Technical University of Crete
School of Mineral Resources Engineering
Master of Science on Geotechnology and Environment

# THESIS: TREATMENT OF WATER PRODUCED FROM OIL WELLS - PROCESSES AND TECHNOLOGIES

**Vallianou - Setta Danai - Evgenia**

*Supervisor:* 1. Prof. Varotsis N.
2. Prof. Pasadakis N.
3. Dr. Marinakis. D.

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*To my family,*

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## Abstract

Water produced during oil and gas extraction operations constitutes the industry's most important waste stream on the basis of quantity. For every single barrel of oil produced, three to nine barrels of water are produced, which can be a useful by-product or even a product for sale. However, due to the increasing volume of produced water all over the world during the current decade, the effect of discharging produced water on the environment has lately become a significant issue of environmental concern, because of the undesirable toxic or other substances that pose a threat to the environment and living organisms. Produced water is conventionally treated through different physical, chemical and biological methods. The overall treatment and management of the produced water is a vital consideration for the oil and gas producers, presenting multiple technical and economic aspects.

The water contained in an oil field or a gas field is actually an aquatic mixture containing inorganic salts, oxides, mud, sand etc. All these suspended and diluted substances are brought to the ground level during the extraction process, along with oil and water, as well as other chemical substances (emulsifiers etc.) used during the extraction and the drilling process. The first treatment process taking place after the produced water extraction is typically the separation of the aquatic (inorganic) phase from the organic phase. Subsequent processes involve the removal of undesirable inorganic components so that the treated water may be safely disposed to a natural recipient or recycled.

The present thesis, presents the water treatment of the produced water during the oil extraction. Therefore, it analyzes the different technologies which are actually used for an effective initial separation and the secondary treatment of waste waters which are scientifically documented.

**Key-Words**: Water treatment, Produced water, produced oil and gas, extraction and drilling process, environmental regulations.

# Table of Contents

# Table of Pictures

# Index of Tables

The current thesis comprises the following chapters:

- First, an introduction to the main subject of this dissertation is presented which is defined as the different methods of treatment of produced water from oil wells.
- Chapter 1 deals with historical data, environmental legislation and regulations.
- Chapter 2 explains analytically the role, the sources, and the possible uses of produced water (PW), as well as the factors that affect the quality and the volume of PW.
- Chapter 3 presents the different ways of disposing produced water such as underground injection, the evaporation method, the constructed wetlands and some impacts of oil and gas operations during treatment of PW.
- Chapter 4 presents the types of hydrocarbons that are mainly produced and their interconnection with the characteristics of PW.
- Chapter 5 presents the chemical and physical properties of PW, the oil and gas constituents and major elements of concern found in PW and as a result, the challenges that have to be addressed.
- Chapter 6 presents different alternatives of processing produced water, using different equipment and technologies and shows off the criteria which are applied. The separation of the three phases - oil, gas and water, and the role of emulsion, are also described.
- Chapter 7 presents all the latest technologies used for the oil/water separation, discussing their advantages and disadvantages.
- Chapter 8 presents a summary of the most widely applied technologies for the treatment of PW in a tabular form and a discussion among the available treatment methods of PW.
- Chapter 9 presents the parameter of cost.
- Chapter 10 presents the survey that was conducted on the latest used equipment for the PW treatment.
- Chapter 11 comprises the conclusions of this dissertation
- The Appendix, includes the Glossary and the Abbreviations used in this thesis, some representative definitions of terms used in oil and gas extraction field, a table with the characteristics and composition of a typical oilfield sample of PW and a case study.

## Introduction.

The present thesis intends to provide a wide knowledge, scientifically documented, but at the same time being comprehensive enough about the different technologies which are actually used for an effective separation and the secondary treatment of waters produced during the oil extraction process.

Water produced during oil and gas extraction operations constitutes the industry's most important waste stream on the basis of quantity. Along with every barrel of oil approximately three to nine barrels of water are produced. The above waste varies greatly in quality and quantity while its composition depends on location and climate. In some cases, the waste water can be a useful valuable by-product or even a product for sale rather than a waste for disposal. The cost of managing such a large volume of water is a key consideration to oil and gas producers. Moreover, today's innovative water - control technology can lead to significant cost reduction and improve the procedures of oil production. Although produced water is considered to be a 'waste', it could also be regarded as a potential profit source.

It is absolutely necessary to ascertain how these vast quantities of produced water should be treated before any other use or disposal to natural recipients, since they bring undesirable chemicals, biological contaminants, suspended solids and gases. The removal of these constituents is of great importance.

The oil and gas industry, as many other industries in the world, must process its waste before its final disposal to the environment or even re-use it as an alternative choice. The major waste of the oil and gas industry that has to be processed is the production of water after the separation of oil and many other admixtures. The treatment of produced water is a necessity, since otherwise, the majority of the conventional produced waters could not have any other uses.

Consequently, characteristics of the produced water in combination with environmental factors, economic considerations, and local regulatory framework are evaluated to select the optimal option for treatment of produced water in a, whatever the case - offshore or onshore - , oil and gas exploration.

# 1. A Historical Review

During the first years of oil and gas production, little or no attention was given in managing produced water. For example, amounts of Produced Water (**PW**) were disposed in large evaporation ponds or released to surface without much treatment. However, from both environmental and social perspectives, this treatment should not be considered as an acceptable disposal method. Since then, producers have developed some beneficial re-uses for PW, or at least, methods for a better PW treatment.

Early in the history of oil and gas production, petroleum engineers realized that injecting water into hydrocarbon-producing reservoirs could increase production. This process, known as **waterflooding**, began approximately at 1865, in Pennsylvania. Waterflooding technology was spread from Pennsylvania to Oklahoma and Texas in the 1930s, but it was not widely used until the 1950s [3].

Firstly, a well drilled for oil or gas may produce oil, gas or both of them. Whatever the case, as production goes on, the produced fluids begin to contain formation water (in addition to oil and gas), the proportion of which increases over time.

The first well at a fixed offshore platform was drilled in 1947. By 1949, 11 fields were found in the Gulf of Mexico, with 44 exploratory wells. The common method used for managing offshore PW was simply to discharge it to the ocean, after the initial separation of oil and water. Gravity separation used to leave in the PW sufficient oil to create a gloss, after the water was discharged. In view of this severe environmental threat, industry was obliged to take drastic measures in order to remove a higher percentage of oil before discharging the PW.

In some cases, a larger amount of water was generated than the one that was really needed for waterflooding. In those cases, companies used to inject the extra PW into other, non-hydrocarbon-producing formations, suitable for disposal.

Concluding, injection - either for waterflooding or disposal, had been the dominant method for managing onshore PW for years. [3]

## 1.1.Establishing Regulations

Substantial waste water treatment and management of the PW started **in 1974** with the *Environmental Protection Agency* (**EPA**). EPA conducted a research work on oil and gas platforms of coastal and *Outer Continental Shelf* (**OCS**) areas. In particular, this research work points out the differences in treatment between offshore and onshore platforms.

*Environmental Protection Agency's (***EPA'**s) regulations require that all discharges of pollutants to surface waters (streams, rivers, lakes, bays and oceans) must be authorized by a permit issued under the *National Pollutant Discharge Elimination System* – (**NPDES**) program. [9, 39].

The *Safe Drinking Water Act* (**SDWA**) of 1974 gave the EPA the authority for *Underground Injection Control* (**UIC**) regulation [9]. The UIC program is designed to protect underground sources of drinking water. [27]

The EPA has formed three categories for the pollutants under the NPDES program:

1. **Conventional pollutants** (5-day BOD, total suspended solids, and oil and grease),
2. **Toxic or priority pollutants** (including metals and artificial organic compounds) and
3. **Nonconventional** (including ammonia, nitrogen, phosphorus, chemical oxygen demand - COD and whole effluent toxicity). [9]

Later **in 1974**, EPA published a "*Draft Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Oil and Gas Extraction Point Source Category*". Based on this publication, and the Clean Water Act *Best Practicable Control Technology Currently Available* (**BPT)** a temporary guide, came into existence.

According to BPT for onshore areas, PW was not allowed to be discharged. On the other hand, discharge of PW in offshore areas was allowed due to the special technologies that were used for the removal of oil and grease. These techniques included analytical tests that measure the content of water in organic compounds, before the discharging. [3]

In **1978** the Oslo-*Paris Commission* (**Oslo-Paris or OSPAR**) set the limits for discharges for offshore oil case at **40** ppm, discouraging, at the same time, the disposal into fresh water. [20]

However, in **1987**, Neff claimed that PW disposed into oceans contains about 48 parts per million (ppm) petroleum, due to the fact that it comes into contact with crude oil under the reservoir rocks. Additionally, the same disposed water, contained more metals such as barium, beryllium, cadmium, chromium, copper, iron, lead, nickel, silver, and zinc including traces of the natural radionuclides, radium226 and radium228 and several hundreds ppm of non-volatile dissolved organic material of unknown composition that include dissolved gases (hydrogen sulfide and carbon dioxide). [35]

The BPT limits (***48** mg/L on average and **72** mg/L maximum value for oil and grease)* reflected the capability of the operating platforms in the early 1970s. Technologies such as separators, filtration, skim piles and gas flotation were used to remove additional oil and grease. **In 1979** the **BPT** discharge regulations (known *as effluent limitations guidelines)* were disclosed.

**In 1992**, Jacobs et al. mentioned that produced waters discharged from gas and condensate platforms are far more toxic than the produced waters discharged from oil platforms. Their claim was based on a study that was conducted with sample of PW from Shell, operated oil and gas fields in North Sea. [20]

**In 1993,** a more advanced guide for existing facilities came into force, known as ***BAT** (Best Available Technology Economically Achievable*). During this period, the BAT limits for oil and grease for offshore facilities decreased to ***29** mg/L on average and **42** mg/L maximum* value. Improved gas flotation, granular filtration, membrane filtration, hydrocyclones and centrifuges were the additional technologies used to reach the strict BAT limits. [3]

**In 1998**, Cline noted that produced waters from petroleum production operations were in most cases, more saline than sea water. [20] Studies have shown that, the samples of PW, where the dilution was achieved, were not expected to be found beyond 50 meters from the discharged point. Yet, they did. [35]

The maximum admissible PW oil concentration (**OIW**) discharged in the sea according to *Oslo-Paris Convention* (**OSPAR)** is 30 ppm. This limit was reduced by 15% from what it was **in 1999**. In the U.S the daily maximum PW oil and grease concentration is ***42*** ppm while in China the corresponding monthly average limits are ***10*** ppm. In Australia the daily maximum PW oil and grease concentration is about ***30*** ppm. In the North-East Atlantic Ocean, the Convention for the Protection of the Marine Environment decided to set the annual average limit at ***40*** ppm. [10]

The "zero discharge" regulation was adopted by the EU **in 2000** and Norway. The oil operators, agreed to "zero discharge" rule by *2005*. For this purpose, the Norwegian Oil Industries Associations developed the *Environmental Impact Factor* (**EIF**), which considers all the contaminants in PW. Similarly, the Convention for the Protection of Marine Environments of the North-East Atlantic has agreed on zero discharge of pollutants into the sea. Nowadays, most of the oil and gas companies all over the world are working on this target.

The current global best practices on PW management were established **in 2005.** It is about a three-stage approach. These fundamental regulations aim to reduce discharges to zero. [20] PW management practices should always protect the environment. In any other case, the operator should face prosecution under the law. [2]

Because of the increase in environmental awareness, disposal of surface waters or evaporation ponds tends to be prohibited. PW is now considered as an industrial waste with specific limits of concentration, defined by the Environmental Protection Agency.

The standards for water quality usually include minimum and maximum concentrations of contaminants, depending on the intended purpose of water use. In addition, austere regulations and measures need to ensure that the water quality is appropriate not only in relation to the treatment of the water, but also to its transition and distribution after treatment.

According to the above, the oil and gas industry, as every industry, has to follow specific regulations concerning its waste water products. If a company aims to use a low-cost disposal method, such as discharge to surface waters, the PW quality should not above authorized limits. These limits may include specific constituents of concern, such as ammonia, heavy metals, *Total Dissolved Solids* (TDS) or *Sodium Adsorption Ratio* (SAR). All these parameters could affect several aspects of the environment. [2]

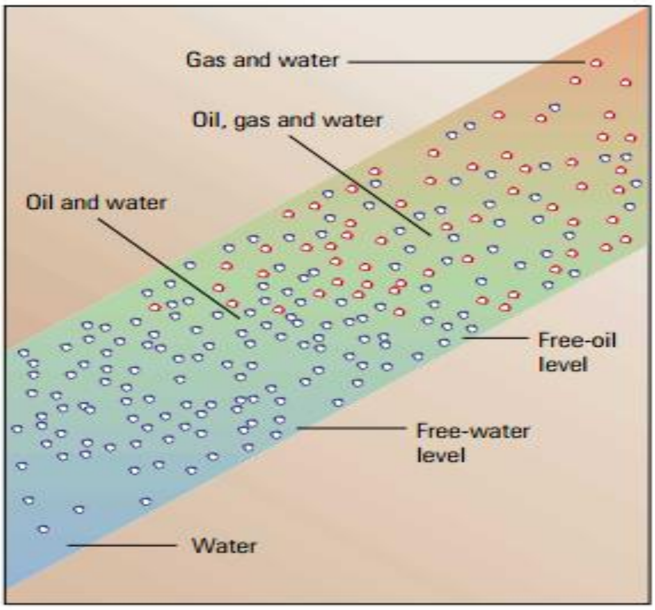
In general, injection was the safest and least expensive choice for disposing the industrial waste byproducts during the 1950s. There are now about 180,000 wells in the U.S. mostly in Texas, Oklahoma, California, and Kansas where operators inject 2 billion gallons of brine every day. Late last year, operators of a water injection well in Kansas started facing difficulties. Bad quality of the water is the highest problem. Poor water quality causes a list of problems and leads to mechanical failure, damage from water/rock interactions, permeability issues, biological impairments and interactions between fluids. [38]


**Picture 1. The life cycle of Produced water. [34]**

## 2. Produced Water

The term "produced water" refers to the aquatic mixture that is produced, along with the oil and gas in the surface, during the extraction process. PW is also generated during the whole drilling process of a well. [3] However, this byproduct – through an appropriate treatment, can contribute in dry areas, where water supplies are limited. [4]

All types of reservoirs, (oil and gas) contain water mixed with hydrocarbons (*picture 2*), in a zone that lies under the hydrocarbons as well as in the same zone with the oil and gas. Oil wells tend to produce large quantities of water along with oil, whereas gas wells tend to produce water in smaller proportions. [16] This is a consequence of the higher compressibility and absorption capacity of gas. [4] Globally, approximately 250 million barrels of water are produced daily from both oil and gas fields compared with around 80 million barrels per day of oil and more than 40% of these are discharged into the environment. [10]




**Picture 2. A fluid distribution in a typical reservoir before production/injection begins. [26]**

PW concentration can contain significant quantities of precipitated solids, sand, silt, carbonates, clays, asphaltenes, waxes, bacteria, corrosion products and other suspended solids, derived from the producing formation and well bore operations, as well. The water generally reflects the depositional environment for the reservoir (marine, brackish or continental fresh water) [1, 9, 10, 23]

## 2.1. The role of water in production

Water is present in every oil field, since it affects every stage of oilfield life, from exploration through development production, up to its final abandonment. Although water is the most abundantly produced fluid, no operator wants to produce water. [26] However, water is necessary in many processes in oil and gas operations, such as drilling, hydraulic fracturing, sustaining aquifer pressure, fracture stimulation process and enhanced recovery operations where it is used as injection fluid. Much of the water is sent downhole for drilling and well completion it comes back to the surface and it is considered as a waste stream. [2]

A solution aiming to reduce the quantity of PW is a separation of oil and gas, that can occur either onshore or offshore. For example, on the bottom of the ocean, the use of *down-hole oil/water separation* (DOWS) is suitable, where a hydrocyclone separates water from oil and gas inside the well space and then, reinjects it. This technique is restricted to suitable wells and water injection zones. [2, 31] Generally, separation techniques found at the bottom of the sea are very similar to topside water treatments. However, subsea systems are quite expensive and the industry has limited experience in implementing this technique. [31]

## 2.2. Sources of Produced Water:

1. ‘Connate’ or ‘formation’ water that present in the reservoir prior to production (mixture of saline water and hydrocarbons comes to the surface)

2. Natural water from formations, holding oil and gas

3. Condensed water from produced gas: water that used to be in vapor phase during reservoir conditions and then, condenses into liquid state in the production separation system at surface. [11]

4. Injected water in order to increase oil production [7]

   Water injection can be performed in the following ways:

   I. As fluid injection for primary, secondary or EOR treatment
   II. As injected fluid in underground rock formations which are not productive anymore. This method is used for the treatment of the saltwater. [27]

In oil and gas production activities, additional water is injected into the reservoir to maintain the pressure and achieve greater level of recovery. Both formation water and injected water are produced along with hydrocarbon mixture. At the surface, processes are required to separate hydrocarbons from the produced fluid.

## 2.3. Factors Affecting Water Production

Given that PW is an inextricable part of the hydrocarbon recovery process, the volume of PW during the whole life cycle of a well will be affected by the following factors: [9]

**Type of the drilled well**: A horizontal well can be more productive than a vertical one, producing fluids in higher rates.

**Location of the well within reservoir structure**: An improperly drilled well could affect water production in the reservoir. As a result, there could be water production earlier than expected.

**Type of completion**: A perforated completion (versus to open hole completion) provides a greater degree of control in the hydrocarbon-producing zone. Specific areas can be accessed, for increased hydrocarbon production or plugged to minimize water production.

**Water flooding for enhanced oil recovery**: The main purpose of waterflooding is to place water in the reservoir where the oil is located, so that the latter will be driven directly into a producing well. As the water flood comes to the well, the volume of PW will be significantly increased. In many cases, it is advantageous to shut in these producing wells or convert them to injection wells.

**Insufficient produced water volume for water flooding**: If the amount of PW available is insufficient for water flooding purpose, then an additional source water must be obtained successfully to increase the PW injection. For this purpose, the water used for injection must be of a suitable quality so that the reservoir rock is not damaged. Over the past years, freshwater was extensively used in water flood, but nowadays it is not anymore used as a reliable source for water flooding. However, regardless of the source, any addition of water to the reservoir will lead to an increased volume of PW.

**Loss of mechanical integrity**: Holes caused by corrosion and splits in the casing caused by flaws, excessive pressure or any deformations created during the well operation may allow undesirable reservoir or aquifer waters to get into the well bore and be pushed to the surface as PW.

**Subsurface communication problems**: Near well bore communication problems such as channels behind casing or barrier changes may lead to increased PW volumes. In addition, reservoir communication problems such as *coning, cresting, channeling through higher permeability zones* or *fracturing out of the hydrocarbon producing zone* can also provide higher produced water volumes.

## 2.4. Possible Uses of Produced Water

For the PW management, three major directions can be considered which are minimizing the production of PW, reusing or recycling the PW and if none of them could be applied, disposing of the PW must be considered.

Depending on the quality of the untreated PW and the one needed for the final use, many different treatment technologies or combination of technologies can be used.

Some options for reuse of PW are the following: [7]

- ✓ Injection to a hydrocarbon-bearing formation to contribute to the hydrocarbon production
- ✓ Commercial exploitation and management
- ✓ Re-use for oil and gas operations (drilling fluids, frac fluids)
- ✓ Re-use in the agricultural field.

Re-uses of PW for oil and gas operations refer mainly to *hydraulic fracturing* of oil and gas sites, power generation, dust and fire control. To initiate production operations and enhance production, wells may have to be hydraulically fractured. Another possibility is the use of PW as cooling water for power generation. [11] In any case, we have to consider every possible exploitation of PW along with the economic and technological parameters.

As far as the **agricultural** field is concerned, PW could be reused for land restoration, stream flow augmentation, livestock watering, wildlife watering and habitat as well as aquaculture. [2, 11] However, re-use of PW represents only a small percentage of total agricultural requirements. A significant challenge using PW for agricultural purposes is the *salinity* and the *sodicity* of the water, meaning the amount of sodium in it. [11] The uses of PW in agriculture field is divided into three specific categories:

**A.** Irrigation subsurface, can be a great benefit to arid areas however, the water should be treated before applying it to the soil or adding soil supplements.

**B.** Livestock and wildlife watering, provide a source of water for animals. It must be ensured that the water is clean enough to avoid illness or other impacts to animals.

**C.** Constructed wetlands, that provides a “natural” form of treatment and creates a stable habitat for wildlife, however it needs to meet space requirements and extensive oversight and management during the whole procedure, as well.

In the case of irrigation, large water volumes are necessary and strict water quality criteria must be followed. The main criterion used to ensure the irrigation water quality, to avoid crop damage is sodium adsorption ratio (SAR). When irrigation water has more than three SAR values, a stronger control of salt accumulation is required. Water with high SAR value can be used only in cases where enough water is applied to wash the salts down below the root zone of the crops. [4]

In the case of flow augmentation, parameters such as temperature, dissolved oxygen levels, biological and chemical oxygen demand (BOD and COD) need to be taken into account. In that way, the ecosystem and its physicochemical characteristics will not be affected negatively and as a result, erosion and deterioration of aquatic life will be avoided. [4]

In the case of livestock and wildlife watering, water consumption can be affected by lots of factors, such as environmental temperature, gender and size of the animals. To be more specific, sulfate should not to exceed 2,000 mg/L, pH should range between 5.5 – 8.5 and TDS concentration should not exceed 10,000 mg/L. Levels of specific ions and salinity are of high importance, too. [4]

**The quality of PW which is suitable for drinking consumption**. The ultimate use of PW is for drinking and other domestic uses. In this case PW can be beneficial, providing water especially in arid areas.

However, there are some disadvantages as this method:

a. It is considered very expensive to treat the PW in order to be drinkable, without any contaminants
b. The quality of the water needs to be tested before consumption
c. It may be more cost-effective and energy-conserving to treat other water sources like saline groundwater rather than treating PW.

<u>Just to give an idea of the TDS specifications, depending on the water final use:</u>

Produced water TDS average values range from 370 mg/L to 1940 mg/L. Maximum permitted concentrations for five uses are presented below: [4]

- drinking water 500 mg/L
- ground water recharge 625 mg/L
- surface water discharge 1,000 mg/L
- irrigation 1,920 mg/L and
- agriculture 10,000 mg/L.

## 2.5. Injection – Improved Oil Recovery – {IOR}

The most common way to re-use PW is to re-inject it into a producing formation to improve production. In primary production, the oil and gas is being forced out by the natural reservoir pressure. However, after a period of time, the natural reservoir pressure will subside. Therefore, an enhanced recovery technique has to be employed to continue the production. Re-injection for improved recovery occurs in tens of thousands of injection wells throughout the world. Considerable efforts are ongoing to develop economic methods to treat PW, and put it to a better use. Some PW has low salinity that may be suitable for re-use without any treatment. However, it may be not productive to spend high amounts of energy to treat PW with a high saline level, when a smaller amount of energy could be used to treat an alternative water source more efficiently. [3, 7]

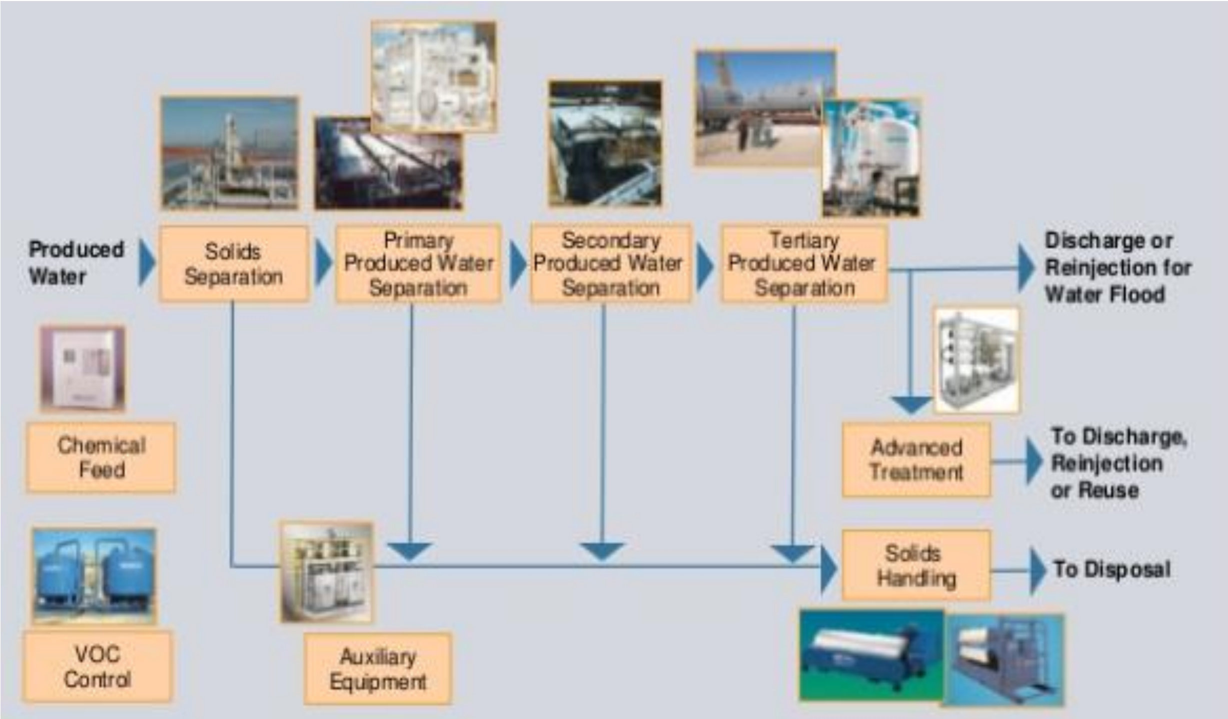
**Underground Injection for Improved Oil Recovery**

Most PW generated onshore is injected to retain reservoir pressure and hydraulically drive oil toward a producing well. This technique is often referred to as waterflooding or steam flooding, depending on the temperature of the water. Studies have indicated that injection for EOR can manage up to 71% of the PW. In this case, PW should be seen rather as a resource than a waste product. [11]

- ❖ Crude oil production in oil reservoirs takes place in three distinct phases: *primary, secondary* and *tertiary (or enhanced) recovery*.
- ➢ During *primary recovery*, it is the natural pressure of the reservoir or gravity that drives oil into the wellbore and can be assisted by some artificial lift techniques (such as pumps), oil comes to the surface. However, during primary recovery only about 10 % of the reservoir's original oil in place is produced.

- ➢ *Secondary recovery* techniques extend reservoir's productive life by injecting water or gas to displace oil and drive it to the production wellbore. As a result, we get 20 % - 40 % of the original oil in place. [4] Waterflooding is the most common technique for secondary recovery. It is used as injection of water as a barrier through the producing formation from a series of injection wells toward the producing well. Such injection wells can either be converted producing wells or new wells drilled specifically for injection of flooding water.

- ➢ However, because of the fact that most of easy-to-produce oil has been already recovered from oil fields, producers attempt several *tertiary or enhanced oil recovery (EOR)* techniques that offer prospects for 30 % - 60 % of production, of the reservoir's original oil in place. In other words, EOR is used to extract additional oil in place in a reservoir. [47] The tertiary recovery is the steam flooding technique where steam is injected into a well that is taken out of service to heat the oil-bearing rock for a period of several weeks. After the stimulation, the well is returned to service. More commonly, steam flooding technique involves the introduction of a steam-water mixture into the well. Generally, after these recovery techniques, the well produces 6-8 bbls of water per bbl of oil. The PW and oil need to be separated and the water further processed before it is suitable for reuse or disposal. [48]




**Picture 3. Produced water treatment Process Map. [40]**

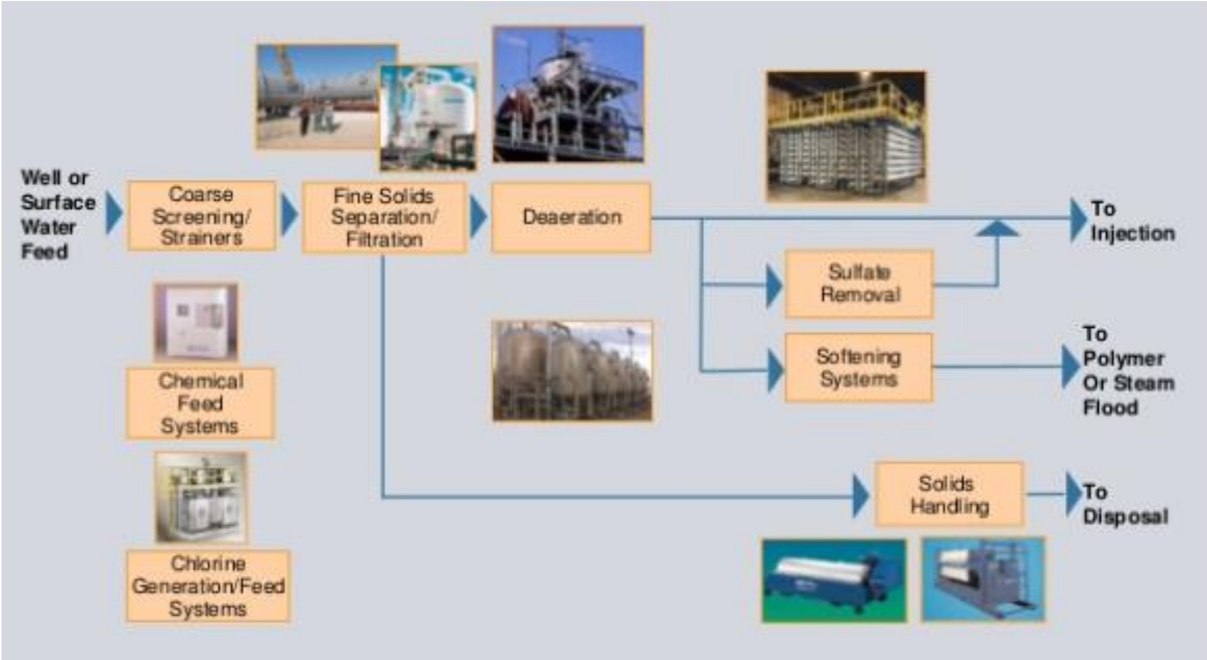
Three major of EOR methods have turned out to be commercially successful:

- Thermal recovery involves the use of heat - such as injection of steam, to lower the viscosity of heavy viscous oil and improve its ability to flow through reservoir. Thermal techniques account for 40 % of worldwide EOR production, predominantly in California.

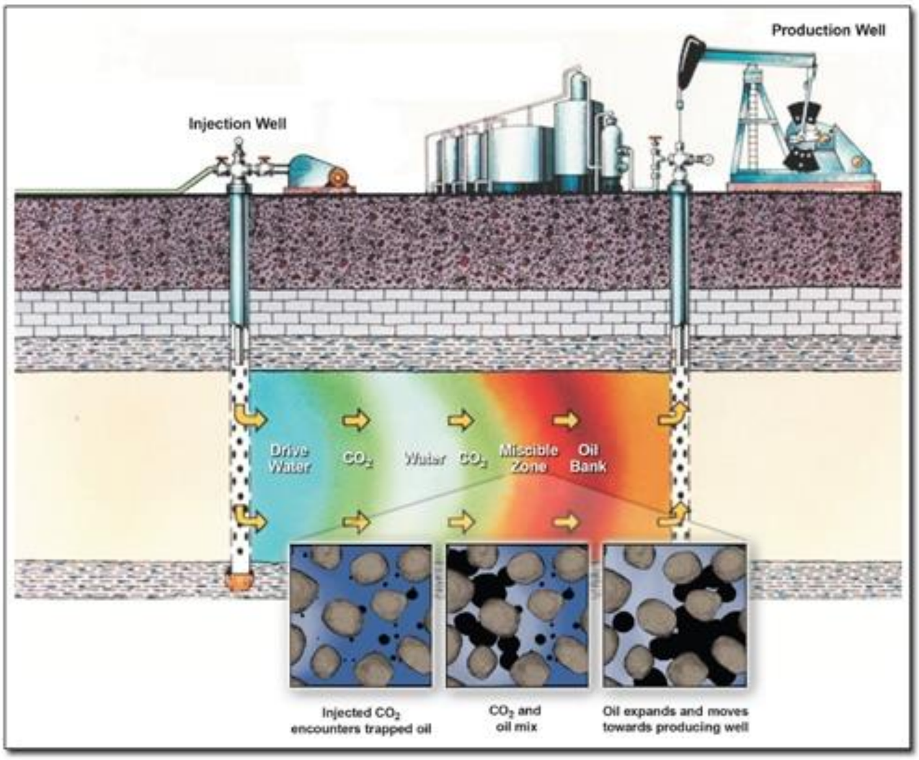
- Gas injection uses gases - such as natural gas, nitrogen or carbon dioxide ($CO_2$), to push additional oil to a production wellbore or other gases dissolved in the oil in order to lower its viscosity and improve its flow rate. Gas injection accounts for nearly 60 % of EOR worldwide production.

- Chemical injection involves for example the use of polymers, to increase the effectiveness of waterfloods and lower the surface tension that often prevents oil droplets from moving through a reservoir. [47] The main role of polymers is to promote the hydrocarbon movement through formation. [4] Chemical techniques account for nearly 1 % of EOR production. [47]

Each of these techniques is limited by its relatively high cost and by the uncertainty of its efficiency. [47] Water injection into an aquifer will displace oil towards the production well. EOR involving the injection of water into depleted oil fields, since it can extract up to 10 % of the remaining oil. The volumes of water used depends upon the reservoir, while water quality concerns for injection include lowering divalent cation and silica levels to minimize scaling. During EOR, one barrel of crude oil can give up to ten barrels of water, which can be treated and re-used for further EOR. [4] The re-injection of PW changes the reducing waste related with liabilities and costs from a waste product to a resource commodity. [8]




**Picture 4. Water Injection-Reinjection Process Map. [40]**




**Picture 5. Injection of $CO_2$ and $H_2O$. [47]**

Picture 5 shows a cross-section illustrating how $CO_2$ and $H_2O$ can be used to displace residual oil from a subsurface rock formation between wells. [47]

<u>Water injection features may be summarized as follows: [8]</u>

| | |
|---|---|
| • Increased volumes of PW | • Reduction of capital and operating costs |
| • Stricter environmental regulations | • A water source for pressure maintenance and EOR |

# 3. Disposal of Produced water.

## 3.1. Underground Injection for Disposal

Injection wells are designed and generally constructed so that we could inject fluids to zones in a way that migration into the *underground sources of drinking water (USDWs)* will be avoided. Injection wells for disposal are often located in formations that enable water entry at pressures below the fracture pressure and which are isolated from USDWs and hydrocarbon producing formations.

In addition to locating a formation with appropriate characteristics for receiving the water, it is also important that the PW is chemically compatible with the receiving formations. This may require a specific treatment prior to injection to manage excessive solids, dissolved oil, corrosion, chemical reactions or microorganisms. [11] Offshore PW discharges should be used under a specific monthly average and daily maximum limit for oil and grease compounds according to the applicable national environmental regulation. [11, 28]

## 3.2. Offsite Commercial Disposal

When onsite management is not practical, then as an alternative choice, operator may send the PW offsite to a commercial disposal facility. Typically, PW is removed from well locations systematically and transported by trucks to an offsite facility. Offsite commercial disposal is usually chosen by small producers who find this option more feasible than constructing, operating and closing onsite facilities or by operators who do not have access to suitable formations for PW injection. [11]

Offsite facility provides service to the oil and gas community by accepting and disposing water for a regular fee. According to that, the water management responsibility is removed from the operator. However, this procedure requires infrastructure such as disposal facilities and a transportation network to move the water to a disposal site making this solution rather costly.

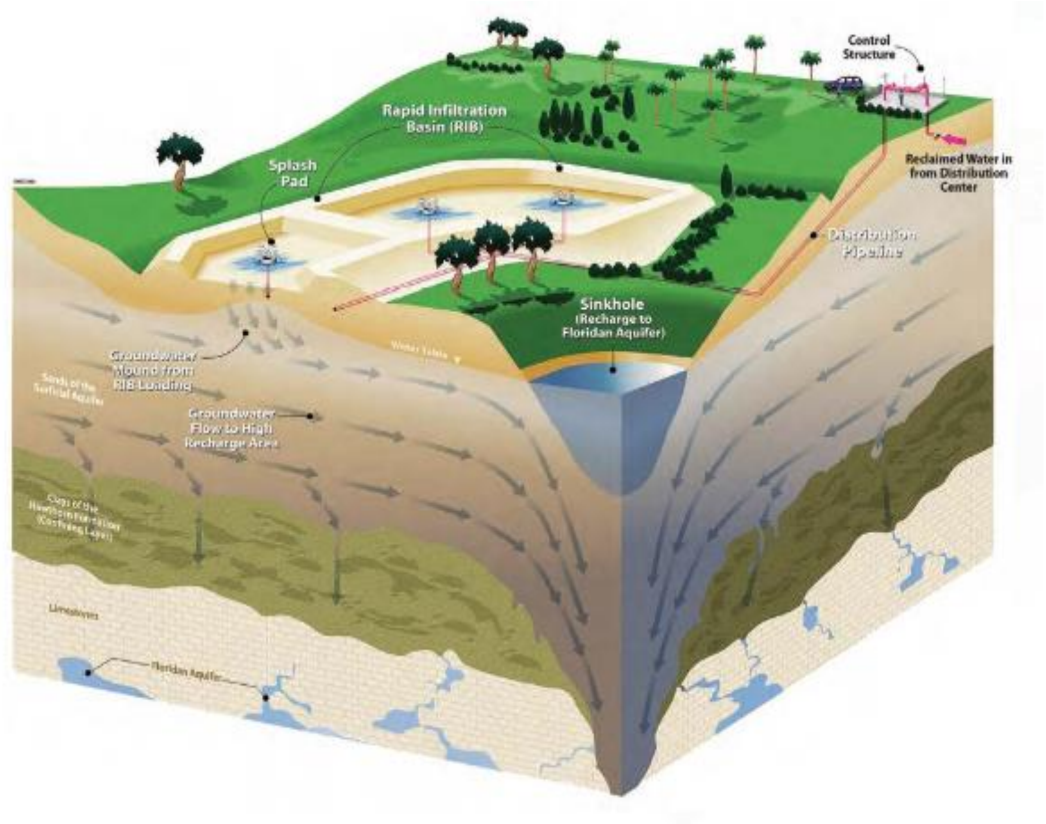
## 3.3. Constructed Wetlands

The development of constructed wetlands started approximately 40 years ago to exploit the biodegradation ability of plants and since then has been used for PW management. Wetland treatment systems utilize natural filtration systems to remove suspended matter, organic matter, nutrients, metals and certain pathogens. Constructed wetlands also provide an approach to treat raw PW or post treatment to further clean treated water. [15]

Results after one year of operation indicated that the wetland system could effectively treat iron and possibly barium but not affect SAR. Wetlands could be designed for specific desired results, depending on PW quality and prevalent environmental conditions. The appropriate plants are the halophytic which have dense fibrous root systems, uptake salts and can be used as forage. [15]

The advantage of the constructed wetland systems is their low construction and operation costs. They are easy to maintain, provide an excellent wildlife habitat, but they have a slow operation rate. The average lifespan of a constructed wetland for organic removal treatment is 20 years. [4, 15]

On the other hand, constructed wetlands have some restrictions on their application: 1) Wetlands require a large amount of land per unit volume of water 2) A sufficient supply of water is necessary to support the wetland 3) Periodic release of captured contaminants during high flow periods or periods when vegetation decomposes may occur.




**Picture 6. A wetland construction [46]**

## 3.4. Concerns on Disposal into Environment

Although PW is a waste product, under a suitable treatment it may become a valuable source contributing to the investment profitability. Nevertheless, the most important benefit coming from the development and the implementation of PW treatment technologies is the protection of the environment and the natural resources (sea water, ground, etc.).

This environmental protection is not only beneficial for human beings and the wild life, but in the long run is also beneficial for economic activity itself. An eventual deterioration of the environment will affect the efficiency and the profitability of any industrial or even economic activity. So, the only sustainable economic development is one which is based on environmental protection and invests in environmental technologies.

Additionally, many water-stressed countries with oilfields are looking for supplements of their limited fresh water resources by focusing on efficient and economical methods to treat PW, so that it could have agricultural or industrial uses. [10, 28]

The discharge of PW into the environment is beginning to be of great importance because the potential pollutants (hydrocarbons, inorganic salts, heavy metals, production chemicals and oil field chemical residues) are extremely harmful, and in some cases exceptionally toxic. [35] This is the reason PW disposal is one of the significant environmental issues receiving major attention within the oil and gas industry. [8]

The most commonly reported environmental concerns are degradation of soils, contamination of ground water, surface water and the supported ecosystems. [4] Discharges to small streams are likely to have a larger environmental impact than discharges made to the open ocean due to the dilution that takes place following discharge. [35]

Due to the multitude of potential health and environmental impacts of hydrofracking, source contamination can be complicated, and thus there are some risks concerning the fracking operation. The well location where drilling takes place is only one piece of the frack puzzle. Since each well can require up to eight million gallons of water and up to 40,000 gallons of chemicals, a well site may need up to 2000 tanker truck trips, per frack. A well can be fracked up to 20 times. Storage for the waste water can take place either on site, in an injection well, or in open air ponds in the surrounding areas. Transport of the waste poses a contamination risk outside the actual well location. Air pollution also extends beyond the immediate drilling site and transportation route, since a by-product of natural gas drilling is methane gas, one of the worst greenhouse gas pollutants contributing to climate change. [53]

Additionally, it has been reported that metals and hydrocarbons from oil platforms are very toxic to the ecosystem. Fish exposed to oil face disturbances in vital organs and fertility. For this reason, companies have to pay more attention to the dissolved organic components, heavy metals and production chemicals, since their long-term effects on living organisms cause general degradation and irreversible results. [10]

Chemical additives are used in the drilling mud, slurries and fluids required for the fracking process. Each well produces millions of gallons of toxic fluid containing not only the added chemicals, but other naturally occurring radioactive material, liquid hydrocarbons, brine water and heavy metals. Fissures created by the fracking process can also create underground pathways for gases, chemicals and radioactive material. [53]

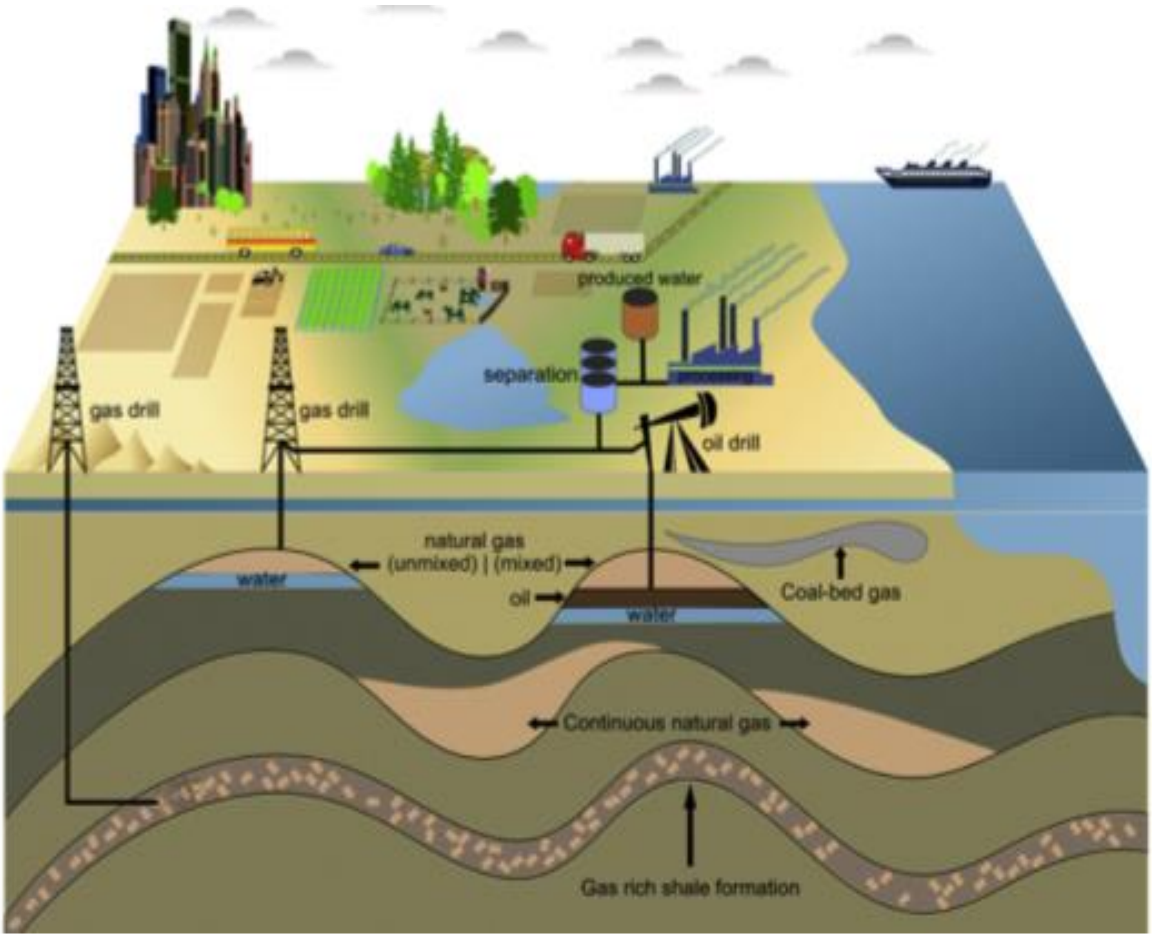
Earthquakes constitute another problem associated with deep-well oil and gas drilling. Scientists refer to the earthquakes caused by the injection of fracking wastewater underground as "induced seismic events." Although most of the earthquakes are small in magnitude (the strongest measured 5.2), their relationship with the storage of millions of gallons of toxic wastewater does little to ease the fears over fossil energy's long list of externalities. [53]

# 4. Types of Hydrocarbon Production.

**Types of hydrocarbon production & the characteristics of the PW associated with them.**

According to the Energy Information Administration - (EIA) **conventional** oil and natural gas production are defined as "*crude oil and natural gas that are produced by a well drilled into a geologic formation in which the reservoir and fluid characteristics permit the oil and natural gas to readily flow to the wellbore*."

On the contrary, EIA defines **unconventional** oil and natural gas production as "an umbrella term for oil and natural gas that is produced by means that do not meet the criteria for conventional production." [7]



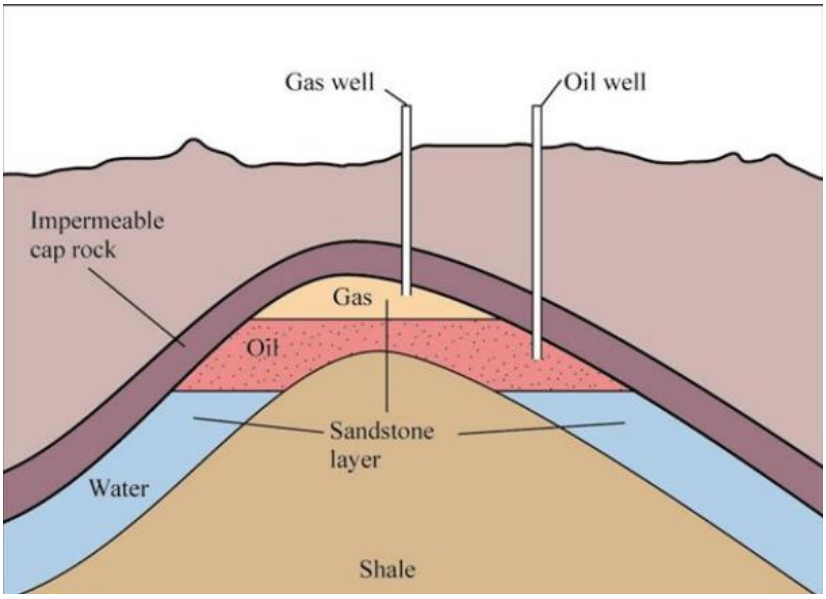

**Picture 7. The different types of hydrocarbon occurrences. [30]**

## 4.1. Conventional Petroleum Resources

The volume of PW from oil and gas wells does not remain constant over time and can even vary during the lifetime of a reservoir. [9, 14, 36]. For example, early in the life of an oil well, oil production is high and water production is low. In particular, the water-to-oil ratio [W/O] and water-to-gas ratio [W/G], more commonly known as the *'water cut'*, increases over the life of a conventional oil or gas well. [9, 36] For such wells, water amounts to a small percentage of produced fluids when the well is new. Consequently, for a given well, as the percentage of water increases over time, the percentage of oil product declines. For crude oil wells nearing the end of their productive live, water can constitute as much as 98% of the material extracted to the surface. [9] At some point, if the cost of managing PW exceeds the profit from extracting and selling oil, then production stops and the well is closed since it is no longer profitable.

### 4.1.1. Crude Oil and Natural Gas

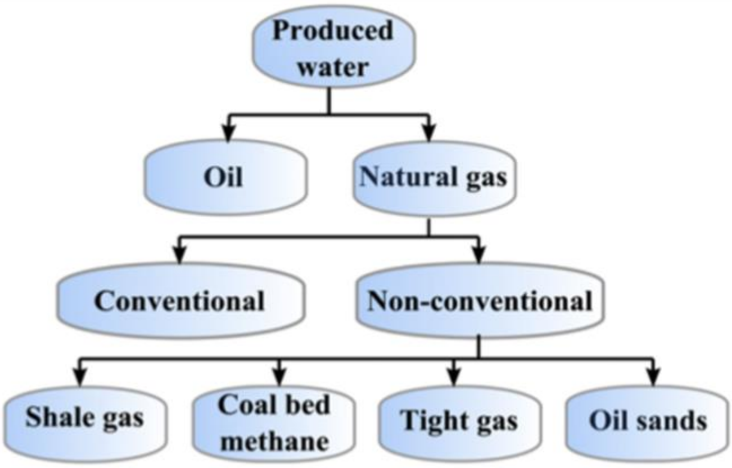
Natural gas wells typically produce much lower volumes of water than oil wells. Among all, onshore extraction operation is the most common procedure. The produced fluids are transferred to the surface where they are separated by means of a machine known as *free water knockout unit*. This water will follow an alternative route into an additional settling unit, such as a *corrugated plate* or *inclined plate separator*. *Coalescers* may be used to make small oil droplets form larger oil droplets. Additionally, *hydrocyclones, media filters, membrane filters,* and *gas flotation units* may be used. In case the oil and grease contains a high percentage of dissolved oil, that was not previously removed by physical processes, other technologies such as *organic clay adsorbents* or *activated carbon* can be used. [3]




**Picture 8. Crude oil and natural gas. [49]**

## 4.2. Non - Conventional Petroleum Resources.

Unconventional oil and gas resources can be found in subsurface formations with low permeability. Producers import water for onsite use for drilling, hydraulic fracturing (as flow back or frac water) and during production operations in general. [4]

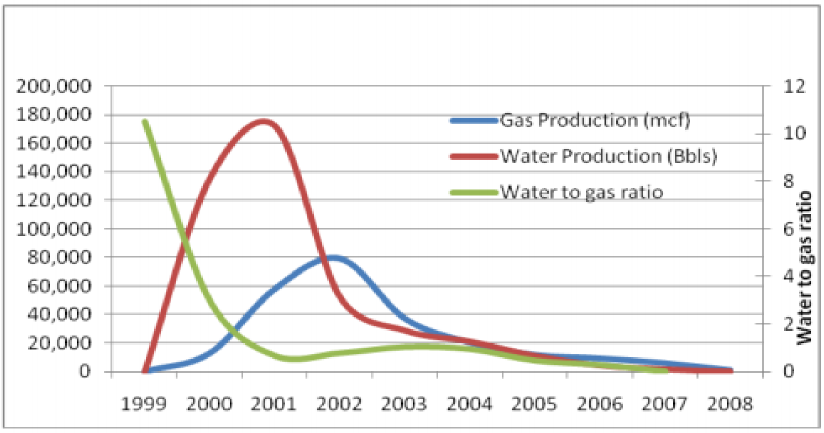



**Picture 9. Various sources of produced water [30]**

### 4.2.1. Coalbed Methane (CBM)

CBM produces the largest quantities of water early in a well's life during gas production compared to other unconventional sources. CBM produced water is generated when the water that permeates the coal beds that contain the methane is removed. [9] The water in coal beds contributes to the pressure in the reservoir which keeps methane gas adsorbed up to the surface of the coal. The water must be removed by pumping to reduce the pressure in the reservoir and allow the methane extraction from the coal. As the amount of water in the coal decreases, the amount of methane production increases. Initially, PW comes to the surface at a high rate, but later the flow rate decreases. Gradually, as the gas production increases, the water production decreases and as a result the volume of CBM-produced water generated decreases over time. CBM produced water is re-injected or treated and discharged to the surface. [4, 9]

When the hydrostatic pressure becomes sufficiently low, methane is released from the coal and rises to the surface through the well. [7] Coal beds contain fractures and pores that can transmit large volumes of water. The volume of water varies significantly from basin to basin, depending on the rank of the coal, the depth of the coal and the hydrologic connectivity to other water bearing aquifers. Water to gas ratio [W/G] is used to describe the volume of water produced per million cubic feet of natural gas as it is a tool to predict the volume of water that will be generated in each producing basin. [4]




**Picture 10. Typical water and gas production for CBM. [4]**

The quality of water from CBM formations varies with the original depositional environment, depth of burial and coal type. It is mainly characterized as salty. However, some CBM formations may produce water with lower salinity. [3, 7]

### 4.2.2. Shale Oil and Gas

The flowback-frac water derives from large water volumes linked to oil shale and gas shale production and is mainly used during drilling, since it returns to the surface at the completion of the hydraulic fracturing job. The main problem is that the produced mass of water is very difficult to be handled, and therefore, its management takes a lot of time. [3, 4, 36]

**The possibility of using PW from shale gas depends on two major factors**:

The first factor, is the **volume** of the flowback and PW generated. Wells that produce significant volumes of flowback water are preferable for re-use because of the specific requirements for storing and transporting the water for re-use.

The second factor is **the quality** of PW. The most important is the composition of PW since it may have salt contents (expressed as TDS), and *Total Suspended Solids* - (TSS). TDS can be treated during the re-use process by mixing PW with freshwater to reduce the concentration of TDS. TSS can be treated by means of low cost equipment, such as specific filtration systems. Chemical additives can be helpful with scale causing compounds. Of course, each additional treatment step increases the cost of the process. The ideal PW for re-use has low TDS and TSS and little or no scale causing compounds. [3]

A serious disadvantage is that the fluid of frac water (that has not initially returned to the surface) remains in the new rock surfaces, which are created through the fracturing process and it is able to dissolve specific high salted constituents from the pores. The longer the water remains in touch with pore spaces, the higher the dissolved constituents are likely to be up to some saturation or equilibrium point. As a result, treatment of the later PW becomes more challenging than treatment of the early flowback water. [7]

The following table compares water needs and PW generation for each major type of oil and gas production. [7]

**Table 1. Comparison of Water Needs and Produced Water Generation [7]**

| Type of Oil and Gas Production | Water Needs for Production | Produced Water Generated |
|---|---|---|
| **Conventional Oil and Gas** | ▪ Not much need for drilling, for some wells that use hydraulic fracturing<br>▪ Typically, much water is needed for EOR as a field matures | ▪ Initially at low volume<br>▪ Increased volume with time<br>▪ High lifetime PW production |
| **Coalbed Methane** | ▪ Not much need for hydraulic fracturing | ▪ High PW volume initially<br>▪ Decreased volume with time |
| **Shale Oil and Gas** | ▪ Great need for hydraulic fracturing | ▪ Initial flowback rate is high, but quickly drops to very low<br>▪ Low lifetime flowback and PW product. |

# 5. Characteristics of Produced Water

## 5.1. Physical and Chemical properties

According to Arnold [1], the composition and the concentration of the PW components depends on the specific field and the various production zones, even in the same field. Trapped water has been in contact with hydrocarbon-bearing formations for centuries and as consequence, it has acquired some of the chemical characteristics of the formation and the hydrocarbon. [11, 14] However, oil and gas production procedure can give PW with similar composition.

**Physical and chemical properties of produced water vary considerably and depend on**: [3, 4, 9, 11, 31, 36]

- **a)** the geographical location of the oil or gas field
- **b)** the geochemistry and the geological host formation
- **c)** the geological contact materials of water in the past
- **d)** the type of hydrocarbon composition being produced
- **e)** the age and type of reservoir
- **f)** the water injection history
- **g)** the artificial lift technique

## 5.2. Composition of Produced Waters from Oil Wells

### 5.2.1. Organic Compounds

<u>The **organic** matter on PW is found either as '**Oil and Grease'** or as **Dissolved Components.**</u>

Oil and grease - *(O&G)* are the most important constituents in both offshore and onshore PW. Their removal from produced wastewaters is often challenging and involves the combination of different treatment technologies, according to the desired use of the treated water and the O&G substances involved. O&G can be classified according to its type and source and this influences the choice of the treatment process. [59]

Therefore, 'O&G' as a class of pollutants, are not specific chemical compounds, but rather a measure of many different types of organic materials. Different methods will measure different organic fractions and compounds. [9, 11] These are identified by an analytical test method that measures the presence of families of organic chemical compounds associated with hydrocarbons in the formation. [3, 7, 11] Average value for oil and grease content typically ranges from 40 mg/L to 2,000 mg/L. [7, 11]

**A.** 'Oil and Grease' are made up of two forms:

1. **Free oil** forming large droplets removable mainly by gravity separation methods.
2. **Dispersed oil** is referred to small, individual droplets, suspended in the aqueous phase and difficult to remove. [9, 10, 31]

Concentrations of dispersed oil found in PW can be very high in some oil fields. [10] Factors that affect the concentration of dispersed oil in PW are oil density, interfacial tension between oil and water phases, type and efficiency of chemical treatment and type, size and efficiency of the physical separation equipment. [9] In particular, PW from crude oil is characterized by high amount of dissolved hydrocarbons, including organic acids, polycyclic aromatic hydrocarbons (PAHs), phenols and volatiles. [9]

**B.** Dissolved Components:

1. **Organic components that are very soluble** in PW consist of low molecular weight ($C_2$-$C_5$) carboxylic acids (fatty acids), ketones and alcohols (e.g. acetic and propionic acid, acetone and methanol). [9] These soluble organics cannot be easily removed from PW and therefore, are discharged to the ocean or re-injected at onshore locations. Generally, the concentration of organic compounds in PW increases as their molecular weight decreases. [9, 31]

2. **Partially soluble** components include medium to higher molecular weight hydrocarbons ($C_6$ to $C_{15}$). They are soluble in water at low concentrations, but as the molecular weight of hydrocarbons rises, they become less soluble. They are not easily removed from PW and are generally discharged directly to the ocean.

   Partially soluble components include aliphatic and aromatic carboxylic acids, phenols, aliphatic and aromatic hydrocarbons. [9] The most toxic hydrocarbons in the soluble fraction are volatile **aromatics**. Alkylated phenols are the most important contributors to toxicity into offshore PW. However, phenols and alkyl phenols could be treated by bacterial in seawater and marine sediments. [9, 31] Concentrations of volatile organic compounds in PW from *gas-condensate-producing* platforms are usually higher than from *oil-extraction*, where concentration is low or nonexistent. On the contrary, semi-volatile organics are rarely found in gas PW whereas in oil PW, they are much more prevalent. [4, 9]

### 5.2.2. Dissolved Gases

**Natural gas** (methane, ethane, propane and butane), **hydrogen sulfide** and **carbon dioxide** are the most significant gases that could be found in PW. As PW flows up the wells, most of these gases turn to vapor separating from the liquid phase. The prevailing conditions of pressure and temperature will indicate the quality of dissolved gas that will be included in the PW flow and finally will end up in water treating facilities.

The higher the separation pressure, the higher the quantity of dissolved gases will be. On the contrary, an inverse relationship exists with temperature: the higher the separation temperature, the lower the quantity of dissolved gases will be. [1]

- **Natural gas** is composed by components slightly soluble in water. The solubility of natural gas (primarily methane) is a function of pressure, temperature and specific gravity of water.

- **Hydrogen sulfide** is corrosive, can cause iron sulfide scaling and is extremely toxic to breathe. This toxicity of hydrogen sulfide demands a special training and life support breathing equipment for protection against exposure when treatment of produced fluid contains this scale. Simultaneously, iron sulfide (the corrosion product of hydrogen sulfide) maintains a possible fire risk since it ignites spontaneously when exposed to air or other sources of oxygen.

- **Carbon dioxide** is corrosive and can cause $CaCO_3$ scaling. If the $CO_2$ and $H_2S$ remove from PW, then the pH will increase causing scaling.

- **Oxygen** is not found typically in PW. Generally, reservoir systems are anoxic. However, oxygen will be absorbed into the water, when the PW is brought to the surface and exposed to the atmosphere. In cases where water comes in contact with the atmosphere such as during pumping and transportation, oxidation is observed. [4] Unfortunately, water containing dissolved oxygen can cause crucial problems, such as severe and rapid corrosion. [1]

### 5.2.3. Dissolved Solids

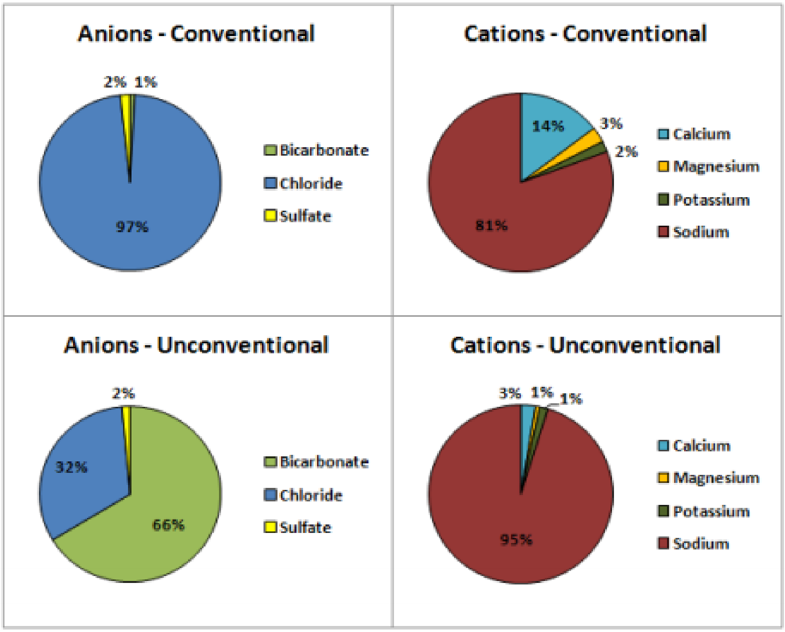
**Dissolved solids** are inorganic constituents that are found in PW [barium (concentration 0 - 850 mg/L), strontium (0.5 – 125 mg/L) and salts mixtures (sodium, calcium, magnesium, potassium or bicarbonate and chloride)]. [3, 4, 31]

Measured in terms of total dissolved solids (TDS), concentration values vary by location ranging from a minimum concentration between 100 mg/L - 1,000 mg/L to a maximum between 300,000 mg/L - 400,000 mg/L [11, 31], with an average value calculated to be a bit less than 100,000 mg/L [7] (to be compared to salinity in seawater that is around 35,000 mg/L).

The reservoir temperature (which is related to subsurface depth) and the amount of *Total Dissolved Solids* (TDS) are related to each other. This can easily explain why PW from hot reservoirs tends to have higher TDS concentrations whereas cooler reservoirs tend to have lower levels of TDS. [1]

Picture 11 shows that sodium and chloride cover the greatest percentage of PW salinity. [31] The dominant cations observed in produced water are sodium (Na+), calcium ($Ca^{2+}$), magnesium ($Mg^{2+}$) and potassium ($K^{+}$). The dominant anions are chloride (Cl-), bicarbonate

($HCO_3^-$) and sulfate ($SO_4$). However, significant differences exist in the dominant ions between conventional and unconventional types of PW. In conventional resources, salinity is mainly up to dissolved sodium and chloride, and less up to calcium, magnesium and potassium. On the contrary, in unconventional resources increased concentration of sodium and bicarbonate are marked. Subsurface anaerobic methanogenesis or creation of biogenic methane are also attributed to increased bicarbonate levels. [4]




**Picture 11. Major cations and anions for produced water [4]**

### 5.2.4. Metals

Metals that are found in PW include <u>zinc, lead, manganese, iron, cadmium, chromium, copper, mercury, nickel, arsenic and barium</u>. Besides toxicity, metals can cause production problems. For example, iron in PW can react with oxygen in the air and produce iron oxides. This could interfere with the processing equipment, e.g. the hydrocyclones or plug formations during injection. [5, 9, 31]

The concentration of metals in PW depends on the field and the geological characteristics of the reservoirs, with respect to the age and geology of the formation. Usually, gas fields provide higher values of heavy metals than oil fields. PW generated from mature fields has significantly less heavy metal content than early production fields. [5, 9]

### 5.2.5. Naturally Occurring Radioactive Materials (NORMs)

Naturally occurring radioactive elements include <u>uranium, thorium, thallium, radium and radon.</u> They are dissolved into water at low concentrations in hydrocarbon bearing formations due to existence of gas shales which are rich in these elements.

NORMs originate from geological formations and they are brought to the surface with PW. As the water approaches the surface, temperature changes cause radioactive elements to precipitate.

The most abundant NORM compounds in PW are Radium 226 and Radium 228, which are derived from the radioactive decay of uranium and thorium associated with certain rocks and clays in the hydrocarbon reservoir. [9, 31] What is more, these elements are not water-soluble in their original form under reservoir conditions ($^{238}U$ and $^{232}Th$) but they can easily decay into different isotopes of radium ($^{226}Ra$ and $^{228}Ra$) that can further decay into radioactive gas, called radon ($^{232}Rn$). Leakage or spill of PW containing NORMs contaminates soil, ground and surface water. [1, 4]

Radioactivity values of Norm samples range from low detectable levels -0.3 and 1.3 Bq/L- to levels between 16 and 21 Bq/L for $^{226}Ra$ and $^{228}Ra$ generating serious concern demanding a special treatment before disposal to the environment. [31] $^{226}Ra$ and $^{228}Ra$ are regulated at a maximum concentration of 5 pCi/L in drinking water. Therefore, most sources require treatment in order to meet this requirement. Both radium and radon are soluble in formation water under reservoir conditions and can be transferred to the surface along with oil, gas and PW. [1, 4]

### 5.2.6. Scale

Some ions react under specific conditions, such as changes in pressure, temperature and composition, forming precipitates. As a result, deposits and oily sludges are formed in tubing, flow streams, vessels and equipment during PW treatment, in general, that must be removed. Sometimes emulsions are formed that are difficult to break. *(see 6.3 Emulsion separation on page 43)*. [1, 9]

Mixing oxygenated water with produced water should be avoided because it could lead in the formation of calcium carbonate ($CaCO_3$), calcium sulfate ($CaSO_4$) and iron sulfide ($FeS_2$) scale, along with oil-coated solids. [1]

- **Calcium Carbonate ($CaCO_3$)** precipitates are formed due to pressure decline accompanied with dissolved carbon dioxide ($CO_2$) release from PW. The produced water's pH increases and as a result, the solubility of $CaCO_3$ is reduced, leading to scale precipitate.

- **Calcium Sulfate ($CaSO_4$)** one of the several sulfate scales, can be formed either by mixing different waters or naturally, due to changes in temperature and pressure.

- **Iron Sulfide ($FeS_2$)** appears when water containing dissolved hydrogen sulfide ($H_2S$) deals with equipment made of carbon, steel or iron. Moreover, mixing water containing iron cations ($Fe2^+$) with hydrogen sulfide ($H_2S$) water will also result in a $FeS_2$ precipitate. Both of these reactions lead to corrosion.

- **Barium and Strontium Sulfate ($BaSO_4$ and $SrSO_4$)** are found hardly ever in PW. However, in case of mixing water stream containing considerable quantities of barium or strontium ions with sulfate-rich water, barium and/or strontium scaling can be formed. [1]

### 5.2.7. Water Treatment Chemicals

Chemicals used to treat PW include:

- ✓ *Biocides* to mitigate bacterial fouling
- ✓ *Emulsion breakers* to break water-in-oil emulsions
- ✓ *Reverse breakers* to break oil-in-water emulsions
- ✓ *Scale inhibitors* to limit mineral scale deposits
- ✓ *Oxygen scavengers* to reduce equipment corrosion.
- ✓ *Corrosion inhibitors* to form more stable emulsions, making O/W separation less efficient.
- ✓ *Coagulants, Flocculant*s and C*larifiers* to remove solids
- ✓ *Solvents* to reduce paraffin deposits

Chemical additives are used to improve drilling, production and separation operations. [7,11] The production from a well can be improved by utilizing the appropriate well-treatment chemicals, according to the characteristics of the formation. [11] Treatment of PW of the above chemicals, is required to avoid aquatic toxicity. However, some of them could be fatal even at levels as low as 0.1 ppm. [9, 31]

The most common problems in treatment of PW in comparison to their causes and possible chemical treatment requirements are presented in the following table:

**Table 2. Chemical treatment of water problems [4]**

| Problem | Cause | Chemical Treatment | Chemical Concentrations |
|---|---|---|---|
| Chemical corrosion | Hydrogen sulfide gas, carbon dioxide or oxygen | Corrosion inhibitor: amine imidazolines, amines and amine salts, quaternary ammonium salts, and nitrogen | Active ingredient concentration 3 –40% |
| Bacterial corrosion | Sulfate reducing bacteria reducing sulfate to hydrogen sulfide | Bactericides: quaternary amine salt, amine acetate, and gluteraldehyde | Concentrations ranging from 10–50% |
| Hydrate formation | Natural gas hydrates formed in the presence of water usually at high pressure and low temperature | Hydrate inhibition: ethylene glycol and methanol | 5–15 gallons per million cubic feet of produced gas |
| Water Vapor | Water vapor present in natural gas is removed to meet sales specifications | Dehydration: Triethylene glycol (TEG) | n/a |
| Mineral deposits | Inorganic mineral compounds causing scale or deposits, such as calcium carbonate, calcium sulfate (gypsum), strontium sulfate, and barium sulfate | Scale inhibitor: phosphate esters, phosphonates, and acid polymers | Treatment concentrations from 3–5 ppm, but depend on the water type |
| Emulsion (normal and reverse) | Normal – water droplets dispersed in the oil phase Reverse – oil droplets suspended in the continuous water phase | Emulsion breakers: oxyalklated resins, polyglycol esters, and alkl aryl sulfonates | Bulk concentrations of 30–50% |
| Foaming | Oil froth | Defoamers: silicones and polyglycol esters | Treatment concentrations are 5–25 ppm |

### 5.2.8. Sand and Other Suspended Produced Solids

Suspended solids can influence PW production, since fine-grained solids can reduce the removal efficiency of oil/water separators. Some of them can form oily sludges in production equipment and require periodic removal and disposal. In the case of sand, if the well is characterized by an unconsolidated formation, then bigger quantities of sand are produced. [1, 9, 23]

### 5.2.9. Salinity – Sodicity - SAR

Salinity, sodicity and toxicity from various metals should be taken under serious consideration. [9]

**Salinity** refers to the amount of total dissolved salts (TDS) in the water and is measured by electrical conductivity (EC),

**Sodicity** refers to the amount of sodium in the soil. Sodium adsorption ratio - **SAR** is the standard measure of sodicity, and along with pH, characterizes salt-affected soils. It is a calculated parameter that relates the concentration of sodium to the sum of the concentrations of calcium and magnesium. It is an easily measured process that gives information on the comparative concentrations of sodium ($Na^+$), calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) in soil solutions.

SAR is calculated using the following equation:

$$SAR = \frac{Na^{+}(meq/L)}{\sqrt{\frac{(Ca^{2+} + Mg^{2+})(meq/L)}{2}}}$$

The higher the SAR, the greater the potential for reduced permeability, which reduces hydraulic conductivity while causing surface crusting [9]. (It should be noted that adding calcium and magnesium to produced water does not reduce sodium, but changes the ratio of sodium to other salts). Although SAR is decreased by adding hardness, the PW becomes more saline with the sodium salt still dissolved in the water. SAR treatment may require the addition of acid (e.g., $H_2SO_4$) to help degassing carbonate to produce the desirable hardness concentration. [15]

# 6. Technologies and Options for Managing Produced Water.

There are four different available options for PW management to oil and gas operators:

1. ***Injection***: injection of PW into the same formation from which the oil is produced or handle to another formation.
2. ***Discharge:*** treatment of PW to meet onshore or offshore discharge regulations.
3. ***Reuse in oil and gas operation***: treat the PW to meet the quality required to use it for usual oil and gas fields operations.
4. ***Consume in beneficial uses***: PW treatment to meet the quality required for beneficial uses such as irrigation, land restoration, animal consumption or even drinking water.

In general, about 93% of PW from onshore activities, is injected underground either to maintain formation pressure and increase the output of production, e.g. wells for enhanced recovery (approximately 59% of the total injected), or for disposal (approximately 40%). Only 3% of onshore PW is discharged by treating it to meet required regulations, whereas most of **offshore** PW - about 90%, is treated on the platform and discharged to the ocean.

A small percentage of the **offshore** PW is injected underground for improved recovery, disposal or offsite commercial disposal. [7, 11] About 3.6% of all PW evaporates. At least 0.6% of the PW and flowback water in 2012 was put to a beneficial reuse. It is likely that a higher percentage was reused, but data is not available to quantify the amount. Much of the reuse was carried out by recycling flowback water and PW to make drilling fluids and frac fluids for new wells in the same fields.

There are several parameters that affect the final amount to be discharged or injected. Proper management of PW should begin with an accurate estimation of the produced quantities.

## 6.1.Produced Water Treatment Processes and Criteria

There is no treatment technology suitable for all produced fluids and producers have to determine the most appropriate one for each case.

The selection of the suitable methodology for PW management should be based on the following criteria:

**a)** Chemical and physical properties of the PW.

**b)** Volume, duration and flow rate of PW.

**c)** Desired end use or disposition of PW.

**d)** Treatment and disposal options in accordance to national regulations.

**e)** Economic criteria.

Generally speaking, several factors should be taken into consideration during the treatment process of PW to remove contaminants and undesirable components. Treatment operations vary considerably depending on the location, quality and quantity, regulatory acceptance, technical feasibility, cost, availability of infrastructure and equipment. Therefore, selection of PW treatment technology is a challenging task.

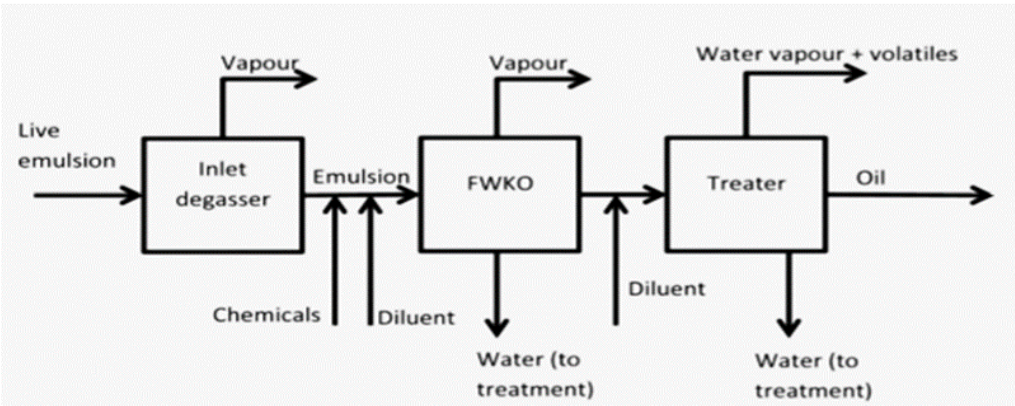
The general principle is to select the most economical, commercially available method that covers the specific technical criteria. For example, PW must be treated to remove oil and grease and toxic chemicals before discharging it to the ocean from an offshore platform. PW that is discharged to onshore freshwater rivers must be further treated to reduce salt content. Water that is injected for either enhanced recovery or for disposal is treated in a different way from water that is discharged. The treatment processes used prior to injection are designed to remove free oil, solids and bacteria. Chemicals are often used to enhance treatment processes and to protect underground formations and equipment. Some characteristics of PW may limit the treatment options. For example, temperature, indicates which type of desalination treatment should be followed, since some technologies are more efficient at high temperatures, whereas others use a low temperature feed stream. In the case of ion removal, the types of ions that need to be removed indicate the treatment method.

Direct discharge or evaporation is the least expensive management option, whereas commercial use of water or brine disposal is the most expensive one. So, PW treatment (and its final ‘safe’ disposal) and the cost should be considered as an integral part of the overall oil or gas production cost. However, if an operator cannot reduce water management costs or even if the cost exceeds the value of the hydrocarbon produced from a well, then the well is usually abandoned and shut down. [14]

## 6.2. Separation of Oil, Gas and Water

The separation of a three phase stream of water, oil and gas produced from the reservoir can be achieved by gravity separation in a horizontal or vertical separator and comprises into the following steps.

Firstly, the stream enters into an *inlet degasser* (two-phase separator) where the separation of gas from liquid takes place. So, gas stream is the first to be removed. In previous years, gas was burned. Nowadays, gas is often collected and sent to markets as an energy source. [9] Subsequently the gas is driven to a vapor recovery unit and the liquid flows to a *free water knockout* (FWKO), which separates the oil from the water based on differences in phase densities (picture 12). Secondly, the water is further treated and the oil flows into a treater unit, where remaining water, solids and gases are removed before the final destination use of oil. [24]




**Picture 12. High-level overview of emulsion separation process. [24]**

However, the separated oil stream may contain some water and the water stream may contain additional dissolved hydrocarbons or emulsified oil. Those elements cannot be removed through basic gravity separation and require an additional treatment. [9] Gravity separation is widely used to separate emulsion ingredients, and in this case the addition of a diluent and a *demulsifier* chemical is required. [24] A common oil field treatment method used to break emulsions is the application of heat generated by burning gas, through a pipe laid in the middle of a tank, known as *heater-treater*. Another approach used to break emulsions is electrostatic precipitation. [9]

## 6.3. Emulsion separation

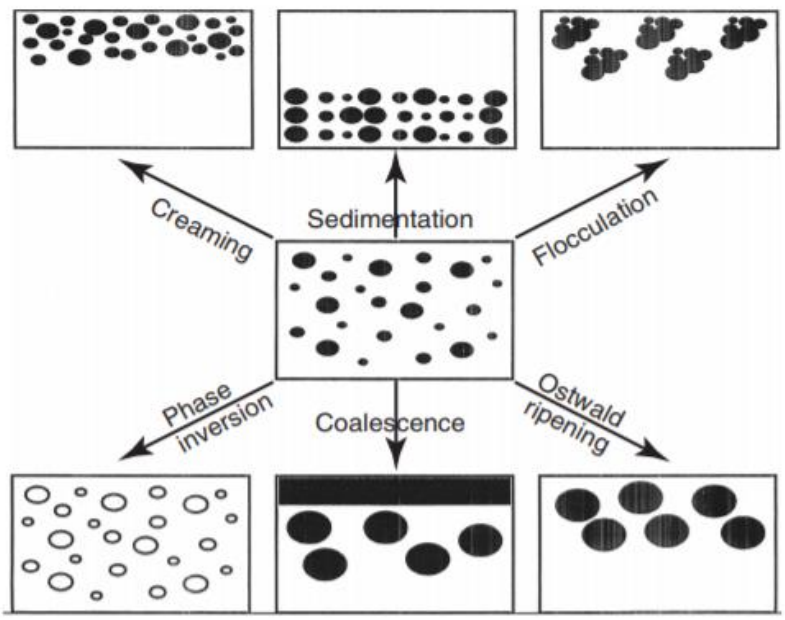
PW can be seen as an oil-in-water emulsion, where the oily phase is dispersed in the aqueous phase, stabilized by surfactants. Surfactants can be chemicals such as corrosion inhibitors, biocides and extraction enhancers. [22] Emulsion separation is sometimes very difficult and expensive. The difficulties associated with oil–water mixtures separation depend primarily on the dispersed phase size and its stability in the mixture.

Mixtures of oil and water are classified in terms of the diameter (d) of the dispersed phase, as

- free oil and water if d>150 µm,
- dispersion if 20 µm ≤ d ≤ 150 µm or as
- emulsion if d < 20 µm.

The stability of oil–water emulsions is greatly increased by addition of surfactants, decreasing the interfacial tension between oil and water phases, preventing the coalescence of droplets. [5] Most emulsions are thermodynamically unstable because of the relatively large positive free energy (interfacial tension) associated with the contact between the oil and water phases, and so they have a tendency to break down over time, e.g. due to gravitational separation, flocculation, coalescence or Ostwald ripening. As a result, the increase of the interfacial area between water and oil when an emulsion is formed, drives to increase the free energy in the system as well.

This is given by $\Delta F = \gamma \cdot \Delta A$, where **ΔF** is the change of free energy, **γ** is the interfacial tension and **ΔA** is the change of interfacial area.




**Picture 13. Schematic representation of the various breakdown in emulsions. [52]**

The stability of an emulsion is determined by *Van der Waals forces and repulsive electrostatic forces* between the droplets. However, the two main factors responsible for emulsion instability are *Coalescence* and *Ostwald ripening* and are both depended on interfacial tension. In both cases, the free energy of the system diminishes because of the reduction of the surface area. [22]

Analytically,

- *Coalescence* refers to the process of thinning and disruption of the liquid film between the droplets with the result of fusion of two or more droplets into larger ones. The limiting case for coalescence is the complete separation of the emulsion into two distinct liquid phases. The driving force for coalescence is the surface or film fluctuations which results in close approach of the droplets whereby the van der Waals forces is strong thus preventing their separation.

- *Ostwald Ripening* results from the finite solubility of the liquid phases. Liquids that are referred to as being immiscible often have mutual solubilities that are not negligible. With emulsions, which are usually polydisperse, the smaller droplets will have larger solubility when compared to the larger ones. With time, the smaller droplets disappear and their molecules diffuse to the bulk and become deposited on the larger droplets. With time, the droplet size distribution shifts to larger values.

- *Flocculation* process refers to aggregation of the droplets (without any change in primary droplet size) into larger units. It is the result of the Van der Waals attraction that is universal with all disperse systems. Flocculation occurs when there is not sufficient repulsion to keep the droplets apart to distances where the Van der Waals attraction is weak. Flocculation may be ‘‘strong’’ or ‘‘weak,’’ depending on the magnitude of the attractive energy involved.

- *Sedimentation* refers to a process that results from external forces usually gravitational or centrifugal. When such forces exceed the thermal motion of the droplets, a concentration gradient builds up in the system with the larger droplets moving faster to the top (if their density is lower than that of the medium) or to the bottom (if their density is larger than that of the medium) within the container.

- *Phase Inversion* refers to the process whereby there will be an exchange between the disperse phase and the medium. For example, an O/W emulsion may with time or change of conditions invert to a W/O emulsion. In many cases, phase inversion passes through a transition state whereby multiple emulsions are produced. [52]

## 6.4. SAGD - Steam Assisted Gravity Drainage

Oil shales commonly produce bitumen. The physical separation of produced bitumen and water remains challenging, as facilities need specific equipment and treatment technology along with highly skilled operators. Further, many oil sands plants have limited access to nearby water sources, forcing them to pump water long distances, thereby increasing their energy demand along with capital and operating costs. [51]

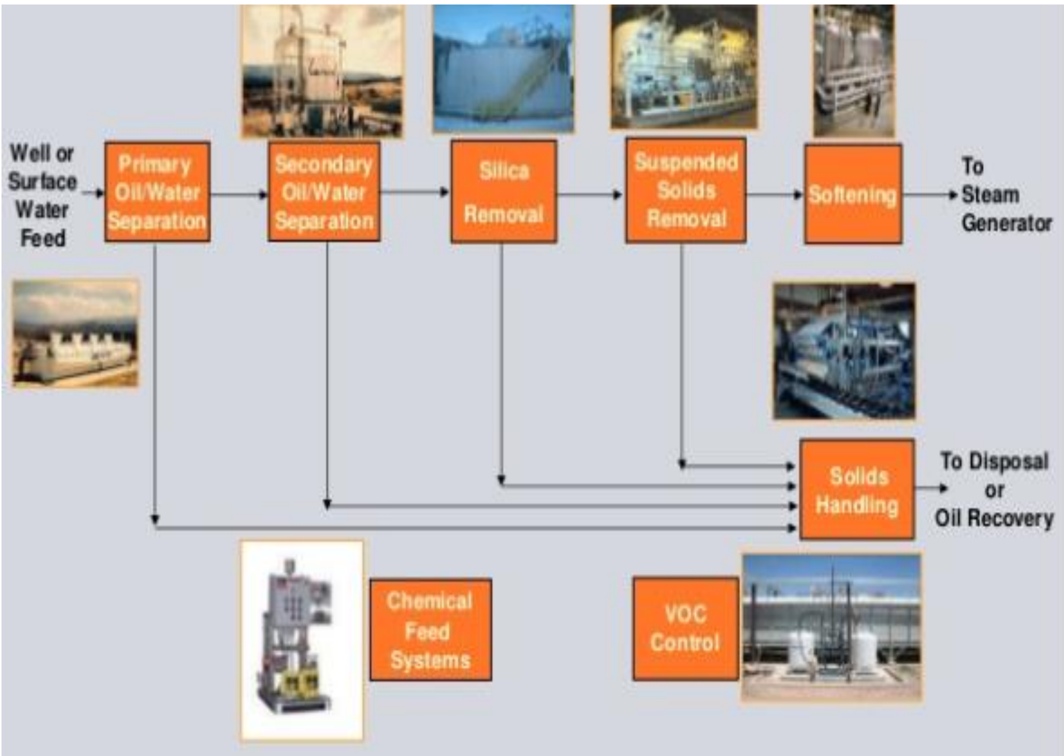
Bitumen are rather heavy and their density is close to that of water. Consequently, gravity separation of bitumen from water confronts a lot of difficulties. The recommended solution is the use of a diluent that is added to emulsion before the FWKO, which dilutes the oil phase, decreases the viscosity and improves the efficiency of the whole separation.

Demulsifying chemicals are additionally added to the emulsion to reduce the interfacial tension between oil and water droplets. Once the water has been initially separated, the following step is the treatment for an efficient removal of dissolved solids, silica and any other remaining oil droplets. [24]

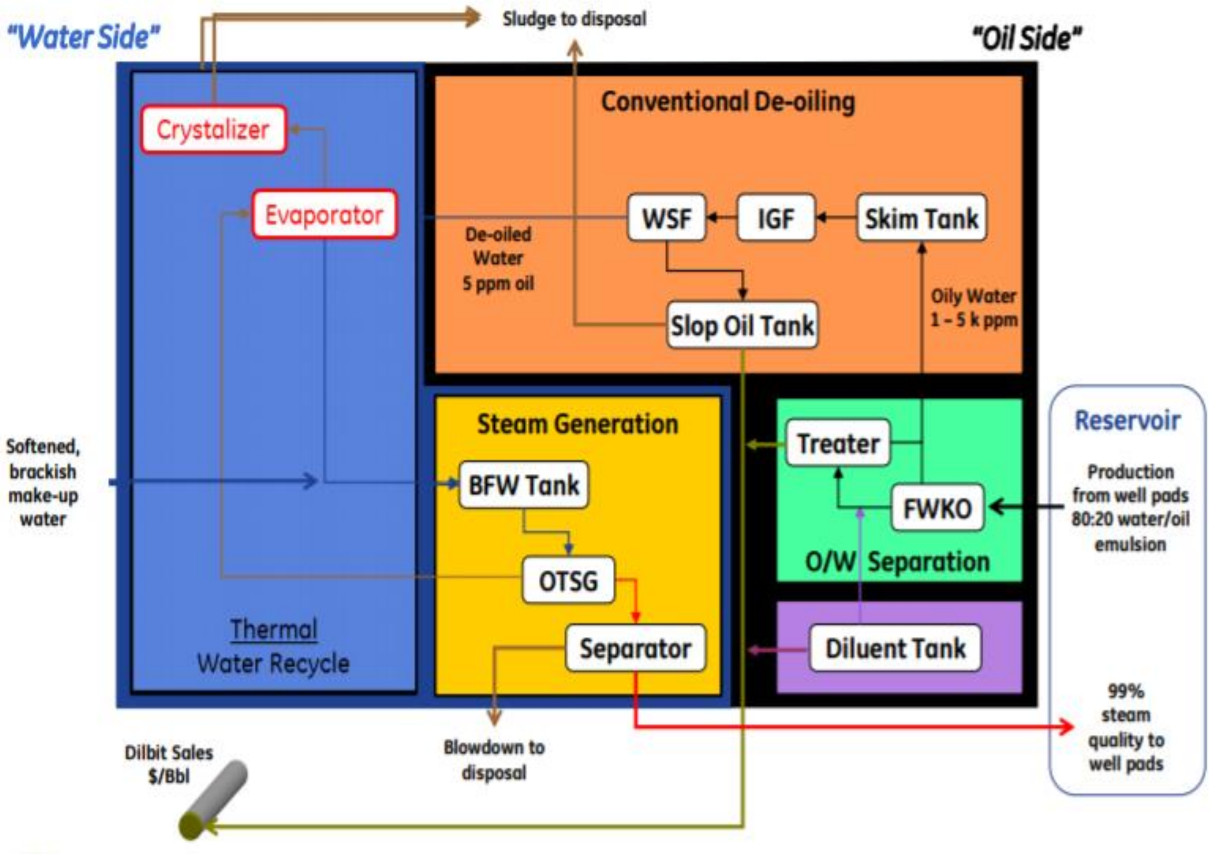
***SAGD*** *(steam assisted gravity drainage)* is a tool that designed to make the treatment of PW a more energy-efficient process. Indeed, SAGD evaporators enable to achieve significantly higher water recycle rates while reducing chemical use and improving plant availability. So, recycle rates of up to 98% can be achieved, reducing total water consumption by 50%, compared to traditional treatment processes. [51]

More specifically, s*team assisted gravity drainage* ***(SAGD)*** is a technique where two horizontal wells are drilled into the deposit. These horizontal wells may extend for miles in all directions. One well is directly above the other. In the upper horizontal well, steam is injected continuously to heat the bitumen. The lower of the two wells is used to pump the bitumen to the surface. The bitumen produced via SAGD contains a significant amount of water from the steam condensate.

Since the quality of the water required for discharge is high and the availability of raw water is limited, the choice is most often made to recycle this water. Some of the major differences from conventional water treatment systems are the desire to preserve as much heat as possible and the need to reduce the high amounts of silica which are common in water at SAGD operations. Heat recovery saves energy in cold climates. In addition, silica reduction via warm lime softening requires temperatures of 140° F for best silica reduction.




**Picture 14. Steam Assisted Gravity Drainage (SAGD) [40]**




**Picture 15. SAGD facility processes. [50]**

# 7. Subsequent steps of a typical Produced Water treatment

In most cases of treatment of PW, these following steps are not used individually but depending on the conditions and the composition of PW, they constitute stages in the treatment system of PW, since in combination could give the appropriate result.

a) **De-oiling** – Removal of dispersed oil and grease present in PW. The concentration of these oils in the treated PW must comply with regulations. [2]
The apparatus through which the oil removal is achieved are the following: API gravity separator, Corrugated plate separator, Gas floatation (with or without flocculants), Hydrocyclone and Centrifuge. [2]

b) **Organic removal** – Removal of dissolved organics includes: Adsorption, (with Granular Activated Carbon (GAC) or Biological Active Carbon (BAC)), Oxidation.

c) **Disinfection** – Removal of bacteria, viruses and microorganisms are necessary to avoid scaling and water contamination. [2] It is achieved by the use of **UV ultraviolet radiation light** (primary treatment, no need for chemicals, no formation of byproduct) and **chlorination** (secondary stage).

d) **Suspended solids – SS removal** – Removal of suspended particles, sand, turbidity.

e) **Dissolved gas removal** - Removal of light hydrocarbon gases, carbon dioxide, hydrogen sulfide - Gas Stream Recovery - Air Stripping

f) **Desalination** – Removal of dissolved salts sulfates, nitrates, contaminants, scaling agents involves the use of either:

- ✓ **Filtration Membranes** processes (Microfiltration, Ultrafiltration, Nanofiltration, Reverse Osmosis, Forward Osmosis and Membranes with selective wet-ability)
- ✓ **Thermal** processes (Membrane distillation) or
- ✓ **Alternative** processes (Capacitive deionization - CDI, Ion exchange - IX)

All these techniques aim to remove TDS, salts, contaminants, impurities and scaling agents. TDS in PW may be up to 150,000 ppm. The final choice of desalination method to be used depends on TDS content and the compatibility of the treatment system. [2].

g) **Softening** – Softening is suitable for removal of excess hardness and silica. [2,4,10] It is a chemical addition so post treatment of precipitated waste is necessary.

h) **NORM Treatment** - Extraction of heavy metals and radioactive material with aqueous solution. PW contains high levels of Uranium or Thorium. Unless treatment is accomplished radioactive scale can form in surface equipment extensive remediation. [2]

## 7.1. Technologies of Treatment of Produced Water

In the following section we will analyze some methods of treatment of PW, specifically the most widely known ones.

Prior to disposing of or re-using water, operators should employ different treatment processes and technologies. The final disposition of the water defines the type and extent of treatment. For example, if water is discharged, the parameter of greatest concern can be related to either the organic content (oil and grease) or the salt content (salinity, conductivity). The salinity of PW discharged to the ocean is not a parameter of concern, but the oil and grease concentration should be regulated. Onshore discharges must remove salinity in addition to oil and grease. When the process of extracting the oil is finished, the remaining water is ready for disposal or for management.

The parameters determining the technologies of the PW treatment are:

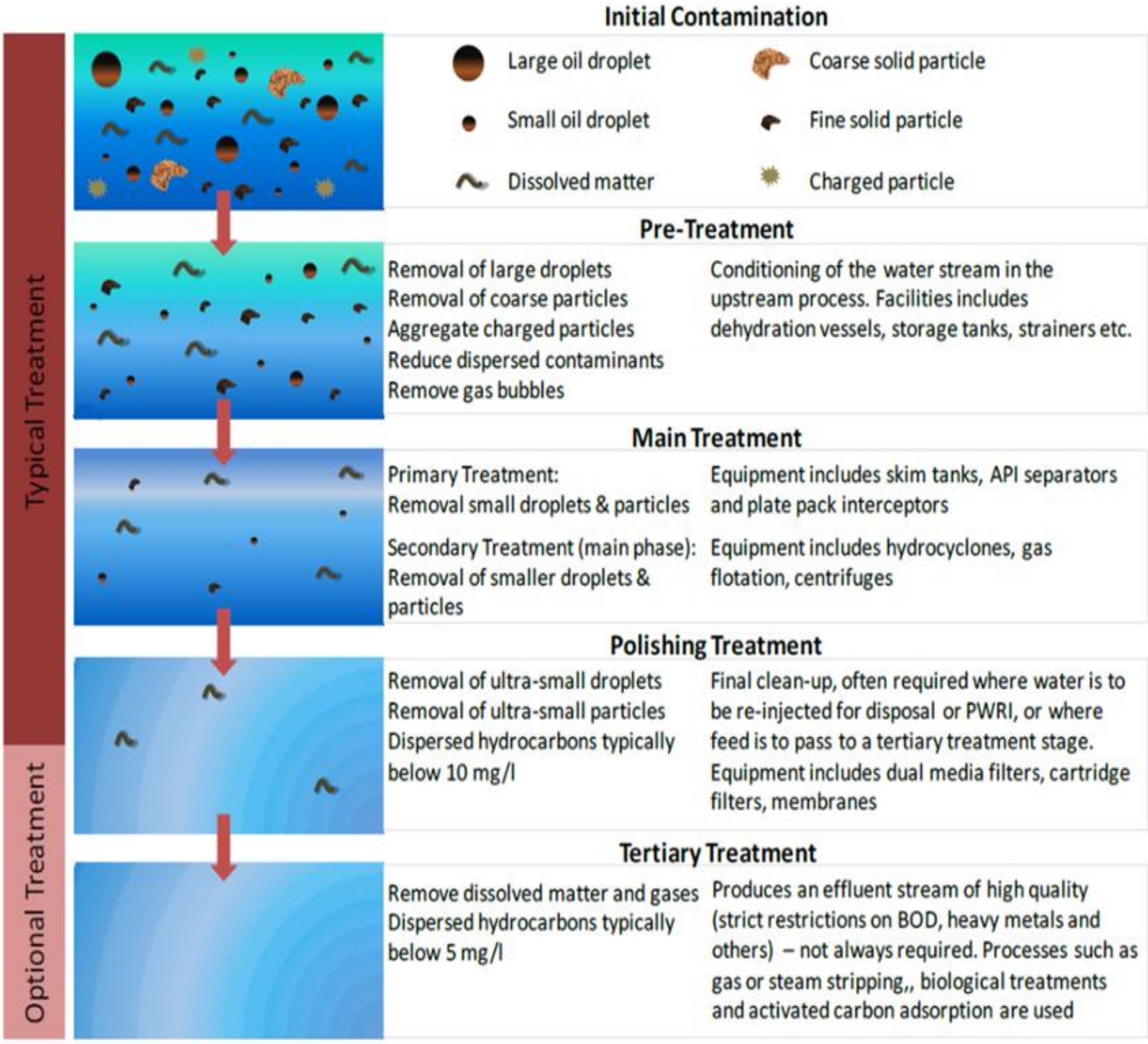
- The quality specifications of the injection water
- The amount of the produced solids
- The characteristics of the PW
- The regulations of the surface PW disposal
- The required supplemental water resources
- The type of the platform (floating, etc.)
- The cost of the procedure and
- The oil production methodology [8]

The next treatment steps are indicated from the desired use of the water. In this chapter the latest technologies and treatment processes which are currently applied by the oil/ gas extraction industry are discussed.

Picture 16 shows the typical treatment of the main stages that PW receives in oil and gas field operations.

In **pre-treatment**, the bulk of the oil and gas, as well as coarse particles are removed. This is followed by the **main treatment**, which focuses on further removal of small hydrocarbon droplets and small particles from the water. This is achieved in two steps of treatment.
The primary step removes larger hydrocarbon droplets and large solid particles, as well as hydrocarbon slugs. A secondary step goes after smaller droplets and particles, and it encompasses the bulk of the de-oiling equipment used in the upstream industry. This secondary step is usually sufficient to reduce the dispersed hydrocarbon content to below the typical offshore discharge level of 40 mg/L.

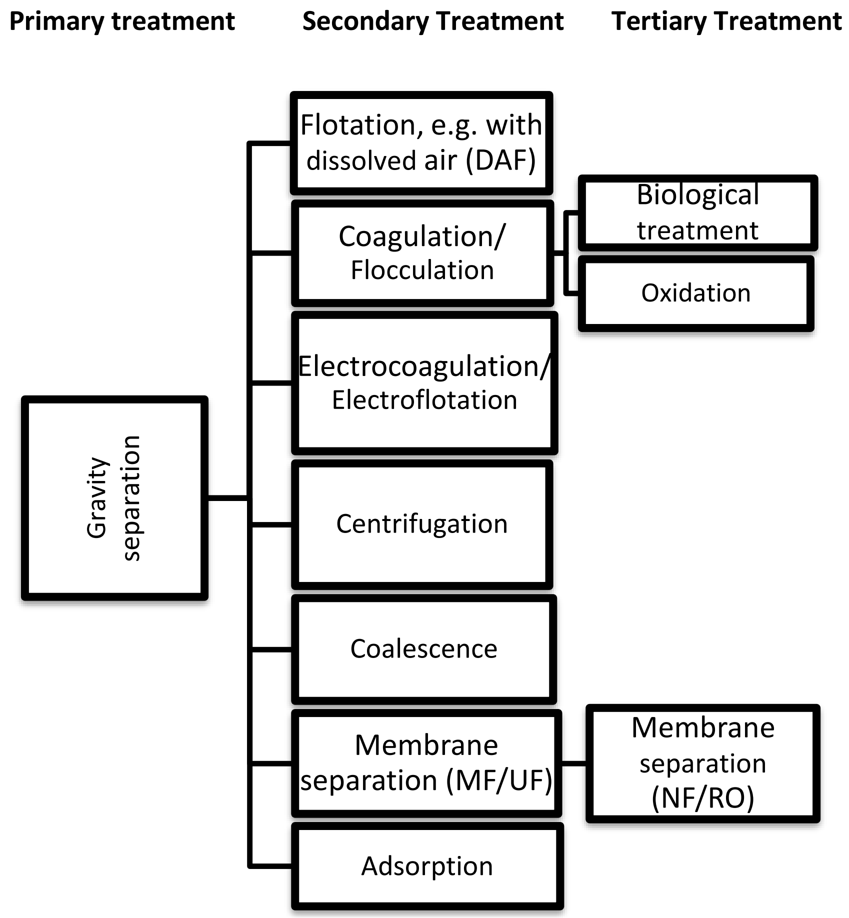
Then, there is a final **polishing treatment**, which can be optional, where the oil concentration is lowered to levels typically below 10 mg/L. The implementation of this last treatment depends on either the regulatory framework or an operational requirement if water is going to be re-injected for either disposal or as part of the waterflooding operations in the field. Sometimes an additional treatment is required, where the final effluent stream must have a high quality. In this case, oil concentration is typically below 5 mg/L, and there are usually other restrictions that must be met such as heavy metals content, biochemical oxygen demand (BOD) levels, and so on.




**Picture 16. Typical water treatment process in the oil and gas industry. [60]**

As picture 17 shows treatment of PW usually involves three steps, including primary, secondary and tertiary treatment.

Gravity separators accomplish removal of free oil as a primary treatment. Secondary treatments include chemical, electrical and physical methods which target emulsified oil, such as, coagulation/flocculation, dissolved air flotation, electro-coagulation/flotation, and membrane separation. Tighter membranes and advanced oxidation processes can refine treatment in a tertiary step.




**Picture 17. Graphic plan of primary, secondary and tertiary treatment of PW. [59]**

## *7.2.* De-oiling processes *(Oil and grease removal).*

Oil and grease discharge, along with PW, should be removed according to stringent regulations. Table 3 presents the typical performance of oil removal methods, as expressed by minimum oil particle size removal.

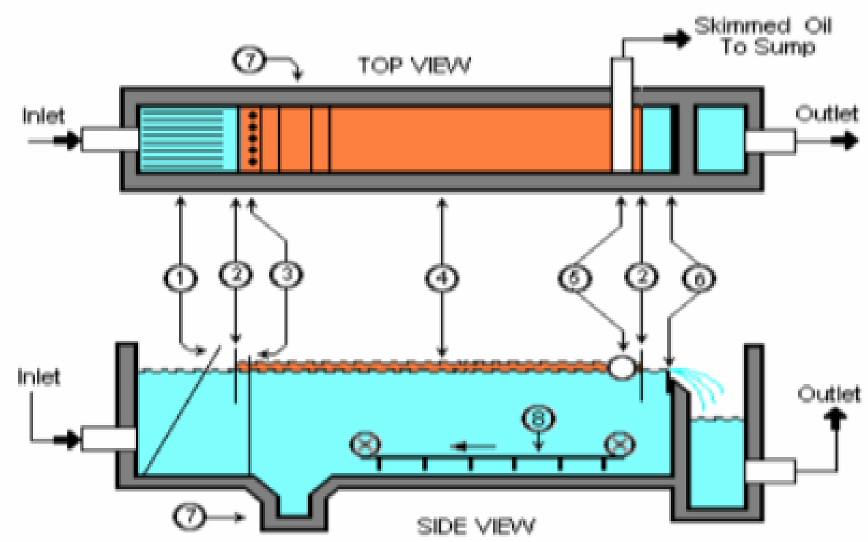
**Table 3. Oil and grease removal technologies based on size of removable particles. [9]**

| Oil Removal Technology | Min. size of particles removed (microns - μ) |
|---|---|
| API gravity separator | 150 |
| Corrugated plate separator | 40 |
| Induced gas flotation (no flocculants) | 25 |
| Induced gas flotation (with flocculants) | 3-5 |
| Hydrocyclone | 10-15 |
| Media filter | 5 |
| Centrifuge | 2 |

### 7.2.1. Gravity separation

The most frequently used type of oil-water separator is the well-known API gravity separator, which can remove up to 60 to 99% of the free oil in a stream. In an API separator the separation of the three phases stream in oil, gas and water takes place through gravity. During the retention of the effluent, pollutants such as oil (lighter) and solids (heavier than water) are separated into floating scum (oil) and bottom sludge (sand and other solids). These are subsequently removed by a scraping device for bottom sludge and a device for floating scum removal for the surface scum. [6]

The efficiency of this process depends on the retention time, tank design, oil properties and the effects of flocculants or coagulants, if added. This method is not suitable for small oil droplets or emulsified oil because, for a given efficiency, as the oil droplet size decreases, the required retention time increases drastically. Additionally, gravity separation for smaller droplets involves higher maintenance cost. [2]




**Picture 18. Schematic diagram of an API oil separator [6]**

Where:

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

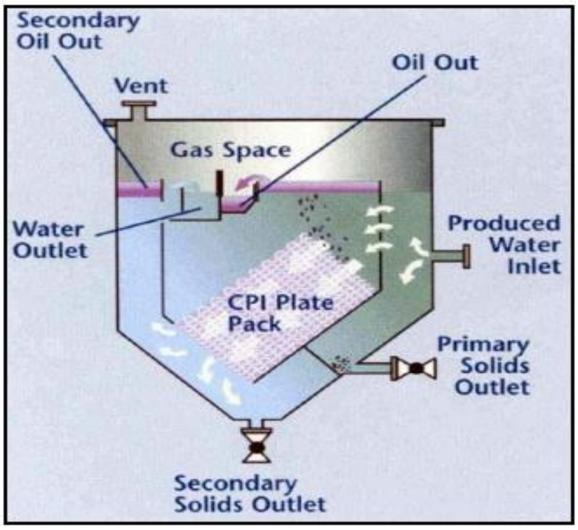
### 7.2.2. Corrugated plate

The separation of free oil from water is achieved by gravity enhanced by its flocculation on the surface of corrugated plates. [2]

Principle of operation: The oil droplets coalesce and form larger oil droplets as the corrugated plates provide a greater surface for the oil droplets making them follow a path and travel towards the top of the tank. [2] The oil droplet size should be greater than 40 μ. for an efficient operation. The picture 19 illustrates the flow pattern of a typical down flow CPI design. In CPIs the parallel plates are corrugated (like roof) and the axes of the corrugations are parallel to the direction of flow. [6]

Advantages: it does not require much energy, it is rather cheap and effective for bulk oil and suspended solid removal, with no moving parts, this technology is robust and resistant to breakdowns. Disadvantages: it is rather inefficient for fine oil particles, since it requires high retention time and maintenance cost. [2]

This method is indicated in oil and gas PW, especially oil recovery achieved from emulsions or water with high oil content prior to discharge. For example, it can treat PW that may contain oil and grease in excess of up to 1000 mg/L. [38]




**Picture 19. Corrugated Plate (CPI) packing separates oil & solids from produced water [2]**

### 7.2.3. Gas flotation

Flotation is widely used for PW treatment, primarily for conventional oil and gas PW. It is a procedure that introduces small gas bubbles in order to separate suspended particles that are difficult to separate by other means like settling or sedimentation. [10]

The gas bubbles acquire a small electronic charge, opposite to that of the oil droplets. [6] Gas is injected into the water and oil droplets suspended in the water are attached to the air bubbles and driven to the surface. As a result, foam is created on the surface, which is often removed by skimming. The dissolved gas can be air, nitrogen or other types of inert gas. Dissolved air or gas flotation can be used to remove volatile organics, oil and grease. [4,15]

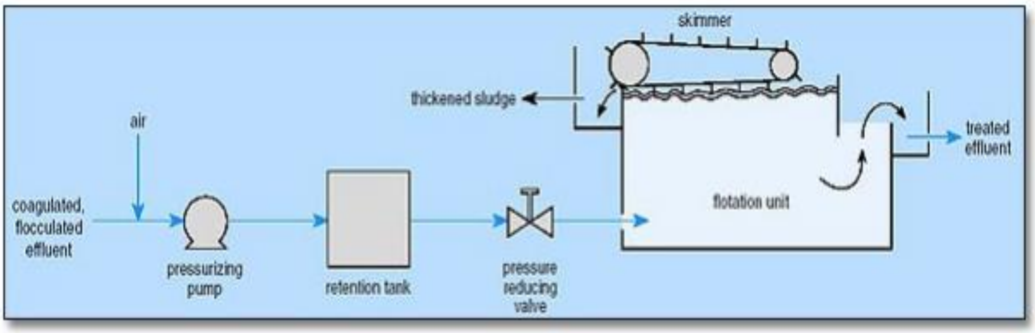
Gas flotation technology is subdivided into **a.** *Dissolved Gas Flotation (**DGF**)* and **b**. *Induced Gas Flotation (**IGF**)*. The two technologies are distinguished by the method used to generate gas bubbles and the resultant bubble sizes.

- In DGF units, gas (usually air) is fed into the flotation chamber, which is filled with a fully saturated solution. The gas inside the chamber, is released either by applying a vacuum or by abruptly decreasing the pressure.
- IGF technology uses mechanical shear or propellers to create bubbles that are introduced into the bottom of the flotation chamber. Coagulation can be used as a pretreatment to flotation. [4, 10, 15]

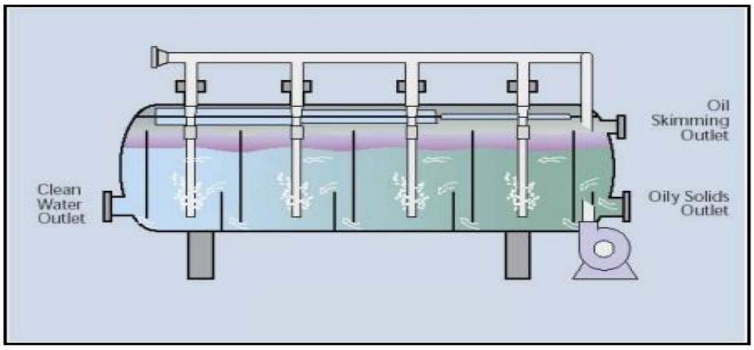
The efficiency of the flotation process depends on the density differences between the liquid and the contaminants to be removed, on the oil droplet size and the temperature as well.

Minimizing gas bubble size and achieving an even gas bubble distribution are critical for the gas removal efficiency. Flotation works well in low temperatures and can be used for waters with both high and low TOC concentrations. It is recommended for the removal of natural organic matter, TOC, oil and grease and particulates. [4] Analysis of PW quality has shown that flotation can lead to 93% of oil removal, 75% of COD and 90% of $H_2S$.

*Dissolved air flotation* (DAF) can remove particles as small as 25μm. If coagulation is added as pretreatment, DAF can remove contaminants 3 to 5 μm in size. Flotation cannot remove soluble oil constituents from water. Because flotation involves dissolving gas into the water stream, flotation works best at low temperatures. If high temperatures are present, a higher pressure is required to dissolve the gas in the water. [4, 10, 15]




**Picture 20. A flotation unit. [15]**

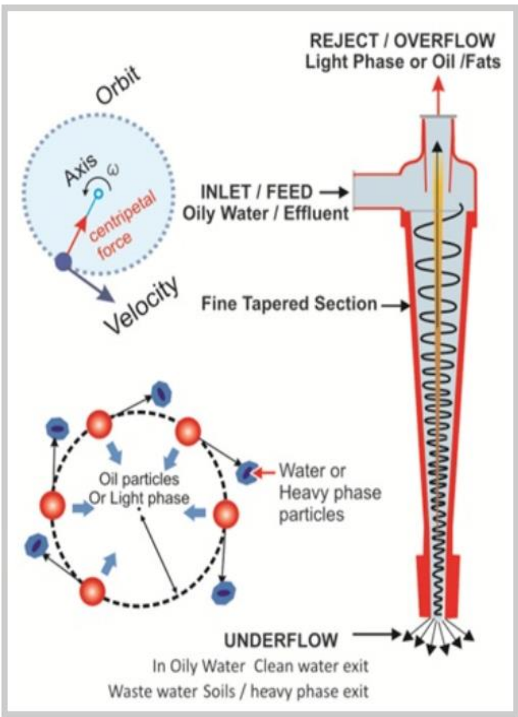



**Picture 21. An Induced gas floatation cell [2]**

### 7.2.4. Hydrocyclones *(physical treatment)*

Hydrocyclones are used for PW treatment from various companies worldwide. They are used to separate liquids from solids (sand) or liquids with different densities, particulates (usually within the range of 5 - 15 μm) and oil from PW. Especially they used to treat PW with great amount of solids and to reduce oil and grease concentrations to 10 ppm. [4]

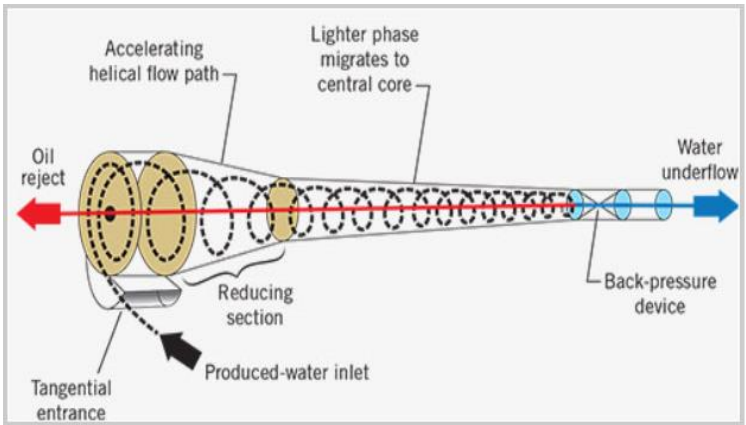
Principle of operation: Hydrocyclones as density separators convert pressure energy into rotational momentum. This momentum provides the centrifugal force to separate solids or heavy oil from the liquid. The denser solids will sink to the bottom whereas the water will overflow to the next treatment chamber– tertiary treatment (if any) or into injection tank. After secondary treatment, water normally contains about 200 ppm of oil. The heavier water phase, which is subjected to higher centrifugal forces, moves to the outer wall of the cyclone and exits the tailpipe of the hydrocyclone by the underflow. The lighter particles, free-oil droplets, are displaced towards the inner core of the cyclone and move axially up the cyclone and exits out the reject orifice as overflow. By maintaining a balanced differential pressure between the overflow and underflow, the oil core is forced out through the overflow outlet. [39]




**Picture 22. Typical Hydrocyclone. [39]**

The oil and water separation is magnified since the ratio between the centrifugal force in the hydrocyclone and the force of gravity is in excess of 1000, meaning that the force is 1000 times greater in the hydrocyclones. With such force, effective oily PW treatment can be achieved even with emulsified oil droplets. [2]

Advantages: it does not require any pre/post-treatment, any chemicals or much energy. The hydrocyclone is the only necessary piece of equipment. However, the energy requirement that pumps the water to hydrocyclone is the pressure drop. [15] It is presents higher efficiency and throughput for smaller oil particles. Drawbacks: the larger pressure drop across the device, the inability to remove solids, the higher maintenance costs and the sensitivity to fouling and blockages from accumulation of solids. [2] The generated waste is a slurry of concentrated solids that requires a final disposal. [15]

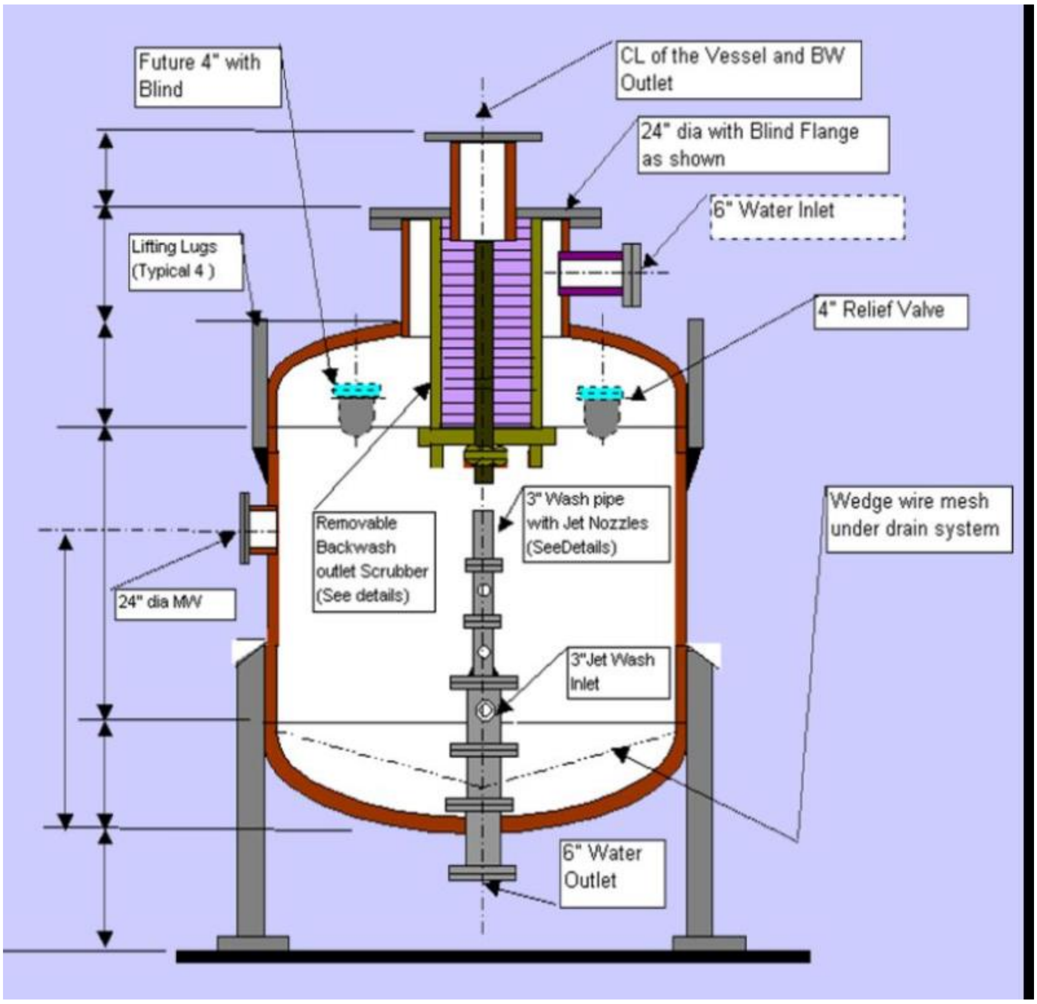



**Picture 23. Hydrocyclone operation [39]**

### 7.2.5. Media filtration

Filtration is a simple but effective method for treating PW and can be accomplished using a variety of different types of media including walnut shell, gravel, sand, anthracite and others. Filtration can effectively remove oil, grease and total organic carbon (TOC), but of course it cannot remove dissolved ions. Moreover, it is widely used on highly salty water. Analysis of PW quality has shown that it is responsible for more than 90% of oil and grease removal. [4, 10, 15] However, the expected lifetime of filters is lower than that of other apparatus. They require a frequent replacement, depending on the type of particles and the water quality. The process also requires appropriate equipment such as a vessel to contain the media, pumps and plumbing to implement backwashes. Chemicals may also be required to increase particle size, enhance separation and for media regeneration. [25]

Energy is required for backwashing the filter. Solid waste disposal is required for damaged filters and the waste produced during the regeneration of the media. [4]



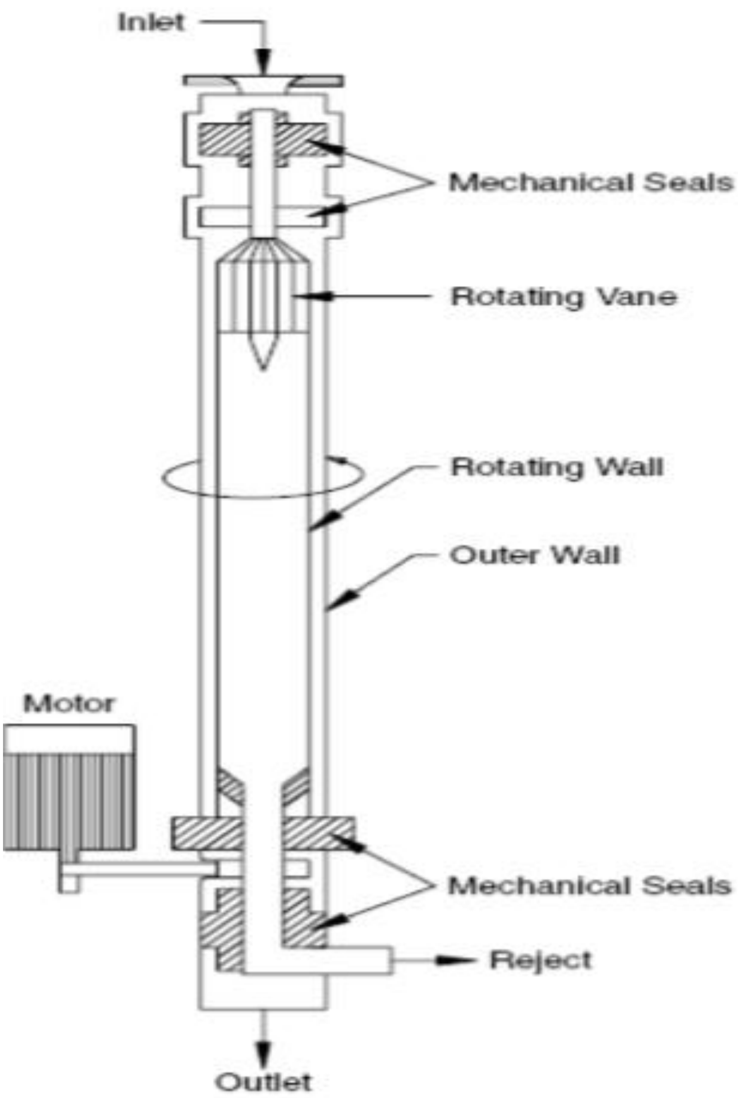

**Picture 24. Walnut Shell Filters are designed as a final stage in the treatment of PW.**

They are typically used after a flotation package (IGF) to ensure that the maximum water quality is achieved.

### 7.2.6. Centrifuges

Centrifuges are sometimes referred to as a dynamic hydrocyclone operating under the same principle with the hydrocyclones (centrifugal force) but in this case it is the moving parts which generate the spinning motion. [2] A centrifuge system consists of a rotating cylinder, axial inlet and outlet, reject nozzle and an external motor. The external motor is used to rotate the outer shell of the hydrocyclone. The rotation of the cylinder creates a "free vortex." Since there is no complex geometry requiring a high pressure drop, dynamic units can operate at lower inlet pressures (approximately 50 psi) than that of static hydrocyclone units. [6]

Advantages: They can effectively remove small oil particles and suspended solids particles as small as 2 microns. They require less retention time while they show high throughput. On the other hand, the disadvantages include energy requirement for spinning and high maintenance costs. [2, 38]




**Picture 25. Centrifuge system for O/W separation [6]**

### 7.2.7. Adsorption *(physical treatment)*

When the aim is to remove an oily phase from a continuous water stream, using adsorbing media is an option. Organic compounds of PW (and some heavy metals) can be adhered to porous media of carbon surfaces. Many compounds can be used as absorbent if they have hydrophobic-oleophilic characteristics.

Adsorption of organics when treating PW is achieved with the use of zeolite or organoclay or activated alumina or activated carbon. These adsorbents, are able to remove iron, manganese, total organic carbon, BTEX compounds, heavy metals and oil from PW. It is noted that chemicals are not required during adsorption procedure however, they may be used later when all active sides of the adsorbents are occupied. [4,15]

Adsorbents are columns filled with porous solid material. Hydrocarbons and other contaminants of PW are attached on the porous surface of the adsorbent materials, remaining inside the porous structure. The overall adsorption capacity depends on the surface area and the porous material. [2] When all active sites of the adsorptive material have been covered with adsorbed organics, the material must either be regenerated or disposed of. [4, 15]

The performance of the adsorbents is affected by pH, temperature, amount of suspended solids/oils, concentration of dissolved contaminants and salts. For example, the removal efficiency could be decreased because of plugging of the adsorption material by the suspended oil or particles of PW. For this reason, the material is backwashed periodically to remove large particulates which blocks its spaces. The input stream can be fed to the adsorption column by gravity, so it does not require any energy supply except during the backwash process.

Analysis of PW quality has shown that this method is responsible for the removal of more than 80% of the heavy metals with the minimum energy consumption. [4, 15]

### 7.2.8. Oxidation

Oxidation is a well-established and reliable treatment of PW technique. [15] It is responsible for removal of COD-*chemical oxygen demand*, BOD-*biological oxygen demand*, organics, iron, nitrite, manganese, cyanides, hydrogen sulfide, sulphur, odor, tastes, color and aromatic hydrocarbons. [2, 10]

Chemical oxidation can take place by one of the following reactions:

**a**. *the oxidation reaction* in which a substance loses or donates electrons, and
**b**. *the reduction reaction* in which a substance accepts or gains electrons.

Since free electrons cannot exist in solution, reactions form simultaneously. During these reactions there is not generated waste. [4, 10, 15] Byproducts involves $CO_2$. Ozone, Hydrogen peroxide, Hydroxyl ions, Chlorine, Chlorine dioxide and Permanganate are strong oxidizers. Advanced oxidation processes require a combination of them. Cost includes chemicals and equipment like pumps. [2, 4]

## 7.3. Dissolved gas removal

### 7.3.1. Natural gas recovery - Air stripping

Air stripping is a proven and widely used technology, with high contaminant removal efficiency (> 99%). Air stripping is primarily used for the removal of volatile organic chemicals (VOCs) including Benzene, Toluene, Xylene, vinyl chloride, oxidizing contaminants such as iron and manganese. Additionally, it is responsible for the improvement of taste and odor removal.

Air stripping is the process of converting a contaminant from liquid to gas phase where air and water are contacted in a packed column designed to maximize the contact surface area between the water and air. Suitable design of the packed column is necessary to ensure that the desired level of contaminant removal is based on the process operating temperature and the Henry's Constant of the target contaminant. [4]

The performance depends on:

- Characteristics of the volatile component (pressure, Henry's constant, gas-transfer resistance)
- Water and air temperature
- Turbulence in gaseous and liquid phases
- Area-to-volume ratio
- Exposure time

However, there are some disadvantages.

1. **Scaling** can occur when
   - calcium exceeds 40 mg/L
   - iron exceeds 0.3 mg/L
   - magnesium exceeds 10 mg/L and
   - manganese exceeds 0.05 mg/L

2. **Biological fouling** also may occur depending on the feed water quality.

There are two main types of <u>pressure aerators</u>:

a) one that sprays water on top of a tank that is constantly supplied with compressed air and

b) one that injects compressed air directly into a pressurized pipeline adding fine air bubbles into the flowing water.

Air stripping systems are designed in this way to provide the proper air and water balance to prevent flooding or excess air flow scaling without affecting the performance of the air stripper. [4]

## 7.4. Macro-porous polymer extraction technology.

*Macro-porous polymer extraction* (***MPPE)*** is one of the best available technologies and best environmental practices for the PW management on offshore oil and gas platforms. It is a liquid–liquid extraction technology where the extracted liquid is immobilized in the macro-porous polymer particles. These particles have a diameter of ∼1000 μm, pore sizes of 0.1–10 μm and porosity of 60–70%. Polymers were initially designed for absorbing oil from water.

In 2002, the first commercial MPPE unit offshore was successfully installed on platforms in the Dutch part of the North Sea. MPPE was used for the removal of dissolved and dispersed hydrocarbons, achieving > 99% removal of BTEX, PAHs and aliphatic hydrocarbons at 300–800 ppm influent concentration. It was also reported that it has a removal efficiency of 95–99% for aliphatics below $C_{20}$ and total aliphatic removal efficiency of 91–95% was possible.

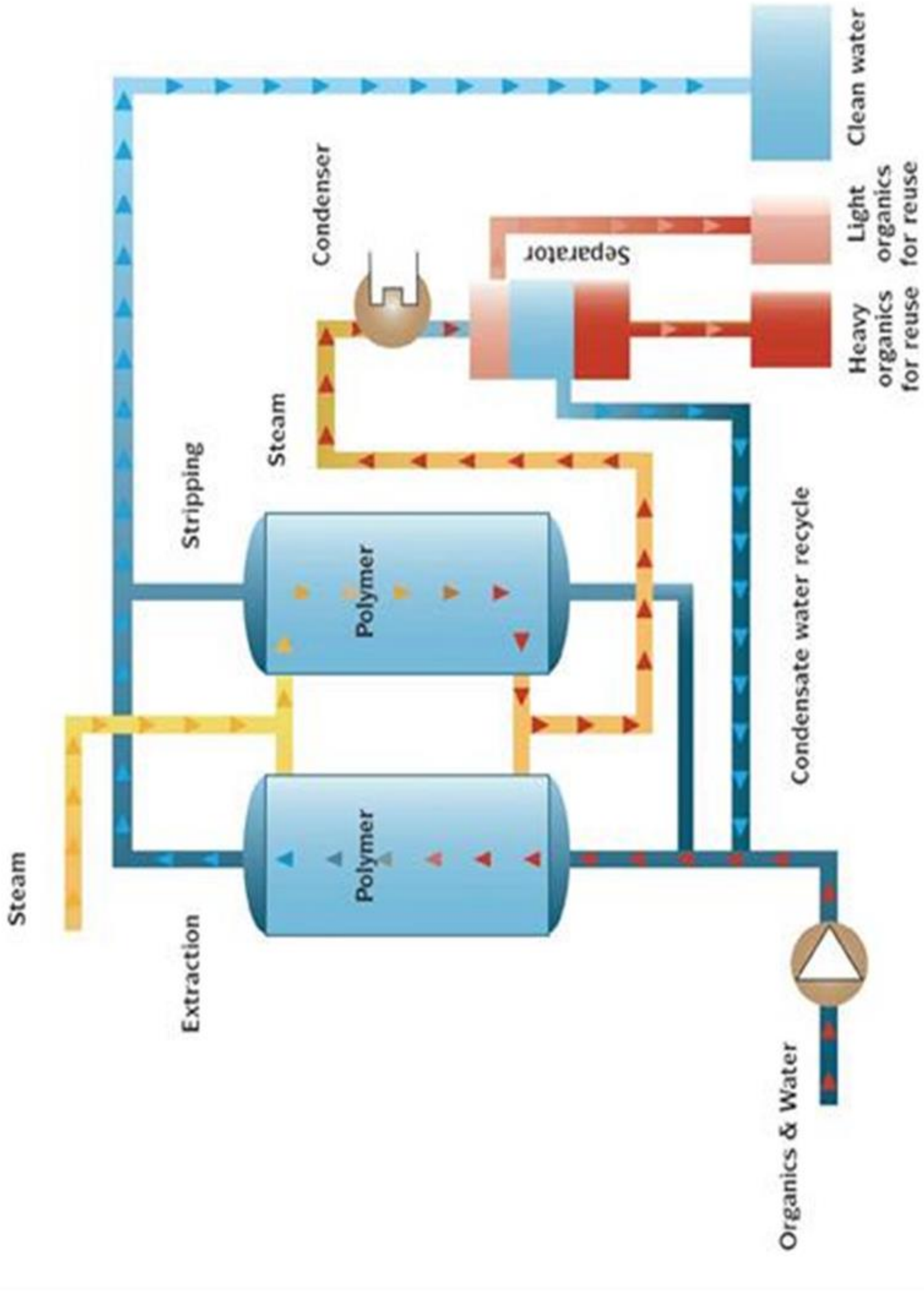
In the MPPE unit, PW is passed through a column packed with MPPE particles containing specific extraction liquid. The immobilized extraction liquid removes hydrocarbons from the PW as shown in the picture 26 below. [10]

Almost all hydrocarbons present in PW can be recovered with this process. Hydrocarbons can be condensed and separated from feed water by gravity and product water is either discharged or reused.

This technology is mainly used to reduce the toxic content of PW containing salt, methanol, glycols, corrosion inhibitors, scale inhibitors, $H_2S$ scavengers, demulsifiers, defoamers and dissolved heavy metals as well.

Pre-treatment through hydrocyclones or other flotation methods is, however, necessary before allowing PW from oilfields to flow into the MPPE unit. Studies have shown that in gas/condensate produced water streams pre-treatment is not required and MPPE can remove the whole spectrum of aliphatics, as well as BTEX and PAHs.

As international legislations seek **'zero discharge'** of contaminants into the environment and focus on contaminants, MPPE will be a major PW technology in the future. A study carried out by Statoil to compare the effect of different treatment technologies of oilfield PW on *Environmental Impact Factor* (EIF) found that the MPPE technology had the highest EIF reduction of approximately 84 %. However, a relatively high cost of unit is a major disadvantage of this technology. [10]




**Picture 26. Shows a MPPE process [10]**

## 7.5. Desalination

### 7.5.1. Filtration Membranes.

Among the important parameters in considering desalination methods are the use of toxic chemicals, the increasing treatment costs, the area limitations for equipment installation and the generation of additional waste stream creating even worst pollution, have led to development of membrane based methods for PW treatment.

So it is the membrane pressure driven separation technique that based on the pore size of the used membrane for separation of the feed stream components. More specifically, membranes are microporous films with specific pore ratings of synthetic materials, which selectively separate a fluid from its dispersed particles and are classified according to pore size (microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO)).

#### 7.5.1.1. Microfiltration (MF)/ Ultrafiltration (UF)

MF separates suspended micro-particles so it can only be used for the pre-treatment of PW, while UF separates ultraparticles from water under applied pressure. [2,38] The MF is characterized by pore sizes that ranges from 0.1 to 3 μm while the UF has pore sizes that ranges from 0.01 to 0.1 μm.

**UF** membranes are widely used for removal of suspended solids, viruses, color, odor, turbidity and some colloidal natural organic matter but they cannot remove salts. [4, 15] The selection of membrane depends on cost, efficiency (recovery), rejection, raw water characteristics and pretreatment while the performance of them depends on the raw water characteristics, pressure, temperature, regular monitoring and maintenance. [4, 15, 34]

**MF** membranes are typically made of oxides, nitrides or carbides of metals such as aluminum or titanium and are able to remove particulates, organic matter, oil/grease and metal oxides. If MF membrane are made of ceramic, then they are much more resilient than polymeric membranes since they are mechanically stronger, chemically and thermally more stable. They consist of at least two layers: a porous support layer and a separating layer.

MF membranes have been employed commercially to treat oilfield PW and research studies have proven that their performance is higher than that of UF membranes when filtering oil waste water. Between those two, energy consumption and acquiring cost is lower for the MF filters. [4, 15]

Advantages: Both membranes do not require chemicals, have low energy costs, are compact modules and are characterized by limited space required for installation. Moreover, UF indicates higher oil removal efficiency. Disadvantages: MF have less efficiency to remove divalent, monovalent salts, viruses. Both of them require high energy. [2, 38]

#### 7.5.1.2. Nanofiltration (NF)

Nanofiltration has been employed in PW treatment for removal of salt, most of the metals (Fe, Mn) and organic compounds. NF membranes are specifically designed to reject contaminants as small as 0.001 µm achieving high rejection of divalent ions ($Mg^{2+}$, $Ca^{2+}$, $Ba^{2+}$, $SO_4^{2-}$), metals (> 99% of Mg) and radionuclides. [15] Advantages: NF are able to remove hardness, divalent salts. Disadvantages: NF require high energy, are less efficient for monovalent salts. [2]

#### 7.5.1.3. Reverse osmosis (RO)

A RO membrane is used to separate dissolved and ionic components [10], but mainly to remove salt. Provided that greater than the osmotic pressure of the feed solution is applied to the system to force water through the membrane, the salt will be rejected. The osmotic pressure is a function of the salinity of the water. For waters with very high salinity, the osmotic pressure and the required operating pressure are very high so RO is not an acceptable and effective procedure. RO generally is considered as a cost effective treatment technology to use when PW salinity (TDS) does not exceed 40,000 ppm. [4]

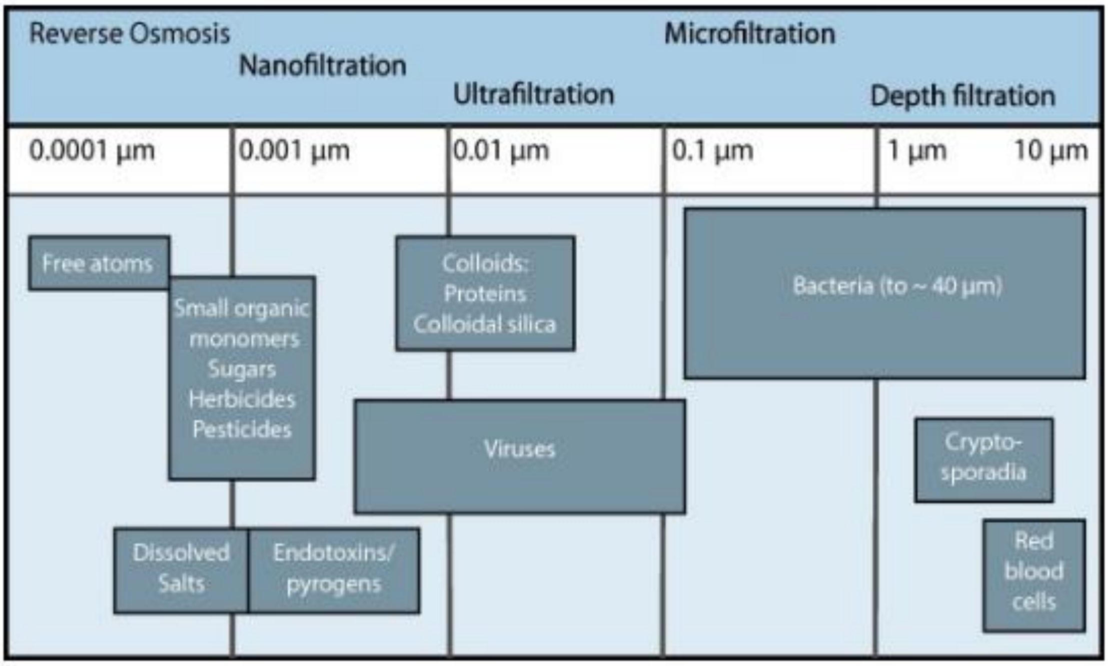
Specifically, on oil and gas PW indicated a removal of sodium chloride, on monovalent salts, and on organics. Some organic species may require pretreatment. While energy costs increase with higher TDS, RO is able to efficiently remove salts in excess of 10,000 mg/L. [38]
Advantages: RO is able to removes monovalent salts, dissolved contaminants etc.
Disadvantages: High pressure requirements, even trace amounts of oil and grease can cause membrane fouling [2,38]

#### 7.5.1.4. Forward Osmosis (FO)

Forward osmosis - **FO** is an emerging technology for separation and treatment of PW from oil and gas exploration. FO membrane system was studied for certain time during PW treatment. As a result, it was proved that FO system was economically and environmentally favorable compared to the common practice of deep-well injection. [15]

Principe of operation: It consists of two membranes, a *cellulose triacetate - **CTA*** and a *polyamide thin film composite - **TFC***. [21] These FO membranes are semipermeable and use osmotic pressure differences to drive the diffusion of water from the feed solution that is concentrated, across the membrane to a more dilute with higher salinity *draw solution* - ***DS*** often composed of NaCl. [15]

FO membranes aim to reject dissolved constituents in PW and provide high quality water for direct reuse in the upstream oil and gas industry or to feed into advanced separation processes such as reverse osmosis (RO) for recovery and reuse in many other processes. This technology is capable of recovering up to 85% of PW and operating with a feed of total dissolved solid - TDS concentrations as high as 150,000 mg/L. The membranes are expected to have a lower fouling impact compared to pressure-driven membrane processes, which minimizes pretreatment requirements.




**Picture 27. Classification of membranes based on pore size. [22]**

Membrane-based methods have become increasingly attractive for the separation of oil–water mixtures because they are relatively efficient and they do not need as much energy as other methods. These methods, can be readily used to separate a variety of feed streams providing consistent quality. The types of membranes with **selective wetability** are subdivided by the level of the wettability.

The design strategies include the parameterization of two important physical characteristics:

- *the surface porosity* (affects the rate of liquid permeation through the membrane) and
- the breakthrough pressure (defined as the maximum pressure differential across the membrane of a given liquid). [5]

Several methods have been used to separate oil–water mixtures. Research on membranes with selective wetability promises to improve the separation efficiency. If a membrane demonstrates a different wetability with water versus oil, then it seems a valuable tool for an efficient separation of oil–water mixtures. This idea has led to the development of a large number of membranes with selective wetability. In the following section the principles of membranes for separation of oil–water mixtures with differing wet abilities are presented. [5]

## 7.5.2. Membranes with selective wetability.

### 7.5.2.1. Hydrophobic and oleophilic membranes - HP/OL

HP/OL membranes allow various oils to permeate while repelling water. They are developed by coating a material with selective wetability onto porous substrates. A range of flexible and rigid substrates have been used for this purpose, including stainless steel and copper meshes, polymers, textiles and filter papers.

### 7.5.2.2. Hydrophilic and oleophilic membranes - HL/OL

HL/OL membranes are characterized by the non-wetting behavior of oil droplets on fish scales underwater. In the presence of HL rough structures, water readily wets and fills all the cavities present on the surface, leading to a composite solid–oil–water interface. Such super hydrophilic and underwater super oleophobic surfaces exhibit excellent oil fouling resistance, which is attributed to the low affinity for oil droplets when submerged in water.

### 7.5.2.3. Hydrophilic and oleophobic membranes - HL/OP

HP/OL-(1) membranes are unsuitable for most gravity-driven separations. Although HL/OL-(2) membranes are applicable for the gravity-driven separation of oil-in-water emulsions, they do not work for free oil–water or water-in-oil emulsions, unless they are repeatedly pre-wet by water. HL/OP-(3) membranes are expected to overcome these limitations. However, fabrication of such membranes has been considered as challenging due to the surface tension of water being significantly higher than that of oils.

The development of membranes with selective wetability is an ongoing process, which aims to more effectively meet today's needs for efficient oil and water separation. They are a promising alternative to traditional separation methodologies. The numerous sources of oily wastewater and increasingly strict environmental guidelines impose a highly effective, economical and durable membrane, with a long service life, for purifying oily waste streams.

The type of membrane used will depend on the waste stream composition, fouling potential and the system employed for the separation. The form of oil, whether free or emulsified, will indicate the pore size for the membrane and thus is directly related to the permeation rate through the membrane. All these parameters must be taken into account for utilizing membranes with selective wetability.

A multitude of selective wetability systems have been used to successfully separate oil and water mixtures with efficiency of more than 99.9%. However, the future lies in imparting these wetting properties to membranes that withstand high trans-membrane pressures, have greater permeation rates for the desired liquid, are anti-fouling and can be manufactured at a reasonable cost. [5]

## 7.6. Thermal Technologies

Technologies based on thermal treatment of water are employed in regions where the cost of energy is relatively cheap such as in the Middle East region. It must be noted that about 95 % of the operating cost for thermal treatment processes in an industrial scale is related to the energy consumption. Although membrane technologies are typically preferred to thermal technologies, recent innovations in thermal process engineering make thermal process more attractive and competitive in treating highly contaminated water. [10]

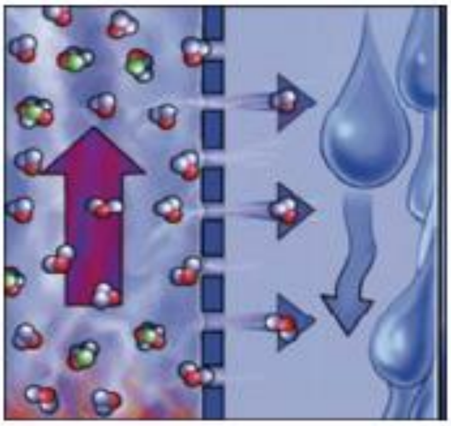
**Thermal distillation** can effectively treat water with TDS levels above 50,000 mg/L. In some cases, companies are treating flowback water with thermal distillation systems to produce very clean water and concentrated brine. The clean water can be re-used or discharged. [3]

The advantages of these methods could be summarized as:

- No sludge production
- No need of chemicals for treatment
- Lower costs of waste and life cycle
- Lower requirement of maintenance and human power

#### 7.6.1.1. Membrane Distillation (MD)

MD is considered as a novel thermally driven membrane separation process because it is capable of treating feed waters with TDS concentration in excess of 35,000 mg/L. Theoretically, rejection for all non-volatile solutes (including Na, $SiO_2$, and heavy metals) is 100%. However, compounds with higher volatility than water, like BTEX and other organic compounds, will diffuse faster through the membrane. [15]



**Picture 28. Generalized illustration of the principles of MD [15]**

Principle of operation: it utilizes a low-grade heat source to facilitate mass transfer through a hydrophobic, microporous membrane. The driving force for mass transfer is a vapor pressure gradient between a feed solution and the distillate. [15] The flux and salt rejection of this process is independent of feed water salinity. [4]
Pros: MD is capable of producing ultra-pure water at a low cost. [15]

## 7.7. Alternative Processes for treatment of Produced Water

### 7.7.1. Capacitive Deionization

In capacitive deionization, water is passed through pairs of carbon electrodes and retained at a potential difference of 1.2 volts. Ions and other charged particles are attracted to the oppositely charged electrode. When the electrodes have become saturated with ions, they must be regenerated by removing the applied potential. The carbon gel electrodes have a relatively high surface area (500 $m^2/g$) providing high electrical conductivity and therefore, high ion permeability. [4] The advantage of this method is that requires low energy and shows higher efficiency. [2] The disadvantage is that the electrodes are expensive and have a relatively low ion storage capacity. [2, 4]

### 7.7.2. Ion exchange

In this case, dissolved salts or minerals are ionized in order to be removed. This method that is a reversible chemical reaction process is able to remove:

a) *cations* as calcium, magnesium, barium, strontium, arsenic, radium, uranium and other heavy metals, and
b) anions as nitrates, fluorides, arsenates, fulvates, humates, selenates, chromates

It uses: a) *cationic solutes* columns to exchange the above cations by cation exchange resins.
*b) anionic solutes* columns to exchange the above anions by anion exchange resins.

Additionally, ion exchange is associated with some other water processes capable of removing hardness, alkalinity, radioactive waste, ammonia and softening (removal of Ca and Mg). [2,15]

## 7.8. Disinfection as Treatment of Produced Water

### 7.8.1. UV - Ultraviolet radiation light

Removal of bacteria, viruses and microorganisms, from the PW is necessary to prevent fouling of the reservoir, tubulars and surface equipment. Microorganisms occur naturally in the PW from subsurface reservoir, or can be introduced during production or de-oiling treatments. Filtration technology is one of the effective techniques used to remove microorganisms. However, *UV light treatment,* is another available technique to disinfect PW.

The principle operation of UV light is the inactivation through UV damage of the microorganism's DNA or RNA. PW is pumped through a UV reactor, which is equipped with an array of UV lamps that provide disinfection dosages of 30–50 $MJ/cm^2$. As pathogens path through the reactor, they are exposed to the UV light for a predetermined period of time, depending on the desirable level of disinfection, in order to be inactivated. Removal of suspended solids from the feed water through UV is important to avoid shielding of microorganisms. It should be noted that disinfection is usually the last treatment step in most water treatment facilities because most suspended solids or dissolved ions, if any, have been already removed prior to disinfection. UV disinfection is a highly efficient method and does not generate any waste. [2, 4, 15]

## 8. Summary Tables of methods of Treatment of PW

After the analytical description of each method for treatment of PW in chapter 7, this chapter and the following two tables merge a summary of advantages and disadvantages of each presented technology. Therefore, the treatment technologies can be divided into two general categories, depending on which types of pollutants are removed.

The Table 4 presents the treatment technologies designed for the removal of oil and grease and other organic compounds from PW. [3, 7, 9]

**Table 4.**

| Technology | Subcategory | Pros | Cons |
|---|---|---|---|
| | ***Deoiling*** | | |
| **Physical separation** | Advanced separators (inclined plate, corrugated plate) | Provide enhanced oil capture compared to basic oil/water separators. | Work well for free oil, but not as effective on dispersed and soluble oil. Performance can be improved by adding flocculants. |
| | Hydrocyclone | No moving parts results in good reliability. Separates free oil very well. | Does not work well on dispersed and soluble oil. |
| | Media Filtration | Different types of filter media and filter operations provide a good range of oil and grease removal. | Requires regular back-flushing. Does not treat soluble oil. |
| | Centrifuge | Provides good separation of free and dispersed oil. | More expensive than other technologies in this group. |
| **Flotation** | Dissolved air flotation, induced gas flotation | Removes free and dispersed oil. | Does not remove soluble oil. |
| ***Soluble organic removal*** | | | |
| **Adsorption** | Organoclay, activated carbon, zeolites. | Does a good job at removing oil and grease. Used primarily for polishing. | Media cannot be re-used or regenerated – results in large volume of solid waste. |
| **Oxidation** | Advanced processes using combinations of ozonation, cavitation, and electrochemical decomposition | Creates nearly sterile brine. | Has high energy input. Limited use to date. |

Table 5 illustrates the treatment technologies that are designed to remove salt contents and other inorganic materials from PW. [3, 7, 9]

**Table 5.**

| Technology | Subcategory | Pros | Cons |
|---|---|---|---|
| ***Desalination*** | | | |
| **Filtration Membrane** | Microfiltration, Ultrafiltration, Nanofiltration | They are good pretreatment steps for more advanced processes like reverse osmosis (RO). They operate at lower pressure and lower cost than RO. | These levels of filtration cannot remove most salinity. Potential for membrane fouling. Sensitivity to fluctuating water quality. |
| | Reverse osmosis (RO) | RO can remove salinity (up to about 50,000 mg/L TDS. | Requires pretreatment and regular membrane cleaning. Not suitable for high-salinity flowback water. Potential for membrane fouling. Sensitivity to fluctuating water quality. |
| | Forward osmosis (FO) | May offer future treatment opportunities. | Have not been used in full-scale oilfield treatment systems yet. Potential for membrane fouling. Sensitivity to fluctuating water quality. |
| **Thermal Treatment** | Distillation | Can process high-salinity waters like flowback. Generate very clean water as one product (can be re-used). | High energy usage and cost. Generates concentrated brine stream that requires separate disposal. Potential for scaling. |
| | Evaporation | Can treat to a zero liquid discharge standard. | High energy usage and cost. Limited usage in oilfield applications. Potential for scaling. Challenges in disposing of salt residue. |
| **Alternative processes** | Capacitive deionization | Low energy cost. | Limited usage in oilfield applications. |
| | Ion exchange | Successfully treat low to medium salinity water (e.g., Powder River Basin). | Large acid usage. Resins can foul. Challenges in disposing of rinse water and spent media (resin). Also ineffective on high salinity PW. |

## 8.1. Summary and Discussion

Regulations concerning the waste water discharge impose the implementation of a variety of different technologies in the treatment of PW. Conventional technologies such as gas flotation focus on the dispersed oil and emulsified oil, while more advanced technologies should be used for the separation of smaller oil droplets. Secondary treatment technologies are used for the reduction of toxicity of smaller dispersed oil droplets and these technologies should be used in combination with conventional technologies. [31]

All mentioned treatment methods of PW have their advantages and disadvantages. There are four main types of treatment of PW.

These are: 1) Physical 2) Chemical 3) Biological and 4) Membrane based

I. ***Physical*** methods are based on natural forces like gravity, electrical attraction and Van der Walls forces. Physical methods do not consume as much energy compared with other methods and at the same time they do not use any chemicals. However, more time is required to treat the PW. All of them generate a waste product and their cost is quite high. For example, hydrocyclones can remove smaller oil droplets but they need much more energy compared to other methods and their maintenance cost is very high. Physical filtration methods using natural aggregates, sand and walnut shells have been implemented in offshore platforms.
The disadvantages of physical methods are likely to be the high initial capital costs and the sensitivity to the feed stream quality.
In general, Physical methods of PW treatment include hydrocyclones, gas/induced flotation, adsorption of dissolved organics, media filtration, evaporation and macro-porous polymer extraction (MPPET).

II. ***Chemical*** technologies can treat more than one component of PW but, on the other hand, they require a huge amount of energy and have a high operational cost. Therefore, they produce sludge and large quantities of chemical waste that has to be disposed safely.
However, hazardous sludge generation, high operating costs and sensitivity to the initial concentration of effluents in feed stream are some of disadvantages of chemical methods.
Chemical precipitation (flocculation, coagulation), chemical oxidation (chlorine, oxygen), catalysis, ion-exchange, ionic liquids and electrochemical techniques are some typical examples of this type of treatment.

III. ***Biological*** methods are used for removal of organic material since they are able to separate the compounds of the pollutants into small and simple non-toxic forms. High retention time (hours to days) and the large quantities of produced sludge are the major disadvantages of these methods. Membrane based methods combine to biological methods and are characterized by higher efficiency. [6,30]

IV. ***Membrane*** based methods are used in relation to the grade of purity required. They are categorized according to the pore size as nano, ultra and micro. However, fouling or scaling issues and high module price are the disadvantages of membrane-based treatment methods. Examples of this case include microfiltration, ultrafiltration, nanofiltration, reverse osmosis, forward osmosis and membrane distillation. Fouling and high cost are some of the biggest challenges that have to overcome. [30]

Among the available technologies for treatment of PW, centrifuges provide much stronger centrifugal forces than hydrocyclones (via the rapid spinning bowl) and therefore are able to remove smaller oil droplets than a hydrocyclone. However, the higher energy and maintenance costs which are required, are a major barrier, though the centrifuges can reach high flow capacity. Coalescers merge small oil droplets into larger droplets to improve efficiency in other oil removal processes.

Membrane filtration processes remove suspended and dissolved particles larger than the membrane pore size. In onshore platforms membrane filtration processes are used in order to remove particles with sizes greater than 0,01 μm but a pre-treatment stage is needed with the use of chemicals to remove the larger particles.

Solid adsorption, as a secondary treatment technology is quite effective in removing oil and organic materials from PW. In an adsorption process, molecules of contaminants adhere to the surface of solid media (adsorbents). Adsorption material can be zeolite and organic clay while the combination of zeolite with membrane technologies can produce higher efficiency. However, the high cost is a major barrier while high retention of water limits the overall performance.

Chemical oxidation is mainly a conventional chemical method for PW treatment but the enhanced oxidation by ultraviolet - UV, is able to give very good results in the PW treatment according to the latest research. The sequential use of UV radiation and ozone oxidation may result in a positively effect of organic contaminants elimination. Research has demonstrated that while natural microbial populations in seawater partially biodegrade oil when sufficient nutrients were supplied, pre-treatment with photo-oxidation increased the amount of crude-oil components sensitive to biodegradation, leading to significantly increased biodegradation of hydrocarbons. However, the reaction dynamics of the combination of ozone and ultraviolet are unclear, and it is questionable whether the process is fundamentally different from either ozone or UV treatment alone in such a wastewater with high salinity and high concentration of organic compounds.

To sum up, treatment of PW is a complicated procedure as concentrations of constituents change over time, additional chemicals affect the quality of PW and it is necessary take into consideration the oil field settings that often have extreme temperatures.

Some potential problems associated with managing PW water include: 1) Plugging of disposal wells by solid particles and suspended oil droplets 2) Plugging of lines, valves and orifices due to deposition of inorganic scales 3) Corrosion due to acid gases and electrochemical reactions of the water with piping and vessel walls and 4) Growth of bacteria that plug lines and valves or result in the formation of harmful products.

# 9. Discussion of Produced water treatment & management cost

PW treatment is a complex technological problem, comprising economic and other social aspects. This is particularly true when considering the broader problem of *Produced Water management*, which comprises its chemical or other treatment, its storage, its transfer and its final disposal or its eventual recycled use. PW management is a procedure to be reconsidered on a regular basis, because the parameters determining the best economically advantageous solution (produced quantities, constituents, legislation for pollutants concentration, market prices of equipment, materials and services, free market demands, social context, etc.) change over time, and what was an optimal PW management solution will not certainly be an optimal one after five or ten years.

In the light of the above remarks, and given the extremely diversified prevailing circumstances of each specific exploitation (climate), any attempt to establish generally applicable cost factors concerning PW treatment or management, is a risky exercise. So, the present chapter 9 provides some indicative cost elements highlighting the importance of the problem and its growing significance with respect to society.

**A.** *The quantitative aspects of the PW treatment and management problem*.

According to the USA Department of Energy, for every barrel of oil produced globally three barrels of PW also come to the surface. Nevertheless, this value does not apply everywhere. Indeed, in the United States, for which the most reliable data is available, for every barrel of oil produced, seven up to ten barrels of PW come to the surface (mainly because of the extended use of the hydraulic fracturing technology in a production well, which demands the use of extremely high quantities of water coming out subsequently as PW). It seems that the latest value is going to be stabilised to this level, although some reports estimate that later it may reach the value of 50 barrels of PW per barrel of oil.

Additionally, the reported ratio for the gas production wells varies between 0.1 and 1 barrel of PW per MCF (1000 cubic feet) of natural gas. In the rest of this section, any data concerning PW quantities and its management refers almost exclusively to the USA oil and gas production activities, since information and data concerning similar activities in the rest of the world are difficult to find on the internet and not necessarily accurate.

In the USA there are almost 1 million producing oil and gas wells. According to estimates for 2019, the actual USA water production may exceed 25 million barrels per day. [41] Specifically, in the U.S.A. 97% of total of PW comes from onshore wells located in 31 states and the remainder comes from offshore platforms. More than one third of the USA PW is generated in the state of Texas.

Long term production forecasts predict that within the next ten years, globally, some 200 million barrels of PW will require a kind of treatment and management per day. [41]

Obviously, the treatment and management of such huge quantities of PW is a challenging problem. Under the circumstances of the collapse of the crude oil spot prices prevailing in the global market since 2014 the cost efficiency of oil or gas production activity will depend strongly on the proper management of PW. [56]

**B.** *PW management indicative cost factors. The USA case*.

When barrels of oily water are produced, producers must find ways to treat and dispose of the PW. This procedure involves use of latest technologies (e.g., to compress operational cost as far as possible or to minimize the treatment time interval) and a costly management.

According to data concerning the oil and gas exploitations in USA, the main cost factors associated with PW handling is transportation of the PW from the well to the disposal site, fees for disposal into an injection well and the treatment of PW to be disposed to any natural recipients, or recycled in a socially useful way. The high cost factor associated with the PW transfer to its final disposal site is an immediate consequence of its extremely high quantities.

The disposal or discharge of such huge quantities is very rarely possible close to the production well so they often have to be transferred to a site outside of the limits of the State of origin, which may be found some dozens of miles away.

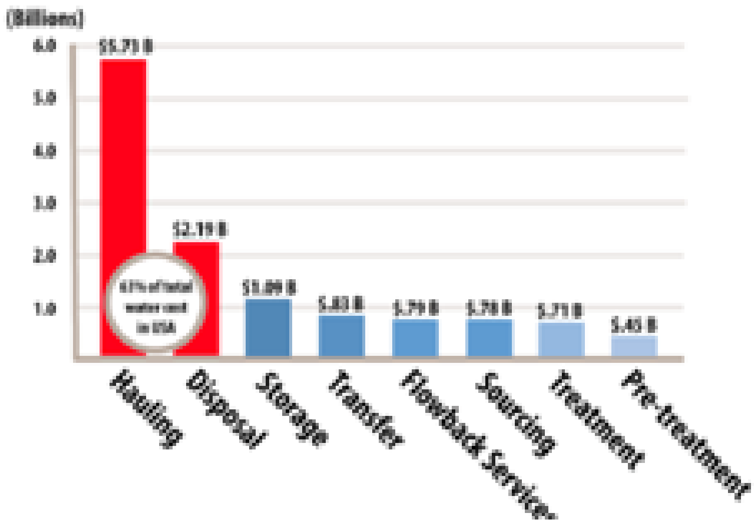
Trucks are by far the predominant method of transporting the PW and the cost of a typical truck carrying about 100 barrels (or 4,200 gallons) normally ranges between $95/h to $150/h just for hauling. Hauling time varies substantially, depending on proximity of source water and disposal wells. Typically, about 1,000 truck visits are needed to service a single well to deliver the source water and a large number of truck loads to dispose of the flowback and PW. Trucking costs alone for these operations are estimated to run close to 1.5 million dollars. [58]

Because of the high operational cost of trucks hauling and its high environmental footprint, (traffic jams on motorways, atmospheric pollution, etc.), producers are considering the development and use of a pipelines network to transfer the PW from its origin to the final disposal site. Moreover, oil and gas operators will attempt to minimally treat the PW and use it ideally for hydraulic fracturing. If this application is not permissible in the region, then it will be a tradeoff between the cost of treating and discharging to the environment or the cost of trucking and deep-well disposal.

As an alternative solution, some producers, in order to reduce their overall production costs, use recycled water for drilling and completion operations instead of having water trucked in or out. In 2016, for example, a specific USA producer, Apache, was paying upwards of $2.00 per barrel to dispose of water in the Permian Basin, but only $0.17 per barrel to recycle it. [57]

In addition to hauling, disposal costs on average are about $1.00 per barrel and can be substantially higher. Halliburton claims that disposal costs can range from $3 to $12 per barrel. Overall, USA oil and gas producers spend an average of $1 to $6 billion dollars per year for the PW disposal purposes. In onshore operations, the PW must be hauled to re-injection sites or disposed of in evaporation ponds.

The cost of disposal is about $0.5-$8 per barrel of water, depending on the location of disposal from the production sites. This amounts to more than $5 million per year to dispose of 5,000 barrels per day of PW. Moreover, discharge into evaporation ponds requires that there is no visible oil layer or (equivalently) that the oil content of the PW is less than 10 ppm. Some reinjection disposal methods also require that the oil content should be less than 10 ppm. [55]




**Picture 29. PW management market by service type. USA, 2015 [57]**

Arguably, water transportation and disposal costs may be the high cost elements of water management and also a very large percentage of total costs. [58] Picture 29 depicts a decomposition of USA PW management market by service type [57].

It is possible to assume that this graph reflects the decomposition of the overall management of PW cost factors and their relative importance. We should also point out the relative low budget (compared to the extremely high hauling budget) of pre-treatment and treatment activities, although these activities are always indispensable, regardless of the final PW disposal or recycling. Obviously, this statement does not apply to offshore wells, where PW has to be treated in situ and immediately after its production, and disposed in the aquatic environment.

**C.** *Cost factors of PW treatment*. Generally, the PW is contaminated with various organic and inorganic compounds, particulate matter, grease and oil, where the concentration values of those compounds are constantly changing in concentration during production, posing additional challenges for the treatment adjustment.

***C1.*** *Oil removal.* According to companies providing consultancy and waste treatment services to the oil and gas production industry, hydrocarbons dissolved or suspended in PW could be removed to the extent required by the applicable legislation concerning the waste disposal in the appropriate deep wells (oil concentration not greater than 10 ppm, for most of USA states), at a cost as low as $1 per PW barrel. It should also be noted that hydrocarbons received as a by-product of this treatment may compensate part of this oil removal cost. According to some reports, these hydrocarbons have a market value of about $0,20 per PW barrel.

***C2.*** *Minerals removal*. According to the same companies, removal of minerals dissolved or suspended in PW could be achieved at an additional cost of about $1 per barrel of PW. Some indicative information concerning the variation of PW unit treatment cost as a function of process scale is given below.

According to Dr. T.Y. Cath, PW desalination scaling may reduce the treatment cost to approximately $ 0.25 per barrel (to be compared to a typical cost for disposal, of about $ 0.50 per barrel), while small scale water desalination along with pre- and post-treatments can range anywhere from $0.75 - $1.75 per barrel. Additionally, approximately an additional $1 per barrel can be added to the total disposal costs for every 100 miles of trucking. [57]

Following what it was just mentioned above, when the market price of minerals received from the PW treatment exceeds the threshold of $1 per barrel, the whole cost of the treatment is compensated and an extra profit may arise from the operation.

**C3.** *Treated PW as a socially useful product of a market value*. In some cases, in areas where fresh water is not abundantly available, further treatment of PW may be of interest so that treated water is used in irrigation, road dust elimination, animal watering, or even domestic water supply [57]. For such applications, an inverse osmosis treatment procedure is applied, coupled with various filtration and active carbon absorption techniques, removing more than 99% of TSS, 95-99% of TDS and bacteria. In this case, the operational cost of the treatment depends strongly on the scale. The market price of the treated water should normally at least compensate the overall treatment cost.

# 10. Results from companies - Equipment and methods

There are a lot of companies worldwide that provide treatment to PW for oil and gas wells. In most of the cases, the contact took place via e-mail. Some of them responded whereas some others did not, because companies are often reluctant to give out information about its current equipment and the treatment methods of PW that they use today especially including cost of equipment. The results of this research is presented below:

## 10.1. Schlumberger

**Schlumberger,** is one of the biggest and well known oil company all over the world. It provides a variety of water treatment and management solutions since oil and gas industry generates billions of barrels of PW annually. For example, it could use enhanced gravity separation and filtration solutions to reduce loading on biological systems and ensure that treated PW meets discharge or reuse requirements, protects formation rheology and limits equipment corrosion. [33]

The methods that Schlumberger follows include:

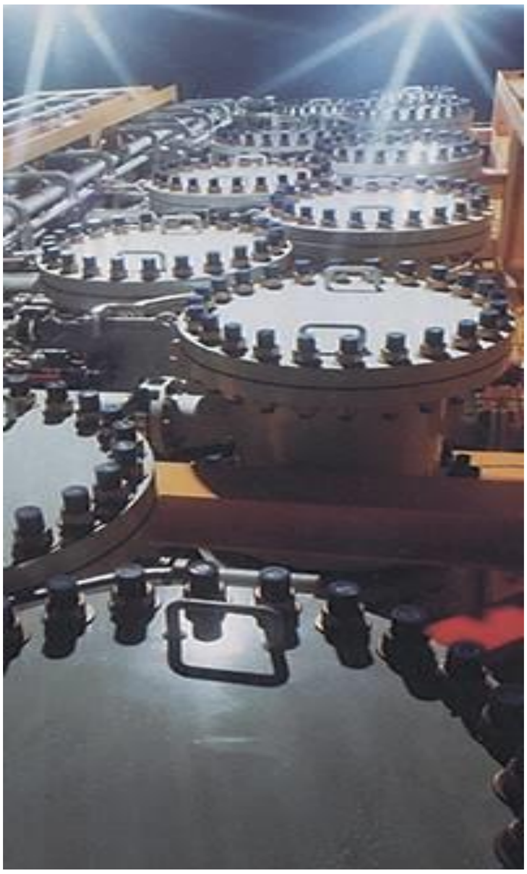
1. PETRECO Hydromation Nutshell filter which are the ideal solution for removal of ***suspended solids and oil*** from PW before discharge into the environment or reinjection. They remove 95% to 99% of suspended solids and 90% to 99% of insoluble hydrocarbons without the use of chemicals, providing oil discharge levels as low as 5 ppm or less.

**Picture 30. Shows the hydromation Nutshell filter. [33]**

2. UNICEL Vertical IGF Induced-Gas Flotation Unit is a simple, hydraulically operated gas flotation machine that delivers efficient oil/water separation with complete process containment.

**Picture 31. Shows the UNICEL Vertical IGF Induced-Gas Flotation Unit [33]**

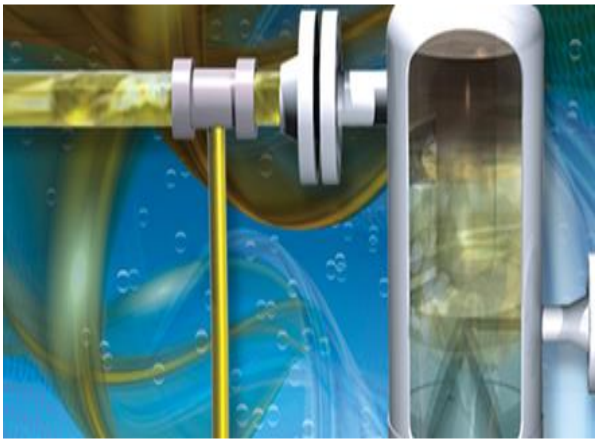
3. VORTOIL De-oiling Hydrocyclone is a highly efficient, compact and inexpensive method of ***removing the bulk of the free oil*** content (particle size 10-20 um) from large volumes of PW. The central feature of these de-oiling hydrocyclones is the internal geometry of each liner design, developed to provide high separation efficiency. With no moving parts inside the vessel and construction materials carefully selected to reduce erosion, this hydrocyclone's functional and elegant design results in operational simplicity and extremely low maintenance.



**Picture 32. The VORTOIL De-oiling Hydrocyclone**

Moreover, it represents the state of the art in PW treatment technology, optimizing the critical balance between oil-removal efficiency and capacity and ensuring that peak separation is achieved in the most cost-effective and space-efficient manner for both onshore and offshore facilities. The de-oiling hydrocyclones achieve liquid-liquid separation using a pressure drop across the unit, with no moving parts for greater reliability.

4. EPCON Dual Compact Flotation Unit (CFU) introduces an engineered internal design that incorporates residual flotation gas in a secondary separation stage to increase oil-in-water (O/W) removal efficiency while fully degassing the clean water outlet. In fact, it is an improved oil-in-water removal method resulting 50% greater efficiency than others. A successful field trial was performed on a Statoil installation in the Norwegian sector of the North Sea. Post-treatment outlet oil concentration was measured at 10 ppm, down from more than 25 ppm before treatment. The results also verified 27% better separation rates compared with conventional technologies.

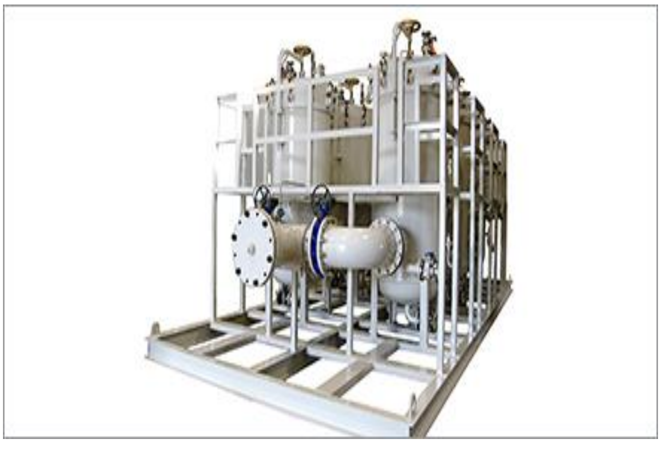


**Picture 33. Shows EPCON Dual Compact Flotation Unit [33]**

5. MYCELX RE-GEN Advanced Water Treatment Media is used for oily PW stream. Coated with a patented polymer, the media provides an economically sustainable treatment for removal of oils and suspended solids down to 5 um with 95% single-pass effectiveness, without the use of chemicals. Additionally, it can function properly as a primary or secondary treatment option for oil and solids removal. For chemical enhanced oil recovery (CEOR) applications, polymer- and chemical-laden water that has been treated with MYCELX RE-GEN media can be recycled for reuse in the injection field and, in the case of polymer, with no viscosity loss across the system. The media removes oils and solids but very little to none of the water-soluble enhanced oil recovery (EOR) products. In thermal EOR, removing the oil and solids before sending the produced water to a softener generates process and cost savings.

**Picture 34. Shows the MYCELX Advanced Water Treatment Media. [33]**

6. MYCELX Polisher Oil-In-Water consisted of a simple filtration system with a patented thin film polymer deposited on filter fibers. This polymer is a suitable surface for hydrocarbons. These filters provide a higher flow capacity and smaller footprint than conventional tertiary treatment technology. It is suitable treatment technology for fast and permanent ***removal of oil and grease*** down to <1-um droplet size from produced water, achieving extremely low O/W discharge levels to offshore or to inland, with the industry's highest flow capacity and smallest footprint. Concluding, it is able to remove oil in the presence of water-soluble polymers used in chemical enhanced oil recovery (CEOR) [33]



**Picture 35. Shows MYCELX Polisher Oil-In-Water [33]**

### 10.2. Aquatech

Aquatech is one of the largest companies globally in water treatment and water operations. It provides services in Pennsylvania in North America performing leadership environmentally friendly methods in desalination, water reuse and the pioneer zero liquid discharge. [42]

***Zero liquid discharge*** (ZLD) is a pioneer and advanced water treatment process in which liquid PW is eliminated, is purified, recycled and therefore, leaving zero discharge at the end of the treatment cycle. Zero liquid discharge can be defined broadly as a process for maximum recovery of high quality water, that would otherwise be discharged. So, the amount of PW is beneficially reused, reducing in that way the environmental footprint and improving the sustainability. The salts and other solids that contained in the PW are separated and disposed in a landfill. It combines ultrafiltration, reverse osmosis, evaporation/crystallization and fractional electro deionization with membrane processes and hybrid systems. Additionally, it is considered as a reliable and cost effective solution with more than 160 installations worldwide.

The design objectives are to minimize the capital investment and system operating cost, while not significantly impacting the manpower required for operation. Further, the system must be designed with operational flexibility to meet the facility needs and be safe and reliable.

Zero liquid discharge can be achieved in different ways. There is no "one size fits all" solution, as the optimal system design is site specific. The PW composition, the various streams that have to be treated, the site specific operating costs, the foot print availability and some other parameters are determining factors for an optimal design.

***Principle of operation***: Vertical tube falling film brine concentrators are generally used to concentrate lower total dissolved solids (TDS) brine solutions up to 12 % to as high as 25 % total solids and are used to minimize the design capacity of a downstream forced circulation crystallizer. Brine concentrators are specifically designed to manage the scaling of sparingly soluble divalent salts such as calcium sulphate and calcium carbonate, as well as silica that is also commonly present. Forced circulation crystallizers are generally used to concentrate brine blowdown from upstream concentration equipment, although small waste water flows are sometimes treated directly with a forced circulation crystallizer. Crystallizers are designed to manage crystallization of all salts, less soluble as well as highly soluble sodium salts such as sodium chloride and sodium sulphate, without excessive scaling and cleaning frequencies. This robustness comes at the expense of higher specific energy consumption and higher specific capital cost.

The solids generated by a forced circulation crystallizer are generally harvested and dewatered by a centrifuge. In such case the solids are collected and typically landfilled in a conventional landfill as long as the waste passes *Toxicity Characteristic Leaching Procedure* (***TCLP***) testing. However, in some applications involving zero liquid discharge equipment, the highly concentrated brine is discharged to an evaporation pond. Unfortunately, such a configuration reduces the footprint of the evaporation pond and expense the operating dewatering equipment. [42]

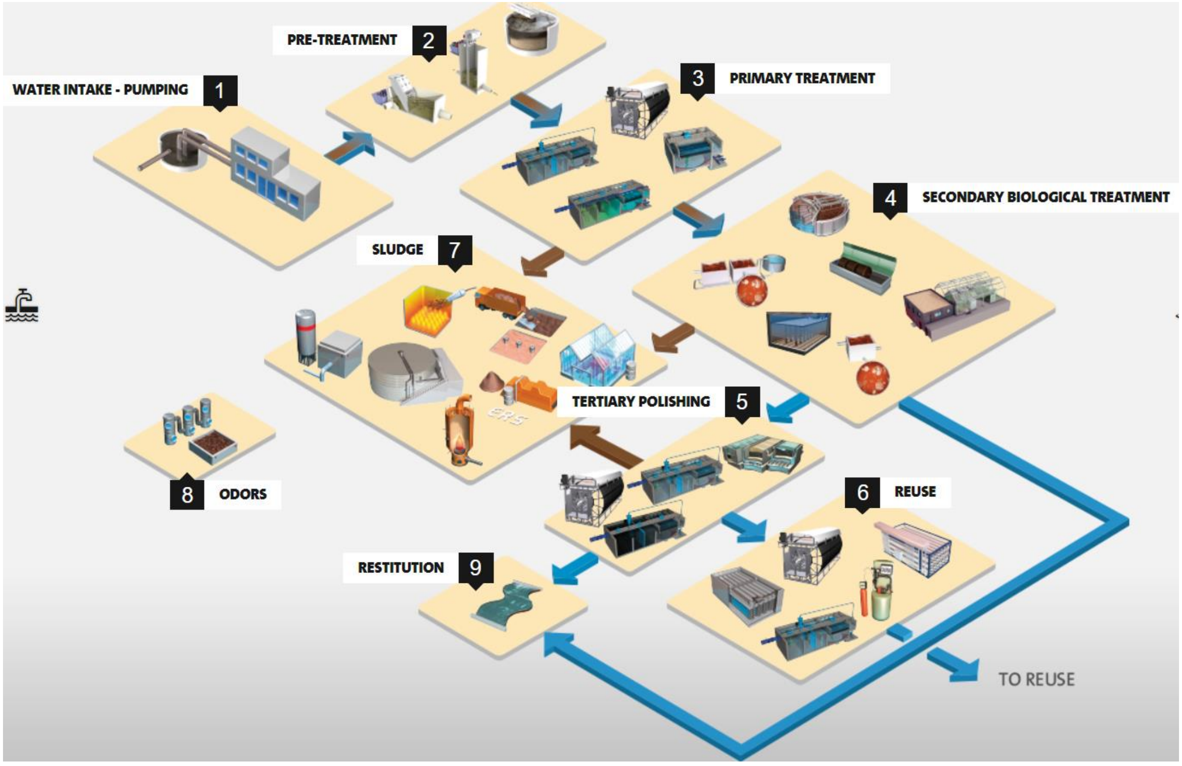
### 10.3. Veolia

Veolia specializes in PW treatment and provides sustainable water management solutions for handling PW and for production of water injection, as well as appropriate services required to design, maintain and upgrade water treatment facilities for oil and gas industry. Veolia mentioned that PW it is not solely wastewater but it is resource water, since it is a major component in all phases of oil and gas production. According to this, many different water technologies have been implied to extract the full value from PW while they help to generate reusable water that meet the most austere standards.

Veolia provides applied techniques both onshore and offshore for: Enhanced oil recovery (EOR), Treatment of injection water, Treatment for beneficial reuse of PW, Treatment of PW for surface discharge, Treatment of PW from gas production [37]

The stages include:

| | |
|---|---|
| 1. Water Intake - Pumping | 2. Pre -Treatment |
| 3. Primary Treatment | 4. Tertiary Polishing |
| 5. Reuse | 6. Sludge |
| 7. Odors | 8. Restitution |




**Picture 36. Schematic diagram of PW treatment through stages. [37]**

Prior to injection, PW is treated to remove contaminants that could plug the reservoir or damage injection equipment. Veolia provides an ultimate solution incorporating a variety of options to treat PW and remove undesired elements in order to meet the high performance demands of the Oil and Gas industry:

- Efficient treatment for increased productivity
- Robust and reliable installations and processes
- Operational safety in harsh environments
- Environmental compliance through efficient removal of pollutants.

A wide array of treatment technologies and process expertise is available from Veolia to provide solutions for pretreatment, primary, secondary and tertiary treatment applications. The treatment solutions are suitable for applications in both conventional and unconventional methods such as oil and gas field production, water flooding, chemical enhanced oil recovery (CEOR), steam assisted gravity drainage (SAGD), hydraulic fracturing, coal bed methane and shale gas.

Veolia, as the world Leader Company in offshore desalination and *Sulphate Removal Technology* (***SRP***) provides a schedule of water injection treatment which includes:

- Pre-treatment systems (microfiltration, ultrafiltration or multi-media filtration)
- Sulphate removal membrane systems (nanofiltration)
- Controlled salinity membrane systems (reverse osmosis / nanofiltration)
- Water treatment chemicals (storage, dosing, injection)
- Seawater reverse osmosis for wash and service water
- Integrated modules, fully compliant with offshore engineering specifications. [37]

Regulations for produced water are becoming more and more strict, incorporating the Zero-Harmful Discharge principle. Veolia's *Macro Porous Polymer Extraction* (***MPPE***) system removes precisely these toxic compounds, making direct discharge after MPPE treatment possible. Veolia offers treatment systems that are suitable for Oil field and Gas field PW.

Producers are faced with tightening restrictions on the handling and discharge of water from:

- Conventional oil and gas fields
- Aging oil fields
- Flowback and PW from shale gas fracturing
- Reservoir over-pressurization
- Tailings water
- Coal bed methane [37]

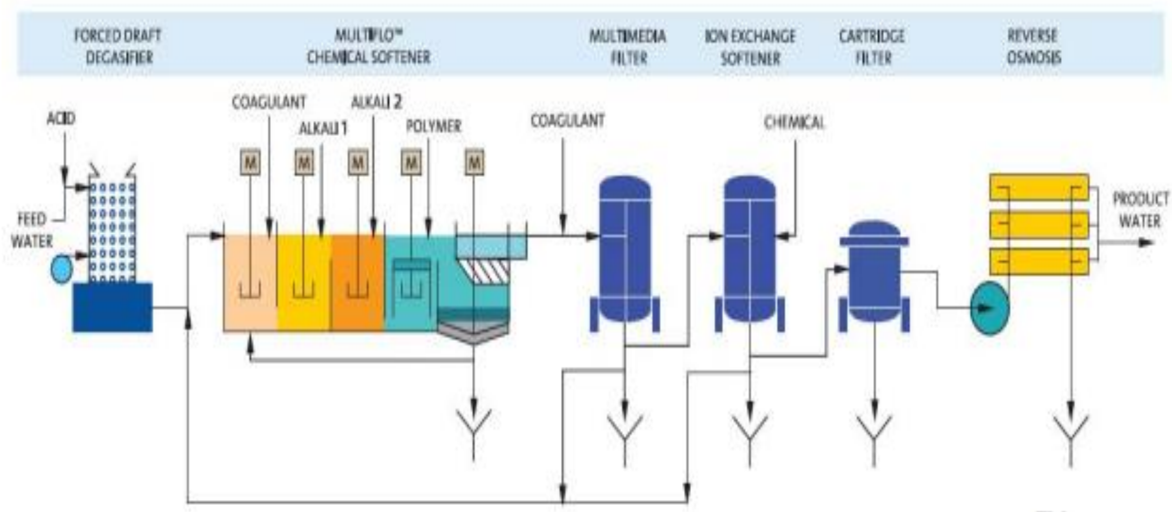
These streams are subject to quality limitations, especially concerning *Total Dissolved Solids* (***TDS***), oil and grease, solids, organics and sodium absorption ratio (SAR).

Treating PW so that it can be safely reused requires technologies that can operate oil and grease, slightly soluble inorganic salts, volatile organic compounds or hazardous trace contaminants. These constituents create challenges to traditional water treatment processes. Veolia has the pre and post treatment systems permitting water treatment technologies to meet the higher expectations. Water injection is often necessary to maintain reservoir pressure. Offshore, the source of injection water is the sea, however seawater contains naturally occurring sulphate which may need to be removed to prevent scaling of production equipment and the reservoir itself. [37]

- **Veolia Water Solutions and Technology - Designed the *OPUS* system**.

OPUS is an exclusive optimized pretreatment and unique separation process for desalination of water with high concentrations of partly soluble solutes (for example $SiO_2$, $CaSO_4$ and $Mg(OH)_2$), organics and boron. [15] It uses filtration and ion exchange as pretreatment to an RO system operated at high pH level. [4]

Principle of operation: the process initially starts with acidification and degasification of the raw feed water. After this, other processes such as conventional coagulation, flocculation, and high-rate plate settler sedimentation process are followed. It is noted that the feed stream should be clear from all high-molecular-weight organic molecules and oxidized metals (particularly iron and manganese). Additionally, colloidal silica is partially removed by co-precipitation. Decant from the sedimentation basin is then filtered by a packed-bed media filtration column, which removes any microflocs and most suspended solids that did not settle out in the plate settlers. The media filter may also achieve additional removal of low to medium molecular weight hydrophobic organic molecules, including any remaining oil and grease. As a result, OPUS product literature shows removals for TDS of 99.6%, TOC of 99%, silica of 99.9%, and boron of 99.4%. [15]




**Picture 37. Process schematic of Veolia Water Solutions and Technologies: OPUS PW treatment system [15]**

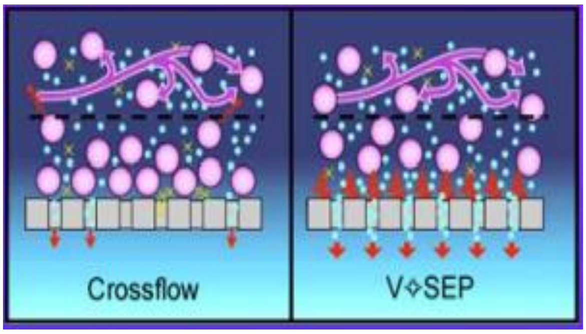
## 10.4. V*SEP - Vibratory Shear Enhanced Membrane Filtration

The patented V*SEP® technique membrane for treatment of PW (offshore and onshore) was developed by New Logic Research in California. It is an alternative method for producing intense shear waves into the membrane and is known as *Vibratory Shear Enhanced Processing (**VSEP**)*. [15]

Principle of Operation: The V*SEP® membrane filter pack consists of elements lined in parallel discs and separated by gaskets. The produced shear waves by the membrane vibration cause solids to be lifted off as suspended particles into the membrane surface and remixed with the bulk material flowing through the membrane. This high shear processing exposes the membrane pores for maximum throughput that is typically between 3 and 10 times the capacity of conventional cross-flow systems. [36]

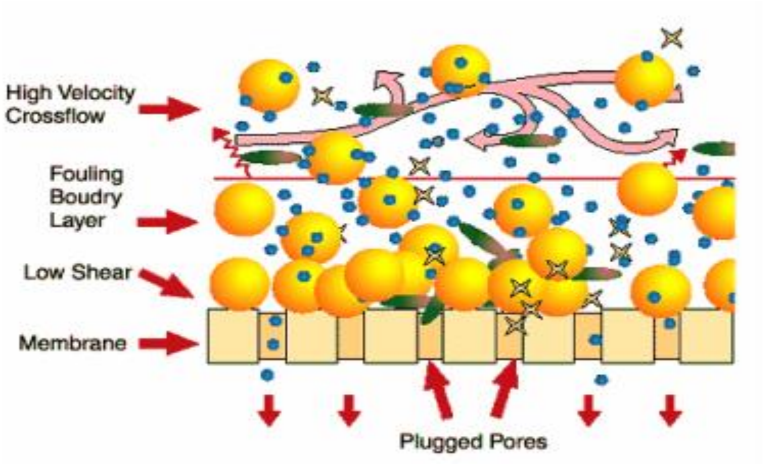
At startup, the V*SEP system is fed with slurry and the concentrate valve is closed. Permeate is produced and suspended solids in the feed are collected inside the VSEP filter pack. After a programmed time, interval, valve one is opened to release the accumulated concentrated solids. The valve is then closed to allow the concentration of additional feed material. This cycle repeats indefinitely. [36]

Membrane selection is the most important parameter that affects the quality of the separation, while pressure, temperature, vibration and residence time are affecting less the system performance.




**Picture 38.**

Compared to conventional reserve osmosis, V*SEP® is not limited by the solubility of minerals or the presence of suspended solids. It can be used in the same applications as crystallizers or brine concentrators and is capable of high water recoveries of up to 90%. The V*SEP system can be configured to employ either RO or nanofiltration membranes in a single-stage or multiple-stage arrangement. The formation depends on feed water quality, water quality goals of the V*SEP permeates and targeted water recovery. [36]




**Picture 39. Fouling reduction mechanisms of V*SEP [36]**

The manufacturer mentions that the V*SEP® process has numerous advantages which are considered attractive. It is a pioneer technology for treatment of PW.

**These include:**

- Minimal pretreatment: Because of high shearing energy at the membrane surface and near the pores, colloidal fouling and concentration polarization are greatly reduced but the use of pretreatment to prevent scale formation is not necessary.
- Low fouling and scaling potential: Sinusoidal shear waves from the membrane surface help to repel approaching particles and colloids, thus it is a source of fouling and scaling reduction.
- High permeate flux: The performance rates of V*SEP are 5-15 times higher. The shear waves propagating from the membrane surface act to hold suspended particles above the membrane surface allowing free transport of the liquid through the membrane.
- Low energy consumption: High flux and minimized membrane scaling and fouling make V*SEP very energy efficient (0.27 kWh/kgal filtrate). [36]

Experiments on sample of PW have conducted and the results are presented in the table 9.

**Table 6. V*SEP® produced water projects [36]**

| Produced water type | Location | MGD | bbl/day |
|---|---|---|---|
| CBM Produced Water | Utah | 0.72 | 17.143 |
| Offshore Produced Water | Santa Maria, CA | 0.86 | 20.571 |
| Oil Produced Water | Santa Maria, CA | 0.22 | 5.143 |
| Oil Produced Water | Bakersfield, CA | 12.24 | 291.429 |
| Produced Water | Kuwait | 1.44 | 34.286 |
| Offshore Produced Water | Peru | 0.05 | 1.200 |
| Note: 1 barrel = 42 US gallons | | | |

Experiments and results

In 2006, the first full-scale V*SEP system was selected to create steam quality water from oilfield produced brine at a Breit Burn Energy facility in Santa Barbara, California. Breit Burn implements steam flooding in the process and uses steam generators in the operations to enhance oil production. Re-injection of PW into the source formations was the method of disposal. After on-site trials, Breit Burn determined that the V*SEP system provided a cost-effective solution capable of removing the contaminants and providing the needed boiler feed water. As a result, was given the eradication of expensive pretreatment and chemical usage. The BreitBurn PW characterized from high alkalinity, silica, sodium, carbonate and TOC. The feed to the V*SEP contains 25,900 mg/L TDS and 870 mg/L hardness. The TOC was mostly made up of paraffins, waxes and asphaltenes that are colloidal materials that do not readily separate using conventional methods. Asphaltenes tend to adsorb at water-in-crude oil interfaced to form a rigid film surrounding the interface. The treatment employs both NF and RO membranes. The final permeate, after two stages of filtration, has non-detectable concentrations of hardness and water quality that is suitable for boiler feed water. The V*SEP process achieved an overall recovery of 70% of the oil PW as clean boiler feed water. Concluding, V*SEP process has proven effective in treating high solids water although may not be suitable for economic reasons, for PW that has less solids and can be treated by conventional membrane processes. [15]

## 10.5. MIOX - Mixed Oxidant Solution (MOS)

***MOS*** is an oil and gas water management company that deals with on-site generated Chemical with the lowest cost. Among all microorganisms the most detrimental to the oil and gas industry are the *sulfate-reducing bacteria* ***(SRBs)*** that are able to convert sulfate ions to hydrogen sulfide ($H_2S$) especially into the injection water. For this reason, biocides play a major role in frac fluid treatment and any water injected downhole.

The most common are non-oxidizing organic biocides, referred to as 'conventional' biocides. The problem is that many *SRBs* become resistant to conventional biocides, limiting effectiveness and requiring operators to increase their concentrations. Many conventional non-oxidizing biocides are also carcinogenic, so using more chemicals can present potential health risks for workers. [43] Oxidizing biocides fall into the other category of biocides which include sodium hypochlorite, hydrogen peroxide and others. Oxidizing biocides are considered green chemistry and work well against all strains of SRBs. Sodium hypochlorite is among the top 10 disinfection chemicals used in the world and was used downhole in the oilfield as early as the 1960s. However, the wide spread use of sodium hypochlorite in the oil and gas industry has been limited by the high costs associated with transporting a product, that is mostly composed of water, to the remote oil and gas fields around the world.

**MIOX** has developed a highly effective disinfection technology for use in the oil and gas industry which creates *Mixed Oxidant Solution (**MOS**)* biocide consisting predominantly of sodium hypochlorite and hydrogen peroxide. When applied correctly, MOS can completely eliminate SRBs and all other bacteria.
Electrolysis process: The electrolytic cell of a MIOX on-site generator uses common salt combined with water and electricity to generate high performance Mixed Oxidant Solution (MOS) or hypochlorite, eliminating the need to transport and store hazardous chemicals. [43]

## 10.6. GE Power Water & Process Technologies.

It is a water processes company for oil and gas operations that optimizes water use for exploration, production and refining in an efficient and profitable way. Offshore water injection consists of injecting seawater into oil reservoirs to maintain or increase oil production. A number of reservoirs, such as those found off the coast of Brazil and West Africa, in the North Sea or in the Gulf of Mexico, require the water be treated before injection.

This company uses nanofiltration membranes for this application, which when in combination with a proper pre-filtration scheme and chemical program, ensure that practically all the sulfate is removed from the seawater. Enhancing oil production can also be achieved through membrane technology by designing water injection systems where water salinity can be adjusted. Recent experiments have shown that reduced salinity water can positively impact the amount of oil being recovered from a series of different reservoirs. According to GE power this technology can be used for existing fields in the North Sea and the Gulf of Mexico where oil production is declining. In addition, it may be beneficial to use low salinity technology instead of sulfate removal in early stages since GE's salt reducing membranes also remove sulfate from seawater. [44]

## 10.7. Ecosphere: Ozonix

Eco-Sphere is a leading company near Florida, USA that offers on site produced water treatments solutions. Innovative Ecosphere's patented Ozonix® technology is the only *Advanced Oxidation Process* (***AOP***) proven to provide high-volume, chemical-free water treatment and recycling services at the frac site, as it has been used to recycle billions of gallons of PW and hydraulic fracturing fluids on hundreds of wells in the United States, reducing costs, microbial growth, corrosion and increasing operational efficiencies and capacity. [45]

Ecosphere's proven, chemical-free **Ozonix technology** will enhance industrial operations achieve cost-effective water pretreatment to produce environmentally safe effluent that is suitable for discharge. Specifically, flowback water had to be loaded into tanker trucks and transferred away to deep-injection sites or holding ponds. The Ecosphere Ozonix® water treatment technology has eliminated the need for wastewater trucking and allows operators to re-use 100% of their water in current and future operations. [45]


**Picture 40. [45]**

**Ozonix**® is a patented, liquid chemical-free advanced oxidation process, which saturates contaminated water with ozone using hydrodynamic cavitation, acoustic cavitation and electrochemical oxidation to oxidize and destroy micro-organisms, while generating no harmful disinfection byproducts. It is considered as highly effective in water recovery, treatment and recycling. Ozonix, 10 to 20 times multiplier over the use of ozone and cavitation when used by themselves, removing 99.99% of bacteria in water and eliminating the need for chemical biocides, scale inhibitors and friction reducers. Disinfection time is fast making it perfect for on the fly use, mobile wastewater treatment applications when Ozonix® generates no harmful disinfection byproducts. [45]

Results: Pilot scale study carried out with frac water flowback in the Woodford Shale Play of eastern Oklahoma. System piloted for 2 weeks and treated 4,200 gal/hour was tested with highly challenging feed water have shown TDS of 14,000 mg/L, presence of dispersed oils, over 1,000 mg/L of total hardness, and presence of barium.

Pilot study reports 99.1% TDS rejection, and 97% removal of BTEX compounds in quality of produced water. Furthermore, as far as production efficiency concerned pilot study reports purified water recovery approaching 75%. The vendor claims a 1% waste stream for disposal, with the rest of the solution being retained for reuse as frac water. [15]

## 10.8. GeoPure Water Technologies

The GeoPure desalination process is an innovative combination of pre-treatment, ultrafiltration and reserve osmosis. The aim of those three steps is to treat a wide range of produced water compositions and produce clean water that may then be discharged or reused. This technology was specifically developed for the desalination of oil and gas produced waters, containing up to 50,000 mg/L TDS. Depending on raw water quality, this process employs various pretreatment processes to remove dispersed oil, suspended solids or dissolved hydrocarbons. The pretreated water is then further purified with polymeric UF and RO. The UF system provides a final barrier to suspended solids (such as colloids) prior to the RO subsystem. [15]

Case study: GeoPure performed a field test of its commercial desalination unit in the Barnett Shale Play of central Texas in 2006. In this field trial, frac flowback water was treated at a feed rate of 210,000 gal/day (5,000 barrel/d). The feed water from this field trial also contained 4,200 mg/L of TSS, 170 mg/L of Fe and 940 mg/L of Ba. After coagulation/flocculation, the water was treated with GeoPure’s UF and RO units. Influent and RO permeate TDS concentrations were 15,000 and 190 mg/L, respectively, corresponding to 98.7% TDS rejection. When including the coagulation/flocculation pretreatment process, total treatment costs were estimated to average $0.94 per barrel.

A second field trial was conducted at a CBM well field in Western Wyoming. The GeoPure treatment process was tested with CBM produced water containing corrosion inhibitor, alcohols, and surfactants. Other feed water parameters include a feed TDS of 9,700 mg/L (dominated by NaCl) and 41 mg/L of dissolved hydrocarbons. 99% rejection of TDS was achieved. No electrical or other cost information was provided from this study. GeoPure focuses on optimizing pretreatment technologies to protect its core UF/RO treatment processes from membrane material that causes fouling (especially dispersed oils). [15]

Results: Oil and natural gas related field trials have reportedly been conducted at 12 sites. Two summary documents from field trial experiences with frac flowback water in Texas and CBM produced water in Wyoming were located. The vendor reports treating water in excess of 50,000 mg/L TDS. Available field trial reports claim treating water with TDS ranging from 9,700 to 15,000 mg/L. Frac flowback water constituted high concentrations of barium, dissolved hydrocarbons and iron. PW water recovery in one field test was reported to be 50%. 60-70% recovery is estimated for feed water of 7,000 and 17,000 ppm chlorides, respectively. [15]

## 11. Conclusions

Our bibliographic research confirmed the increasing importance of an efficient PW treatment, which was stated from the first pages of the present thesis.

Every treatment method depends on:

**1**) characteristics and the origin of the PW quality - *Coal bed methane (CBM)* PW is usually more acidic than the oilfield PW, and also volatile components concentrations are lower in accordance with gas field produced waters

**2**) the final purpose of its use after the treatment – injection, IOR, location of disposal, (surface or underground), reuse.

Regional regulation is also an important key parameter that has to be taken into consideration since the permissible values change from country to country, as the PW amount the oil content can be up to 42 mg/l into the Gulf of Mexico while the amount decreases up to 15 mg/l oil content in the Persian Gulf as it is a closed aquatic region and has more austere limits.

An efficient and reliable PW treatment (before its disposal to the natural recipients or its recycling in other uses) is required nowadays for two distinct reasons:

**a.** It is already established that the capacity of Nature to "digest" any pollution coming from human economic activity is not unlimited. In fact, there is evidence that these limits have already been violated. So, the development of technologies for the protection of the environment, which should be respected by every producer along the planet, give rise to an "environmental sustainability" and a reasonable natural resources management, gains extremely urgent importance. The importance of such a policy as above is self-evident, especially with regard to the international context of climate change. National and international environmental legislation, setting ever stricter upper limits for every specific pollutant concentration contained in a waste water solution to be discharged to a natural recipient is just a proof that human community recognizes the threat of an environmental degradation coming from current human economic (and other) activities.

**b.** As it was explained in the previous pages, during the exploitation of an oil well (or a gas deposit) water is produced at increasing quantities. Besides, the exhaustion of reservoirs close to the surface leads inevitably to the exploitation of other reservoirs found deeper and deeper, producing greater quantities of PW compared to the exhausted ones, close to the surface. Because of this effect, the overall global quantities of PW are always increasing, although the global quantities of pumped oil had a tendency to stabilize over the last decades. As a consequence, oil and gas producers are forced to treat increasingly greater quantities of PW and for this purpose they have to develop and implement specific and effective technologies.

The extensive study of the various techniques which were developed for the PW treatment, or for other problems and later applied in the field of PW treatment shows that from a "technical" point of view, a great variety of methods and solutions are available to the oil producers, depending on the PW origin, the chemical characteristics of pollutant to be removed and the final desirable concentration level of each pollutant. Of course, pioneering scientific research never stops and new methods will be certainly developed in the future, giving better results and performances.

Central to PW treatment is the idea that because of the extremely great variety of the dissolved or dispersed pollutants contained in PW (hydrocarbons, oils and greases, emulsifiers, other organic substances, minerals, salts, metals, gazes, etc.), there is no one single technology capable of removing all pollutants. A combination of different techniques and technologies is almost always required, each of which targets a certain group of pollutants, or even a specific "fraction" of a given pollutant (for example the case of membranes removing particles of a given size). Choice of the best technology is based on PW chemistry, cost, space availability, reuse and discharge plans, durable operation, and overall byproducts. Furthermore, the order of succession of the different techniques is in most cases critical, since the presence of a specific pollutant might be prohibitive to the implementation of a given technique (this is for instance the case of some heavy metals "poisoning" or spoiling biological treatment bacteria).

On the other hand, any technological solution applied in the waste water treatment and the environmental protection have their "economic", as well as their "technical" aspects. PW treatment, even if the obtained "treated" water which is recycled for other uses, represents a considerable part of the overall oil or gas extraction cost, and (as it was explained in the previous pages) sometimes it is because of this extremely high cost that an oil exploitation has to stop. So, it can be concluded that a lot of work has to be done to compress PW economic cost to affordable levels where it is not the case, or to lower the overall oil (or gas) production cost, and their market price.

In any case, PW treatment is always a problem, depending strongly on the nature and the characteristics (size, etc.) of the contained pollutants, their concentration, the PW quantities to be treated per day, the characteristics and the quality of the treated water to be obtained, as well as the specific conditions (climatic conditions, available area, etc.) of the exploitation. This means that there are no "ready to buy" or "ready to apply" solutions, and that the suitable technology to be implemented in a given exploitation requires a specific "case study" which has to be investigated.

# Appendix .

## I. Glossary and abbreviations

**BAT:** Best Available Technology Economically Achievable

**BPT:** Best Practicable Control Technology Currently Available

**CAPEX**: Capital Expenses

**CBM:** Coalbed Methane

**DGF:** Dissolved Gas Flotation

**EIA:** Energy Information Administration

**EPA:** Environmental Protection Agency

**GAC**: Granular Activated Carbon

**GWPC**: Ground Water Protection Council

**IGF:** Induced Gas Flotation

**IOGCC**: Interstate Oil and Gas Compact Commission

**MPPE**: Macro Porous Polymer Extraction

**NPDES**: National Pollutant Discharge Elimination System

**OCS:** Outer Continental Shelf

**OPEX**: Operational Expenses

**SRBs:** Sulfate Reducing Bacteria

**TCLP**: Toxicity Characteristic Leaching Procedure

**TDS:** Total Dissolved Solids

**TSS:** Total Suspended Solids

**UIC**: Underground Injection Control

**WHO**: World Health Organization

**ZLD**: Zero liquid discharge

## II. Definitions.

In order for somebody to reading this thesis, it is required to define some key words: [19]

**A petroleum reservoir or oil and gas reservoir** is a subsurface pool of hydrocarbons contained in porous or fractured rock formations. Petroleum reservoirs are broadly classified as *conventional* and *unconventional* reservoirs.

In case of conventional reservoirs, the naturally occurring hydrocarbons, such as crude oil or natural gas, are trapped by overlying rock formations with lower permeability.

While in unconventional reservoirs the rocks have high porosity and low permeability which keeps the hydrocarbons trapped in place, therefore not requiring a cap rock.

**Aquifer**: A single underground geological formation, or group of formations, containing water. It contains less than 10,000mg/L total dissolved solids – TDS [13]

**Clean Water Act:** The federal law that regulates discharges into waterways.

**Coal Bed Methane (CBM)**: A form of natural gas extracted from coal beds. Along with tight and shale gas, CBM is considered an unconventional natural gas resource.

**Demulsifiers**: specialty chemicals that are used to separate the oil from water.

**Flowback:** Water used as a pressurized fluid during hydraulic fracturing that returns to the surface via the well. This occurs after the fracturing procedure is completed and pressure is released.

**Fossil Energy**: Energy derived from crude oil, natural gas or coal. Shale gas is a form of fossil energy.

**Frac Focus**: A joint effort by the Ground Water Protection Council (GWPC) and the Interstate Oil and Gas Compact Commission (IOGCC) that is an online registry for companies to publicly disclose the chemicals used in their hydraulic fracturing operations. As of November 2012, more than 30,000 well sites and 200 companies were registered on the site.

**Fracturing fluid:** The primarily water-based fluid used to fracture shale. It is basically composed of 99 % water, with the remainder consisting of sand and various chemical additives. Fracturing fluid is pumped into wells at very high pressure to break up and hold open underground rock formations, which in turn releases natural gas.

**Geological Formation**: A body of earth material with distinctive and characteristic properties and a degree of homogeneity in its physical properties.

**Groundwater**: The supply of usually fresh water found beneath the surface usually in acquirers', which are a body of permeable rock containing water and supplying wells and springs with drinking water. [12]

**Hydraulic fracturing:** The use of water, sand and chemical additives pumped under high pressure to fracture subsurface non-porous rock formations such as shale to improve the flow of natural gas into the well. Hydraulic fracturing is a mature technology that has been used for 60 years and today accounts for 95 % of all new wells drilled.

**Natural gas:** A naturally occurring mixture of hydrocarbon and non-hydrocarbon gases beneath the surface, the principal component of which (50 to 90 %) is methane.

**On-site water treatment:** A practice employed by many shale gas producers to facilitate reuse of flowback fluids. In this instance, mobile and fixed treatment units are employed using processes such as evaporation, distillation, oxidation and membrane filtration for recycling and reuse. On-site treatment technologies may be capable of returning 70-80 % of the initial water to potable water standards, making it immediately available for reuse.

**Produced water:** Naturally occurring water found in shale formations, it generally flows to the surface during the entire lifespan of a well, often along with natural gas. Produced water and flowback from natural gas extraction may be reused in hydraulic fracturing operations, disposed of through underground injection, discharged to surface waters as long as it doesn't degrade water quality standards or transferred to a treatment facility if necessary, processed and discharged into a receiving water body in compliance with outflow limits.

**Safe Drinking Water Act (SDWA):** A federal law whose provisions also apply to shale production activities related to wastewater disposal through underground injection and discharge to surface waters.

**Scale**: A mineral salt deposit that may occur on wellbore tubular and components as the saturation of produced water is affected by changing temperature and pressure conditions in the production tubing. In severe conditions, scale creates a significant restriction or even a plug, in the production casing. Scale removal is a common well-intervention operation, with a wide range of mechanical, chemical and scale inhibitor treatment options available.

**Shale:** A fine-grained sedimentary rock composed mostly of consolidated clay or mud. Some large shale gas formations were formed more than 300 million years ago during the Devonian period of Earth's history, where conditions were particularly favorable for the preservation of organic material within the sediment. Methane that remained locked in the shale layers is the source of today's shale gas.

**Surface water:** Water that is in contact with the atmosphere, such as rivers, lakes, ponds, reservoirs, streams, seas and estuaries.

**Well**: a drilled borehole whose depth is greater than the largest surface dimension. It consists of subsurface fluid distribution system that may more than one wells are connected underground forming path up and down for transformation of fluids. [13]

## III. Typical characteristics and composition of an oilfield sample of PW.

**Table 7. Values of constitutes of oilfield produced water. [10]**

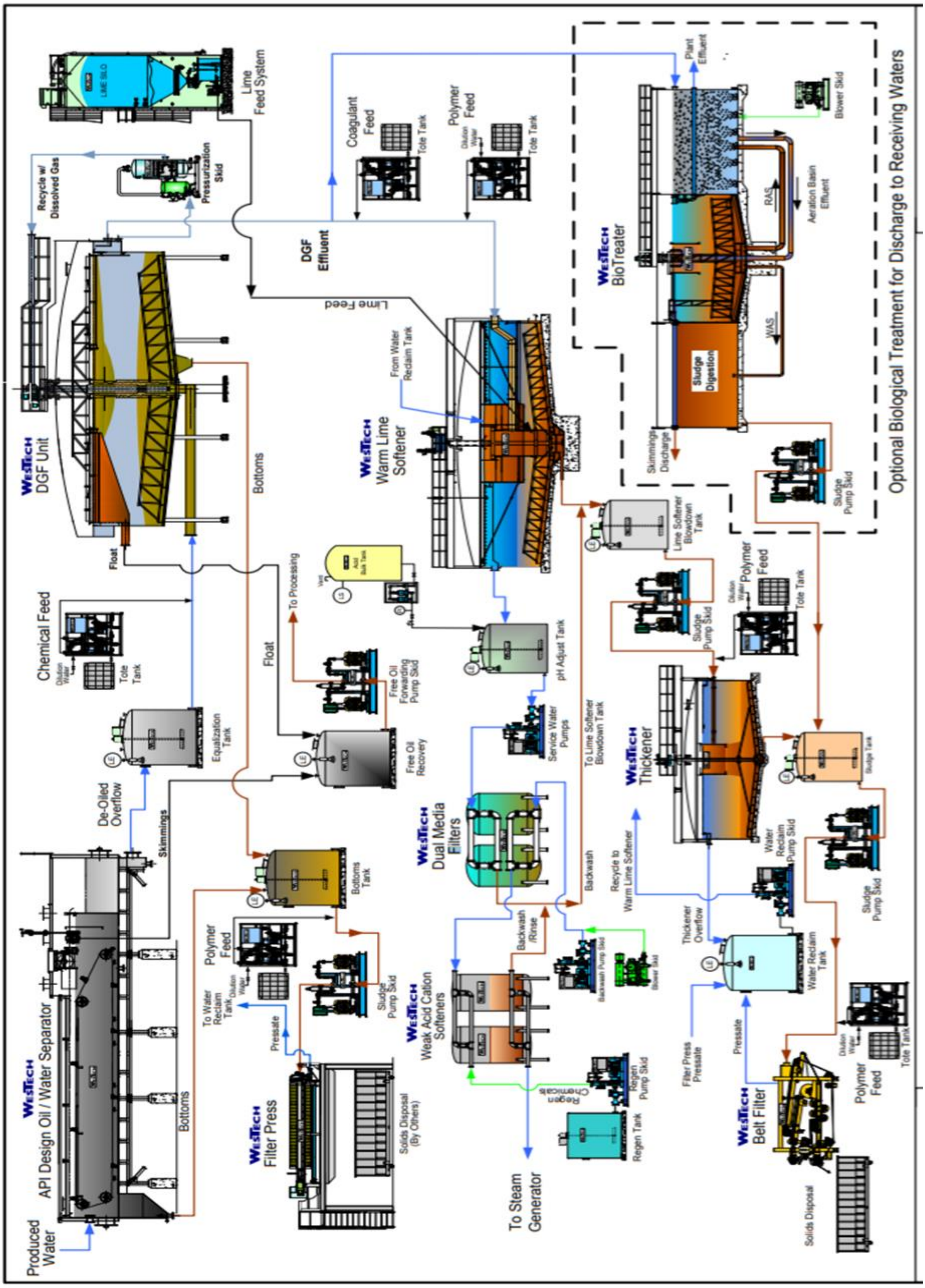
| Parameter | Min. value | Max. value | Metal | Min. value (mg/l) | Max. value (mg/l) |
|---|---|---|---|---|---|
| **Density** (kg/m$^3$) | 1014 | 1140 | Calcium | 13 | 25 800 |
| **Conductivity** (µS/cm) | 4200 | 58 600 | Sodium | 132 | 97 000 |
| **Surface tension** (dyn/cm) | 43 | 78 | Potassium | 24 | 4300 |
| **pH** | 4.3 | 10 | Magnesium | 8 | 6000 |
| **TOC** (mg/l) | 0 | 1500 | Iron | <0.1 | 100 |
| **TSS (**mg/l) | 1.2 | 1000 | Aluminium | 310 | 410 |
| **Total oil** (IR, mg/l) | 2 | 565 | Boron | 5 | 95 |
| **Volatile** (BTX, mg/l) | 0.39 | 35 | Barium | 1.3 | 650 |
| **Base/neutrals** (mg/l) | — | <140 | Cadmium | <0.005 | 0.2 |
| **Chloride** (mg/l) | 80 | 200 000 | Copper | <0.02 | 1.5 |
| **Bicarbonate** | 77 | 3990 | Chromium | 0.02 | 1.1 |
| **Sulphate** (mg/l) | <2 | 1650 | Lithium | 3 | 50 |
| **Ammoniacal nitrogen** (mg/l) | 10 | 300 | Manganese | <0.004 | 175 |
| **Sulphite** (mg/l) | — | 10 | Lead | 0.002 | 8.8 |
| **Total polar** | 9.7 | 600 | Strontium | 0.02 | 1000 |
| **Higher acids** | <1 | 63 | Titanium | <0.01 | 0.7 |
| **Phenol** (mg/l) | 0.009 | 23 | Zinc | 0.01 | 35 |
| **Volatile fatty acids** (mg/l) | 2 | 4900 | Arsenic | <0.005 | 0.3 |

# IV. Summary of current technologies PW treatment

**Table 8. Comparison of current technologies for oil and gas produced water treatment.**

| Treatment | Description | Advantages | Disadvantages | Waste stream | Oil and gas produced water applications |
|---|---|---|---|---|---|
| Corrugated plate separator | Separation of free oil from water under gravity effects enhanced by flocculation on the surface of corrugated plates | No energy required, cheaper, effective for bulk oil removal and suspended solid removal, with no moving parts, this technology is robust and resistant to breakdowns in the field | Inefficient for fine oil particles, requirement of high retention time, maintenance | Suspended particles slurry at the bottom of the separator | Oil recovery from emulsions or water with high oil content prior to discharge. Produced water from water-driven reservoirs and water flood production are most likely feed stocks. Water may contain oil and grease in excess of 1000 mg/L. |
| Centrifuge | Separation of free oil from water under centrifugal force generated by spinning the centrifuge cylinder | Efficient removal of smaller oil particles and suspended solids, lesser retention time high-throughput | Energy requirement for spinning, high maintenance cost | Suspended particles slurry as pretreatment waste | |
| Hydroclone | Free oil separation under centrifugal force generated by pressurized tangential input of influent stream | Compact modules, higher efficiency and throughput for smaller oil particles | Energy requirement to pressurize inlet, no solid separation, fouling, higher maintenance cost | | |
| Gas floatation | Oil particles attach to induced gas bubbles and float to the surface | No moving parts, higher efficiency due to coalescence, easy operation, robust and durable | Generation of large amount of air, retention time for separation, skim volume | Skim off volume, lumps of oil | |
| Extraction | Removal of free or dissolved oil soluble in lighter hydrocarbon solvent | No energy required, easy operation, removes dissolved oil | Use of solvent, extract handling, regeneration of solvent | Solvent regeneration waste | Oil removal from water with low oil and grease content (<1000 mg/L) or removal of trace quantities of oil and grease prior to membrane processing. Oil reservoirs and thermogenic natural gas reservoirs usually contain trace amounts of liquid hydrocarbons. |
| Ozone | Strong oxidizers oxidize soluble contaminant and easy operation, efficient for primary treatment of soluble constituents remove them as precipitate | Easy operation, efficient for primary treatment of soluble constituents | On-site supply of oxidizer, separation of precipitate, byproduct $CO_2$, etc. | Solids precipitated in slurry form | |
| Adsorption | Porous media adsorbs contaminants from the influent stream | Compact packed bed modules, cheaper, efficient | High retention time, less efficient at higher feed concentration | Used adsorbent media, regeneration waste | |
| Lime softening | Addition of lime to remove carbonate, bicarbonate, etc. hardness | Cheaper, accessible, can be modified | Chemical addition, post-treatment necessary | Used chemical and precipitated waste | These technologies typically require less power and less pretreatment than membrane technologies. Suitable produced waters will have TDS values between 10,000 and 1000 mg/L. Some of the treatments remove oil and grease contaminants and some of them require oil and grease contaminants to be treated before these operations. |
| Ion-exchange | Dissolved salts or minerals are ionized and removed by exchanging ions with ion-exchangers | Low energy required, possible continuous regeneration of resin, efficient, mobile treatment possible | Pre- and post-treatment require for high efficiency, produce effluent concentrate | Regeneration chemicals | |
| Rapid spray evaporation | Injecting water at high velocity in heated air evaporates the water which can be condensed to obtained treated water | High quality treated water, higher conversion efficiency | High energy required for heating air, required handling of solids | Waste in sludge form at the end of evaporation | |
| Freeze–thaw evaporation | Utilize natural temperature cycles to freeze water into crystals from contaminated water and thaw crystals to produce pure water | No energy required, natural process, cheaper | Lower conversion efficiency, long operation cycle | – | |
| Microfiltration | Membrane removes micro-particles from the water under the applied pressure | Higher recovery of fresh water, compact modules | High energy required, less efficiency for divalent, monovalent salts, viruses, etc. | Concentrated waste from membrane backwash during membrane cleaning, concentrate stream from the filtration operation | Removal of trace oil and grease, microbial, soluble organics, divalent salts, acids, and trace solids. Contaminants can be targeted by the selection of the membrane. |
| Ultrafiltration | Membrane removes ultraparticles from the water under the applied pressure | Higher recovery of fresh water, compact modules, viruses and organics, etc. removal | High energy, membrane fouling, low MW organics, salts, etc | | |
| Reverse osmosis | Pure water is squeezed from contaminated water under pressure differential | Removes monovalent salts, dissolved contaminants, etc., compact modules | High pressure requirements, even trace amounts of oil and grease can cause membrane fouling | | Removal of sodium chloride, other monovalent salts, and other organics. Some organic species may require pretreatment. While energy costs increase with higher TDS, RO is able to efficiently remove salts in excess of 10,000 mg/L. |
| Activated sludge | Using oil degrading microorganisms to degrade contaminants within water | Cheaper, simple and clean technology | Oxygen requirement, large dimensions of the filter | Sludge waste at the end of the treatment | Removal of suspended and trace solids, ammonia, boron, metals, etc. Post-treatment is normally required to separate biomass, precipitated solids, dissolved gases, etc. |
| Constructed wetland treatment | Natural oxidation and decomposition of contaminants by flora and fauna | Cheaper, efficient removal of dissolved and suspended contaminants | Retention time requirement, maintenance, temperature and pH effects | | |

## V. Example of Treatment of PW sample




**Picture 41. Oil sands Produced water treatment. [52]**

# VI. Case study 1.

**A.** The following sample of produced water is consisted of hydrocarbons (primarily methanol, amines and lubricating oils), heavy metals and naturally occurring radioactive materials (NORM). According to the environmental regulatory authorities firstly, the amount of PW has to be treated and be characterized with in permissible limit values in order to be discharged into the sea. Treatment processes was responsible for reduction of each category of contaminants concentration. [17]

**Table 9. Preliminary Process Design Basis [17]**

| Contaminants | Units | Influent | Effluent |
|---|---|---|---|
| Oil and Grease | mg/L | 118 | 50 |
| Amines | mg/L | 106 | 10 |
| Phenols | mg/L | 9 | 15 |
| Methanol | mg/L | 1440 | 400 |
| Arsenic | mg/L | 0.06 | 0.01 |
| Aluminum | mg/L | 2.6 | 2.0 |
| Cadmium | mg/L | 0.17 | 0.01 |
| Chromium | mg/L | 0.02 | 0.05 |
| Copper | mg/L | 0.06 | 0.1 |
| Iron | mg/L | 313 | 100 |
| Manganese | mg/L | 12 | 1.0 |
| Mercury | mg/L | 0.02 | 0.001 |
| Molybdenum | mg/L | 0.01 | 0.01 |
| Lead | mg/L | 5.4 | 0.01 |
| Zinc | mg/L | 63 | 0.5 |
| Nickel | mg/L | 0.04 | 0.05 |
| Suspended solids | mg/L | 803 | - |
| Radium, total | Bq/g | 0.02 | 0.001 |
| Lead 210 | Bq/g | 0.02 | 0.005 |
| Salinity | % | 20 | - |
| pH | - | 4.5 to 6.8 | 6 to 9 |
| Flow Rate - Design | $m^3$/hr | 100 | |

### 1. Free-Floating Oils-Suspended Solids

The existing oil/water separator can be expected to consistently reduce free-floating hydrocarbon (oil and grease) concentrations from 118 to the proposed discharge limit of 50 mg/L. However, the potential downstream treatment processes needed to reduce soluble organics and inorganics would require that oil and grease concentrations be reduced to 10 mg/L or less. Although no discharge limit had been placed on suspended solids concentrations, the influent concentration of 803 mg/L would have to be reduced significantly to 30 mg/L in order to prevent affecting the performance of other potential treatment processes.

The oil/water separator would not be able to achieve these required treatment levels for either oil and grease or suspended solids. Two similar treatment processes were considered for further reducing free-floating hydrocarbons and suspended solids concentrations to the required levels: dissolved air flotation (DAF) and induced air flotation (IAF). Both processes use air bubbles to float free-floating hydrocarbons and suspended solids to the surface of the wastewater, where they are removed by skimming. Both processes also normally use chemical conditioning pretreatment steps to promote oil droplet and suspended particle agglomeration and have been proven effective in high salinity applications. However, the DAF process typically achieves a slightly better effluent quality than IAF, and therefore, was selected as a component in the treatment system options.

**2. Soluble Organics**

Soluble organic contaminants consist mainly of amines and methanol residuals that remain in the PW after hydrocarbon processing operations. Methanol serves as a transport medium for the amine-based corrosion inhibitor chemicals.

The process design basis requires that methanol be reduced from 1440 to 400 mg/L and that amines concentration be reduced from 106 to 10 mg/L. Potential downstream treatment processes would also require a reduction in soluble organics concentrations to avoid interfering with process reactions and kinetics. Reducing the amines concentration is particularly important, since amines form complexes with heavy metals, which would adversely affect the efficiency of heavy metal treatment processes.

Three methods were considered for reducing the soluble organics concentrations to the necessary limits: biological oxidation, advanced chemical oxidation and source minimization. Biological treatment was not selected, however, because the extremely high salinity concentration in the PW would result in high osmotic pressure. This high osmotic pressure would adversely affect micro-organism development. Advanced chemical oxidation using hydrogen peroxide or ozone with UV light can reduce amines and methanol concentrations in high-salinity solutions, but results in high operating costs.

Methanol and amines concentrations in the PW could be reduced at source but some question remained as to whether the required effluent concentrations could be consistently achieved. Based on this information, advanced chemical oxidation was selected for further consideration in the treatment system options.

**3. Aluminum, Iron, Manganese and Zinc**

The concentrations of aluminum, iron, manganese and zinc can be reduced to the proposed limits (2.0, 100, 1.0 and 0.5 mg/L, respectively) by using traditional alkaline precipitation processes. The alkaline reagents typically used include hydrated lime (calcium hydroxide) and caustic soda (sodium hydroxide). Polyelectrolytes are normally added to the reaction to cause the newly formed metal hydroxide precipitates to flocculate, resulting in more rapid precipitation rates. Hydrated lime was selected as the preferred reagent because it was more cost effective for this application and precipitate sludges that are generated by hydrated lime treatment are typically more easily dewatered.

The insoluble metal hydroxide precipitates generated are usually removed from solution by a clarification step. Typical clarifier types include standard open-area settlers, tilted plate or

tube settlers, and solids-contact units. The solids-contact clarifier was selected as the best treatment option, because in this type of clarifier, the precipitates are filtered from the wastewater as the water up flows through the sludge blanket. The other clarifier types rely strictly on gravity settling to cause solids-liquid separation, which is difficult to achieve in a high-salinity, high-density solution, such as the PW.
To ensure that the treated wastewater stream consistently satisfies the discharge limits for aluminum, iron, manganese and zinc, a final filtration step would be required to reduce the concentration of the residual metal hydroxide precipitates and other suspended solids to below 10 mg/L. Multimedia deep-bed filtration and membrane-based micro-filtration were considered for this application. Multimedia deep-bed filtration was selected over micro-filtration because it has a much longer track record in treating high-salinity wastewaters to the quality limits required in this application.

### 4. Arsenic, Cadmium and Lead

Reducing arsenic, cadmium and lead concentrations to the very low concentration of 0.01 mg/L (10 ppb) would require additional treatment stages beyond alkaline precipitation. Microfiltration and electro membrane processes, such as reverse osmosis and electro-dialysis, were considered but rejected because the extreme salinity of the water stream was beyond the range of the systems' processing capabilities. Sulfide precipitation was also considered, since metal sulfides are generally less soluble than metal hydroxides. The sulfide precipitation process is similar to hydroxide precipitation, except that sulfide-based reagents are used to react with the heavy metal ions in solution to form insoluble metallic sulfide precipitates. The sulfide precipitation process would reduce arsenic, cadmium and lead concentrations to approximately 0.02 mg/L, although this concentration is much lower than the expected to remain after hydroxide precipitation, it is still twice the proposed discharge limit of 0.01 mg/L. The process of ion exchange was also evaluated. In this process, the ions of the metallic contaminants in the wastewater are selectively removed from solution by surface-active resins, which are periodically regenerated by a strong acid to remove the accumulated heavy metal ions and to restore the attraction activity of the resins. The ion exchange process would consistently reduce arsenic, cadmium, and lead concentrations to the required effluent quality levels.
Based on the above information, the sulfide precipitation process was selected to reduce arsenic, cadmium, and lead concentrations to 0.02 mg/L, and the ion exchange process was selected to reduce residual concentrations to the proposed discharge limit of 0.01 mg/L.

### 5. Mercury

Consistently reducing the concentration of mercury from 0.02 mg/L to 0.001 mg/L (1 ppb) would be very difficult to achieve using any treatment process or processes, and difficult to accurately measure by laboratory analysis on a consistent basis. The ion exchange process should be able to consistently reduce mercury concentrations to 0.005 mg/L, and reduce mercury concentrations to 0.001 mg/L sporadically.
To ensure that the required effluent concentration would be met consistently, complete mechanical desalination (evaporation) of the produced water stream would be necessary. This process would generate a pure distillate that would be free of any dissolved ions. It would

have relatively very high capital and operating (energy) costs, and large quantities of solid residuals would be generated by the dissolved solids-reject stream. Since residual methanol and amines would become volatile and carry over with the distillate stream, a post-treatment chemical oxidation step would be required before the distillate could be discharged.
The evaporation process was selected as a component for the treatment system options because, despite its economic and operational drawbacks, it is the only process commercially available that would satisfy the proposed discharge concentration limit for mercury.

### 6. NORM

Total radium radioactivity would have to be reduced 95% (0.02 to 0.001 Bq/g) to satisfy the proposed effluent limit. For Lead 210, radioactivity levels would have to be reduced 75% (0.02 to 0.005 Bq/g). Experience has shown that NORM radioactivity has been reduced by 95 to 99% in similar wastewaters using alkaline precipitation processes.

### 7. Residuals Handling and pH Requirements

Sludges generated in the oil/water separator, DAF, and clarifier would be collected in a holding tank and dewatered by centrifuge, filter press, or vacuum filter. Each is a proven technology with comparable performance characteristics, equipment costs, and operating costs. For this study, filter press treatment was selected for sludge dewatering. The centrifugation process was selected for treating the high-volume residual-reject stream generated by the evaporation process, because it was considered to be better suited for continuous, high flow rate operations than filter presses or vacuum filters. If the pH of the wastewater stream does not meet the proposed 6 to 9 range after the other chosen treatment stages have occurred, it can be adjusted to this range with the addition of a post-neutralization step.

## B. Treatment System Options

The treatment processes that were considered the best for satisfying the process design basis were designed into three treatment system options, which are presented below. Each treatment option was designed to generate different levels of effluent quality and capital cost.

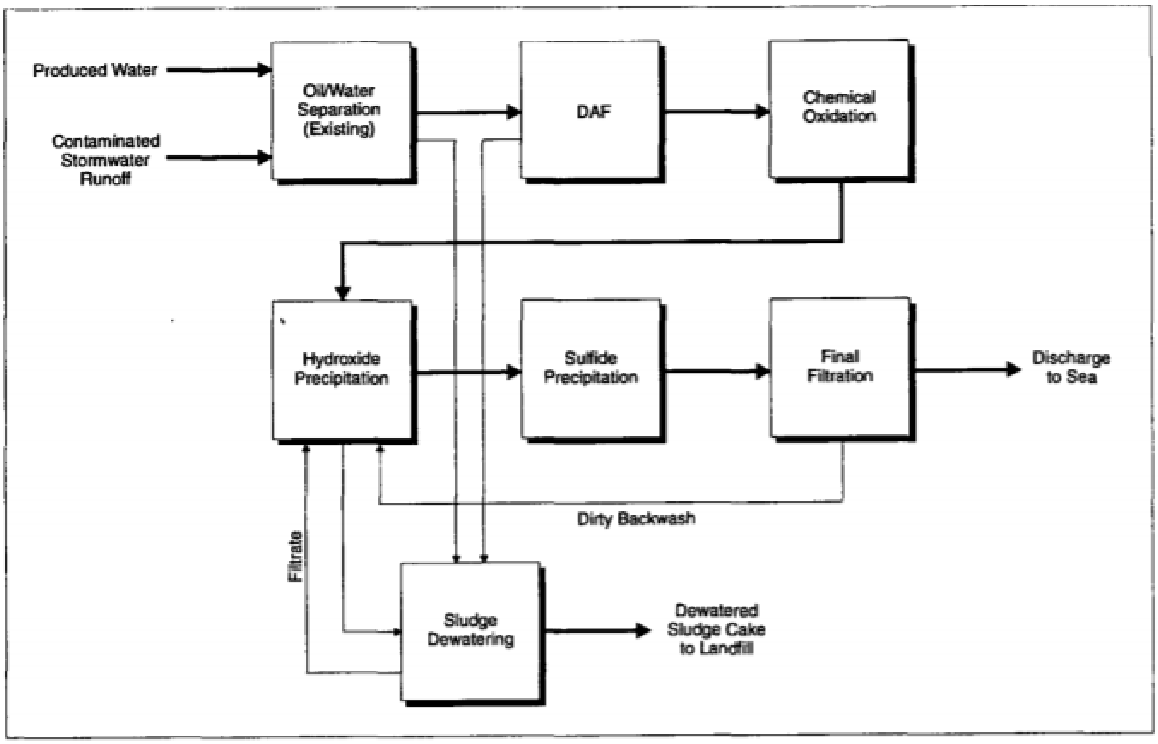
- **Option 1 (OAF-Chemical Oxidation-Metals Precipitation)**

As picture 42 shows, the facility's wastewater stream, consisting of PW and contaminated water, flows by gravity through the existing oil/water separator to remove free floating oils and solids and then is pumped to the DAF system, where residual oils are reduced to 10 mg/L, and suspended solids concentrations are reduced to 20 mg/L.
The wastewater stream then flows by gravity to the chemical oxidation system, which consists of a multi-chambered reactor tank fitted with UV lamps and an oxidant feed system that may include an ozonator or a hydrogen peroxide feed pump and storage tank. The concentrations of the hydrocarbons, mainly methanol and amines, are reduced by 90%.
The effluent from the chemical oxidation process flows by gravity to the metal hydroxide precipitation system, which consists of pH adjustment/coagulation, flocculation and clarification steps. Hydrated lime is blended with the wastewater to increase pH and cause metal hydroxide precipitates to form. These precipitates are flocculated into larger particles with the aid of a polyelectrolyte and are removed from solution through solids-contact

clarification. The precipitates are concentrated at the bottom of the clarifier in a sludge, which is pumped to the sludge handling area for dewatering and disposal. The clarifier effluent has a suspended solids concentration of approximately 30 mg/L.

The pH of the clarified wastewater is readjusted toward neutral with the addition of acid, and the neutralized wastewater flows by gravity to the sulfide precipitation system. A sulfide reagent and polyelectrolyte are blended with the wastewater in a reactor tank to further reduce residual metal concentrations through the formation of metal sulfide precipitates, which are less soluble than metal hydroxides.

The effluent from the sulfide precipitation process then flows into the multimedia deep bed filters, which are used to remove metal sulfide precipitates, residual metal hydroxide precipitates and any remaining residual suspended solids and free-floating oils. The wastewater flows down through the filter media where the particulates collect in the media voids. The filtered effluent is pumped to sea for final discharge. Periodically, the filters are backwashed to remove accumulated particles. The dirty backwash water is collected in a surge tank and pumped to the clarifier at a controlled rate. The suspended solids concentration in the filtered effluent is approximately 5 mg/L.




**Picture 42. Treatment Option 1 (DAF/Chemical Oxidation/Metals Precipitation) [17]**

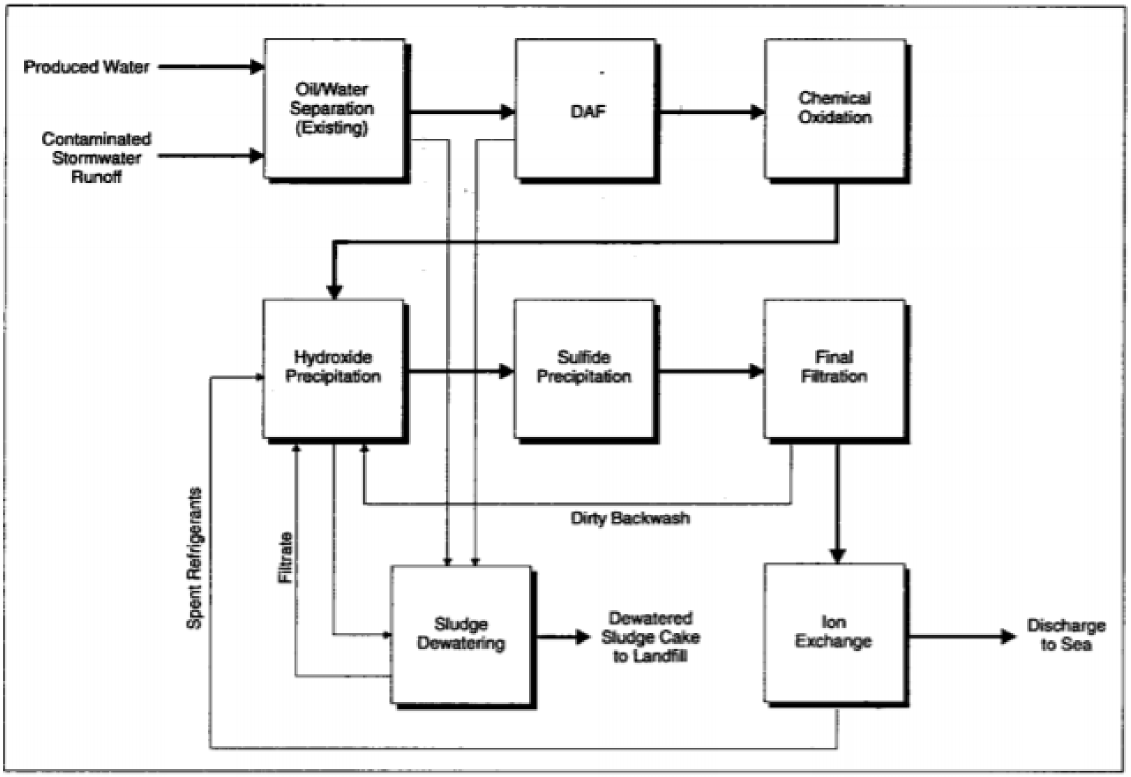
The sludges generated during the oil/water separation, DAF, and clarification processes are collected in the sludge holding tank and blended. Periodically, the tank's contents are pumped to the filter press and the sludge is dewatered. The filtrate is discharged to the clarifier, and the dewatered filter cake is disposed of in an approved landfill.

This treatment system option should satisfy all the requirements of the process design basis, with the exceptions of arsenic, cadmium, mercury, and lead, all of which would have treated effluent concentrations of 0.02 mg/L, rather than the required 0.01 mg/L. The estimated budget capital cost for this treatment system option is approximately $14 million.

- **Option 2 (Option 1 + Ion Exchange)**

This treatment option has all the treatment processes provided in Option 1 and an additional ion exchange process for further reducing arsenic, cadmium, mercury and lead concentrations.

As picture 43 shows, the filtered effluent from the deep bed filters is pumped to the ion exchange system's activated carbon absorbers, where residual soluble organics are removed from solution. This treatment step is necessary to protect the ion exchange resins from organic fouling. The activated carbon beds are periodically backwashed to remove a buildup of suspended solids, with the dirty backwash water discharged to the clarifier. Over time, the activated carbon will become loaded with adsorbed organics and will require replacement or regeneration, which will be provided as a service by the activated carbon suppliers.



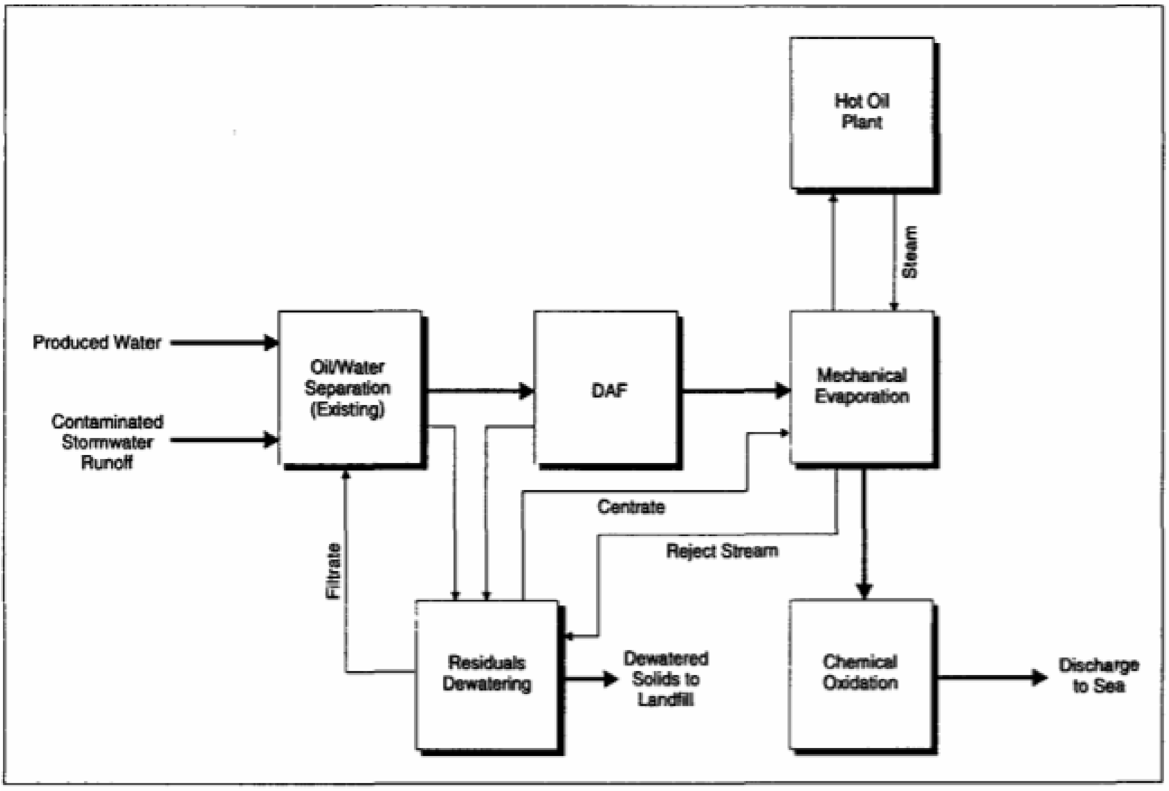

**Picture 43. Treatment Option 2 (DAF/Chemical Oxidation/Metals Precipitation/Ion Exchange) [17]**

After carbon adsorption treatment, the pH of the wastewater stream is readjusted to the acidic range and the wastewater is then pumped into the ion exchange units, which selectively remove the residual heavy metal ions remaining in solution. Periodically, the resin beds are regenerated with acid to remove the metal ions that have accumulated on the surface of the resins. Spent regenerant solutions are discharged to the clarifier. After ion exchange, the pH of the treated effluent is readjusted to the required range before final discharge to sea.

This treatment option should consistently satisfy the discharge requirements for all the contaminants except mercury, the 0.001 mg/L (1 ppb) discharge limit for mercury could be met using this option, but not on a consistent basis. The estimated budget capital cost for this treatment system option is approximately $15 million.

- **Option 3 (OAF/Mechanical Evaporation! Chemical Oxidation)**

As picture 44 shows, the wastewater stream for this method is treated in the oil/water separator and DAF unit and the resultant sludges are handled as described in Option 1. The wastewater is then conditioned with chemical reagents and pumped to a mechanical evaporation system. As water is evaporated from the wastewater stream in the evaporator, a reject stream consisting of crystallized salts and residual suspended solids and oils is formed. The distilled water stream is condensed by heat exchange with the influent stream. The heat required to generate the steam for the evaporation process is supplied by a hot oil plant.




**Picture 44. Treatment Option 3 (DAF/Mechanical/Chemical Oxidation) [17]**

Because the condensed distillate will also contain residual organics that will have been evaporated with the water, the distillate is discharged to the chemical oxidation system (as described in Opt. 1) to reduce methanol and amine concentrations to the proposed discharge limits before the distillate is discharged to sea. The evaporator reject stream, which contains all the dissolved solids that were in the wastewater, is discharged to the residuals handling area to undergo dewatering by centrifugation. The dewatered solids are disposed of in an appropriate landfill and the rest is returned to the evaporator for retreatment. The effluent from Option 3 will consistently satisfy all the proposed discharge permit requirements and the estimated budget capital cost for this treatment system option is approximately $27 million.

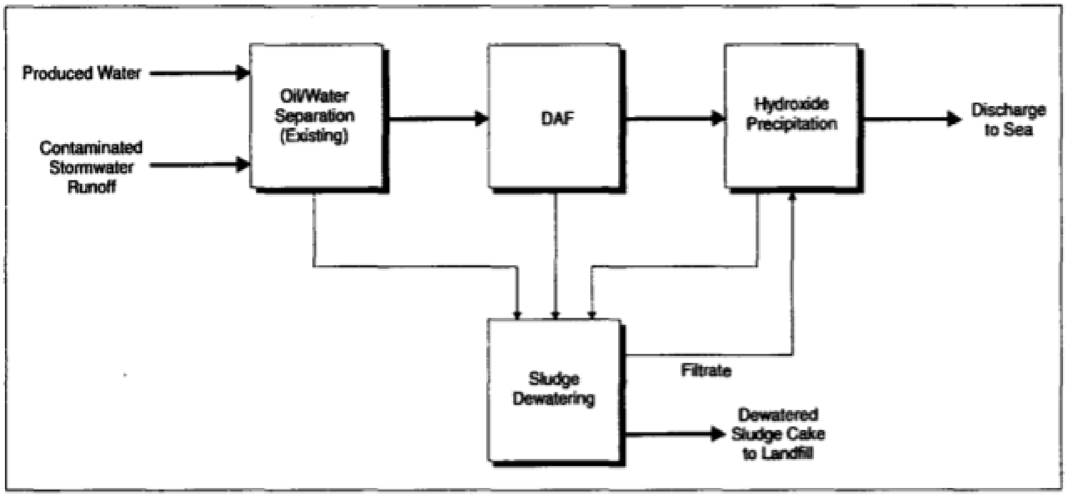
### C. Conclusions

Based on the information in the previous sections, the following conclusions are obtained:

- ✓ Option 1 has the lowest budget capital cost ($14 million), but does not quite satisfy all proposed discharge permit requirements.
- ✓ Option 2 has a slightly higher budget capital cost ($15 million). Although it produces a higher effluent quality, it is not expected to satisfy all the proposed discharge permit requirements consistently.
- ✓ Option 3 has a significantly higher budget capital cost ($27 million), and is expected to generate large volumes of solids requiring off-site disposal, but will ensure compliance with the proposed discharge permit requirements.

During a meeting with regulatory authorities, facility representatives discussed all three options and posed the following arguments against the proposed permit-to-discharge:

- ✓ Implementing Option 3 would have an adverse impact on the public living near the facility because of the heavy truck traffic that would be required to transport the large volumes of dewatered solids to landfill. In addition, it would be very difficult to find an approved landfill that could accept such large quantities of waste.
- ✓ A mechanical evaporation system and hot oil plant would also detract from the scenic beauty of the surrounding area.
- ✓ The large incremental capital cost of going from Opt. 1 to 3 does not justify the slight incremental improvement in the effluent water quality.
- ✓ The authorities agreed with the facility representatives' arguments and stated that they would relax the proposed discharge limits, requiring that only hydroxide precipitation treatment would be needed to satisfy future treatment requirements of heavy metals.
- ✓ Based on these requirements, a new treatment option was developed that included oil/ water separation, DAF, hydroxide precipitation and pH adjustment (pic. 45). After examining the results of the study, facility management chose to pursue source minimization rather than chemical oxidation treatment to reduce methanol and amine concentrations. The initial estimated budget capital cost for this option is $8 million. [17]




**Picture 45. Revised Treatment Option [17]**

# VII. Case study 2.

## A. **Case study**: *Warm lime softening* (***WLS***) optimization reaps substantial savings. [51]

One of the largest SAGD operators in Alberta was facing challenges related to the carryover of oil and solids from the WLS into the plant's water stream. Mostly resulting from poor performance of *Lime Softener Filters* ***(LSF)*** and *Ion Exchange* vessels ***(IX**),* the operator was experiencing a shortened resin life, increased maintenance and cleaning costs and a decrease in production, reducing the plant's overall efficiency and profitability.

Turning to SUEZ's proven technological solutions, the operator installed SUEZ's water flocculent and coagulant polymer products Klaraid and Novus. Partnering with SUEZ enabled the operator to see significant improvement in its filter performance operations:

- 95 % reduction in turbidity
- 90 % reduction in total suspended solids (TSS) and
- 65 % reduction in oil and grease from the resulting water stream.

The benefits and resource savings from the new treatment program are plentiful. As a result of the introduction of the new polymer water treatment program, the operator was able to:

- reduce LSF cleanings from two to one per year,
- reduce LSF Backwash screen cleanings from four to three per year,
- reduce IX Resin cleanings from four to three per year and
- extend resin life by 25 %.

With a projected savings of nearly $13 million per year, the operator is looking to transform the way it operates, while also reducing its impact on the environment. [51]

## **B. Case study**: Alberta oil producers reduce water and carbon footprints. [51]

In 2008, Connacher Oil and Gas Ltd selected SUEZ's produced water evaporation technologies to dramatically reduce the amount of water used at its Algar Oil Sands Project in Alberta, Canada and to help protect regional water resources. The system can recycle up to 98% of the water recovered from the SAGD bitumen extraction process and eliminate all wastewater discharge to the environment.

SUEZ utilized its experience, research and development efforts in produced water evaporators and ZLD systems to incorporate a new energy-saving two-stage evaporation process for the Algar project. The new design, SUEZ's second evaporator project with Connacher, reduces electricity demand by as much as 25% and significantly decreases plant size compared to previous configurations. The process also incorporated standard drum boilers to produce steam, which can reduce natural gas consumption by 5% over conventional once-through steam generators. With water savings potentially reaching 73 million gallons (276,000 cubic meters) per year, the system will play a significant role in reducing the carbon and water footprints of the Algar Oil Sands Project.

The SAGD process is becoming more widespread in Canada's Alberta Oil Sands as the extraction of deeper bitumen reserves, which are beyond the reach of surface mining equipment, continues to increase. SUEZ's thermal evaporators, crystallizers and dryers are used by six major companies in the oil sands and provide reliable, highly efficient water treatment and recycling for sites that extract as much as 60,000 barrels of bitumen per day. SUEZ's fourth generation modular system offers scalable and cost-effective performance and is currently being evaluated at significantly larger production sites, ranging as high as 200,000 barrels of bitumen per day.

At the Algar Oil Sands site, the produced water evaporator system will be capable of treating up to 1,000 gallons (3.78 cubic meters) of produced water per minute, and will decrease make-up water requirements by more than 200,000 gallons (757 cubic meters) of water per day.

Since nearly all of the water recovered from the extraction process is reused, SUEZ's ZLD system also eliminates water discharge to the environment by an equivalent amount. The robust process helps protect critical steam generators from any upsets in the de-oiling process and is capable of using lower quality, brackish water sources as make-up water. [51]

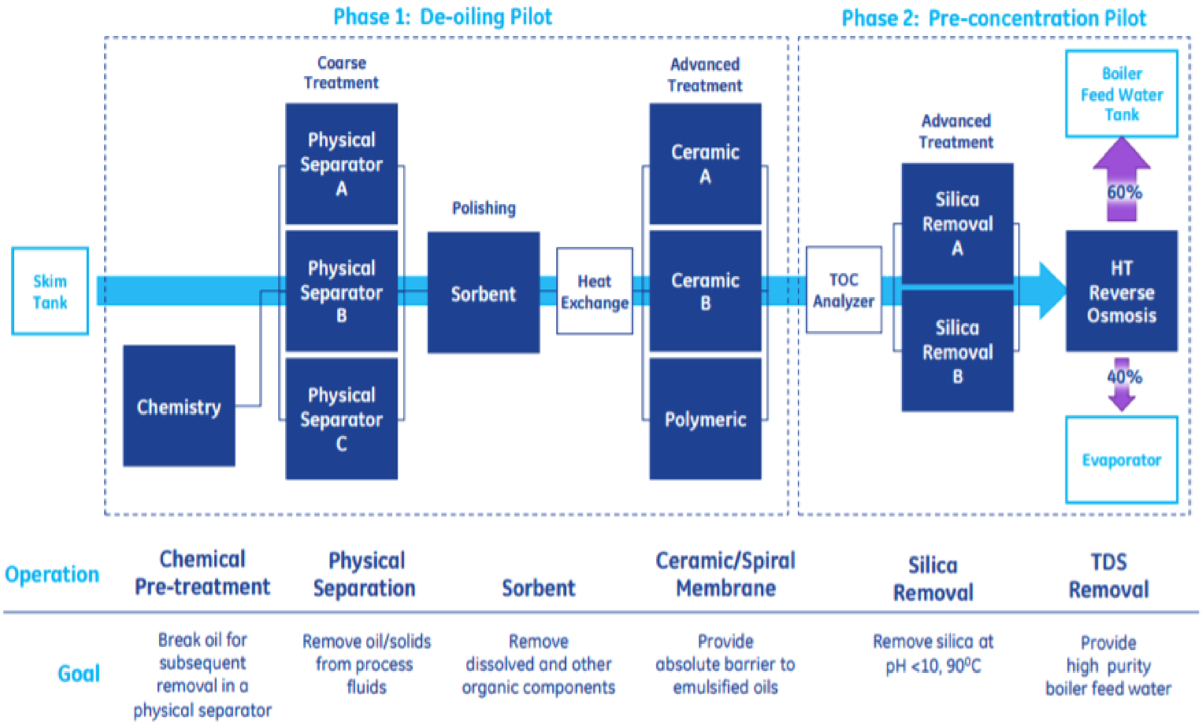
**C.** **Case study.** SAGD pilot program of next generation. [50]

According to the SAGD pilot program of GE Power & Water of Next Generation, the objective goals are distinguished as:

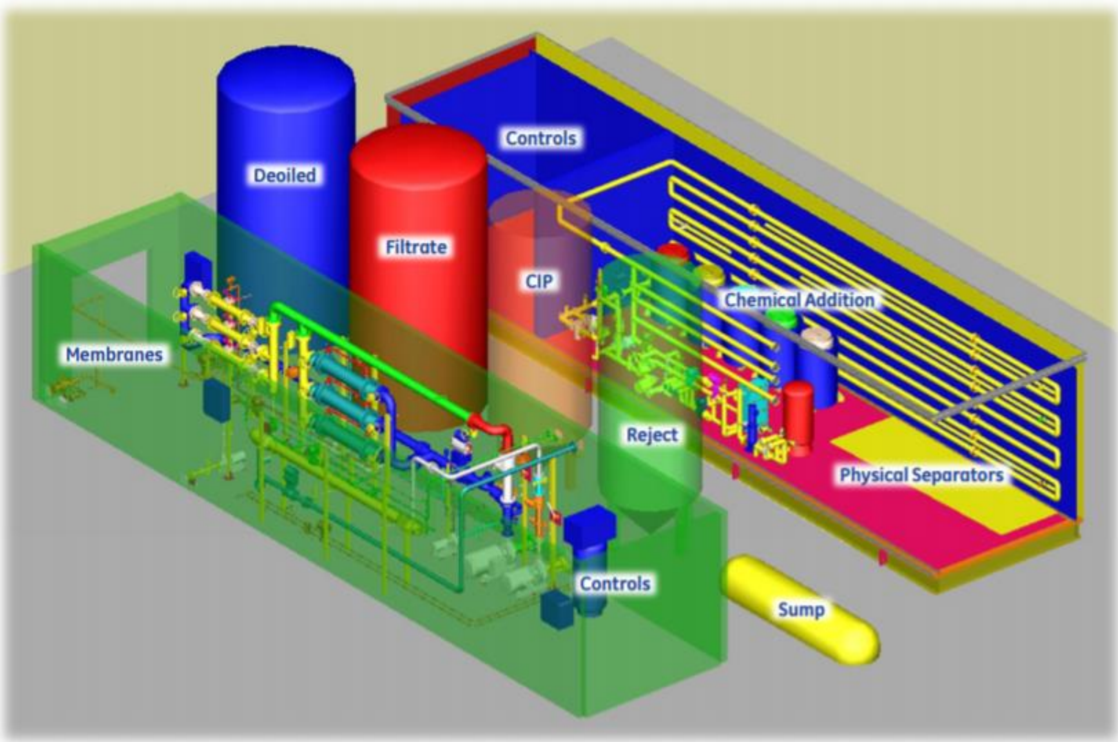
1) **De-oiling field pilot** which aims to
    - deliver treated water with no more than 1ppm oil-in-water at $90^0$C
    - establish optimum system design
    - recovery rate and operating conditions for de-oiling system across a broad range of SAGD produced water inlet conditions
    - determine options available for control and monitoring the efficiency of oil separation to validate total lifecycle cost model and value proposition for existing and next gen. SAGD de-oiling unit operations
    - identify most promising pathways for future technology development

**2)** **Pre-concentration field pilot** which aims to
    - deliver boiler feed water quality and concentrate stream compatible with evaporator treatment at $90^0$C and pH >10
    - design and build robust, high temp/high pH tolerant RO membrane
    - establish optimum system design, recovery rate and operating conditions for pre-concentration system
    - determine options available for control and monitoring the pre-concentration process
    - validate total lifecycle cost model and value proposition for combined de-oiling and pre-concentration system
    - Identify most promising pathways for future technology development

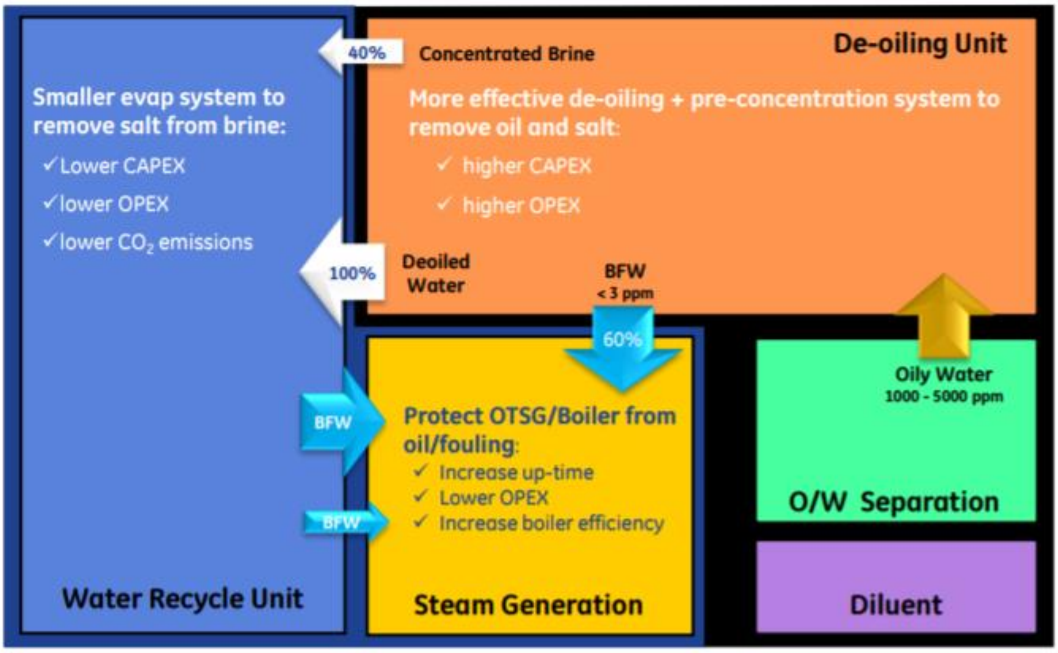
**3)** **Demonstration plant with best technology** which aims to
    - demonstrate the achievement of the above criteria at a scale sufficient to support commercialization
    - validate total lifecycle cost model and value proposition for best combined de-oiling and preconcentration system




**Picture 46. Phase 3-Scale up best performing technologies to 100gpm demo plan. [50]**




**Picture 47. De-oiling pilot layout. [50]**




**Picture 48. Value proportion–Increase plant availability & decrease overall CAPEX/OPEX [50]**

**Direct Benefits:**

- 40% smaller evaporator required
- 26% lower capital cost
- 29% lower annual operating cost
- 30% lower $CO_2$ emissions

**Indirect Benefits:**

- Reduced risk of boiler issues/tube failures – barrier to oil
- Smaller areal footprint
- Improved plant availability - down time costs ~ $2.4M/day

| Conventional Deoiling ($M) | | |
|---|---|---|
| Equip. | CAPEX | OPEX/yr |
| Skim tank | No change | |
| IGF | 6.8 | 2.0 |
| WSF | 4.5 | 0.6 |
| Evaporator | 76.0 | 6.7 |
| Boiler | No change | |
| Total | 87.4 | 9.4 |

| NextGen Deoiling ($M) | | |
|---|---|---|
| Equip. | CAPEX | OPEX/yr |
| Skim tank | No change | |
| Deoiling | 15.4 | 2.1 |
| HT RO | 11.0 | 1.8 |
| Evaporator | 38.0 | 2.7 |
| Boiler | No change | |
| Total | 64.4 | 6.6 |

* Estimates based on 30,000 BOPD SAGD facility

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