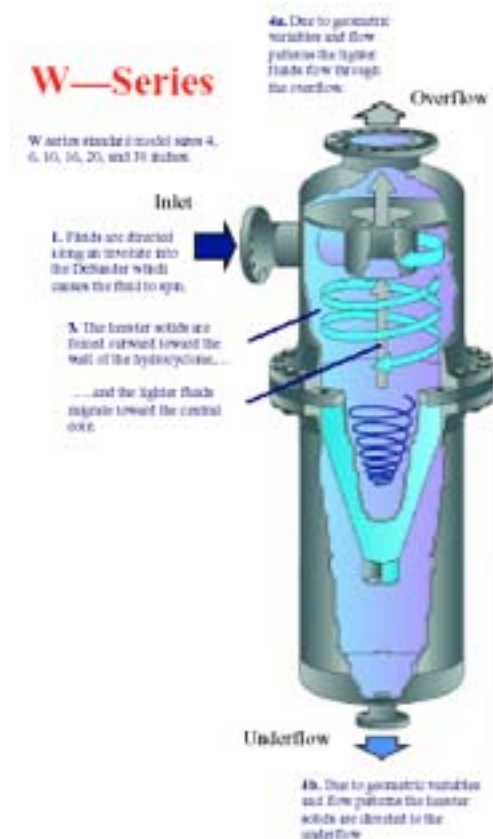
Typical sand removal options are shown. The ideal position being that the downhole sandscreens efficiently remove sand but this is often not the case and the screens pass solids hence topsides sand processing is required.



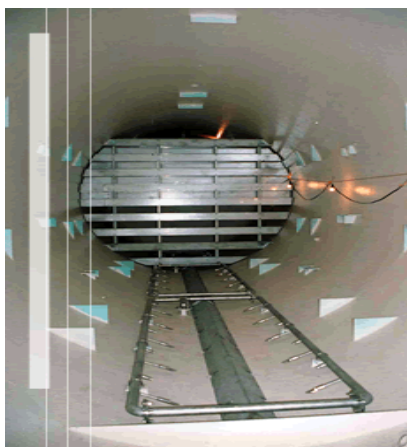
13.2 Desanding Cyclones

Sand cyclones are simple pieces of equipment for coarse and medium grade sand separation from bulk fluids utilising centrifugal sources to effect separation. Sand, being heavier will follow the under flow into a storage vessel while lighter fluids exit at the top of the unit.

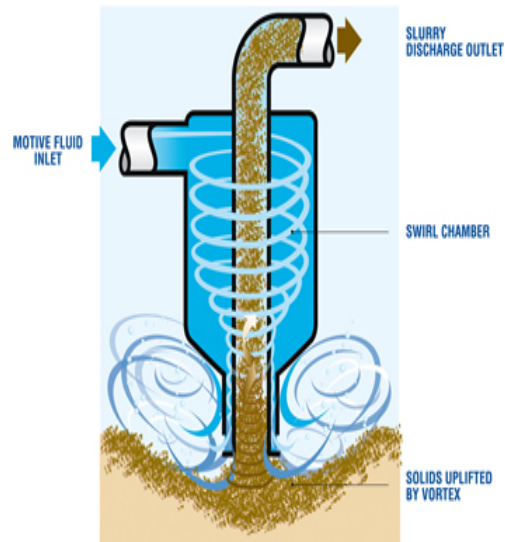
As the sand and water circulate the scouring action also cleans oil from the sand surface. Sand can be removed from at the wellhead or from separator outlets.



It can be difficult to remove sand from the base of a vessel. Spray bars can be used which introduce a fanned stream of water to fluidise the sand and allow removal with the water. Sprays are prone to leaving valleys and ridges may not fully clean the vessel. Typical spray bar arrangements are shown.



As a result of the ineffectiveness of some spray bar arrangement the proprietary Tore device is often utilised. The Tore induces a vortex that ‘sucks’ up the sand from the vessel as indicated.



14 Key Learnings

Produced water components

Principles of water-oil hydrocyclone

Hydrocyclone control system

Pressure and velocity effects

Principles of a depurator

Use of chemicals

Principles of sand cleaning