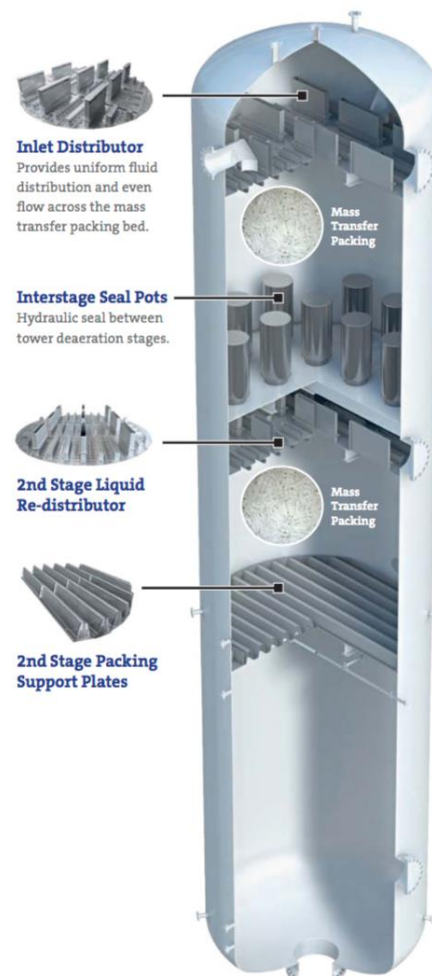


Water Injection



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9 KEY LEARNINGS

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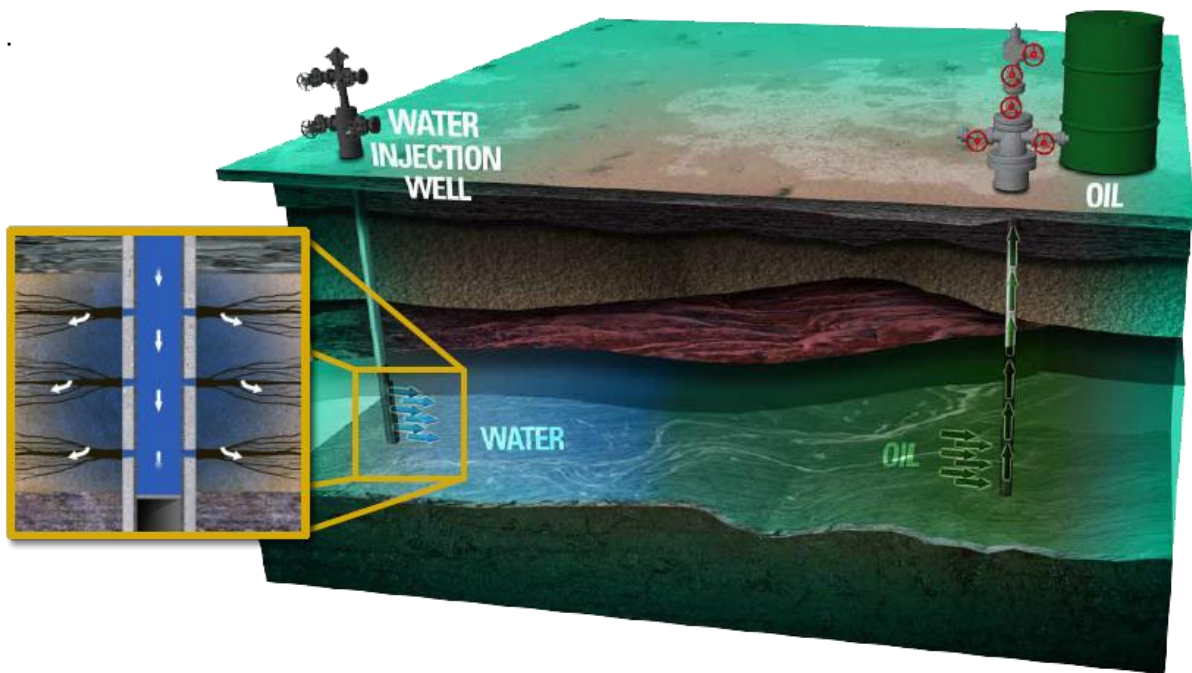
1 Introduction

Water injection serves two primary purposes;

Reservoir Pressure Support

As hydrocarbons are withdrawn from the reservoir formation, the pressure in the reservoir will decline and ultimately production will cease due to lack of pressure although there may be considerable hydrocarbon reserves remaining.

However, if the volume of produced fluids extracted is replaced by an equal volume of water at reservoir conditions then reservoir pressure can be maintained and recoverable reserves enhanced.



To avoid dumping produced water to the environment

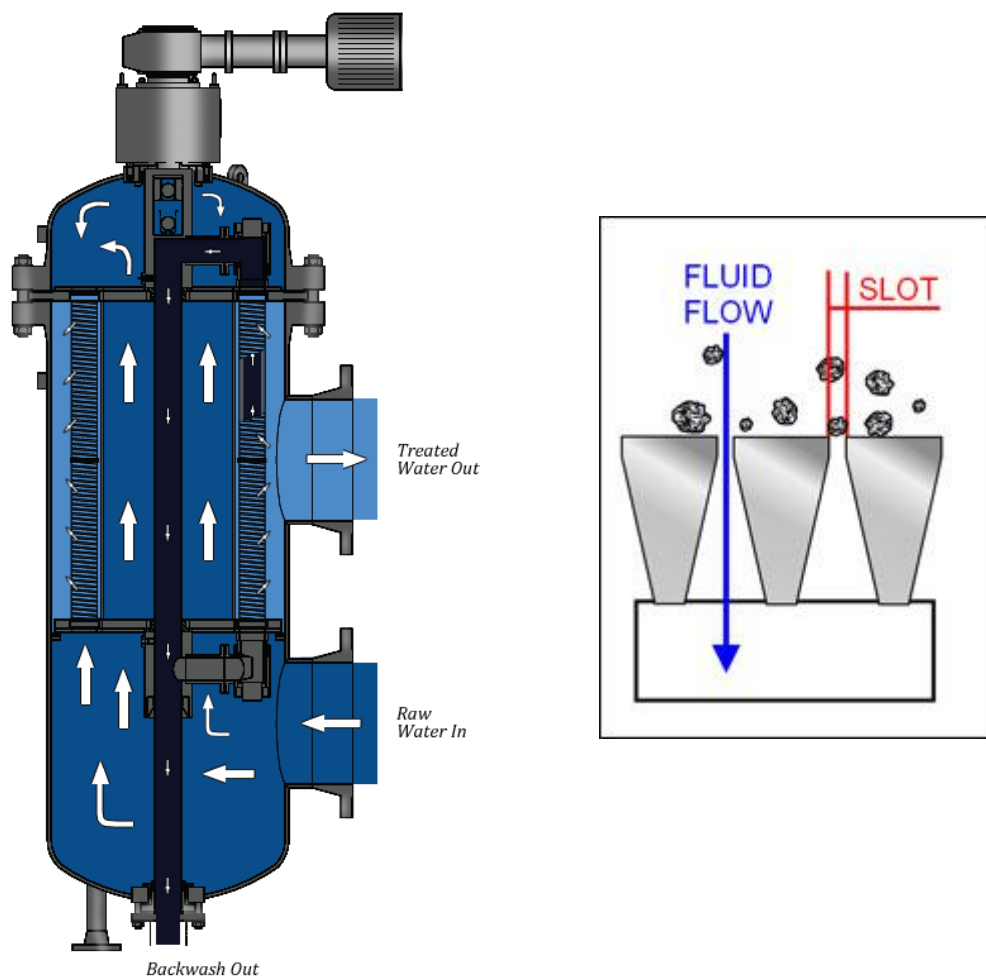
The water produced as a result of production operations needs to be disposed in an environmentally acceptable manner. The most common disposal method is surface disposal whereby water treatment facilities reduce the hydrocarbon concentration of the water to or below regulatory limits prior to discharge to sea. The alternative to surface disposal is re-injection into the reservoir.

Prior to injection the seawater has to be treated. Treatment involves filtration, oxygen removal, biocide treatment and possible scale control. This module cover these water injection treatment processes.

2 Solids Filtration

2.1 Seawater Coarse Filtration

Offshore, seawater is delivered onto an installation by lift pumps with delivery pressures typically 8-10 bar. The water will contain solid particles – plankton skeleton, sand – and these required to be removed. A typical specification being 95% removal of all particles greater than 50 microns. Wire wedge filters with automatic back flush are commonly used for this application. These units contain a number of cylindrical wedge filters. Seawater flows into the vessel and into the cylinders flowing through the wedges where solid particles are captured. An arm rotates over the cylinders and presents a low pressure, this reverses the flow through the wedge and displaces the captured particles as shown.



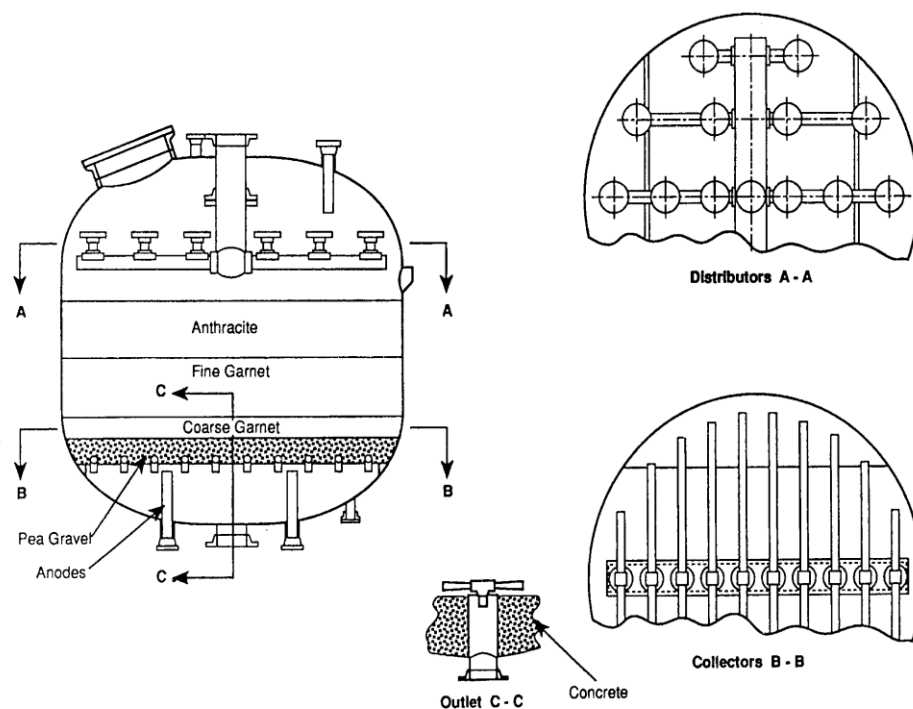
Design of these units is usually undertaken by a specialist vendor. A typical P&ID follows.



2.2 Fine Filtration

To prevent reservoir rock blockage due to injected solids, seawater historically was filtered to remove typically 98% of 2 micron particles. This was undertaken using batching of parallel filter beds. Filter beds consist of dual media; anthracite and garnet material, supported by graded gravel underbeds. The units are commonly referred to as sand filters. The sand beds are located in pressure vessels with internal seawater distribution and collecting systems. As the seawater flows the media the fine sold particles are trapped in the pores.

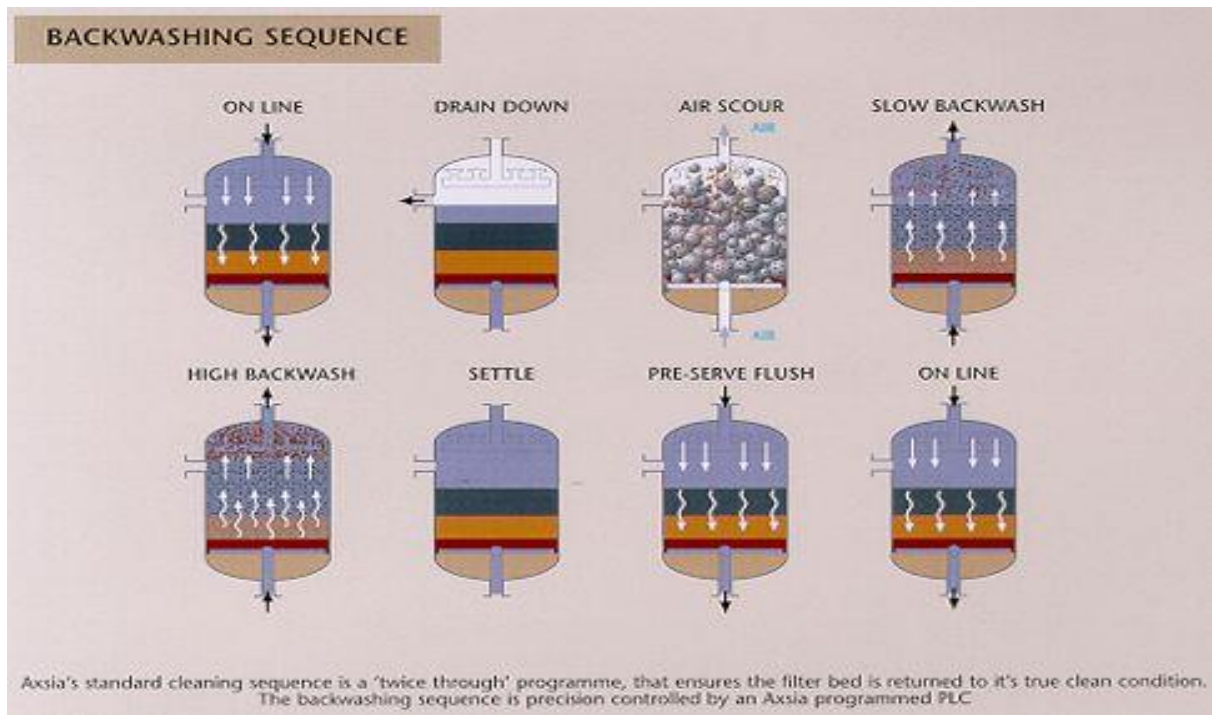
A typical sand filter arrangement is shown.



Typical flux rates $60 \text{ m}^3/\text{hr}/\text{m}^2$ which can be used for preliminary sizing.

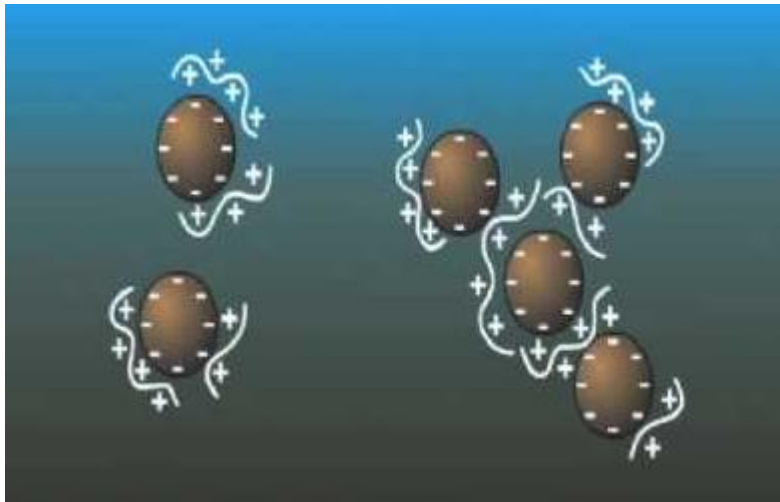
In time the bed will become clogged with the sand requiring regeneration for continued use. Regeneration is initiated at a pre-set pressure drop or by time in service. The bed is taken off line and a regeneration sequence commences. Regeneration typically involves - air scouring, backwashing and a pre-service flush. The back air scouring fluidises the bed and opens up the pores where the back flush removes the trapped solids.

A filtration sequence is shown.



2.2.1 Coagulation and Flocculation

Suspended matter in water may contain very small particles that will not settle out by gravity or that may pass through filters. These particles may be removed by a coagulation-and-flocculation process. Coagulation is the process of destabilization by charge neutralization, and flocculation is the process of bringing together the destabilized or coagulated particles to form a larger agglomerate, or floc.



Media filter performance is therefore enhanced by use of chemicals.

- Coagulant - ferric chloride

The coagulant affects the negatively charged cloud around small particles

- Flocculant - polyelectrolyte

These are long chain polymer which bridges particles and attaches them to the filter media.

Coagulation and flocculation results can be difficult to predict based on a water analysis; therefore, laboratory jar tests are performed to simulate the coagulation and flocculation condition. The laboratory data are then used to determine the basis for design and efficient operation. The tests are run to establish;

- Optimum pH for coagulation,
- Most effective coagulation and coagulation aid,
- Most effective coagulation dosage and order of chemical addition,
- Coagulation and flocculation time,
- Settling time or flocculation time

For seawater the above effects are well known.

Modern Practice

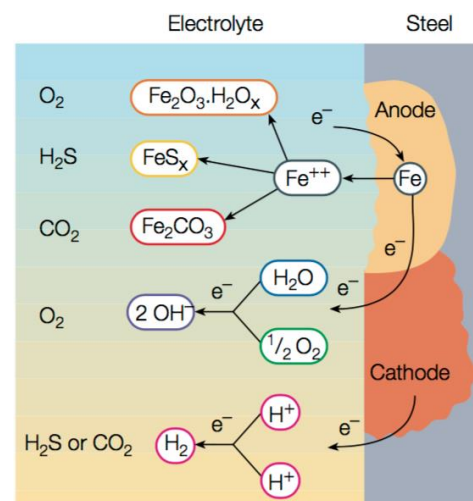
Through work by BP the need for Sand Filters has been reviewed. Many reservoirs do not require water to be filtered to 2 microns and can rely solely on coarse filtration; 40 -50 microns. This results in significant equipment savings by eliminating bulky sand filters.



3 Deaeration

3.1 Seawater Corrosion

Iron corrosion is illustrated in the following figure. At anodic sites iron readily goes into solution as Fe^{++} which readily combines with O_2 , H_2S and CO_2 to form scales/rust.



3.2 Oxygen Removal

The removal of oxygen from seawater is an established means of corrosion control and allows the use of carbon steel material for flowlines and downhole tubulars in place of corrosion

resistant alloys. An injection water oxygen-in-water specification is typically < 5 ppb, often 2-3 ppb mol fraction.

There are various methods for the deaeration of seawater:

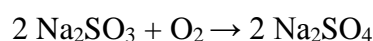
- Chemical Injection
- Gas Stripping
- Vacuum

Gas Stripping and Vacuum deaeration are referred to as a mechanical process.

3.3 Chemical Injection

Deaeration to the required levels using oxygen scavenger chemical is possible. However due to high operating costs it is usually used in conjunction with stripping or vacuum systems.

The most widely used materials in this application are sodium sulphite (Na_2SO_3) and hydrazine (N_2H_4). The sulphite reaction to sulphate is;



3.4 Gas Stripping

The traditional method of mechanical deaeration is by stripping. A stripping gas flows countercurrently against the seawater. The oxygen equilibrium is disturbed and oxygen migrates from the liquid to the gas.

The downside of this method is the continuous disposal of hydrocarbon emissions if process gas is used as the stripping gas. For that reason process gas is now seldom used. An alternative approach is to use inert gas such as nitrogen as the stripping gas and to have nitrogen regeneration facilities to remove the stripped oxygen. A derivative of this approach is the MINOX 'compact tower' system which is described later.

3.5 Vacuum Deaeration

Here oxygen mass transfer is facilitated by introducing a vacuum over the seawater. Thus reducing the partial pressure of oxygen and inducing oxygen movement from liquid to vapour. Two packed beds located in the same tower are often utilised. The upper bed operates at a higher pressure than the lower bed with 90% of the oxygen removal occurring in the upper bed. The two bed system offers energy saving requirements over a single bed. With a single bed all gases are liberated at the low pressure and requires a larger gas handling system.

A typical two bed tower is shown. Pall or Beta rings are the most common packing material. The upper bed typically operates at 40 Torr (750 Torr = 1 bar) with the lower at 15 Torr.

To achieve the necessary suction on the deaerator, a combination of vacuum pumps and atmospheric air driven ejectors are used.

A vacuum is pulled on each individual stage this lowers the partial pressure of oxygen and promotes oxygen mass transfer from liquid to vapour.

As the oxygen is removed, other inert gases are also drawn off e.g. nitrogen and carbon dioxide, as well as water vapour.

The design needs to allow for air leakage into the system and the pressure drop between the deaerator and the vacuum pump/ejector.

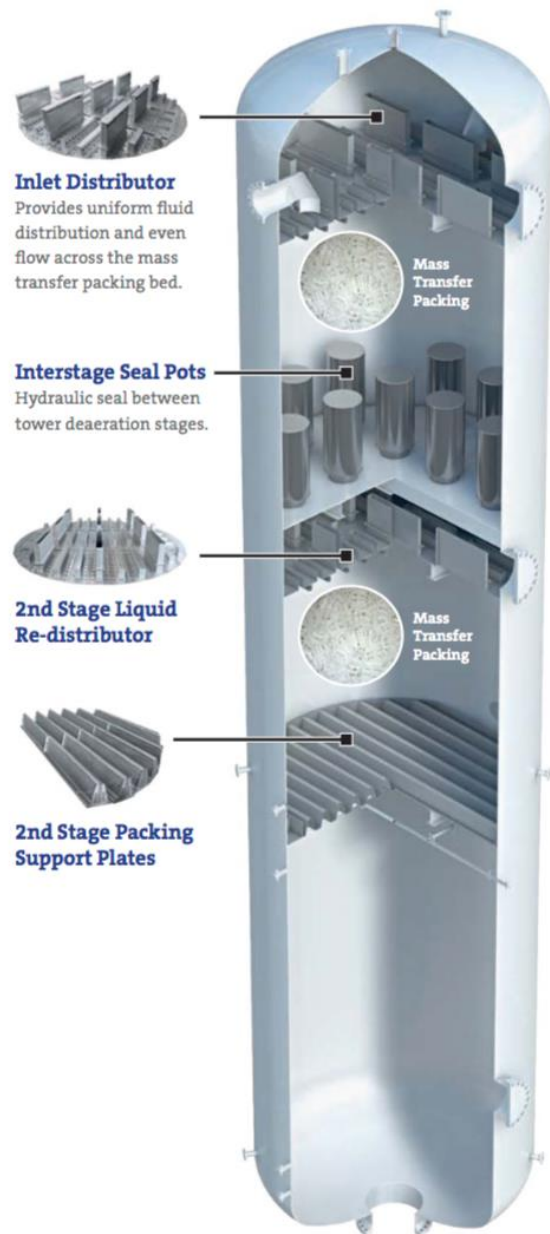
The sum of the inert gases, water vapour and leakage is the duty that is used to specify the vacuum equipment. Because of the large differential in the internal and external pressures, air will always tend to permeate into the deaerator.

Very low dissolved oxygen levels are required, and it is therefore critical that leakage is

minimised, particularly in and around the column sump. Experience has shown that sealing can be achieved by minimising connections and ensuring correct installation e.g. good quality gaskets, torqued flanges and utilisation of non-permeating measuring devices.

For lower oxygen residuals, lower operating pressures are required. But, the lower the pressure, the higher the proportion of water vapour is drawn off.

To achieve a 50 ppb wt outlet oxygen concentration in a single stage at an operating temperature of 10°C, for every 1 kg of oxygen removed a further 8 kg of water vapour would be removed.



This is facilitated by using 1, 2 or 3 mass transfer stages within the column, each operating at successively lower pressures e.g. the first stage operating at around 40 Torr and the second at around 10 Torr, the water vapour removal can be greatly reduced, with consequent reduction on vacuum loading.

The first stage removes the bulk of the oxygen (>93%), but because it is operating at a higher pressure, for every 1 kg of oxygen removed only 0.6 kg of water vapour is removed.

The second stage still has the ratio of 1 kg oxygen : 8 kg water vapour, but with a much smaller oxygen load. This is shown as follows;

Deaerator Stages	2	1
Total Oxygen Load	1 kg/h	1 kg/h
<u>Stage 1</u>		
Operating Pressure	40 Torr	-
Oxygen Load	0.93 kg/h	-
Water Vapour Load	0.558 kg/h	-
<u>Stage 2</u>		
Operating Pressure	10 Torr	10 Torr
Oxygen Load	0.07 kg/h	1.0 kg/h
Water Vapour Load	0.56 kg/h	8.0 kg/h
Total Vacuum Pump Load	180 m ³ /h @ 40 Torr	1100 m ³ /h @ 40 Torr
Pump Power	22 kW	75 kW

The reduction in vacuum duty is clear and this will be balanced against the higher cost of a two stage tower.

The sump of the column section provides residence time to allow chemical scavenging and final polishing to achieve the lowest residual oxygen levels from around 50 to less than 5ppb. The sump also provides a suction head for the downstream pumps and also acts as a buffer for pump run down.

3.5.1 Henry's Law

Henry's Law for dissolved gases is key to deaerator design. Recall Henry's Law as –

The partial pressure of the contaminant above the liquid

$$pp = H \cdot x$$

where;

H – Henry's constant

x – mol fraction of component in the liquid phase

The partial pressure of the species in the vapour phase is;

$$pp = y \cdot P_T$$

P_T – system pressure

y – mol fraction of component in the vapour phase

Henry's constant for common gases together with water vapour pressures are shown.

Perry 7th Edition (Pure Water)

T(°C) Units	VP H ₂ O Torr	H _{N₂} x 10 ⁻⁴ atm/mole fraction	H _{O₂} x 10 ⁻⁴	H _{N₂}	H _{O₂}
0	4.58	5.29	2.55	52,900	25,500
5	6.54	5.97	2.91	59,700	29,100
10	9.21	6.68	3.27	66,800	32,700
15	12.79	7.38	3.64	73,800	36,400
20	17.54	8.04	4.01	80,400	40,100
25	23.76	8.65	4.38	86,500	43,800
30	31.82	9.24	4.75	92,400	47,500
35	42.18	9.85	5.07	98,500	50,700
40	55.32	10.40	5.35	104,000	53,500
45	71.88	10.90	5.63	109,000	56,300
50	92.51	11.30	5.88	113,000	58,800
60	149.38	12.00	6.29	120,000	62,900
70	233.70	12.50	6.63	125,000	66,300
80	355.10	12.60	6.87	126,000	68,700
90	525.76	12.60	6.99	126,000	69,900
100	760.00	12.60	7.01	126,000	70,100

Note deaeration system vendors have corrections to H for water salinity.

Example - calculate the concentration of oxygen in water for an air water system in equilibrium at 15 °C? Oxygen concentration of air is 20.95 mol%.

$$H = 36400 \text{ atm/mf at } 15^\circ\text{C}$$

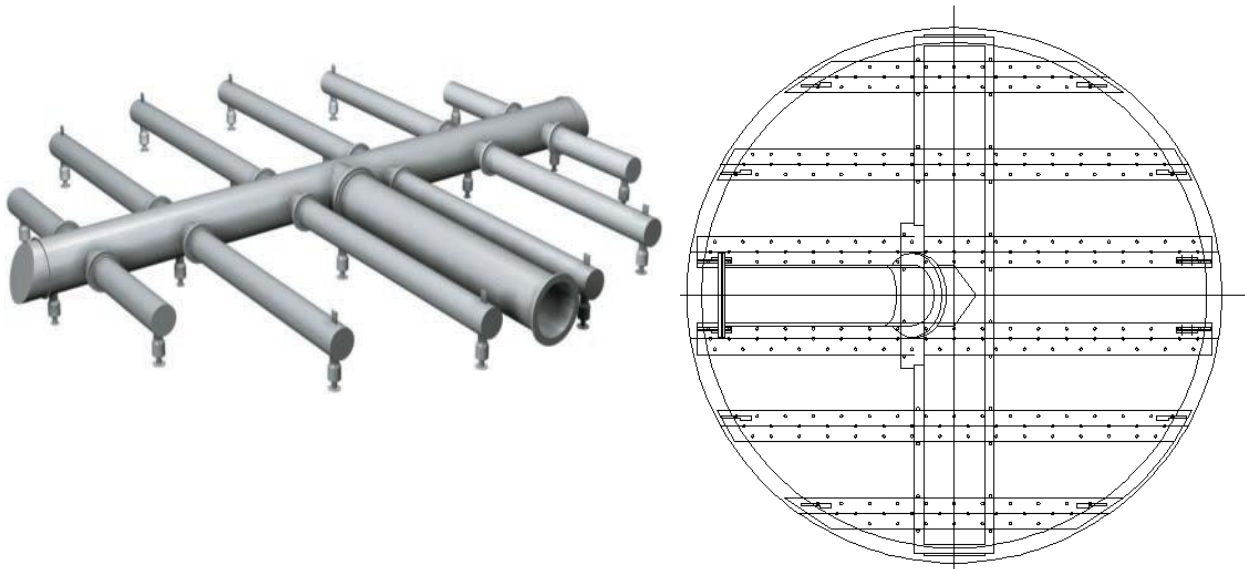
$$ppO_2 = 0.2095 \text{ atm}$$

$$X_{O_2} = 0.2095/36400 = 5.7 \times 10^{-6} = 5.7\text{ppm}$$

3.6 Colum Internals

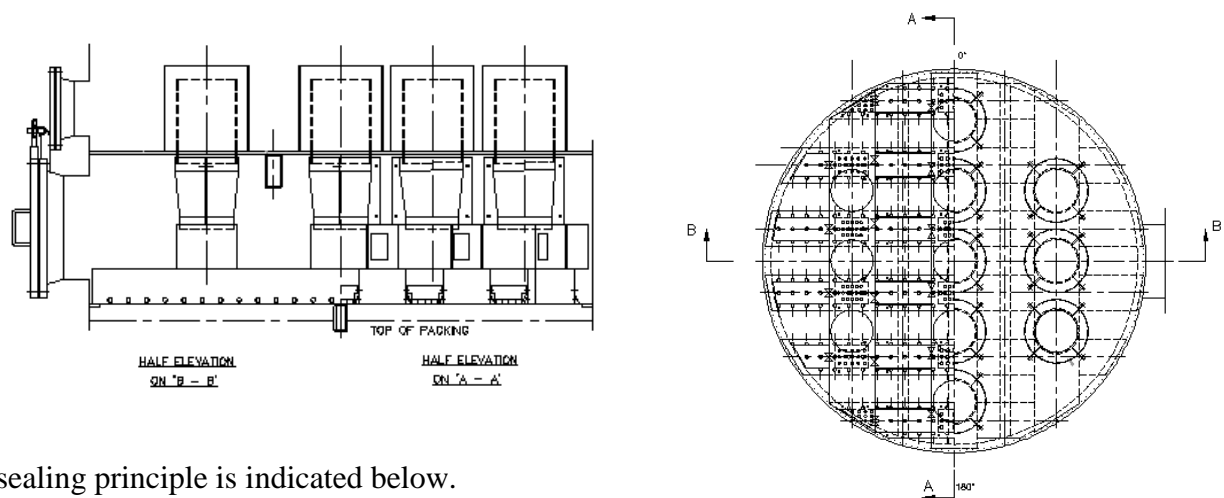
3.6.1 Top Distributor

A distributor is required to provide even flow over the packing. A typical Top Distributor arrangement is shown.

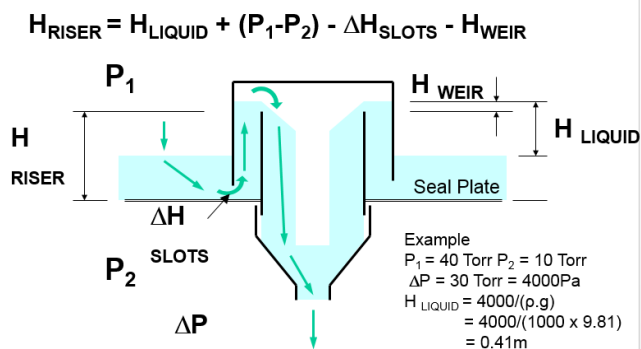


3.6.2 Seal Plate

For a multi-stage vacuum column a sealing system is required to allow operation at differing vacuums levels.



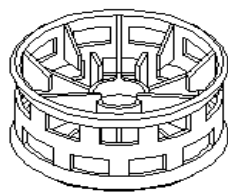
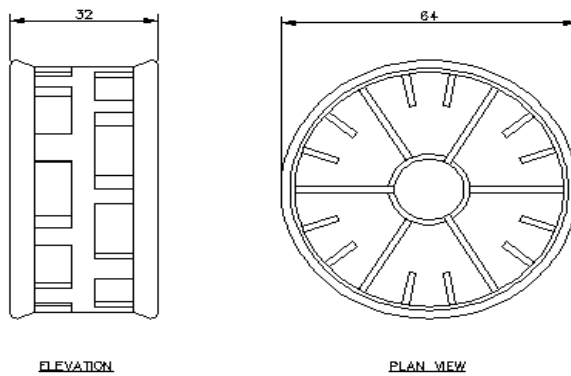
The sealing principle is indicated below.



3.6.3 Packing

Until recently the preferred packing material has been Beta Rings. However developments with structured packing have allowed improved mass transfer and pressure drop characteristics with some vendors claiming a 30% throughput improvement.

Beta Ring



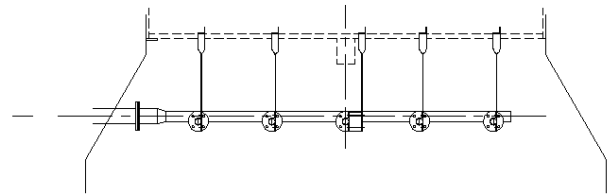
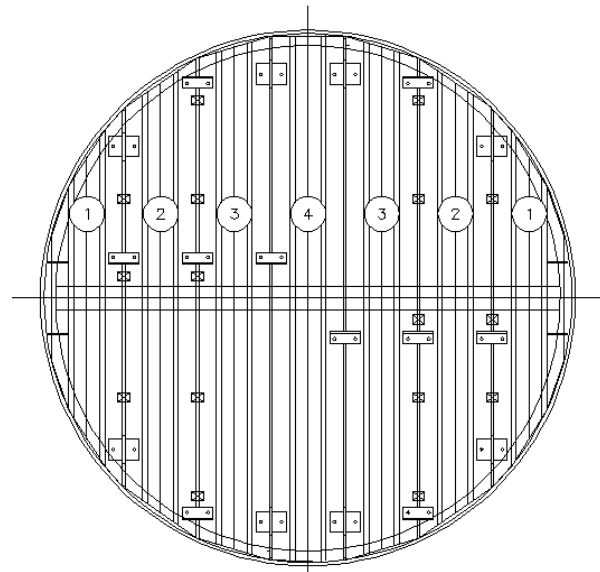
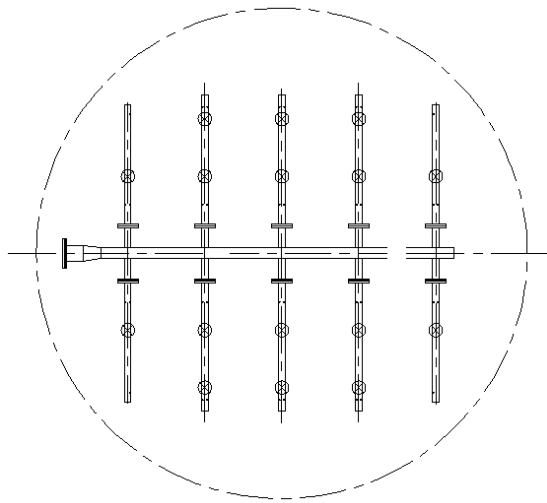
Structured packing



3.6.4 Support Plate

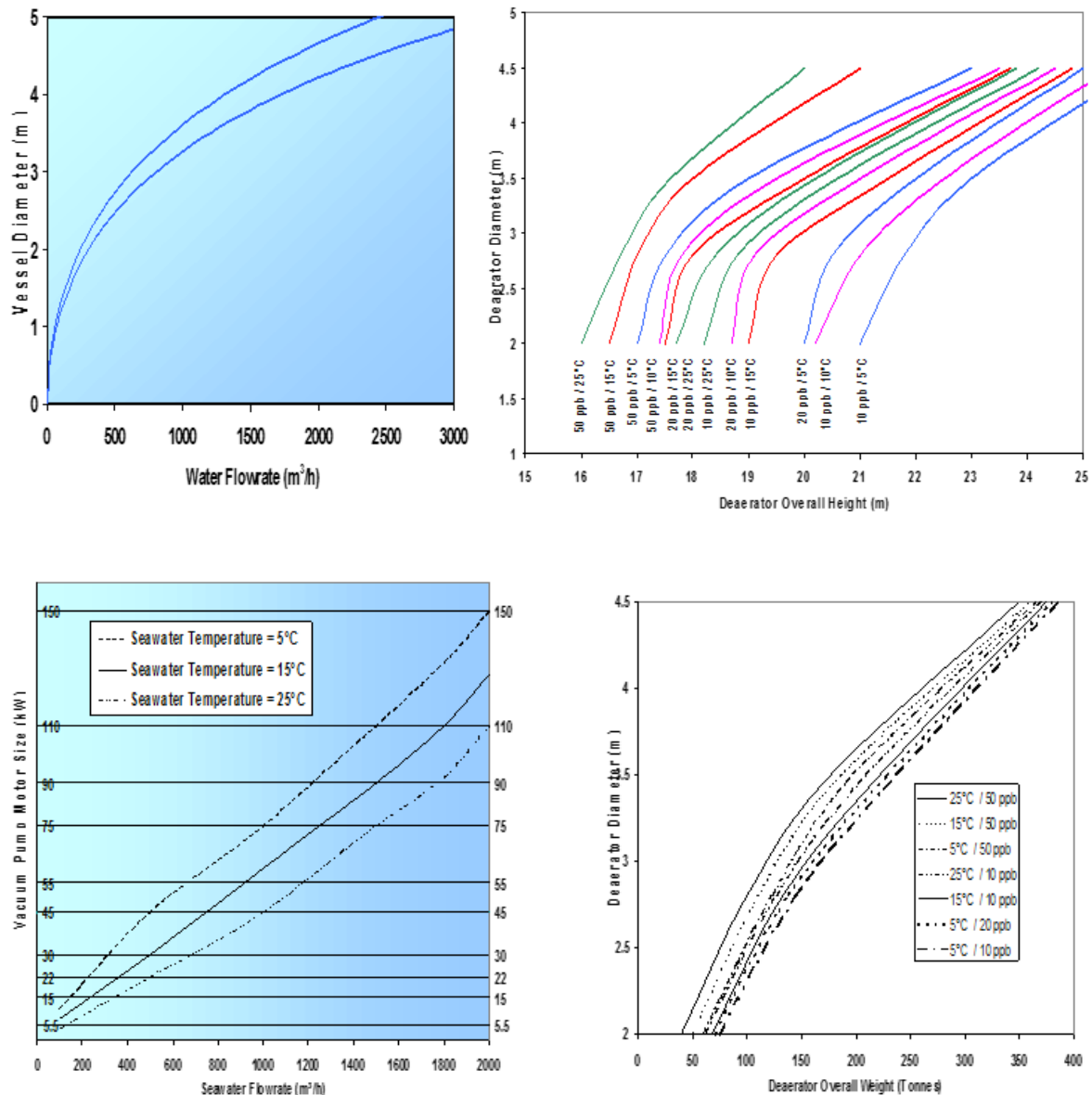


3.6.5 Oxygen Scavenger Spray Arrangement



3.6.6 Deaerator Preliminary Design

Preliminary Vacuum Deaerator sizing can be taken from the following;



4 Chemical Injection

A number of chemicals are required for the Water Treatment system:-

4.1 Oxygen Scavenger

Irrespective of the oxygen levels attainable by the deaeration equipment, oxygen scavenger will be provided to supplement and provide back-up to the deaeration system. Oxygen scavenger reaction requires residence time hence use of deaerator sump - 2 mins typical. Sodium and ammonium bisulphite are commonly used. It should be noted that the scavenger reacts with free chlorine hence preventing further biofouling control. This is usually dosed into the recycled carrier water flow from the booster pumps, back to the tower (approximately

1% of the tower throughput) to give good distribution into the sump. Based on ammonium bisulphite as the scavenging chemical, dose rates are typically;

8 ppm Scavenger per 1 ppm oxygen

2.4 ppm Scavenger per 1 ppm chlorine

1-2 ppm Scavenger to drive the reaction

At temperatures $<15^{\circ}\text{C}$, the reaction time is $\leq 1\frac{1}{2}$ minutes.

At temperatures $>15^{\circ}\text{C}$, the reaction time is ≤ 1 minute.

4.2 Biocide

Biocide injection points are provided downstream of the deaeration equipment. Biocide is normally injected periodically as required to kill any bacterial growth in topsides and downhole equipment. Chlorine and Gluteraldehyde ($\text{CH}_2(\text{CH}_2\text{CHO})_2$) are commonly used

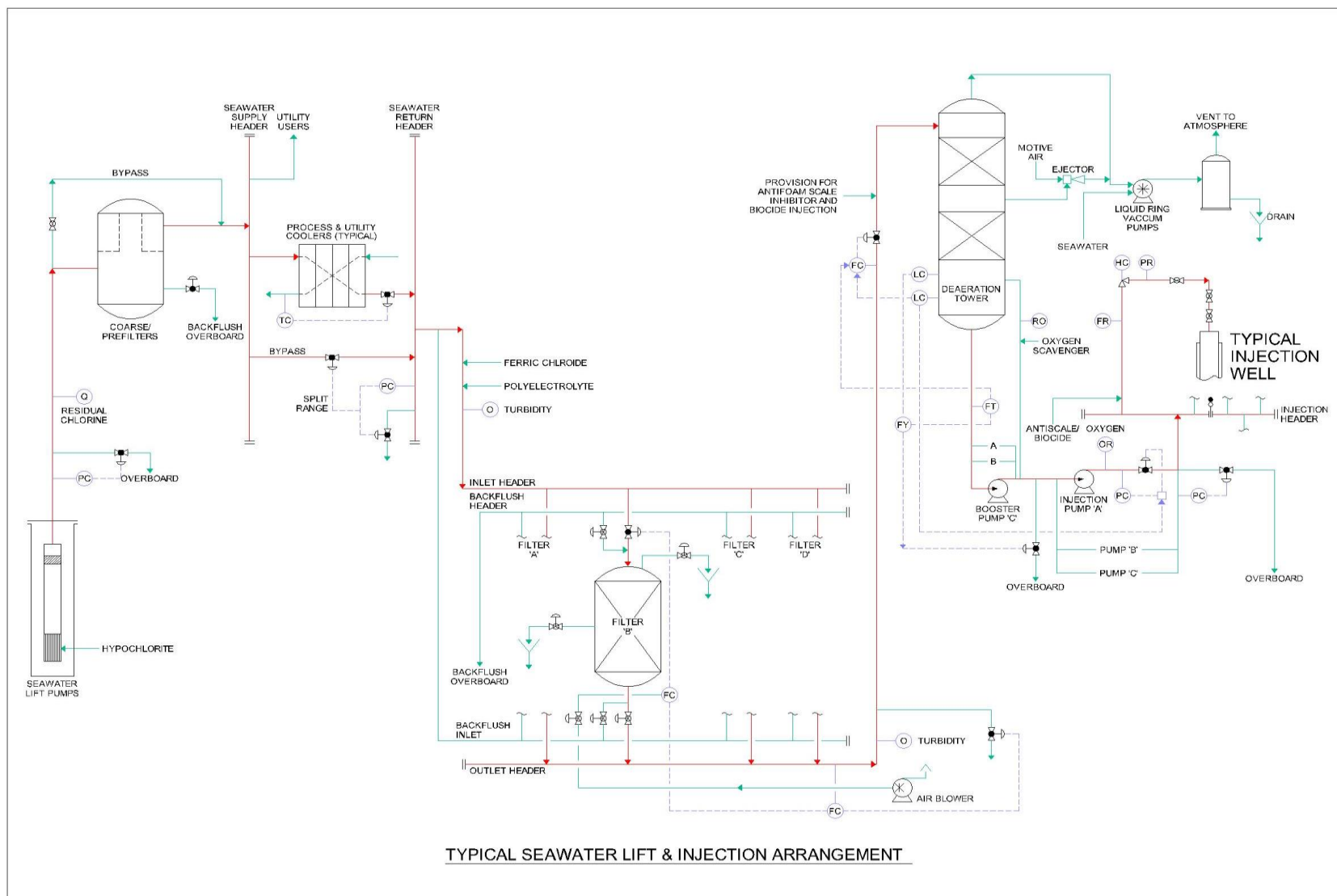
4.3 Anti-foam

Anti-foaming agents will be injected upstream of the deaerator if and when foaming within the deaerator impacts the outlet water specification. Dose rates are typically 1ppm.

4.4 Nitrate Addition

Biogenic formation of hydrogen sulphide can occur in most oil and gas reservoirs - particularly those flooded with seawater. The bacteria which produce H_2S are referred to as SRBs (sulphate reducing bacteria). Hydrogen sulphide requires specialist materials and also gives serious operational problems; sulphide corrosion, iron sulphide plugging, reduced product value, and health and environmental hazards. Historically, the sulphide problem has been treated with toxic biocides, which have proven to be costly and mostly ineffective. Nitrate-based microbial treatment technology can be used to limit H_2S . Nitrate addition encourages the production of non SRB bacteria and by bio exclusion SRB growth is minimised.

A typical vacuum deaerator PFD follows.



5 Gas Stripping

As stated earlier some of the early platforms oxygen stripping was performed using fuel gas which is now not preferred due to the loss of hydrocarbon gas. The Minox system is achieving wide acceptance. This system is based on nitrogen gas stripping, with stripping gas continuously recycled and regenerated through a catalytic combustion process, using methanol as the combustion fuel.

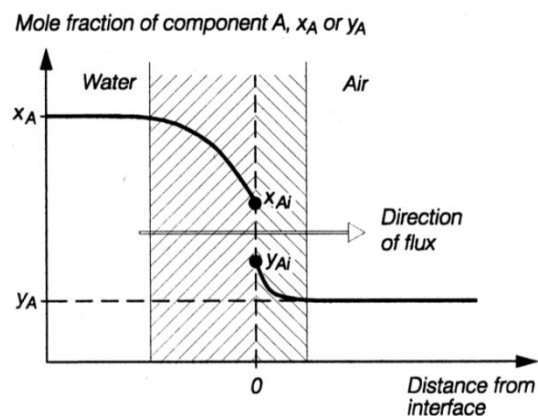
It is capable of achieving 10 ppb oxygen-in-water specification without the requirement of scavenging chemicals. A major advantage of Minox system over a vacuum system is the reduced stripping column height which in turn minimises motion effects and eases structural considerations. The system operates around 5 bar which provides a favourable suction head and can negate need for booster pumps.

5.1 Film Theory

Most techniques for designing packed columns for stripping (and absorption) are based upon the Whitman two-film theory concept.

Steady mass transfer equates the mass rate through the liquid film to that through the gas film.

$$\text{Mass flux} = K_{La} \cdot (x_A - x_{Ai}) = K_{Ga} \cdot (y_{Ai} - y_A)$$



The overall stripping mass transfer

coefficients K_{Ga} and K_{La} are based upon the driving force between the liquid and the gas.

This concept has been developed for the analysis of packed columns using the method of transfer units. In this method, the height of packing required can be evaluated either based on the gas-phase or the liquid-phase. The packed height (z) is calculated using the following:

$$Z = L_m / (\rho_m \cdot K_l) \cdot \int dx / (x_e - x)$$

Where;

L_m is the molar velocity, mol/hr.m²

K_l is the mass transfer coefficient

ρ_m is the molar density, kgmol/m³

x is the mole fraction of the solute in the main body of liquid

x_e is the mole fraction of the solute in equilibrium with the main body of gas

If the equilibrium and operating lines are straight, as is the case for O₂ stripping, then the integral may be replaced with the following;

$$(x_1 - x_2) / \Delta x_{lm}$$

$$\Delta x_{lm} = ((x - x_e)_1 - (x - x_e)_2) / \ln((x - x_e)_1 / (x - x_e)_2)$$

1 and 2 are top and bottom of column. e is the equilibrium oxygen level.

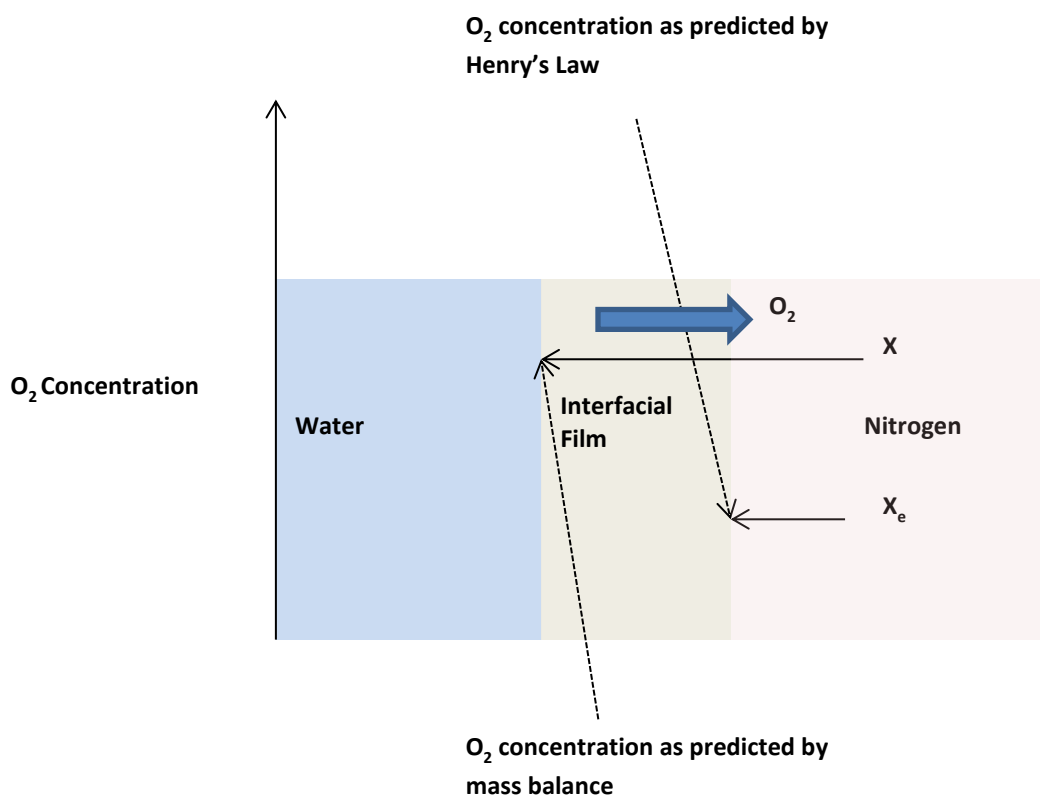
This is simplified to;

$$Z = N \times H$$

where ;

N = number of transfer units (NTU) – dimensionless = $(x_1 - x_2) / \Delta x_{lm}$

H = height of transfer units (HTU) - dimension of length = $L_m / (\rho_m \cdot K_1)$.



The number of transfer units (NTU) required is a measure of the difficulty of the separation.

A single transfer unit gives the change of composition of one of the phases equal to the average driving force producing the change. The NTU is similar to the number of theoretical

trays required for trayed column. Hence, a larger number of transfer units will be required for a very high purity product.

The height of a transfer unit (HTU) is a measure of the separation effectiveness of the particular packing for a particular separation process. As such, it incorporates the mass transfer coefficient. The more efficient the mass transfer (i.e. larger mass transfer coefficient), the smaller the value of HTU. HTU is generally supplied by the mass transfer equipment vendors. The values of HTU can be estimated from empirical correlations or pilot plant tests, but the applications are rather restricted.

Onda, Takeuchi, and Okumoto (1968) published useful but cumbersome correlations for the film mass-transfer coefficients k_G and k_L and the effective wetted area of the packing a_w , which can be used to calculate the HTU.

Their correlations were based on a large amount of data on gas absorption and distillation, with a variety of packings that included Pall rings and Berl saddles. Their method for estimating the effective area of packing can also be used with experimentally determined values of the mass-transfer coefficients, and values predicted using other correlations.

The equation for the effective area is shown:

$$\frac{a_w}{a} = 1 - \exp \left[-1.45 \left(\frac{\sigma_c}{\sigma_L} \right)^{0.75} \left(\frac{L_w^*}{a\mu_L} \right)^{0.1} \left(\frac{L_w^{*2}}{\rho_L^2 g} \right)^{-0.05} \left(\frac{L_w^{*2}}{\rho_L \sigma_L a} \right)^{0.2} \right]$$

The mass transfer coefficient is calculated from:

$$k_L \left(\frac{\rho_L}{\mu_L g} \right)^{1/3} = 0.0051 \left(\frac{L_w^*}{a_w \mu_L} \right)^{2/3} \left(\frac{\mu_L}{\rho_L D_L} \right)^{-1/2} (ad_p)^{0.4}$$

$$\frac{k_G}{a} \frac{RT}{D_v} = K_5 \left(\frac{V_w^*}{a\mu_v} \right)^{0.7} \left(\frac{\mu_v}{\rho_v D_v} \right)^{1/3} (ad_p)^{-2.0}$$

where $K_5 = 5.23$ for packing sizes above 15 mm, and 2.00 for sizes below 15 mm

L_w^* = liquid mass flow rate per unit cross-sectional area, kg/m²s

V_w^* = gas mass flow rate per unit column cross-sectional area, kg/m²s

The mass transfer coefficient is calculated from:

$$k_L \left(\frac{\rho_L}{\mu_L g} \right)^{1/3} = 0.0051 \left(\frac{L_w^*}{a_w \mu_L} \right)^{2/3} \left(\frac{\mu_L}{\rho_L D_L} \right)^{-1/2} (ad_p)^{0.4}$$

$$\frac{k_G}{a} \frac{RT}{D_v} = K_5 \left(\frac{V_w^*}{a \mu_v} \right)^{0.7} \left(\frac{\mu_v}{\rho_v D_v} \right)^{1/3} (ad_p)^{-2.0}$$

where $K_5 = 5.23$ for packing sizes above 15 mm, and 2.00 for sizes below 15 mm

L_w^* = liquid mass flow rate per unit cross-sectional area, kg/m²s

V_w^* = gas mass flow rate per unit column cross-sectional area, kg/m²s

a_w = effective interfacial area of packing per unit volume, m²/m³

a = actual area of packing per unit volume (see Table 17.2), m²/m³

d_p = packing size, m






σ_c = critical surface tension for the particular packing material given below:

Material	σ_c mN/m
Ceramic	61
Metal (steel)	75
Plastic (polyethylene)	33
Carbon	56

σ_L = liquid surface tension, N/m

k_G = gas film mass-transfer coefficient, kmol/m²s atm or kmol/m²s bar

k_L = liquid film mass-transfer coefficient, kmol/m²s (kmol/m³) = m/s

	Size		Bulk Density (kg/m ³)	Surface (m ² /m ³)	Packing Factor F_p m ⁻¹
	in	mm			
Raschig rings ceramic 	0.50	13	881	368	2100
	1.0	25	673	190	525
	1.5	38	689	128	310
	2.0	51	651	95	210
	3.0	76	561	69	120
Metal (density for carbon steel) 	0.5	13	1201	417	980
	1.0	25	625	207	375
	1.5	38	785	141	270
	2.0	51	593	102	190
	3.0	76	400	72	105
Pall rings metal (density for carbon steel) 	0.625	16	593	341	230
	1.0	25	481	210	160
	1.25	32	385	128	92
	2.0	51	353	102	66
	3.5	76	273	66	52
Plastics (density for polypropylene) 	0.625	16	112	341	320
	1.0	25	88	207	170
	1.5	38	76	128	130
	2.0	51	68	102	82
	3.5	89	64	85	52
INTALOX [®] saddles ceramic 	0.5	13	737	480	660
	1.0	25	673	253	300
	1.5	38	625	194	170
	2.0	51	609	108	130
	3.0	76	577		72

The units for k_G will depend on the units used for the gas constant:

$$R = 0.08206 \text{ atm m}^3/\text{kmol K} \text{ or}$$

$$0.08314 \text{ bar m}^3/\text{kmol K}$$

The film transfer unit heights are given by

$$\mathbf{H}_G = \frac{G_m}{k_G a_w P}$$

$$\mathbf{H}_L = \frac{L_m}{k_L a_w C_t}$$

where P = column operating pressure, atm or bar

C_t = total concentration, kmol/m³ = ρ_L /molecular weight solvent

G_m = molar gas flow rate per unit cross-sectional area, kmol/m²s

L_m = molar liquid flow rate per unit cross-sectional area, kmol/m²s

Typical HTU values for a gas stripping unit are 0.6 – 1.0 m

5.2 Minox System

‘Minox’ technology uses nitrogen stripping gas to remove oxygen from the seawater to typically below 15-20 ppb prior to the seawater being injected into the reservoir. Oxygen is subsequently removed from the stripping gas using a catalytic de-oxidising process. This system is often selected in preference to the more normal vacuum de-aeration systems as the ‘Minox’ column operates with a single stage of packing which leads to a lower column height.

The stripper is a conventional counter-current flow (stripping gas against seawater) within a compact deaerator tower which contains structured packing to promote contact between the nitrogen and seawater. The oxygen-contaminated stripping gas leaves the tower and passes through blowers and a heat exchanger before the oxygen is removed utilising a catalytic reaction with methanol vapour. The oxygen free stripping gas is then recycled to the deaerator tower. The de-aerator package typically comprises:

- water injection de-aeration tower
- water injection stripping gas blowers
- stripping gas exchanger
- stripping gas de-oxidiser vessel
- start-up heater

Seawater is often supplied from downstream of cooling medium coolers. This pre-heats the seawater to between 22°C and 27°C with typically a minimum supply temperature of 5°C and a maximum supply temperature of 33°C. The oxygen content of the seawater entering de-aeration is approximately 8-10 ppm wt.

Seawater enters the top of the tower after passing through an inlet flow control valve.

Seawater entering the stripper falls under gravity through a distributor and a bed of structured packing, and exits at the bottom of the tower before being routed to the water injection pumps. Seawater leaving the stripper is normally routed to the water injection pumps. In the event that the seawater demand is low, seawater is routed overboard via a dump valve.

Over-pressure protection is from PSVs which relieve to a safe location. The deaerator may be protected by a high integrity pressure system (HIPS) which shuts the seawater inlet valves. A HIPS system may be required on the deaerator if the vessel relief valves are not designed for full seawater flow relief.

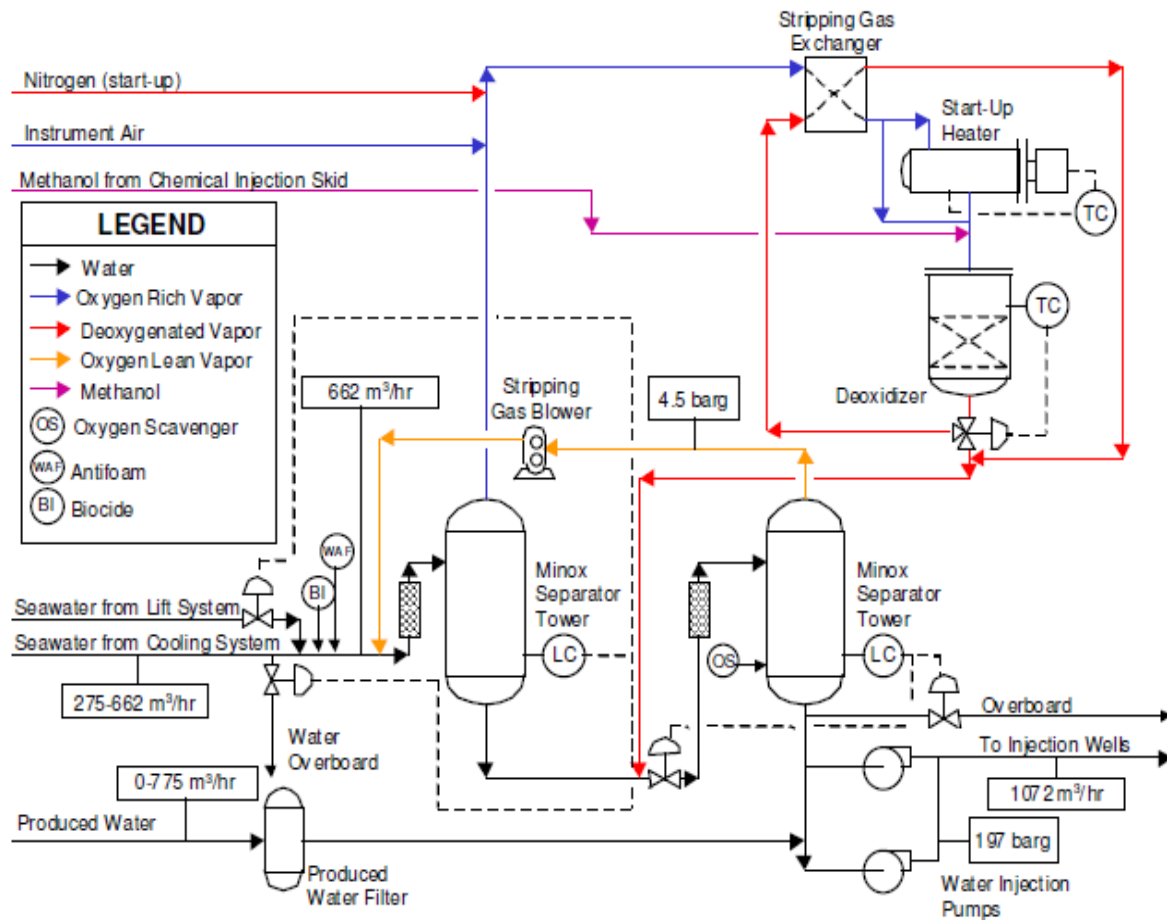
The water passes down through the tower and mixes with a counter-current flow of stripping gas (nitrogen) fed into the tower at a mid-vessel point, below the packing column. The

stripping gas absorbs oxygen contained in the seawater and then passes through a demister. As the nitrogen passes through the tower packing, some of it is dissolved in the seawater and, therefore, there is a requirement to add nitrogen to the system to maintain the required stripping gas flowrate. In addition, to achieve the required oxygen concentration in the stripping gas, so as to maintain reactor efficiency, more oxygen must be added. The required nitrogen and oxygen make-up is achieved by using a combination of instrument air and nitrogen top-up lines.

Stripping gas is drawn off by the water injection stripping gas blowers, which are often rotary lobe, positive displacement type blowers. On leaving the blowers, the stripping gas passes through the tube side of the stripping gas exchanger where it is pre-heated against stripping gas returning from the stripping gas de-oxidiser vessel.

Stripping gas enters the de-oxidiser vessel at a controlled temperature. The gas flows downwards into a de-oxidiser catalyst bed containing an electric start-up heater. The catalyst is palladium pellets on an aluminium oxide core supported on a perforated plate. To create the catalytic effect, methanol is added, as a fuel, to the stripping gas. This is injected as a side stream into the main stripping gas flow. The catalyst needs to achieve a threshold temperature before the required catalytic reaction can take place. The catalyst bed is pre-heated by to this threshold temperature, typically 150°C. Once this temperature is achieved then the power supply to the startup heater is shut off as the resulting reaction is exothermic - temperatures of 240°C to 260°C are generated. Stripping gas leaving the reactor is virtually oxygen free (i.e. oxygen content below 20 ppb). Stripping gas from the bottom of the vessel passes through the shell side of the pre-heater.

A system PFD follows.



6 Water Chemistry

Scale is a deposit of the inorganic mineral components of water. This is in contrast with wax and asphaltenes which deposit from the crude oil. Oilfield scale is generally inorganic salts such as carbonates and sulphates of the metals calcium, strontium and barium. Scale may also be the complex salts of iron such as sulphides, hydrous oxides and carbonates.

The major forms of oilfield scale can form in one of two ways:

As a brine (e.g. formation water) undergoes a temperature or pressure change during production, the solubility of some of the inorganic constituents will decrease and result in the salts precipitating. Scales formed under these conditions are generally calcium/magnesium carbonate scales.

When two incompatible waters (such as formation water rich in calcium, strontium and barium and sea water rich in sulphate) are mixed. Scales formed under these conditions are generally sulphate scales.

Other minor forms of scale are also possible:

Iron scales which are usually a result of corrosion in the system. The source of the iron is predominately the pipework and vessels.

Halite (NaCl) can occur as a result of water flash-off into the gas phase as the pressure decreases or simply due to reduced halite solubility as the temperatures declines during production of very high salinity brines.

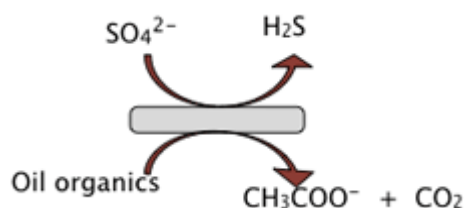
Witherite (BaCO_3) and others such as calcium fluoride (CaF_2) have been observed in high pressure/high temperature reservoirs.

<u>Chemical formula</u>	<u>Common name</u>
NaCl	halite
BaCO_3	witherite
SrSO_4	celestite
BaSO_4	barite
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	gypsum
$\text{CaSO}_4 \cdot \text{H}_2\text{O}$	hemihydrate
CaSO_4	anhydrite
CaCO_3	calcite

Scale inhibitors are chemicals which stop or interfere with the nucleation, precipitation and/or adherence of solid scale. Typical inhibitor concentrations for oilfield production are in the 10 - 100 ppm range.

7 Reservoir Souring

As previously stated, souring in oil field systems is most commonly due to the action of sulphate-reducing bacteria, a diverse group of anaerobic microorganisms that respire sulphate and produce hydrogen sulphide. Such biological sulphide production is a detrimental, widespread phenomenon in the petroleum industry, occurring within oil reservoirs or in topside processing facilities, under low- and high-temperature conditions, and in onshore or offshore operations. Sulphate reducers can exist either indigenously in deep subsurface reservoirs or can be "inoculated" into a reservoir system during oil field development (e.g., via drilling operations) or during the oil production phase. In the latter, souring most commonly occurs during water flooding, a secondary recovery strategy

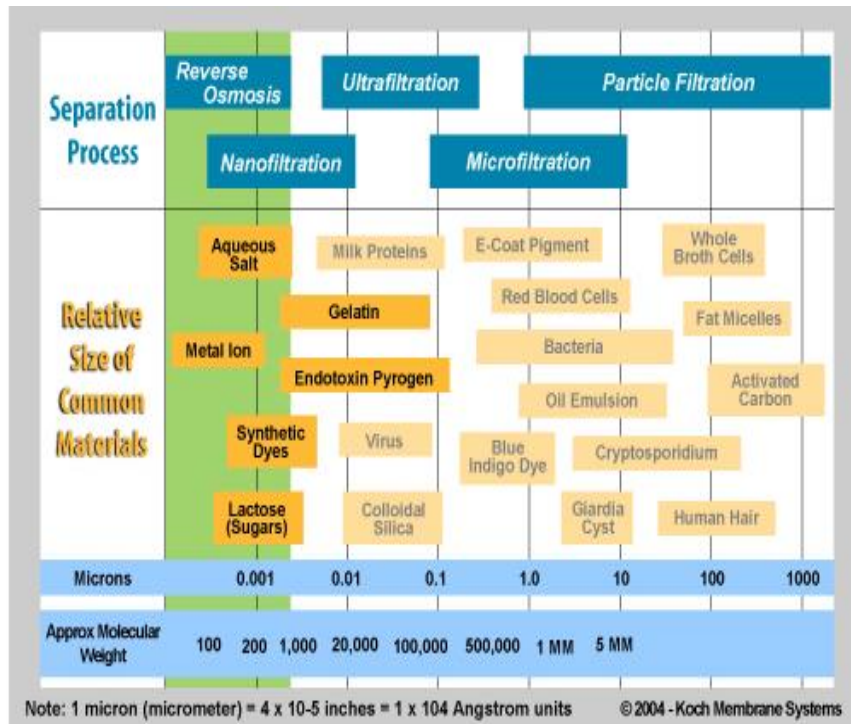


wherein water is injected to re-pressurize the reservoir and sweep the oil towards production wells to extend the production life of an oil field. The water source and type of production operation can provide multiple components such as sulphate, labile carbon sources, and sulphate-reducing communities that influence whether oil field souring occurs. Souring can be controlled by biocides, which can non-specifically suppress microbial populations, and by the addition of nitrate (and/or nitrite) that directly impacts the sulphate-reducing population by numerous competitive or inhibitory mechanisms.

7.1 Sulphate Removal

When seawater, generally high in sulphate, is injected for reservoir pressure control it mixes with formation water which in some oilfields can be high in barium and strontium. In this instance a supersaturated solution of barium and strontium sulphate can occur. Under high pressure this solution is relatively stable, but as pressure is reduced around the production well the solution becomes unstable and precipitation can occur resulting in scale formation in production tubing or the formation rock around the well. Production can be severely affected. Removal of sulphate from injection water reduces the potential for scaling. Secondly, removal of sulphate significantly reduces the likelihood of reservoir souring. Sulphur is converted to hydrogen sulphide (H_2S) by sulphate reducing bacteria (SRB). By removing a feedstock that can be converted to H_2S , the need for costly metallurgy and H_2S removal and handling systems is eliminated. Although not too common some Operators use nanofiltration technology to remove the sulphate – membranes. Operating at pressures of 20 - 30 bar (300 - 435 psig), the spiral wound membrane allows monovalent ions to pass while rejecting divalent ions. Additionally, the membrane rejects particles greater than 0.001 micron including silica and bacteria.

7.1.1 Membranes



Reverse Osmosis (RO)

RO membranes will reject dissolved and suspended materials including monovalent salts.

Since essentially all dissolved and suspended material is rejected by the membrane, the RO permeate is pure water.

For example, water can be softened with a nanofiltration (NF) membrane that rejects 85% of salt (sodium chloride) but 99% of the hardness ions (calcium and magnesium). The highest salt rejection rates (99.7% or higher), which can be provided by RO membranes, are required for seawater desalination.

RO is a moderate to high pressure (5 - 80 bara) driven process for separating larger size solutes from aqueous solutions by means of a semi-permeable membrane. This process is carried out by flowing a process solution along a membrane surface under pressure. Retained solutes (such as particulate matter and dissolved salts) leave with the flowing process stream and do not accumulate on the membrane surface. The amount of salt and other impurities is often referred to as TDS, or total dissolved solids. The higher the TDS, the more feed pressure required.

Nanofiltration (NF)

Nanofiltration is a low to moderately high pressure (typically 5 - 30 bara) process in which

monovalent ions will pass freely through the membrane but highly charged, multivalent salts and low molecular weight organics will be rejected to a much greater degree. Typical NF applications include water softening, desalination of dyestuffs, acid and caustic recovery and color removal.

NF is a pressure driven process for separating larger size solutes from aqueous solutions by means of a semi-permeable membrane. This process is carried out by having a process solution flow along a membrane surface under pressure. Crossflow membrane filtration uses a high cross flow rate to enhance permeate passage and reduce membrane fouling. Retained solutes (such as dissolved salts) leave with the flowing process stream and do not accumulate on the membrane surface.

Pores have not been observed in NF membranes under any microscope, however, water can still pass through the membrane and multivalent salts and low molecular weight organics are rejected. It is difficult to predict the performance of NF membranes, especially if more than three solutes are present in the solution, since membrane rejection is influenced by the size, structure and charge of the components in solution. As a result, piloting is highly recommended for NF applications, even if a detailed feed water analysis is available.

Ultrafiltration (UF)

UF is a low pressure (0.3 – 10 bara) process for separating larger size solutes from aqueous solutions by means of a semi-permeable membrane. UF retains oils, particulate matter, bacteria and suspended solids large macromolecules and proteins. They pass most surfactants, water, acid and alkaline compounds.

Pore sizes range from 0.005 – 0.1 micron. The permeate is clear (non-turbid) solution void of suspended solids

Microfiltration (MF)

MF is a low pressure (0.5- 8 bara) process for separating larger size solutes from aqueous solutions by means of a semi-permeable membrane. This process is carried out by having a process solution flow along a membrane surface under pressure. Retained solutes (such as particulate matter) leave with the flowing process stream and do not accumulate on the membrane surface.

8 Low Salinity Water Injection

A significant portion of oil remains unrecovered after a waterflood scheme. The Petroleum industry continues to research techniques for improved recovery. A new understanding of chemistry behind oil wettability – oil adhering to rocks – has indicated that water of low salinity can significantly improve recovery.

Most sandstones are a mixture of sand and clay containing oil and water. The oil molecules are held to the surface of the negatively charged clay by divalent cations – Ca^{++} and Mg^{++} . When flooded with a lower salinity water than the reservoir's formation water, free monovalent cations in the flood water, e.g. Na^+ , exchange with the divalent cations and release the oil molecules. Low salinity water is usually in the range 500 – 1000ppm. These low salinity water are produced using membrane processes.

9 Key Learnings

1. Purpose of water injection and treatment requirements
2. Filtration principles
3. Henry's law
4. Principles of Oxygen removal by Chemicals, Vacuum and Gas Stripping
- 5 NTU and HTU as applied to absorption/desorption operations. $Z = \text{NTU} \times \text{HTU}$
6. Scaling
7. Reservoir Souring, sulphate removal and membrane principles