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Management of Produced Water from the Oil and Gas Industry: Treatment, Disposal and Beneficial Reuse

THESIS

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Eric Angel Aguirre Hernández

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Acknowledgments

To my parents, for being patient and constant into making me the best version of myself.

To my girlfriend, Mary: for staying with me against all odds, to the end.

To my family and friends, for helping hard times become easier.

Abstract

Produced water represents the largest waste effluent generated in the oil and gas industry. As a wastewater volume which can carry a wide variety of pollutants (such as oil, suspended solids, chemicals, and radioactive matter), a proper management and disposal strategy is required, in order for operators to comply with environmental regulations applicable. In recent years, most of the world has begun efforts to transition into greener energy generation, which has resulted in stricter regulation in terms of waste effluents. As a necessary response, research has arisen to propose, test and assess new treatment technologies that allow operations to comply with effluent limits, especially for volumes that cannot be treated by conventional methods only, due to high salinities, water hardness, or high percentage of dissolved organics. Additionally, in order to reduce the need of disposal (traditionally through disposal wells or discharge into the ocean), several water recycling methods have been proposed, such as crop irrigation, aquifer recharge, fluid for hydraulic fracturing, among others. A review of available research on novel technologies and case evaluations showed that it is not possible to identify one management method as the most efficient neither in terms of cost, energy consumption or efficiency, because technology effectiveness and the feasibility of their implementation depends on water composition, site location and logistics associated, among many other factors; additionally, most recent methods proposed have only been proven at laboratory scale with few samples and would require real-scale pilot tests in order to further prove their feasibility. Another issue is the need for new regulation concerning water recycling, as limits in terms of pollutants present only in produced water do not exist for matters like soil pollution, livestock watering, or even for discharges into surface water, leading to higher risks to the environment and human health than disposal, as well as requiring more expensive treatment. In most cases, recycle within the oil and gas industry results more significant to reduce water scarcity than its possible use in other sectors; however, for specific operations, a recycle option may turn more cost effective even than traditional disposal. This research and discussion helped conclude that future research must focus in evaluating proposed methods in real scale experiments, find their optimal configurations, create efficient methods to characterize water composition, support the updating of environmental regulation, and correctly assess the long-term effects of treated produced water disposition and use on different sectors to allow the development of these practices as a response to more strict limits and environmental damage.

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List of Abbreviations

Abbreviation	Meaning
AOP	Advanced Oxidation Process
BAT	Best Available Technology
BCT	Best Conventional Technology
BOD	Biochemical Oxygen Demand
BPT	Best Practicable Technology
Bq	Becquerel
BTEX	Benzene, Toluene, Ethylbenzene, Xylene
CFU	Compact Flotation Unit
COD	Chemical Oxygen Demand
CPI	Corrugated Plate Interceptors
DGF	Dissolved Gas Flotation
DOWS	Downhole Oil/Water Separation
EPA	Environmental Protection Agency
IGF	Induced Gas Flotation
MF	Microfiltration
MVC	Mechanical Vapor Compression
NF	Nanofiltration
NORM	Naturally Occurring Radioactive Matter
NSPS	New Source Performance Standards
PAH	Polycyclic Aromatic Hydrocarbons
PW	Produced Water
RO	Reverse Osmosis
TOC	Total Organic Content
TDS	Total Dissolved Solids
UF	Ultrafiltration

Chapter 1

Introduction

Every year, world population increases continuously and with it, the demand for energy around the world does too. Up until now, the most part of this demand is satisfied through the exploitation of fossil fuels, mainly hydrocarbon oil and gas. Hydrocarbons are a non-renewable resource essential not only energy generation, but also the creation of different materials essential in every area of human life, including plastics, fuels, chemical products, and all their possible derivatives. However, hydrocarbon extraction requires a number of complicated operations in order to locate them, access them, extract them, store them, and transport them in order to be exploited or processed; overall, one way the oil and gas supply chain can be split is in the following operations: exploration, drilling, production, distribution, refining and commercialization to end users. Each of these steps involves techno-economical assessments in order to allow for profit, but also environmental and health related risks which must be managed carefully in order to comply with regulations applicable and avoiding irreparable damage to living beings and the environment, this due to the high level of toxicity of hydrocarbon compounds and other substances extracted with them. As mentioned, environmental damage can be caused at almost every step of hydrocarbon industry in the form of leaks, spills, and waste effluents; leaks and spills are accidental but significant risks for which every piece of equipment and facility must be constantly monitored and maintained. Waste effluents, however, are constant volumes of different materials with little to no economic value such as drilling cuttings, drilling and completion fluids, controlled emissions to the air, sanitary waste from offshore facilities, water required for the cooling of equipment and produced water. Produced water refers to the volume of water extracted at wells along oil or gas from the reservoir and constitutes the largest volume of wastewater generated during hydrocarbon recovery operations (Olajire, 2020) The subsurface is composed by different types of rocks with different properties. Among the grains that compose rocks, pore volumes exist, which are originally filled with water. Hydrocarbons exist only in very specific rock formations where a special sequence of three types of rock are found together; source rocks are those which contain a high percentage of organic matter from their creation, which is degraded along millions of years into hydrocarbons with lower density than water and due to gravitational forces, migrate out of the rocks where they were generated. The second type of rock required for a conventional reservoir to exist are those with high porosity and permeabilities in order to allow for the migration of hydrocarbons into their pores, where they replace water, with only a small portion of unmovable water remaining in the area (called irreducible water). The third type of rock required is one with very low porosity and permeability: a cap rock whose function is to create a trap which keeps hydrocarbons from reaching the surface and escaping to the atmosphere, which allows for the creation of a reservoir. This generation, entrapment and displacement of fluids causes a pressurization of the reservoir, which is the first natural drive that allows for the extraction of hydrocarbons to the surface once a well has been drilled and opened for production, releasing this pressure. As hydrocarbons are extracted, pressure gradually declines and the pore volumes from which hydrocarbons have been removed have water return to fill them. Water saturation continues to increase as hydrocarbon volumes reduce until the point where movable water reaches the well and is extracted to the surface along with target fluids. Although most of the produced water volume comes from naturally occurring underground bodies, it can also include water which is injected into the formation in order to treat wells or help maintain the reservoir pressure in oil fields as a secondary recovery technique. Another possible source for water in the production stream is “flowback water” returning to the surface after hydraulic fracture operations (Ground Water Protection Council, 2019). The percentage of the total volume of produced liquid fluids represented by water is called water cut, which gradually increases during the life of the reservoir. Globally, water to oil ratio is in average 3:1 and continues to increase as fields mature (Reynolds and Kiker, 2003).

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Chapter 2

Produced Water Composition and Environmental Impact

2.1 Produced water composition

2.1.1 Dispersed Oil and Dissolved Organic Compounds

Hydrocarbons can be present in produced water as suspended droplets or dissolved in the aqueous phase and represent the greatest environmental concern when discharged with produced water, because of their toxicity, oxygen demand and their resilience over time in the receiving environment, be it on water or soil bodies.
Organic components that can be found in produced water include suspended oil, organic acids, polycyclic aromatic hydrocarbons, phenols, and volatiles. The toxicity of these compounds is additive, which means that even if individually their toxicity is insignificant, combined they represent a serious risk for the environment. The type of organic matter found in produced water will depend on the type of hydrocarbon and the type of operation to extract it.
Petroleum hydrocarbons represent the highest concern environmentally. The most abundant hydrocarbons in produced water are aromatic hydrocarbons as benzene, toluene, ethylbenzene, xylenes (BTEX), and low molecular weight alkanes, the latter of which are usually found in concentrations much lower than BTEX, mainly because of the higher solubility in water of BTEX and the volatility of low molecular weight alkanes. Polycyclic aromatic hydrocarbons represent the highest risk due to their toxicity and persistence in marine environment. The phase in which these oil particles can be found is key to their management because oil/water separators are efficient in removing suspended oil droplets, but not dissolved organic matter. The volatility of some compounds, such

as BTEX means they are rapidly released from the water steam during stripping and mixing into the ocean. As no treatment procedure is 100% effective, some dissolved oil is still discharged with produced water streams.

2.1.2 Dissolved minerals

Inorganic compounds dissolved into the water due to the extended contact time with the formation include a variety of ions such as sodium, chloride, calcium, magnesium, potassium, sulfates, sulfides, and ammonia. The concentrations of these vary greatly from source to source, and they affect the solubility, salinity, and scale potential of the stream. Sulfides are highly corrosive. They can be generated by the bacterial reduction of sulfates in the anoxic conditions of the formation and are more common in sour gas or oil with high concentrations of sulfur. Hydrogen sulfide and ammonia possess high levels of toxicity, which must be monitored to avoid damage to marine organisms.
Produced water may also contain dissolved metals with extremely variable concentrations in every case, but commonly higher than in seawater. The most common metals present at high concentrations include barium, chromium, copper, iron, lead, nickel, and zinc, but it is possible to find more toxic metals such as mercury and arsenic. Metals can also cause production problems and deposits at discharge sites.
Bacteria in produced water streams can cause clogs or the creation of strong emulsions, as well as hydrogen sulfide as previously mentioned.

2.1.3 Production Chemicals

Chemical compounds used as additives for the optimization of drilling and production processes can be found in extracted water. The type of additives will depend on the specific problems of each operation. The most common functions for which chemicals are necessary include:

- Reduce the risk of corrosion of the equipment (corrosion inhibitors and oxygen removers).
- Control deposits of mineral compounds (crust inhibitors)
- Limit bacterial fouling (biocides)
- Undo water-in-oil or oil-in-water emulsions (emulsion breakers).
- Solid removal (flocculants, coagulants, purifiers)
- Destroy paraffin deposits (solvents)

- For dispersion of asphaltenes.
- Defoamers.
- Clarifiers.
- Coagulants and flocculants to help separation.
- Prevent methane hydrate formation in gas systems.

The group of substances dosed into wells and reservoirs are selected by manufacturers attending to the characteristics and of the site and the fluids of interest. Therefore, the content of additives in produced water will vary from well to well. Environmental problems can occur when toxic additives are used in higher concentrations than necessary. (Neff et al., 2011).

2.1.4 Naturally occurring radioactive material (NORM)

Naturally occurring radioactive materials are originated in the geological formations containing reservoirs, and brought to the surface with produced water, as they dissolve from the formations through their contact with water for millions of years. The most common NORM found are radium 226 and radium 228, which derive from the decay of uranium and thorium which are associated with specific types of rocks, as well as barium. Concentrations of radium 226 and 228 in produced water can vary from the detection limits of 0.3-1.3 [Bq/L] to 16-21 [Bq/L] respectively (Jiménez et al., 2018). These dissolved elements precipitate due to temperature changes when brought to the surface and may accumulate in separation systems as scaling and sludges. Scales can be found normally on the inside of piping and tubing, and the highest scale concentrations of radioactive agents are usually in scales formed at the wellhead piping and production piping near the wellhead, although scale formation is largest overall in water lines connected to separators, heater equipment for treatment and gas dehydrators. The creation of NORM and other scales can be avoided by the use of chemical scale inhibitors. The average scale radium concentration has been estimated to be 17.76 [Bq/g] in the USA, but it can be as high as 14,800 [Bq/g]. (USA Environmental Protection Agency, 2020a) Sludge is composed of solids precipitated as temperature and pressure vary. It is composed mostly of oily material and silica but may contain large amounts of NORM. Conventional drilling generates around 141 cubic meters of NORM sludge every year in the USA, with average concentrations of radium of around 2.775 [Bq/g]. (USA Environmental Protection Agency, 2020a).

Although sludges have lower average concentrations of radioactive matter than scales, they pose a higher risk of exposure due to their higher solubility, which makes their disposal a matter of great concern. The radioactive contamination in produced water has caused countries to place requirements on the amount of radium allowed in discharges.

2.1.5 Produced water composition: average ranges

The following tables show values for different parameters measured and averaged from multiple samples around the world by Costa et al. (2021).

TABLE 2.1: Range of parameters characterization from produced water around the world (Costa et al., 2021).

Parameter	**Oil field**	**Gas field**	**Unit**
Density	1.01–1.14	1.02–1.13	g/cm^3
pH	4.3–10	3.1–8.8	–
Alkalinity	300–380	0–285	mg/L
Conductivity	4,200-58,600	4,200–586,000	$\mu S/cm$
Salinity (NaCl)	0.033–300	n.d.-250	g/L
Chemical Oxygen Demand – COD	1,220–2,660	2,600–120,000	mg/L
Total Suspended Solids – TSS	1.2–1,000	8–5,484	mg/L
Total Dissolved Solids – TDS	100–400,000	2,600–360,000	mg/L
Total Organic Carbon – TOC	0–11,000	67–38,000	mg/L
Total Naphthenic Acids	23.6–88	6.0–56	mg/L
BTEX	0.39–35	0.01–48	mg/L
PAHs	40–3,000	25–2,000	mg/L
Phenols	0.001–10,000	n.d.-1,160	mg/L
Volatile Fatty Acids	2–4900	n.d.	mg/L
Total Organic Acids	0.001–10,000	n.d.	mg/L
Oil and Grease Content	2–565	2.3–60	mg/L
Corrosion inhibitor	0.3–10	2–10	mg/L

TABLE 2.2: Range of average concentration of ions and solids from different produced waters around the world (Costa et al., 2021).

Parameter	**Oil field**	**Gas field**	**Unit**
Ammonium ($NH_4\hat{+}$)	10–300	0–2.74	mg/L
Bicarbonate ($HCO_3^{-)}$	77–3,990	n.d.-4,000	mg/L
Bromide (Br^-)	46–1,200	150–1,149	mg/L
Carbonate (CO_3^{2-})	30–450	20–300	mg/L
Chloride (Cl^-)	80–270,000	1,400–190,000	mg/L
Iodide (I^-)	3–210	n.d.	mg/L
Sulphate (SO_4^{2-})	$< 2 - 1,650$	n.d.-3,663	mg/L
Aluminium (Al)	0.4–410	n.d.-83	mg/L
Arsenic (As)	0.002–11	0.004–151	mg/L
Barium (Ba)	0–850	n.d.-1,740	mg/L
Beryllium (Be)	< 0.001–0.02	*n.d.*	mg/L
Boron (B)	5–95	n.d.-56	mg/L
Cadmium (Cd)	0.005–2	n.d.-1.21	mg/L
Calcium (Ca)	13–25,800	n.d.-25,000	mg/L
Chromium (Cr)	0.02–1.1	n.d.-0.03	mg/L
Copper (Cu)	0.002–1.5	n.d.-5	mg/L
Iron (Fe)	0.1–1,100	n.d.-2,838	mg/L
Lead (Pb)	0.002–8.8	0.2–10.2	mg/L
Lithium (Li)	0.038–64	18.6–235	mg/L
Magnesium (Mg)	8–6,000	0.045–4,300	mg/L
Manganese (Mn)	0.004–175	n.d.-96.5	mg/L
Mercury (Hg)	0.001–26	n.d.	µg/L
Nickel (Ni)	0.02–0.3	n.d.-9.2	mg/L
Palladium (Pd)	0.008–0.88	n.d.	mg/L
Potassium (K)	24–4,300	0.21–5,490	mg/L
Radium (226Ra)	0–1.66	0.65–1.031	Bq/L
Silver (Ag)	0.001–0.15	0.047–7	Bq/L
Sodium (Na)	0-150,000	10.04–204,302	mg/L
Strontium (Sr)	0–6,250	0.03–6,200	mg/L
Titanium (Ti)	0.01–0.7	n.d.-1.1	mg/L
Zinc (Zn)	0.01–35	n.d.-20	mg/L

The values shown in tables 2.1 and 2.2 were derived from multiple samples coming from different wells around the world, and the ranges for concentration obtained vary by some orders of magnitude for most components, which is an indicator of one of the main problems with produced water management: every stream is different, and composition may vary significantly even from well to well in the same reservoir. In further chapters, the challenges associated with these differences will be discussed.

2.2 Environmental concerns related to Produced Water

The discharge of produced water into the environment can have different possible impacts depending on the place it takes place in and its characteristics, and on the concentration of the different components found on it, some of which can pose an important threat to living organisms in aquatic and land environments. Discharges to small bodies or streams of water certainly will have more impact than those made in the ocean due to a larger dilution capacity.

The actual impact of the discharge will depend on parameters such as the concentration and chemical properties of its constituents, its pH, temperature, and the metabolism, reproductive state and feeding behavior of local organisms. The impact of water discharges on such organisms will depend on their exposure to the concentration of chemicals introduced to the area, which will vary depending on factors such as the dilution capacity of the environment, precipitation, volatilization of hydrocarbons, reactions with other chemical compounds previously present in the receiving environment, adsorption onto particles and the biodegradation of organic chemicals. (Pitre, 1984).

The salinity of the discharged water is an important parameter. Elevated concentrations of sodium can cause deficiencies in the absorption of other cations by plant roots, as well as poor soil structures and the inhibition of water infiltration in the soil. Ions like ammonium can result in toxicity and/or stimulatory responses from local biota (Jiménez et al., 2018).

Radioactive trace elements when in high concentrations may remain in the soil after water has been flushed. Many of these elements are phytotoxic and radium-bearing scales and sludge discarded represent a risk for human health and the ecosystem.

Human health exposure related to radiation include direct gamma radiation, inhalation of contaminated dust, ingestion of contaminated water or food, among other exposures. As NORM contamination was not properly recognized in the past, disposal may have resulted in contamination near sites that has not been correctly characterized to the date (USA Environmental Protection Agency, 2020b).

However, the greatest environmental concern related to produced water is definitely its hydrocarbon content. Most countries with an important oil and gas industry have created regulatory frameworks to define limits for the total hydrocarbon concentration in water that is meant to be discharged into the ocean, or for any other allowed end-uses,

although different countries may have different methods to measure this content. For example, in the U.S., total oil and grease is defined as all materials extracted with n-hexane, not evaporable at 70°C and quantified by infrared or gravimetric analysis. In OSPAR countries, total dispersed oil is the concentration of materials extractable with n-pentane, quantifiable by gas chromatography or flame ionization detection. The methods applied in both of these regulatory procedures do not measure quantitatively low molecular weight aromatic hydrocarbons, such as BTEX, which are important contributors to the toxicity of produced water. (Neff et al., 2011).
A treated produced water discharge typically contains dispersed oil (10-100 [mg/L]), dissolved gases, suspended particles, inorganic salts, organic acids, aromatic hydrocarbons, ketones, phenol/alkylphenols, heavy metals, and NORM.

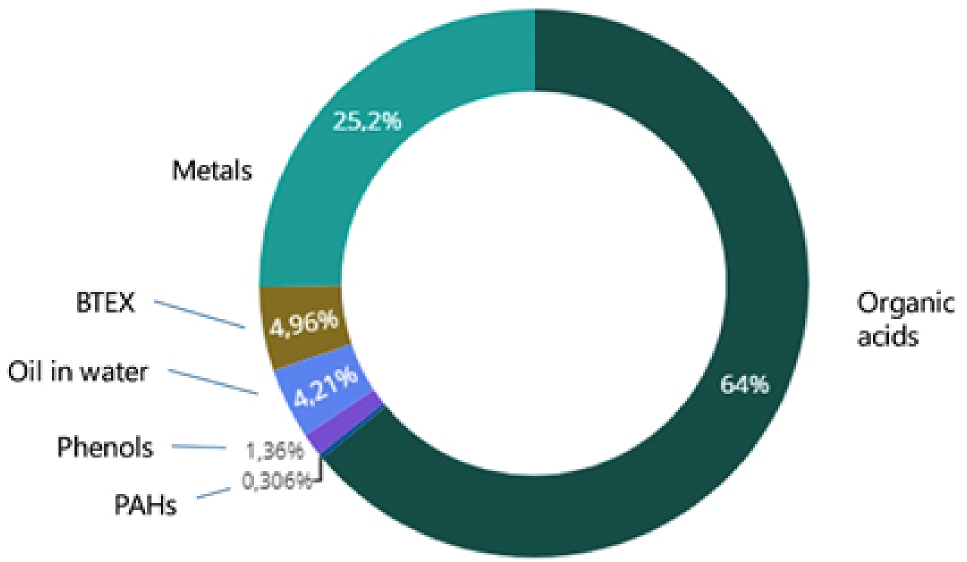

FIGURE 2.1: Percentage of naturally occurring substances contained in produced water discharges in the Norwegian offshore production platforms in 2019. (Beyer et al., 2020)

Produced water will disperse and dilute in the body of water depending on its composition, flow rate, depth, direction and speed, sea current, tides, wind, differences in temperature, salinity, density, buoyancy of the plume, among many others. Even with dispersion, pollutant volumes (especially organic content) might cause concentrations of environmental concern after some time near the discharging platforms, which may cause acute effects on species living in the zone, and effects have been observed in distances as far as 10 km from the nearest discharge, even when pollutant limits by regulation have been complied with mainly due to presence of polycyclic-aromatic hydrocarbons (Beyer et al., 2020).
The degree of effects will depend on different factors but can definitely be reduced by a

complete characterization and the application of the required treatment methods.

2.3 Regulations concerning produced water around the world

Petroleum industry is present in several countries, each with their own politic, economic and cultural differences. Depending on the geographic location of a hydrocarbon reservoir, the government bodies that oversee the operations allowed within their authority are completely different.

Emissions and discharges are two of the most important concerns looked upon by regulatory agencies in order to limit and monitor the impacts that the existence of different types of industry cause in their territory; this means that for every area, operators must carefully investigate about the limits applicable in order to comply, avoiding sanctions, and causing damage to the environment and human health. This section shows some of the limits applied in terms of discharges around the world and associated considerations.

2.3.1 United States of America

In USA territory, environmental issues are controlled by the United States Environmental Protection Agency (EPA). EPA has issued a set of Effluent Guidelines, which are the national regulatory standards for wastewater discharged to surface waters and sewage treatment plants for different industrial categories. For the Oil and Gas extraction industry, EPA indicates that most of the wastewater is disposed by underground injection (regulated by their Safe Drinking Water Act), although injection limits are being reached and new approaches need to be taken. Treatment and renewal for the reutilization of produced water is a matter of investigation, specially to supply areas where water turns scarce such as for the irrigation of crops. Other end uses include enhanced oil recovery and aquifer recharging, as well as managed by evaporation ponds or seepage pits on site. (USA Environmental Protection Agency, 2020a)

Discharge to surface, navigable waters is not allowed in general from any on-land or coastal facilities, unless for specific cases only under a National Pollutant Discharge Elimination System (NPDES) permit, which contains limits for the discharge and monitoring and reporting requirements to ensure that the discharge does not pose a threat to water quality and human health, following regulations stated in the Clean Water Act. (USA Environmental Protection Agency, 2020b)

Offshore facilities can discharge directly into the sea achieving a set of effluent limitations which regulates the maximum daily and monthly average concentration of oil and grease in streams discharged into surface waters. This concentration is measured by the average of four grab samples collected over a 24-hour period and analyzed separately. These limitations are set under specific limitation criteria based on the Best Practicable Technology (BPT), Best Available Technology economically achievable (BAT) and Best Conventional Technology for pollutant control (BCT) for existing operators, as well as values for New Source Performance Standards (NSPS) for new operations; the criteria that each operator must achieve is determined by the type of discharger and the class of pollutant discharged. Such limits are displayed in Table 2.3 (USA National Archives and Records Administration, 2021)

Table 2.3: Effluent Guidelines for oil and grease content in produced water discharges from offshore sources under different levels of control. (Data from USA National Archives and Records Administration (2021))

Guideline Level of Control	**Daily maximum Concentration [mg/L]**	**Average concentration limit over 30 consecutive days [mg/L]**
BPT	72	48
BAT/NSPS	42	29
BCT	72	48

However, upcoming legislation in virtue of cleaner energy production might cause regulation for oil and gas waste to tighten in the close future, as a report by Rice University's Baker Institute for Public Policy (2021) indicates. "The Climate Leadership and Environmental Action for our Nation's Future Act (CLEAN Future Act) seeks to transform the United States into a 100% clean economy by not later than 2050". Among the measures considered in the Act, section 625 indicates that the EPA must "determine whether drilling fluids, produced waters, and other wastes associated with the exploration, development, or production of crude oil, natural gas, or geothermal energy meet the criteria promulgated under this section for the identification or listing of hazardous waste" and promulgate regulations for the new measures required to manage such hazardous waste. (Congressional Bills 117th Congress, U.S. Government, 2021) This classification would change the way in which operators manage their production by becoming large generators of hazardous waste, obtaining cradle-to-grave waste management obligations and additional regulatory structures. Collins mentions that current saltwater disposal facilities cost from $0.50 to 1.00$ per barrel of "non-hazardous waste" water, whereas the type of facility required for the management of hazardous waste would increase the price to over ranges from $7.50to10.50$ dollars per barrel which would probably result in a drastic oil price rise. This transition to clean-energy oriented legislation over the world accentuates the importance of creating more efficient water treatment and recycling end-uses opposed to discharge or underground disposal. Hand to hand cooperation between research workers and agencies responsible for the currently underdeveloped regulatory frameworks surrounding alternative uses of produced water are imperative in creating an environment that facilitates a management of produced water oriented into the protection of the environment and human health.

2.3.2 OSPAR Countries

OSPAR is the commission through which 15 governments and the European Union cooperate to protect the marine environment of the North-East Atlantic, which include Belgium, Finland, Denmark, France, Germany, Iceland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland, and the United Kingdom.
In the matter of produced water, OSPAR indicates that Contracting Parties have made efforts by applying BAT (Best Available Technology) and BEP (Best Environmental Practices) to meet a performance standard for dispersed oil of a maximum of 30 [mg/L], following OSPAR Recommendation 2001/1, last amended on 2011/8 (previously the value was 40[mg/L]), while following OSPAR Recommendation 2012/5 for the management of environmental risks related to added and natural chemicals in produced water discharges. The total oil amount can be calculated by adding BTEX content to the dispersed oil content. Under Recommendation 2012/5, OSPAR members are required to conduct environmental assessments on all produced water discharges from offshore installations which include data collection of the stream and its components, hazard assessment, exposure assessment, risk characterization, risk management and monitoring of the impact of any discharges, as well as submit reports to the OSPAR every four years. (OSPAR Commission, 2011).

2.3.3 Mexico

Regulation in Mexico concerning wastewater from oil and gas industry is overseen by multiple government agencies. The National Commission of Water (CONAGUA), the Federal Authority of Environmental Protection (PROFEPA), the Navy Secretary (SEMAR), and most importantly, the Secretary of Environment and Natural Resources (SEMARNAT) have all their own part to play into the protection of national waters and environmental protection, which leads to multiple laws, technical norms and rules that must be followed by the interested parties. Overall, the most important parameters to determine the possibility of a discharge to Mexican waters depends on the maximum limits for the concentration of pollutants and the hydrocarbon content. SEMARNAT, through the Official Mexican Norm 143 (NOM-143-SEMARNAT-2003) establishes the maximum allowable concentration of hydrocarbons in a discharge to the ocean is of 40 [mg/L], and the maximum total dissolved solids (TDS) must not exceed 32000 [mg/L]. Also, it is established that no discharge can surpass a temperature of 40 [°C]. Specific limits for heavy metals are also specified.

In the case of disposal wells for underground disposal, law specifies several technical parameters for the protection of underground aquifers, such as making sure that the whole well is cemented until the receiving formation, constant monitoring of well hermeticity, the existence of an impermeable layer over the receiving formation to protect overlaying aquifers, and pressure monitoring to avoid fracturing.

2.3.4 Regulation in other countries

In general, all countries with important oil and gas industry economical shares have taken on the task of creating adequate regulation in order to limit discharges into surface water bodies. Table 2.4 shows the limits established in several countries to summarize and give insight on how regulatory framework applicable to every operation changes entirely the level of treatment required in order to allow production of hydrocarbons to continue depending on the geographical location of the operation.

Table 2.4: Oil and grease concentration limits around the world (Costa et al., 2021)

Region	**Limit[mg/L]**	
	Diary	**Monthly**
Canada	44	30
Argentina	–	15
Brazil	42	29
China	70	50
Indonesia	25 (onshore)	50 (offshore)
Australia	50	30

Chapter 3

Produced Water Management

3.1 Produced Water Treatment Methods

Mostly, produced water characterization focuses mainly on total dissolved organic constituents which represent the heaviest environmental concern overall, where dissolved solid characterization commonly looks for concentration of specific components considered of high importance. Methods for other certain chemicals that are not required to be monitored may not exist currently. Additionally, water with very high salinities prove more difficult to characterize because analytical methods commonly do not work accurately for them.
Most of produced water have high salinities, where TDS range from 3,000 [mg/L] to over 300,000 [mg/L] (Ground Water Protection Council, 2019). Water with very high salinity is difficult to treat and results in a high amount of waste product that requires its own disposal strategy.
However, a thorough characterization of produced water is very important for the design of treatment strategies, especially when discharge into the sea or reuse for beneficial purposes is planned. On the contrary, if the produced water will be injected into a disposal well or the same formation, little to no treatment results necessary.
The main treatment objectives are to remove free phase oil which is the main regulatory constraint to meet discharge or injection criteria, and large solids to protect the injection equipment and avoid formation pores to be blocked. Treatment refers to multiple physical, chemical, and biological methods which are used separately or combined.

The following are the objectives pursued by the treatment of produced water:

- Removal of dispersed oil and grease,

- Removal of dissolved organics,
- Removal of suspended particles and sand,
- Dissolved gas removal, which includes hydrocarbon gases, carbon dioxide and hydrogen sulfide,
- Removal of dissolved salts (desalination),
- Reduce water hardness,
- Remove naturally occurring radioactive matter.

Treatment methods can be divided into three levels according to their complexity and their ability to remove more specialized pollutants from the stream to comply with regulations:

- Primary Treatment: Comprehends physical treatment processes which allow the elimination of solid particles and hydrocarbon from produced water. The main mechanism used at this step is gravity separation, which includes separators, hydrocyclones for desanding and deoiling, where flocculants and coagulants can be used to facilitate the coalescence of particles.
- Secondary treatment: Focused on removing dissolved pollutants through the combined use of various methods such as flotation, membrane filtration, and biological processes.
- Tertiary treatment: Also called "water polishing" refers to additional steps to further reduce organic content, turbidity, metals, and pathogens. Techniques developed for these ends include oxidation and degradation-based processes through chemical treatment, as well as Nanofiltration and Reverse Osmosis.

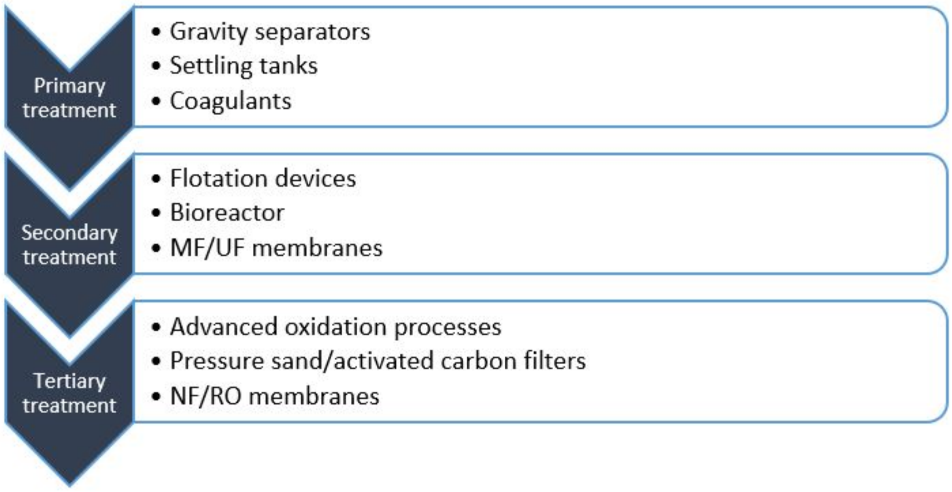

FIGURE 3.1: Treatment processes for produced water from oil and gas operations (Olajire, 2020).

3.1.1 Gravity Separation

Gravity forces can be used in order to separate oil droplets from a continuous water phase; as oil is less dense than the volume of water they displace, a buoyancy effect is exerted over them, causing oil dispersed droplets to flow up and, eventually, form a free phase separate from water. Gas, if present, will follow the same effect and float up to the top part of the vessel.

The effectiveness of this gravity separation depends on the composition of the oil in produced water: density, viscosity, temperature, turbulence, droplet sizes, etc. Usually, in the oilfield, this separation is performed by methods of a separator tank, whose design varies depending on the number of phases to be separated (water, oil and/or gas), their characteristics, and their volumes.

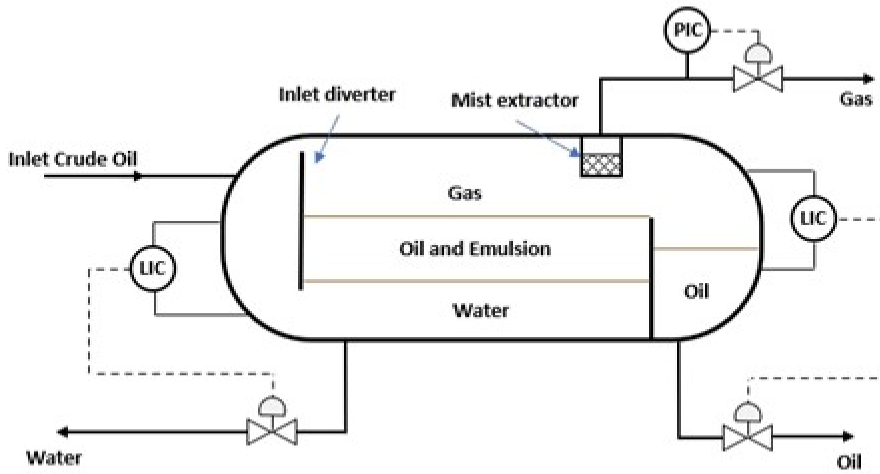

FIGURE 3.2: Basic diagram of a horizontal 3-phase separator

Basically, gravitational separation depends mostly on the residence time inside the vessel, which allows for the separation of the phases. However, several methods can be used in a vessel to facilitate and improve separation, including:

3.1.1.1 Corrugated Plate Interceptors (CPI):

In a CPI unit, the water stream flows through corrugated parallel plates to help gravity-induced separation. The plates are packed in a specific arrangement that provide tortuous channels for the fluids to flow through, which enhance the coalescence of dispersed droplets and help their separation by directing the separated particles out of the water stream thanks to their inclination angle (60° to the horizontal); sediments migrate down, and coalesced oil droplets float up, where they can be removed by specific outlets from the separation device.

The coalescence efficiency is crucially affected by the velocity of the flow, as the inertia force dominates the collision and, therefore, the coalescence between droplets, but also the drag force drives droplets through the surface of the plates. This means that velocity has to be optimized in order to maximize the efficiency of the separator. Corrugated plate separation is important due to its low energy consumption, high efficiency, and absence of secondary pollution, so research is constantly evolving in the interest of creating equipment and internal structures that improve the separation without reducing simplicity of use and durability (Han et al., 2017).

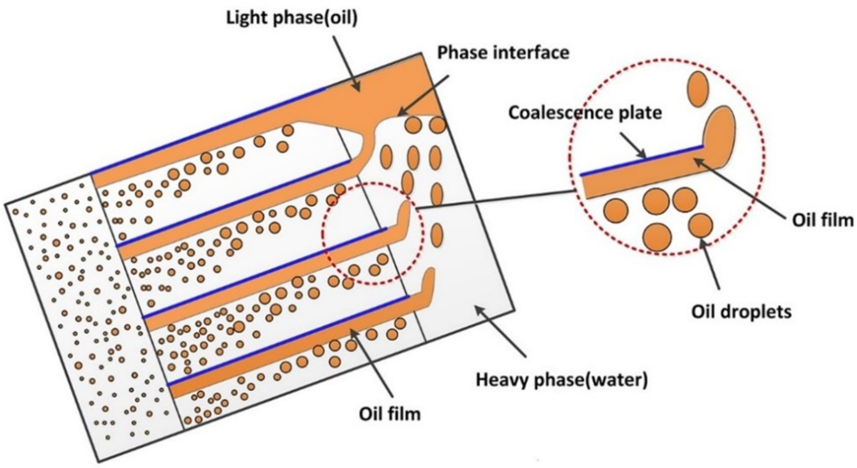

FIGURE 3.3: Principle of coalescence and phase separation used for CPI separation (Han et al., 2017).

3.1.1.2 Hydrocyclones:

Hydrocyclones are compact equipment originally developed for solid-solid separation but can also be used for liquid-liquid and gas-liquid separation. These devices traditionally consist of a cylinder with an inlet at the upper and two outlets, one at the bottom called underflow, and one at the top called overflow. The flow through the device generates a spinning motion of the inflow fluid, which causes the separation of the heavier water from the lighter oil due to centrifugal forces. The less dense phase flows up and is collected at the overflow, while the heaviest phase flows down to the underflow, although different configurations exist.

Cyclonic separators are widely used in the industry to remove solids and oil from produced water; the absence of mobile parts make them simple to use while requiring small space, energy, and maintenance, with high efficiency.

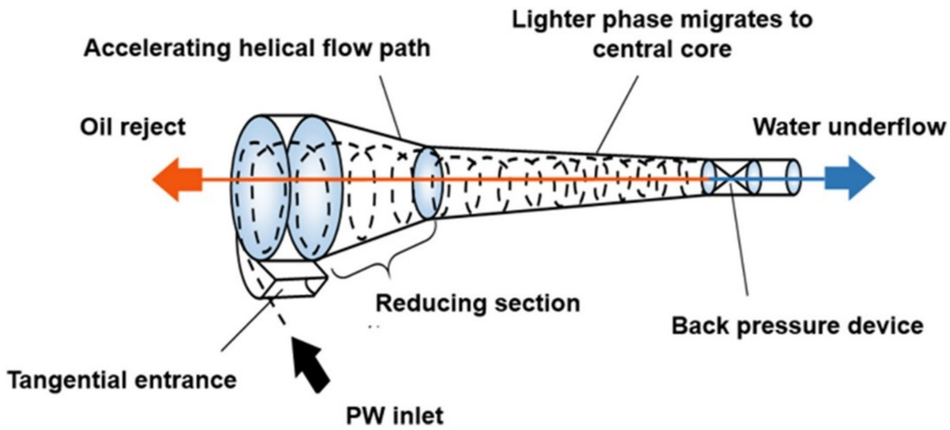

FIGURE 3.4: Separation mechanism of hydrocyclones (Liu et al., 2021).

Experiments on hydrocyclone efficiency have shown that their highest separation efficiency occurs when oil concentration is up to 3%, reaching efficiencies of up to 92%. Latest research is focused on the development of more efficient hydrocyclones that can be used for streams with higher concentrations, oriented at their use in mature fields, by the optimization of their geometry and their parameters with the use of mathematical analysis, optical testing, numerical simulation, among other resources. For example, research by Hamza et al. (2020) documented the possibility of performing downhole oil/water separation (DOWS) to address high water cut characteristic in mature fields. For DOWS, a preliminary separation of oil and water is performed in the wellbore by the use of hydrocyclones which allow the oil to be sent to the surface while underflow water is pumped into the water disposal zone, which helps maintain reservoir pressure. They explain that different types of hydrocyclones have been tried for DOWS up to date, but mostly single-inlet conventional tangential inlet hydrocyclones, due to the space limitation in the wellbore, although axial inlet hydrocyclones show to have more advantages, such as a lower residence time, less pressure drop and less turbulence. Therefore, their work introduced a compact axial inlet conical hydrocyclone which showed separation efficiencies as high as 84% for a water-to-oil concentration of 80:20, at 80° C.
Another disadvantage that future research should focus on is the flexibility of operations as, once installed, the capacity of the hydrocyclonic equipment can only be increased by adding new devices. The development of flexible equipment which can adapt to fluctuations in the amount of produced water would facilitate their use in offshore operations. (Liu et al., 2021)

3.1.1.3 Flotation Devices:

A technique involving flotation processes uses the introduction of fine gas bubbles to separate small, suspended particles which are difficult to remove by sedimentation from the produced water; called Induced Gas Flotation (IGF), this process works by injecting a gas (air, nitrogen, natural gas, or other inert gas) into the water stream, causing oil particles and some suspended solids to attach to the bubbles created, and enhancing their floatability. This results in the creation of a foam on the surface, which can be removed by skimming. Efficient performance depends on the optimization of parameters like bubble size (100-1000 micrometers), gas flowrate, feed flowrates, temperature, and on the content of oil and the size of oil droplets.
Another method, called Dissolved Gas Flotation (DGF), is based on the growth of gas particles dissolved both in water and oil phases by the reduction of pressure. The generated bubble size is smaller than IGF method (10-100 micrometers), which means a longer retention time is required. Overall, IGF has a better removal efficiency than DGF, although both present disadvantages. In IGF systems, the minimum bubble size of 100 micrometers may mean smaller oil droplets are not affected, and the opposite for DGF, where droplets larger than 100 micrometers cannot be floated; therefore, a combination of both methods means the best flotation efficiency.
The separation of oil and water by flotation technique is affected in the microscopic scale by various subprocesses: the approach of bubbles and oil droplets, drainage, and rupture of the water film between them, and the rise of the coalesced particles. Upon coalescence, the difference in density between agglomerates and water enhances separation, where particle flotation at a velocity that can be described by Stokes' Law for particles that experience only their own weight and buoyancy forces, as expressed in the following equation:

$$\mathbf{v} = \frac{2}{9}\frac{R^2 g(\rho_w - \rho_o)}{\mu} \tag{3.1}$$

Where v is the velocity of oil droplets rising to the surface, R is the radius of oil droplets, is the density of oil and water, g is the gravitational constant and μ the viscosity of water. Therefore, the larger size of oil droplets and the difference between oil and water densities, and the lower the viscosity of water, the faster the separation of phases will occur.

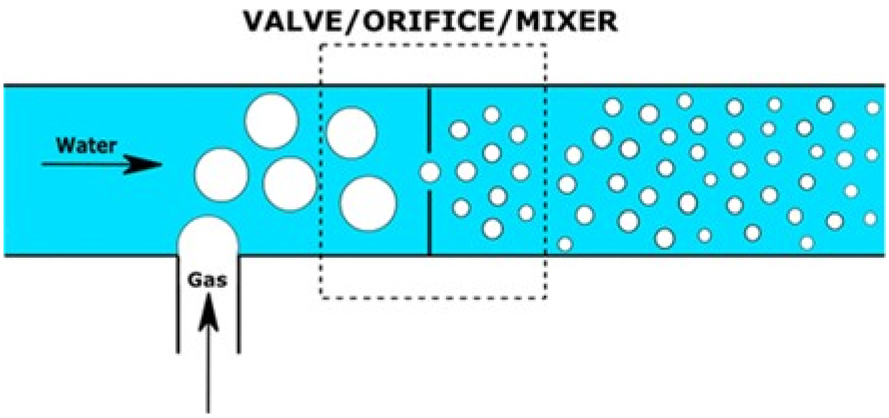

Figure 3.5: Induced Gas Flotation method scheme (Piccioli et al., 2020)

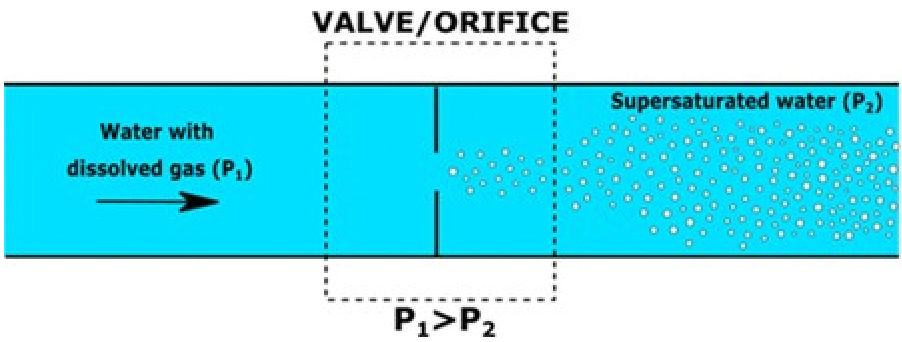

Figure 3.6: Dissolved Gas Flotation method scheme (Piccioli et al., 2020)

Flotation systems, specially offshore, need to be designed for minimal footprint and weight, low motion sensitivity, optimal efficiency, and simplicity of operation. To satisfy this need, a special unit called Compact Flotation Unit (CFU) is used. CFUs use both IGF and DGF to efficiently remove oil droplets from produced water. CFUs are usually vertical vessels, due to lower space requirements, with retention times of typically less than 1 minute. Originally, the process was carried in a single-compartment vessel fed from the top, but more recent designs use a vessel with a separate inlet chamber with the inlet for the water feed at the bottom, avoiding counter-current flow and helping the coalescence and concentration of bubbles and droplets.(Piccioli et al., 2020)

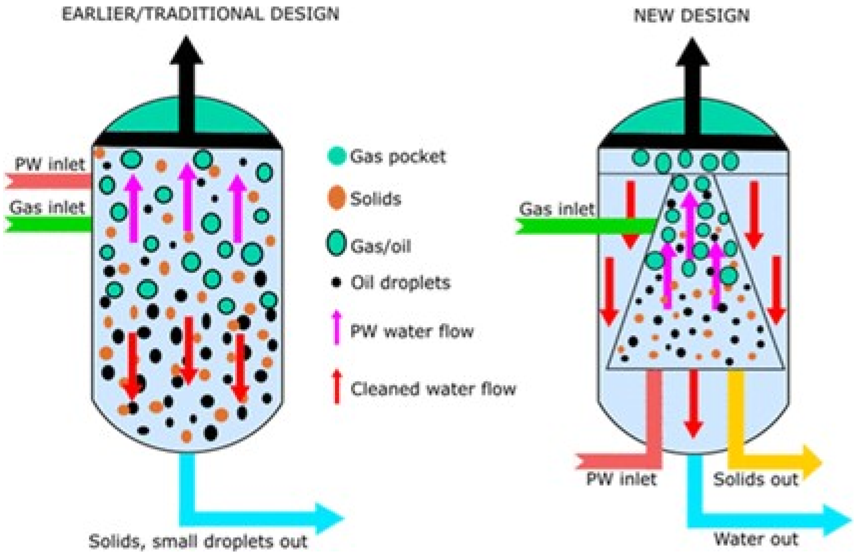

FIGURE 3.7: Schematics comparing original CFU configuration (left) and more recent designs (right) (Piccioli et al., 2020).

Gravity treatment performance can be further enhanced by the use of ultrasonic waves for breaking oil-in-water emulsions (Luo et al., 2019), microwaves, electric fields for phase separation through electro-coalescence (Mhatre et al., 2015), and temperature fields, additional to the physical internal components mentioned, as several recent studies show. Gravity separation is the most adaptable and low-cost technology for water treatment and has a high overall efficiency for removing solids and free-phase oil droplets, even those with smaller sizes, but do not help on the removal of dissolved oil and organic components, which also add up to the TOC.

3.1.2 Medium Filtration

This method uses filter media to remove pollutants and is widely used in the treatment of drinking and industrial water. Medium filtration in produced water allows for the extraction of oil and suspended solids, although some soluble organic compounds, like aromatic hydrocarbons, can also be removed.
Media used for filtration include walnut shells, fiber balls, ceramic particles, and quartz sand. The mechanisms through which these media allow for the separation of compounds are the inertial diffusion and gravity precipitation of particles, as well as mechanical sieving and interception, adhesion based on the characteristics of the filter media or their interface with particles, including electrostatic forces, Van der Waals force and chemical bonds, and the coalescence based on coarse graining, mainly aimed at removing oil, allowing for the fusion of small particles into larger droplets which can be separated.

The main aspects to be considered in order to improve the efficiency of filtration are the proper selection of the filter media and the ability to regenerate such media, as well as the pressure drop through the media. (Liu et al., 2021)

Filtration can occur through two different mechanisms: dead-end filtration, given in most media filters, and crossflow filtration, occurring mainly in membrane filtration methods. Dead-end is the most basic form of filtration. In this mechanism, the feed water is forced through the filter surface by applying pressure, causing particles to be retained and stay behind while water flows through. These particles accumulate and increase resistance to passing through the filter, causing a flow decrease. This means that filter media requires cleaning in order to restore its performance.

Crossflow filtration is performed by passing the feed stream along the surface of the membrane, where the turbulent flow along its surface makes water permeate through the membrane while particles continue flowing through the membrane surface. This causes a perpendicular flow between the water and the particulate streams. This allows for continuous performance with less cleanings.

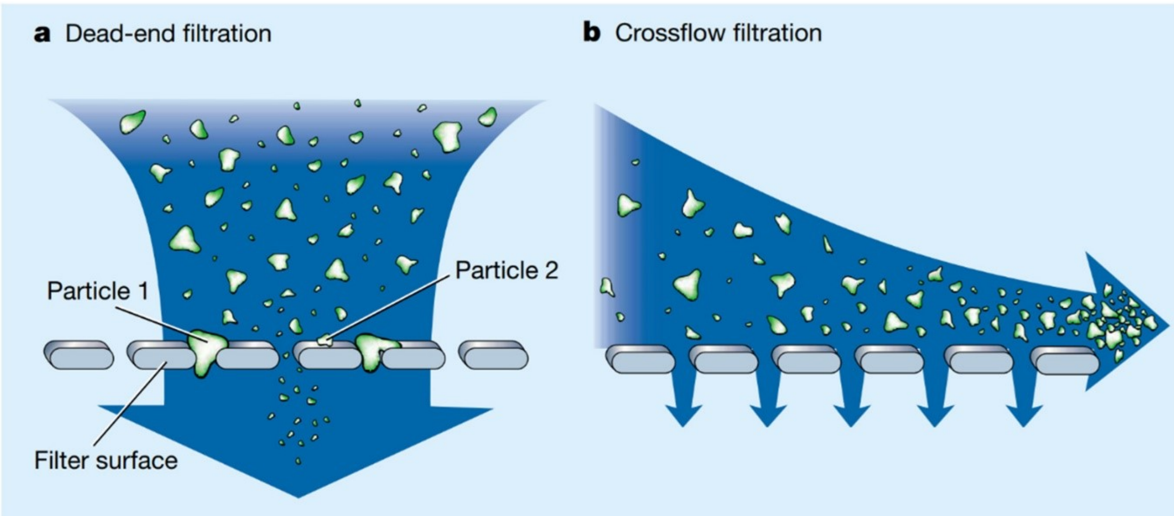

FIGURE 3.8: Filtration techniques for separation (Liu et al., 2021)

Treatment efficiency is improved by two main aspects: the reasonable selection of the filter media, and the capacity to regenerate it. The focus of current research on the subject is directed at developing new composite materials and the modification of existing ones to maximize their efficiency. (Liu et al., 2021)

3.1.2.1 Adsorption:

Adsorption is the ability of a solid material (adsorbent) to attract molecules of solutes dissolved in a liquid or gaseous phase (adsorbates) onto their surface, mainly due to Van der Waals and electrostatic forces, but also from chemical bonding. (35) This process forms the basis of separation by adsorption technologies, which are widely used in many industrial processes, including produced water treatment; the water stream flows through a column packed with a porous and adsorbent material specifically chosen for the targeted pollutant, resulting in an effluent with little to no pollutant molecules. The adsorption capacity of a material and its performance depend on different factors, including (The International Adsorption Society, 2020):

- Their specific surface area, as a larger area of contact within the pores results in more adsorption,
- pore size and its distribution, which determines the accessibility of adsorbates into the internal adsorption surface,
- surface polarity, which defines their affinity to polar substances such as water, allowing to create polar adsorbents called hydrophilic, and non-polar adsorbents called hydrophobic,
- salinity and amount of suspended particles in the stream, which can plug porous media and reduce efficiency of the desired adsorption due to the presence of other dissolved salts,
- temperature and pH, among others.

The benefits of treatment by adsorption include a flexibility of design, no generation of toxic products and ease of recovery, as the media can be regenerated through contact with chemicals to wash particulates trapped (Hedar, 2018).
In produced water treatment, activated carbon is the most commonly used adsorbent for the removal of hydrocarbon molecules, as it is simple to design and very effective for soluble BTEX. Other materials, like organoclays are able to remove hydrocarbons with different characteristics. The use of different materials together can result in effectively reducing hydrocarbon concentration under standards for water quality. (Doyle and Brown, 2000).
As the need for produced water treatment increases, investigation into more economically efficient adsorbents keeps advancing. Additionally, although most studies go into the research of hydrocarbon remediation, the removal of heavy metals is also constantly researched. These studies research many options for improving the efficiency of adsorption

processes, including materials synthesized in laboratories, like, for example, nanostructured carbon materials, especially carbon nanotubes, which has grown interest as their properties can be specifically designed and modified, offering an excellent removal of dissolved organic pollutants due to a better arrangement of carbon atoms than activated carbon. (Adewoye et al., 2021). However, natural adsorbents are also vastly researched, mainly due to their inexpensive economic potential, which makes them favorable when compared to commercial adsorbents. Natural adsorbents come from the Earth's crust or from biological sources such as agriculture or food wastes and have proven to be effective for pollutant removal, such as clay minerals like sepiolite or attapulgite for oil removal, graphene for antimony, plant branches like oil palm or olive branches for the removal of different heavy metals, fruit peels and husks, among many others. (Yousef et al., 2020)

3.1.2.2 Membrane Filtration

Membranes are microporous films of synthetic materials which are able to separate a fluid from its components. There are four processes that use membrane filtration for separation:

1. Microfiltration (MF): Process of sieving of particulates based on the pore size of the membrane. Pore sizes range from 0.1 to 3 micrometers, and is useful as a pretreatment stage to enhance the effectiveness of UF, NF or RO.
2. Ultrafiltration (UF): Pore sizes range between 0.01 and 0.1 micrometers. It is more effective for oil removal in produced water than traditional methods, and better at removing hydrocarbons and suspended solids than MF. UF has proven to be capable to meet effluent standards, opposed to MF which cannot be used by itself.
3. Reverse osmosis (RO): RO membranes are designed to reject all compounds other than water. Osmotic pressure is suppressed by applying hydraulic pressure which forces clean water to diffuse through a non-porous membrane. RO can remove particles as small as 0.0001 micrometers. It requires an adequate pretreatment and regular membrane cleaning to be effective, as scaling and fouling are generated which causes an unavoidable clogging of the membrane.
4. Nanofiltration (NF): Similar to RO, is also operated at relatively high pressure. It is as effective in removing inorganic materials, but instead of blocking all ions like RO, has a selectivity for divalent ions and allows monovalent ions to flow.

In order to remove accumulated fouling on the membranes, a process called backwashing is performed. During this process, the transmembrane pressure is reversed, causing

produced permeate to flow back and wash away the accumulated fouling.
MF and UF operate at low pressure (1-30 psi) and cannot generally remove dissolved salt from water, so they are used as pretreatment steps for RO and NF, which are pressure-driven processes and can be employed for desalination of medium-salinity water (up to about 40,000 mg/L TDS) (Veil, 2015). This means that a combination of filtration methods can be used and has proven to be efficient and reliable for civil and industrial wastewater allowing nearly zero-pollutant effluents. It has been also used for onshore oil and gas industry, but is only an emerging option for offshore facilities, due to space and weight limitations and hard weather conditions, along with other technical challenges discussed previously, like the constant supervision required to avoid clogging, which cause it to become less reliable in the harsher conditions found offshore. This is why current research on the topic is focused in creating filtration methods that can be reliably used in offshore facilities, such as the Smart Filtration Technology proposed by Jepsen et al. (2016), which aims to maintain membrane permeability and reduce energy consumption to make its use in offshore facilities feasible (Jepsen et al., 2016).

3.1.3 Biological Treatment

Biological treatment of water consists in the biodegradation of organic matter into simpler substances and biomass with the use of microorganisms, followed by removal of the resulting mass through sedimentation. Water is then washed out of the reactor for clarification leaving behind solid sludge containing both live and dead bacteria at the bottom. The main obstacle for biological treatment comes from the fact that oilfield-produced water contains toxic substances that can inhibit bacterial activity, which makes it necessary to pre-treat water and select adequate bacteria. (Kardena et al., 2017)
Biological treatment has been mostly used in the treatment of oily and salty wastewater from refineries, shipping, agricultural and textile industries, but a recent research by Camarillo and Stringfellow (2018) recollected proof from multiple studies, mostly in small scale, about the efficiency of biological treatment for oil and gas industry produced water.
Different metrics were compared to evaluate performance, such as Biochemical Oxygen Demand (BOD) which represents the amount of oxygen required by microorganisms when decomposing organic matter and therefore, is an index of the degree of organic pollution (United States Geological Survey, 2020), Chemical Oxygen Demand (COD), total organic carbon (TOC), or oil and grease concentration (OG). Different methods based on biological action exist and have been reviewed:

- Fixed-film treatment: This method is the most commonly used as microorganisms bound in films can be retained and resist extreme conditions of pH, temperature, and salinity. Nutrients can be added to the process to support microbial growth, increasing COD removal from 20% without nutrients to 65-80% when phosphorus and carbon substrates where added. Different configurations showed variable retention times (4 to 48 hours)and COD removals of around 60-80%, with some scaling reported, which did not inhibit biological activity or growth.

- Membrane bioreactors: Membrane bioreactors have the advantage of not requiring settling times as membranes take care of solid separation and therefore have a smaller footprint as they do not require external clarifiers. COD removal was typically higher than 80%, which indicates similar efficiency to fixed-film treatment, requiring retention times varying from 6 to 96 hours. Membrane fouling and scaling were observed in membrane bioreactor studies, which cause a reduced membrane permeability.

- Wetland and pond treatment: This method consists in the creation of an artificial wetland where biodegradation of nitrogen and metals is performed by plant life such as cattails, reeds, or bulrush. Studies have been performed only in small, simulated pilots, but have proven positive outcomes with COD removal of ¿70%, provided an adequate pre-treatment is conducted. Constructed wetland treatment systems require lower costs and maintenance, as well as creating new wildlife habitats.

- Activated sludge: Consists in an aeration tank and a settling tank with a system for the return of the sludge collected in the latter. The system works as a cycle, where activated sludge (loaded with organisms) collected in the settling tank from the removal of organic and dissolved compounds, is returned and mixed with the water influent and loaded with oxygen for some time in the aeration tank, where the organisms use the organic matter as nutrients and continue to grow, being removed as a sludge with the products of the biodegradation in the settling tank, and returned to the beginning of the system, only requiring a periodical remove of excess solids and organisms (Mountain Empire Community College, 2020). It is a mature technology which provides effective removal of oxygen demand, with a low-cost and lower environmental impact than other methods.

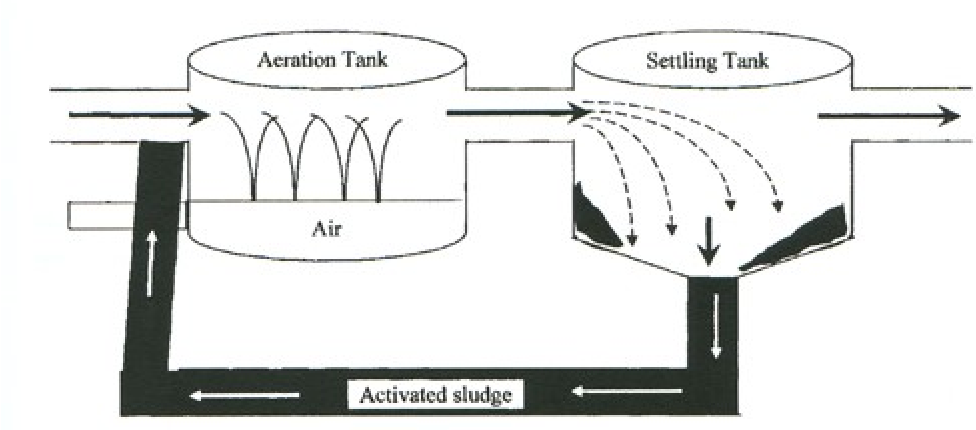

FIGURE 3.9: Diagram describing the process of Activated Sludge treatment (Mountain Empire Community College, 2020).

- Anaerobic treatment: one of the main drawbacks of aerobic degradation is the volatilization of light hydrocarbons, which pollute the air. Degradation under anoxic conditions avoid that problematic but is known for a lower hydrocarbon removal efficiency than aerobic reactions. However, recent studies have achieved a removal of Total Petroleum Hydrocarbons of $> 98\%$ (Ghorbanian et al., 2014), and COD removals ranged from 37 to 87%, identifying possible issues of concern such as mineral precipitation or hydrogen sulfide production.

- Bio-electrical systems (BES): BES combine biological and electrochemical processes to generate electricity. These are cells that consist of an anode and a cathode, joined by an external wire to create an electrical circuit, where special types of microorganisms break down organic material at the anode and release electrons, protons, and carbon dioxide. The anode collects the electrons, which travel to the cathode through the circuit, creating an electric current. Ion capturing at cathodes and anodes allow for the occurrence of desalination additional to the degradation of organic compounds and the oxidation of other contaminants. COD removal was found to be higher than 70%, reaching even 96% in some studies, whereas TDS removal could reach up to 74%. The drawback for bio-electrical system comes from the fact that ion adsorption capacity regeneration is limited (around 75%), which means a decrease in COD removal rates in subsequent runs. However, the advantage that makes it a promising technology for the future is the possibility to not only reduce energy requirement for treatment, but actually allowing for the generation of electricity from the process, as well as other valuable products which can be generated in BES reactions, such as hydrogen (European Commission, 2013). A study by Mohanakrishna et al. (2021) showed positive results with the integration of Electrochemical Cell (EC) and Microbial Fuel Cell (MFC) technologies to treat produced water, resulting in a TPH removal of 89%, COD removal of 90%, sulfate removal of 42.6% and TDS removal of 34.3%, while allowing a net energy production of about 1615 Wh/m3 after balancing energy consumption in EC and generation in MFC, which suggests the possibility of a successful application in the future.

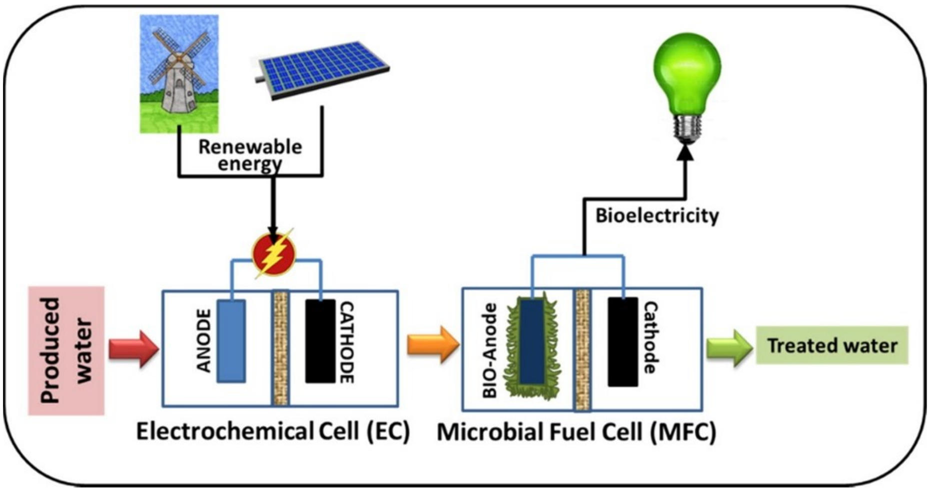

FIGURE 3.10: Diagram describing the EC and MFC integration system used for produced water treatment (Mohanakrishna et al., 2021)

Biological treatment of produced water seems to be a viable strategy, particularly for levels of salinity below 50,000 mg/L. Given that the adequate conditions can be provided in terms of water pre-treatment, toxicity, and nutrient and oxygen availability, bacterial processes show COD removal efficiencies usually higher than 70%, where the main detrimental effects seem to be mineral scaling generated at films or membranes. The future feasibility of biological treatment depend on future studies that bring these laboratory-scale experiments to realistic field conditions to prove their efficiency.

3.1.4 Mechanical Vapor Compression

Mechanical Vapor Compression (MVC) is a thermal desalination process used across water treatment from different sources in general. MVC works through a heat pump principle, where a large compressor continuously recycles and keeps latent heat exchanged in evaporation and condensation steps in the system, thus reducing energy consumption required for feed heaters and removing the need for cooling water essential in other thermal technologies. Saltwater feed entering the system is preheated by heat exchangers that transfer heat from outgoing streams. After pre-heat, saltwater flows into a condenser where it is deaerated prior to the MVC evaporator-condenser, where the seawater is passed through heat exchanger tubes where it flows down as a film.

These tubes act as heat exchangers as they go through a vapor chamber, which causes saltwater to evaporate. Design changes with each technology developer, whereas some make the vapor flow through tubes and spray water on top of them in order to cause the evaporation.
Evaporated water is removed, and the non-evaporated water is recirculated through the heat exchangers until it reaches the desired salinity. It is then rejected from the MVC unit as brine. Generated water vapor is extracted through mist eliminators using a mechanical compressor, which drives the process by compressing the water vapor to a higher pressure and temperature and extracting it into the heat exchanger steps to reuse the heat and then extract it as distillate water.
This process proves to be much more energetically efficient compared to other thermal solutions where heat is not reused. However, as a thermal method it still utilizes larger amounts of energy compared to other methods for salinity removal, such as reverse osmosis or membrane filtration. This has motivated researchers of MVC optimization to assess the possibility of running MVC units powered with renewable energy (IDE Technologies, 2019).

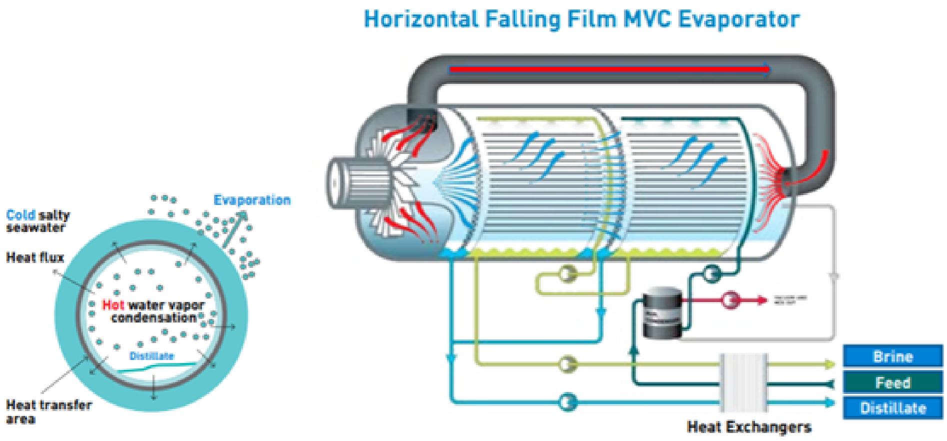

FIGURE 3.11: Process of MVC distillation for saltwater using horizontal tubes for heat exchange. (IDE Technologies, 2019).

3.1.5 Chemical Treatment

Processes of separation such as precipitation due to gravity or degradation can be enabled and enhanced by the addition of specific chemical compounds that alter the behavior of natural occurring compounds in produced water. An aspect of chemical treatment to be taken into serious account is the calculation of chemicals needed for a complete coalescence or reaction, as excess chemicals will add to the total contaminants in water, which is a complete drawback from its objective.

3.1.5.1 Precipitation

Precipitation is considered one of the conventional processes of chemical treatment. It allows for the removal of a large part of the suspended and colloidal particles. Colloid refers to any substance present in very fine particles, ranging from 10 nm to 10 μm (Koohestanian et al., 2008) with an electrostatic charge similar to the particles surrounding them which causes them to be repelled, stabilizing them, and therefore avoiding the coalescence of particles into larger particles, impeding their sedimentation. This makes colloidal particle removal the most difficult aspect of conventional water treatment.
Coagulation and flocculation, achieved by chemical agents, help destabilize colloids in order to facilitate the formation of larger and heavier particles which can be removed by physical treatment.
Coagulation is the process of decreasing or neutralizing the negative charge on the particles to allow the particles to start accumulating. Rapid, high-energy mixing is necessary to ensure that the coagulant is fully mixed into the flow.
Flocculation is the process of bringing together the particles to finally form the large agglomerations expected through the use of coagulant aids such as polymers.
The adequate addition of chemical agents to allow for coalescence of suspended solids allows for the removal of a large part of contaminants in water through simple physical methods.

3.1.5.2 Chemical Oxidation and Advanced Chemical Oxidation

An oxidation process refers to the use of chemical oxidants for the oxidation of the organic components in produced water into less harmful products like CO_2 and H_2O, in order to reduce the Chemical Oxygen Demand (COD), Total Organic Content (TOC), and some inorganics in water. Common oxidants, such as oxygen, ozone or hydrogen peroxide are usually used in oxidation processes, but oil and gas produced water contains recalcitrant, or persistent, organic pollutants, which means they are resistant to conventional chemical and biological degradation methods, such as BTEX, phenols and acetic acids. The use of Advanced Oxidation Processes (AOPs) allows for the degradation of these resistant organic pollutants into CO_2, H_2O, and small molecule compounds, to ensure the complete oxidation of contaminants in water and have become a matter of study for researchers interested in further reducing pollutant content in water produced from the oil and gas industry with the objective of recycling these water volumes instead of conventional disposal methods.
AOPs are based on the in-situ generation of highly reactive radicals with low selectivity, such as hydroxyl radicals (HO·), hydrogen peroxide (H_2O_2), or ozone (O_3), which can

virtually attack and mineralize all oxidizable substances, including organic contaminants, transforming them into CO_2 and mineral salts. Even in case of partial degradation, it results in electronically poorer, smaller (in terms of molecular mass), more hydrophilic and often biodegradable compounds compared to the original contents, which can then be handled by the subsequent treatment step.
New Advanced Oxidation Processes continue to be developed and evaluated by researchers at the time; the research by Coha et al. (2021) describes the following five families of AOPs:

1. **Fenton-based reactions:** Based on the use of H_2O_2 and Fe2+/Fe3+ as catalyst and oxidant. The nature of the reactions allows for the constant recycling of Fe(III) to FE(II) The most important factors determining degradation efficiency are pH and the catalyst/oxidant ratio, although other parameters such as the presence of sulfate ions, dissolved organic compounds and inorganic dissolved solids can significantly reduce efficiency. Best efficiency was reported with a pH of 3.5, whereas produced water streams usually are in the 6-8 range, which means the process requires acidification of the stream. An acidic pH limits the precipitation of Fe(III) as hydroxide during the process, allowing it to be recycled to Fe(II). Efficiency can be further increased by the application of a UV light source (photo-Fenton process) which has proven to increase oil and grease and phenol removal as reported in Table 3.1. Another alternative is the generation of hydroxyl radicals through electrochemical processes, called electro-Fenton technique, and the combination of both (photo-electro-Fenton) have proven to further increase efficiency, although optimal parameters are different for each.

2. **Heterogeneous photocatalysis:** works through the photoactivation of a chemical reaction through the adsorption of a quantum of light (photon) from a photocatalyst. Their use in the treatment of produced water has been widely researched, with titanium dioxide (TiO_2) as the most adopted catalyst, although others such as iron oxide can also be used. This process does not require pH adjustments and its efficiency is mainly regulated by the catalyst concentration.

3. **Ozonation:** Ozone (O_3) is a strong oxidant which can be used to directly oxidize contaminants or as a precursor of other reactive compounds (OH) but is too unstable and reactive to be stocked or transported, meaning it must be produced on site from dry air (to avoid reactions with water vapor) or pure O_2. Ozone reactions are especially useful for breaking double carbon bonds in alkenes, although it can also react with other classes of organic compounds like alcohols and aldehydes. For contaminants that do not react to O_3, it can be used as an OH precursor.

The main drawback of ozonation is that in presence of bromide (Br−)it can produce carcinogenic bromate (BrO_3-). The main parameters affecting degradation efficiency found in literature are high temperature and ozone doses, with low pH and bubble sizes. Varying results have been found in different scenarios, with the highest efficiencies achieved when coupled with other methods.

4. **Anodic oxidation:** Oxidative process at the anode of an electrolytic system. A chain of reactions allows for a continuous oxidation as observable in Figure 3.12. The main mechanism is based on monoelectric oxidation of water to give OH radicals. In the presence of chloride, which is common in produced water, chlorohydroxyl is also created and contributes to the removal of organic compounds. Water and the OH radicals further react creating primary oxidants as oxygen, chlorine, and hydrogen peroxide and, from these, ozone and chlorine dioxide can be created, which further enhance the oxidation.

(1) $H_2O + M \rightarrow M[^{\cdot}OH] + H^+ + e^-$

(2) $H_2O + M + Cl^- \rightarrow M[^{\cdot}ClOH] + H^+ + 2e^-$

(3) $H_2O + M[^{\cdot}OH] \rightarrow M + O_2 + 3H^+ + 3e^-$

(4) $H_2O + M[^{\cdot}ClOH] + Cl^- \rightarrow M + O_2 + Cl_2 + 3H^+ + 4e^-$

(5) $H_2O + M[^{\cdot}OH] \rightarrow M + H_2O_2 + H^+ + e^-$

(6) $O_2 + M[^{\cdot}OH] \rightarrow M + O_3 + H^+ + e^-$

(7) $H_2O + M[^{\cdot}ClOH] + Cl_2 \rightarrow M + ClO_2 + 2Cl^- + 3H^+ + e^-$

Figure 3.12: List of reactions occurring during anodic oxidation

Optimization parameters include electrode material, distance between electrodes, current density, temperature, pH, and reaction time. Several authors have proven anodic oxidation as a promising produced water treatment, with PAH removal of up to 95% and COD reduction of 98% under different optimal conditions.

5. **Other AOPs** which have not been investigated extensively for the treatment of produced water, such as micro-electrolysis, catalytic wet air oxidation, sonolysis and radiolysis. These have all been studied for water treatment, but research on their application on produced water is very recent and, given their complexity, require further research for optimal configurations.

Table 3.1 compares the maximum efficiencies of the application of the different advanced oxidation methods aimed at the removal of different pollutants, as a result of the analysis of the available research up to date by Coha et al. (2021). These removal efficiencies are the highest reported throughout multiple experiments by different authors, which allow in turn to identify the optimal configurations in order to maximize treatment efficiency.

TABLE 3.1: Maximum reported removal efficiency for different methods of advanced oxidation processes, based on information collected by Coha et al. (2021)

Process	**Targeted substance**	**Maximum removal efficiency**
Fenton	COD	91%
	Naphtalene	98%
	Oil and Grease	58%
	Phenol	80%
	TOC	58%
Photo-Fenton	TOC	96%
	Oil and Grease	84%
	Phenol	95%
	TOC	96%
Electro-Fenton	COD	78%
	Oil	90%
Photo-electro-Fenton	COD	86%
Heterogeneous Photocatalysis	BTEX	97%
	Napthalene	85%
	Oil and Grease	100%
	COD	88%
Ozonation	PAH	100%
	TOC	85%
	COD	73%
Anodic Oxidation	BTEX	98%
	Phenol	47%
	PAH	95%
	COD	98%

Chemical oxidation and advanced oxidation processes have been proved to be able to achieve large levels of water cleaning overall. However, the main drawback with the application of chemical oxidation processes is related to their high cost, and the constant requirements of calibration and maintenance in order to maintain their efficiency to the maximum, as scaling, fouling, and efficiencies are always time-increasing.

3.2 Final Fate Alternatives for Produced Water

Produced water management engineers must create an efficient and economically profitable chain that ends with a final fate for the volumes of water produced continuously. The selection of an adequate receiving activity or disposal option is the main factor in order to create the most efficient treatment strategy. Options like underground injection into disposal wells or discharge and dilution into oceanic bodies require way less remediation treatment than any novel use that considers using these volumes of water to supply activities with a risk of human exposure and environmental damage. This section dedicates to the explanation of current options for operators to dispose of produced water.

3.2.1 Discharge into the Ocean

As mentioned before, discharge into the ocean is, logistically, the simplest method to dispose of produced water coming from exploitation facilities, especially for those located in offshore locations; however, concentration of pollutants in produced water has been proved to have the potential of being too large to allow for some oceanic bodies to efficiently dilute and disperse to avoid damages, even after conventional treatment like oil removal, which causes pollutants to settle and accumulate over the course of years of operation which add to the local concentration of these pollutants, which can have several toxic or radioactive risks associated, which might end with damage to local wildlife, and might even result in human health issues if the body of water somehow enables exposure.

All risk factors associated with the discharges of produced water have motivated some nations to increase regulatory limits over discharges, and even reduced them to the minimum if other technologies are available. This is important especially from the point of view of the uncertainty about the real risk of discharging produced water, as complete characterizations of the stream are not usually efficient for operations, and conventional treatment focuses only in suspended solids and hydrocarbons, leaving possible contents present as dissolved matter without remediation, meaning that even water volumes discharged into the ocean in the past because they were considered safe in conventional assessments, might still be discovered to have caused damages to the local environments if a deeper assessment is conducted now, after years of operation.

In order to achieve low-risk operations for petroleum extraction, discharges into the ocean should be minimized, unless a complete assessment of its contents proves it to be safe for the characteristics of the receiving bodies. For cases where no alternatives are available, efficient treatment strategies must be implemented and optimized to comply with applicable limits, keeping in mind that these might be modified in the future, as research on real effects of produced water advances.

3.2.2 Underground Injection through Disposal Wells

The most used method when discharge is not possible is the underground injection of the produced water using saltwater disposal wells, injection wells for enhanced oil recovery through the recharge of aquifers for pressure support in water driven reservoirs, the injection of steam to help increase the mobility of oil, or as fracturing fluid required for hydraulic fracturing in unconventional operations like shale oil and gas reservoirs.

Just like discharges into the sea, underground disposal into non-hydrocarbon-bearing formations has different regulations around the world. The most important technical considerations for water disposal wells are the receiving formation selection, well construction parameters, volumes, pressure, and economics. The main objective, environmentally speaking, is to avoid the pollution of underground aquifers that supply or can supply public water systems. In the USA, wells used for the injection of produced water are considered Class II wells, which includes enhanced oil recovery and disposal wells. Currently around 180,000 Class II wells are in operation in the United States, and it is estimated that over 2 billion gallons of fluids are injected every day (US Environmental Protection Agency, 2020). For the case of EOR, water stops being a waste and becomes a beneficial resource and, as it is being injected into its formation of origin, requires little treatment.

For disposal, produced water is injected into a different formation, which means multiple assessments must be made in order for the operation to be allowed, specifically to make sure there is no risk of contamination of underground drinking water sources through fractures, faults, or other pathways. Geological and geophysical evaluations must prove the presence of an impermeable layer and the absence of open faults or fractures surrounding the selected formation for water disposal. (Veil et al., 2004) Disposal wells are essential, especially for final disposal in unconventional plays where it is not possible to reinject produced water for enhanced recovery due to the low permeability in the area. Operators must demonstrate internal and external integrity of the wells (absence of leaking in casings, tubing, and packers) through mechanical integrity tests (MIT) methods, proven by pressure tests, temperature logs and cementing records. Pressure tests must also determine the maximum allowable injection rates and pressures in order to avoid fracture induction in the formation.

The risk of induced seismicity due to injection is also an important matter of evaluation. Earthquakes can be caused by the slippage of fluids along critically stressed faults

due to the release of stored elastic stress. Being critically stressed means that existing shear forces overcome natural friction. So, for water injection to trigger seismicity in a zone, the presence of a critically stressed fault in the approximates of the operation is necessary. Injection increases pore pressure, which may alter the effective stress on the fault causing it to release its stored energy.
In order to avoid induction of seismicity, a hazard assessment and site characterization is necessary, which includes steps such as examination of historical seismic activity in the area, examination of fault maps, and the evaluation of the proximity of the well to sensitive infrastructure and population. (American Petroleum Institute, 2016) Although underground injection is an environmentally reliable management method, it depends heavily on the availability of underground formations able to receive increasing volumes of fluid.

3.2.3 Recycling of Produced Water

The reuse of produced water requires an adequate characterization of the water quality in order to be suitable for desired uses and paying attention to the environmental risk associated to its transportation and storing, which requires minimizing and remediating spills and leaks, waste management, air emissions and ecosystem protection.
The main advantage of the reuse of produced water from a managemental point of view resides in that this volume becomes a resource rather than a waste to manage. An increase in the reuse of groundwater produced from oil and gas fields represents the return of an important volume of water that could supply water demands in areas where it is necessary, as well as an advantageous alternative to disposal in underground injection wells, which can be costly, limited, or locally unavailable, and discharge into the sea, which is not always allowed, as both of these more traditional practices can become more complicated as future regulation trends to evolve into health and environment protection orientations with zero emission frameworks. The reuse of produced water allows to give a purpose to a volume of water that would otherwise be wasted, saving that same volume of freshwater for other more critical purposes like human consumption.
A transition into more circular, or at least environmentally safe, lifecycles for produced water seems to be the current shared objective, in observance of the sustainability and economics of reuse versus traditional disposal practices. While currently, the reuse of water is being applied and studied mainly for purposes within the oil and gas industry, especially for unconventional extraction, the assessment of alternative uses outside of the industry has gained interest as water scarcity becomes a more important issue in some places, and future research may grant feasible options for the beneficial use of these

large volumes of water that will undoubtedly be produced in the near future.

3.2.3.1 Reuse within the Oil and Gas Industry

Beneficial uses for produced water volumes within the oil and gas industry in certain activities are already a somewhat common practice. Such is the case of the reinjection into conventional fields for pressure maintenance and other enhanced recovery techniques, such as steam injection. Reinjection of produced water into the aquifer layers of a water-driven reservoir helps recharge the aquifer, in order to extent the pressure maintenance effect and help the extraction of larger percentages of oil than what would be extracted by solely the natural pressure. Steam injection is a method for thermal EOR, which consists in the injection of high temperature water steam into the reservoir in order to heat up the crude oil to increase its mobility by reducing its viscosity. (Georgy, 2015)

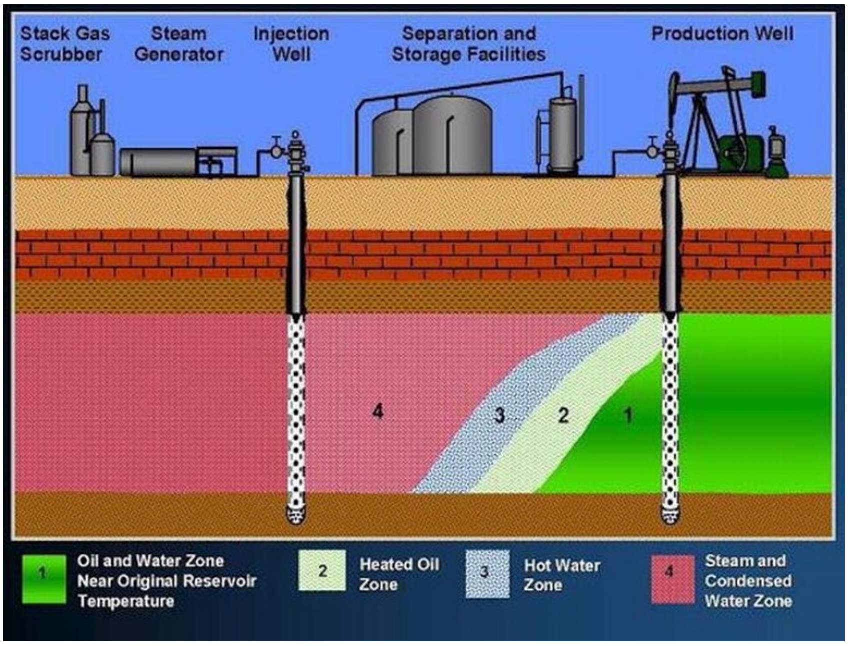

Figure 3.13: Schematic of steam flooding EOR method (Alhakiki, 2021)

However, produced water has also a high potential to be used as a source of water for drilling and completion fluids, and for unconventional drilling operations, specifically in tight oil and gas operations which require hydraulic fracturing to be exploited. Tight reservoirs are defined as those reservoirs found in tight sandstones, carbonates, or shales with very low permeabilities. Without a stimulation technology, fluids in tight reservoirs are impossible to be extracted at an economically viable rate, as the Darcy flow law that works for conventional reservoirs no longer holds true in low-porosity and low-permeability rocks. Hydraulic fracturing is a stimulation process by the continuous pumping of a fluid into a wellbore at an injection rate too high for the formation to accept, which increases the pressure up to the fracture limit, which causes fractures to be formed for the fluid to flow through, where a proppant agent is then placed in order to maintain such fractures open and available for flow. Hydraulic fracturing can be used not only to increase flow rate of low-permeability reservoirs, but also to increase rate of damaged wells, connect natural fractures from the formation to the wellbore, decrease pressure drop around the well to minimize sand production and problems with asphaltene or paraffin deposition, among others. (Wu et al., 2021). The water requirement for hydraulic fracturing varies depending on the rock formation and the type of operation; this value can be anywhere from around 1.5 million gallons to 16 million gallons per well (according to the United States Geological Survey). The replacement of these large volumes required by water produced from oilfields would prove useful in both satisfying the water demand and finding an efficient end-use for these increasingly larger produced water volumes.

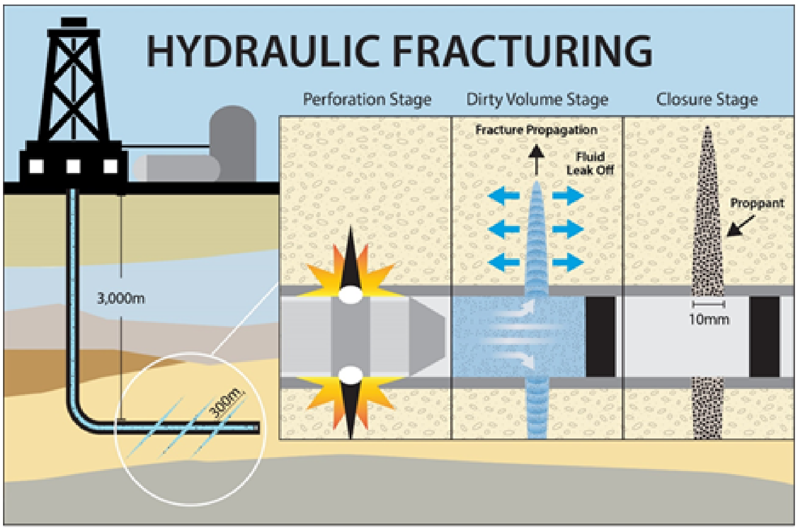

FIGURE 3.14: Schematic of hydraulic fracturing operations (Texas AM University)

For the reuse within the industry, future research must be oriented into detecting, managing and overall minimizing leaks along water management systems, as well as finding cost effective treatment technologies to obtain compatible water compositions to minimize risks to operations, such as minimizing potential scale creating compound concentration, as well as end-uses that can be satisfied by the volumes produces in the oilfield.

3.2.3.2 Reuse in sectors different than the Oil and Gas industry

Produced water has multiple potential uses outside of reutilization within the oil and gas industry. These include land applications such as includes livestock watering, stream augmentation and irrigation of crops, although many other potential end uses have not been put in practice and remain theoretical, due to heavier limitations related to the costs of transportation and storing, as well as treatment for specific end-uses, where water specifications fit to the purpose would require more complex treatment than that for the reuse within oil and gas related operations.

For example, the major concern in reusing PW in irrigation fields is related to increased salinity and soil sodicity, harmful organic compounds, and organic matter to levels that are detrimental to crops and soil, even with little use time, as many of these characteristics may persist even after treatment, altering soil structure. Salt accumulation in soil reduces the infiltration of water, fertility, and its oxygenation. On plants, photosensitivity and nutrient deficiency are the main concerns, reducing their growth.

The main challenge for the future of a reuse strategy for produced water management is the need for effective and economically feasible transport, storage and treatment procedures that allows it to meet specifications for reuse scenarios, which means an in-depth understanding of the water composition, which is complex and variable for every specific source. Another aspect that has to be evaluated is the volumes of water to be produced and their longevity, as the water supply would need to be guaranteed to be continuous and safe for industries to find it beneficial to make produced water their main supply of water in the long term.

However, it is important to continue to study and develop possible applications to reuse produced water in order to reduce the use of freshwater for industrial, agricultural, and other activities such as fire protection, drought relief, irrigation of parks, cooling water for industrial processes, mining, municipal water needs, recreational uses, among many others. The identification of feasible end uses compatible with applicable treatment methods and the regionally available volumes of produced water represent the most important objectives of future investigation (Ground Water Protection Council, 2019).

Chapter 4

Management strategy assessment: review and discussion

There is a growing interest in removing water soluble organic compounds (WSO) from produced water due to them representing in some cases up to 50% of the total organic content (TOC) in the stream, which is a major challenge in order to meet increasingly stricter environmental legislation, as conventional treatments are not useful for efficiently removing this fraction of pollutants. As spoken of before, more recent technologies such as advance oxidation, membrane separation, biological reactions or adsorption show extremely high levels of efficiency in terms of total removal of contaminants, but it is difficult know if their application on certain operations will result feasible, as several factors like space available, costs, energy and chemical consumption, maintenance and management of residue might cause them to result unviable from economic and technical points of view.

The following chapter focuses on the review and understanding of several assessments performed based on previous and new experiments by several authors, search for the most important conclusions shared by their results, and discuss on the future implications of the increasing concern in water treatment management.

4.1 Evaluation of the benefits in terms of water scarcity mitigation from the potential reuse of produced water in the USA

With the continuous expansion of energy production coming from unconventional oil and gas plays in the United States of America, the production of large volumes of produced water has become an important topic, because most of these reservoirs are found in the semiarid west of the U.S., which means water results scarce.
Produced Water volumes in the U.S. during 2017 were estimated to be around 24.4 billion barrels or roughly 3.8 trillion liters from nearly 1 million actively producing oil and gas wells in a report by Veil (2020). Saltwater disposal wells are the most common management method for produced water when discharge to surface water is not allowed, and reuse for EOR is not possible within the same reservoir (in low permeability reservoirs, for example).

The following chart(4.1) shows the distribution of the final management of the reported total volumes of produced water in the country:

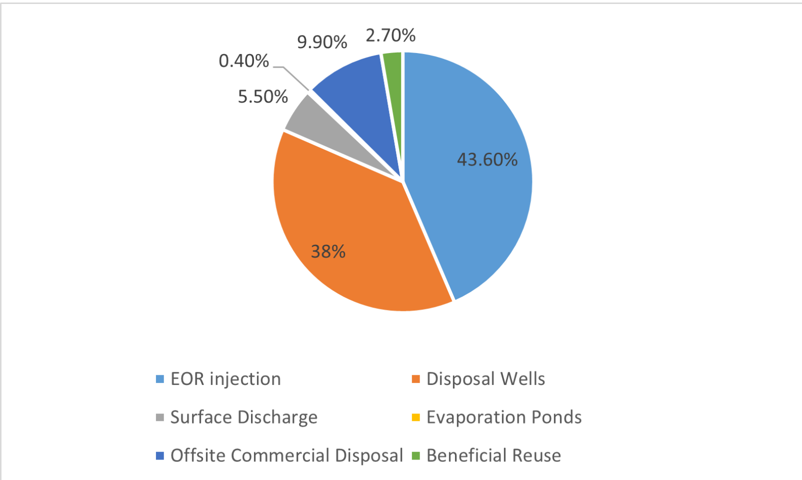

FIGURE 4.1: Produced water management practices in USA during 2017, by final fate. (Information from Veil (2020).

However, the possibility of saltwater disposal wells to pollute overlying aquifers and their relationship with induced seismicity have led to the creation of regulations restricting the use of this method in certain areas.
Due to the increasing restrictions of conventional disposal methods, various produced water management approaches are continuously investigated; use for the supply of hydraulic fracturing for new wells in shale and tight oil plays would reduce the requirement of water sourcing in such operations. The possibility to use produced water for hydraulic

fracturing has been facilitated by advances in fracturing fluid chemistry that changed water quality requirements as, during early years of unconventional exploitation it would require freshwater, and now it can be performed with clear brines that require minimal treatment for most cases. The use outside of the oil and gas sector includes irrigation, municipal, and industrial sectors, or discharge in areas with water scarcity. Several factors determine the feasibility of beneficial reuse (Ground Water Protection Council, 2019):

1. Water quality: the initial quality and the cost of treating to be fit for purpose is a major issue, including the cost factor of the management of treatment residual materials. Additionally, for some of the possible beneficial uses, specifically those not related with oil and gas operations, research is still necessary in order to set quality standards for safe use. Water composition varies greatly from source to source and requires adequate characterization methods that allow to safely assess the environmental and health risks their use may cause.

2. Water volumes and longevity: The amount of produced water and its long-term availability defines how feasible it is to become beneficial for reuse. The operators would need to be able to ensure the availability of sufficient amounts of water with the desired quality over the lifetime of the operations in order for it to be advantageous.

3. Logistics and infrastructure: The cost of logistics and transportation, including the availability of treatment facilities. The trucking cost for a typical water transportation ranges from 1 USD to 3 USD per barrel. The construction of a permanent pipeline is in average 1.45 million USD per mile. In the U.S., midstream water drivers have started to emerge as a solution to handle operators need for transport and management of produced water.

4. Market considerations: The economic attractiveness of reuse requires that water supply is predictable, reliably deliverable, and how high is the cost compared to other available sources. In areas where freshwater is not scarce, the incentive of beneficial use is less, especially due to associated risks.

5. Legal and regulatory concerns: The possibility of beneficial applications of produced water depends heavily on the local regulations applicable. The liabilities and responsibility transference between producer and final user must be clearly defined. Regulations have a heavy impact in the management practices chosen,

and having a clear, consistent regulatory framework that favors water reuse practices and reduces obstacles will encourage operators to consider them as feasible options.

Overall, cost is the key driver of water management techniques chosen, although not the only factor to be considered. This makes the strategies taken vary, where if costs for sourcing of freshwater and disposal of produced water increase, its reuse becomes more cost competitive. As previously mentioned on the USA regulation on water disposal, regulatory changes intended for cleaner, safer energy generation may classify produced water as a hazardous waste, which would increase the overall cost of underground disposal for the difference in requirements for that type of waste. Actually, the areas where water reuse is the highest, Pennsylvania, West Virginia, and the Permian Basin, are regions where disposal options are limited, and disposal costs are high and increasing. If low-cost sourcing and disposal are available, reuse of produced water is not a competitive option.
A study developed by Scanlon et al. (2020) took on investigating the feasibility of the use of the water produced around the country by assessing several factors, especially availability versus demand in different possible sectors, and water quality. The study analyzed data available for around 100,000 unconventional wells in the U.S. from state records and commercial databases and the latest data available on nationally produced water (2017). Scanlon et al. (2020) analyzed the spatiotemporal availability of produced water supply to compare it with potential reuse sector demand. PW volumes from eight major Unconventional Oil and Gas reservoirs (88% of tight oil and 84% of shale gas production) totaled around 600 billion liters.

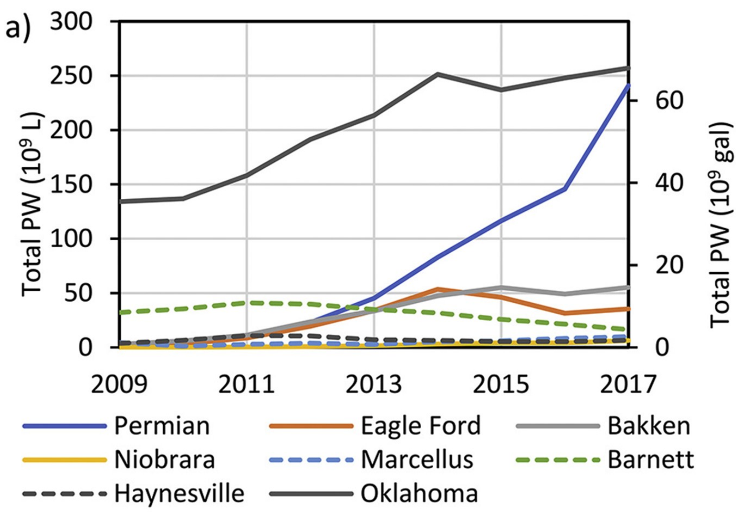

FIGURE 4.2: Time series of produced water volumes for the major unconventional plays in the US (Scanlon et al., 2020)

As observable in Figure 4.2, the Permian Basin is the only play with a continuously increasing trend of produced water volume over time, as other reservoirs have peaked and started the decline of their productions for several factors. Volumes from Oklahoma have stayed stable over the last several years at around 250 [BL]. If water is considered to be reused first within the energy sector for hydraulic fracturing, the PW volumes available are reduced substantially. This sector of reuse should be prioritized as it represents a lower risk compared to others. Hydraulic fracture demand exceeds PW volumes in many of the plays, which means most of it could be used up if logistics allow it. For example, as a part of Texas lease agreements, landowners and organizations can require operators to purchase water from them, disabling them from the reuse of PW. However, in some plays PW exceed hydraulic fracturing (Bakken, Barnett, Oklahoma, and Permian, by almost two times in the latter). These volumes are projected to last around 25 years for Bakken and Eagle Ford plays, 50 years for the Permian Midland Basin and 70-80 years in the Permian Delaware and Marcellus plays, making these latter basins the most reliable feedstock for reuse.

The sector with the largest demand for water is irrigation, which is mostly concentrated in the west of the U.S. This volume exceeds total produced water from unconventional plays by 5 times. The Permian Midland and Delaware basins would represent 1%, 12% and 17% of the total irrigation demand in the counties with highest water uses near to them. These percentages would decrease to 1%, 5% and 11% if used for hydraulic fracturing demand first. Many of the other basins would represent approximately 1% of the water demand for irrigation in their areas. This means that, if technically and environmentally possible, irrigation could accommodate excess produced water volumes easily, but it would have little impact in reducing water scarcity. The water use for livestock was around 25% of total PW from unconventional reservoir in 2017, although areas with high livestock water demand do not coincide with relatively high PW volumes. PW in areas with high water demand for cooling of power plants would represent around 23%-45%.

In terms of water quality limits, the United States regulation does not consider the risks associated with produced water and are inappropriate to assess their use. Most laws contain limitations for contaminants not including volatile and synthetic organics, as well as several inorganics that can be found in PW. Revision of the regulations in order to consider produced water is imperative for the possibility of reuse outside of the oil industry. Plants for the treatment of produced water are still limited, although they are increasing gradually. These are also essential in order to minimize the public health issues associated with pollutants in order to consider use in sectors like livestock feeding and crop irrigation.

The authors conclude that reuse of water is most effective in hitting on water scarcity concern in arid or semiarid zones by reducing hydraulic fracturing water consumption, as the total volume of produced water in 2017 represents only around the total amount of freshwater consumed in the U.S. in 3 days. This is supported by the fact that reuse within the energy sector represents the least risk when compared to reuse in other sectors. The most likely use of produced water out of the energy sector in the U.S. would be in the irrigation sector in some of the semiarid zones with larger produced water volumes, where after treatment, PW would represent 2% of the demand in the Bakken basin, 5% in the Permian Delaware Basin, 63% in the Barnett basin, 77% in Oklahoma, assuming a 50% recovery factor from treatment. Some areas, like California already reuse PW for irrigation, but initial quality of PW is already high and requires minimal treatment. Other sectorial uses are possible, such as municipal or industrial sectors, but only at a local scale. This means PW reuse will not mitigate substantially water scarcity in the country. Discharge into water streams is also difficult as most western streams would be incapable of efficiently diluting produced water. Aquifer recharge is also a consideration, but water quality issues must be thoroughly assessed. This also indicates a need for more efficient methods for the evaluation of produced water composition and profitable advanced treatment methods.

4.2 Reuse of produced water for crop irrigation in Oman

Oman is the largest producer of oil and natural gas of the Middle East (Oman, 2018). A matter of recent concern in Oman fields comes with the fact that most extraction wells currently have higher water production than oil production. This volume rises up to 910,000 cubic meters of water per day, from which 55% is used in reinjection, 33% is discharged in disposal wells and the remainder, around 109,200 cubic meters, is used in seeking alternative methodologies for the management of produced water in order to achieve lower energy consumption and environmental impact. Irrigation of crops is a constantly reviewed possible end-used for treated produced water, with the major drawbacks found in the difficulty to remove salinity and dissolved organics in an efficient way, which can dangerously affect soil quality and plant growth if not carefully managed. The following table describes the treatments used and the results in soil quality after irrigation with produced water.

TABLE 4.1: Technical parameters of produced water used for irrigation of two different fields in Oman.

PW Treatment	**Water quality after treatment**	**Irrigated soil type**	**Modifications used in soil**	**Irrigated crop**
Reed bed and solar distillation	TDS $\leq 50[mg/L]$	Not specified	None	Eucalyptus, Kuwaiti tree, paspalum, cotton
Air flotation, anthracite filtration, activated carbon	Conductivity of 8000 [µS/cm] and TDS of 3000–6000 [mg/L]	Mixture of gravel, sand and organic matter	None except than organic matter initially added to create an experimental soil	Alfalfa, barley, Rhodes grass

In the first case, as water salinity was initially low, the resulting levels after treatment were satisfactory for plant irrigation and no detectable changes were made to the soil or plan growth, allowing for continuous cultivation of eucalyptus, Kuwaiti tree, paspalum and cotton.
In the second case analyzed by Costa et al. (2021), the selected process composed of air flotation, sand filtration and activated carbon adsorption methods allowed for the treatment of large quantities of produced water, between 60 and 430 L per hour. After adsorption, which works as a polishing step, residual oil concentration were reduced to values lower than 0.5 [mg/L], meeting Oman wastewater reuse standards. However, salinity was not efficiently removed, with a concentration of 3000-6000 [mg/L]. That is the reason why crops resistant to high salinity were the target for cultivation, which resulted in no significant differences between crops irrigated with freshwater and those where produced water was used. However, soil salinity increased from 1.63 to 7.08 [dS/m] (deciSiemens is a unit for the measurement of electrical conductivity) after 102 days of irrigation, and sodium concentration increased dramatically from 2.31 to 68.1 [meq/L] causing a reduction in soil permeability. These effects do not allow for effective agricultural development and an effective way to deal with the salinity is required, such as leaching of excess salt below root zones by the use of freshwater mixed with the wastewater. Additionally, the use of extra adsorption steps would allow for a lower salt

concentration, but technical feasibility assessment is required.

4.3 Reuse of treated water produced in China.

China has an estimated production 25 billion cubic meters of natural gas coming from shale reservoirs, with one of the largest reserves around the world. Shale gas requires hydraulic fracturing, which, after consuming large quantities of water, generates equally large quantities of produced water, reaching 25,000 cubic meters per reservoir. Shang et al. (2019) studied a treatment system that uses four processes: coagulation, adsorption, ultrafiltration and reverse osmosis. Water produced in six different wells from the Weiyuan reservoir were evaluated. The following table shows the main characteristics of the batches:

Table 4.2: Parameters observed in produced water from the Weiyuan reservoir at every treatment step, as an average from three samples (Shang et al., 2019)

Param.	Initial composition	Coagulation	Adsorption	UF membrane permeate	RO membrane permeate
Turbidity (NTU)	187	15.8	2.1	0.08	0.07
TDS (mg/L)	116,320	15,715	15,930	15,410	224
Conductivity (mS/cm)	26.79	26.29	26.2	25.85	0.52
DOC (mg/L)	38.03	13.61	5.21	5.19	1.71
pH	7.48	6.93	7.31	7.51	6.65
Na+ (mg/L)	6151	6065	5920	5931	105
Ca2+ (mg/L)	274.7	257.9	201.2	200.9	1.1
Mg2+ (mg/L)	36.5	34.8	26.5	26.4	–
K+ (mg/L)	255.1	246.2	175.7	173.3	2.5
Sr2+ (mg/L)	66.3	57.3	28.9	28.4	–
Ba2+ (mg/L)	94.4	90.2	63.9	61.3	–
NH4+ (mg/L)	60.4	60.2	50.1	50.3	1.3
Cl− (mg/L)	9412	9275	9158	9133	119
NO2− (mg/L)	35.7	31	28.5	28.5	1.3
F− (mg/L)	12.6	11.5	9.4	9.3	0.2
Br− (mg/L)	97.9	94.2	89.8	89.8	1.7
NO3− (mg/L)	161.9	151.9	139.9	138.8	1.2

Adsorption and coagulation processes served as pre-treatment for the advanced treatment techniques of ultrafiltration and reverse osmosis. For coagulation and flocculation, aluminum sulfate octadeca hydrate ($Al2(SO4)3 \cdot 18H2O$) was used. For adsorption, three types of activated carbon were utilized. For ultrafiltration, a polyvinylidene fluoride hollow fiber membrane was employed. Several tests were run, where the pre-treatment steps where added or removed, specifically coagulation alone, adsorption alone and the sequence of both to observe if they positively affected the reverse osmosis procedure. Experiments showed that the more the pre-treatment steps, the less fouling effect was observed at the RO membranes, which is the main drawback to the use of this technology.

This treatment train proved to provide very good results, with a dissolved organic carbon content removal of 95.5% and 98.6% in total ion concentration. As, regulation in China does not provide chemical limitations for hydraulic fracturing, this effluent is more than safe for its reuse within the shale operations in the reservoir. However, Costa et al. (2021) mention that this might not be a long-term solution, as produced water volumes are expected to exceed the water demand of hydraulic fracturing operations with the geological maturation of reservoirs and changes in drilling schedules due to economical variations. Thus, irrigation is a second alternative evaluated: in Chinese environmental laws for crop irrigation, the following minimum parameters are defined: 5.5-8.5 pH, TDS content must be less than 1000 [mg/L], COD must not exceed 150 [mg/L] and sodium concentration must be below 920 [mg/L]. Compared with the results from Shang et al. (2019), this treatment procedure allows water effluents to fit into the criteria applicable for the country.

4.4 Feasibility evaluation of recycling of shale gas produced water from the Sichuan Basin in China.

The research performed by Zhang et al. (2019) used the water effluent from 15 wells in the Eastern Sichuan Basin in 2015, periodically collected and used for experiments. Three setups were evaluated:

1. PW treatment for discharge: laboratory and on-site pilot scale physicochemical pre-treatment reverse osmosis process
2. PW RO concentrate treatment for external reuse: laboratory-scale of the sequential physicochemical process

3. PW biological co-treatment with sewage in WWTPs: laboratory scale of a sequential chemical pre-treatment biological process

Figure 4.4 shows the complete diagram of the procedures implemented for the first two treatment processes.

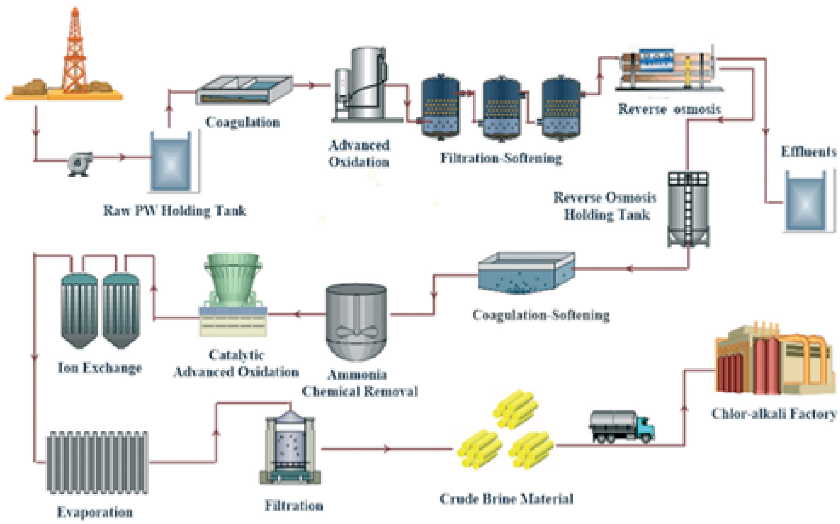

FIGURE 4.3: Flow diagram of the treatment and recycling of produced water researched by Zhang et al. (2019)

The first step after extraction is the containment of water in a holding tank, which allows for some settling time. The following coagulation step allows for the coalescence of floccule and further sedimentation. A Fenton-based oxidation method was then used combined with multi-media filtration to eliminated dissolved and suspended solids, colloids, and organic and inorganic compounds to reduce the membrane fouling at the RO step. Laboratory and on-site scale experiments where performed, where for the latter, a 5 [m3/d] tank was set near a typical well.
After reverse osmosis, a physicochemical process was used to recycle RO concentrates for a chlor-alkali factory near the centralized produced water treatment plant visualized in the area.
A chemical-biological process was then established for the treatability of PW biologically mixed with standard municipal wastewater in order to save disposal costs, with the same Fenton oxidation as a pre-treatment. This step used a moving-bed biofilm reactor process as the biological treatment.

Table 4.3: Water parameters minimum, maximum and mean values of the samples taken from the Easter Sichuan Basin (Zhang et al., 2019)

Parameters	**Minimum**	**Mean**	**Maximum**
pH	6.45	7	8.29
TDS (mg/L)	4900	26500	52500
COD (mg/L)	556	2356	3767
Turbidity (NTU)	500	750	1000

In general, pollutant concentration in the produced water came from chemical additives from hydraulic fracturing. Zhang et al. (2019) mention that TDS content is considerably low in comparison with that of research done in mostly hypersaline water, making membrane adsorption a cost-effective process.

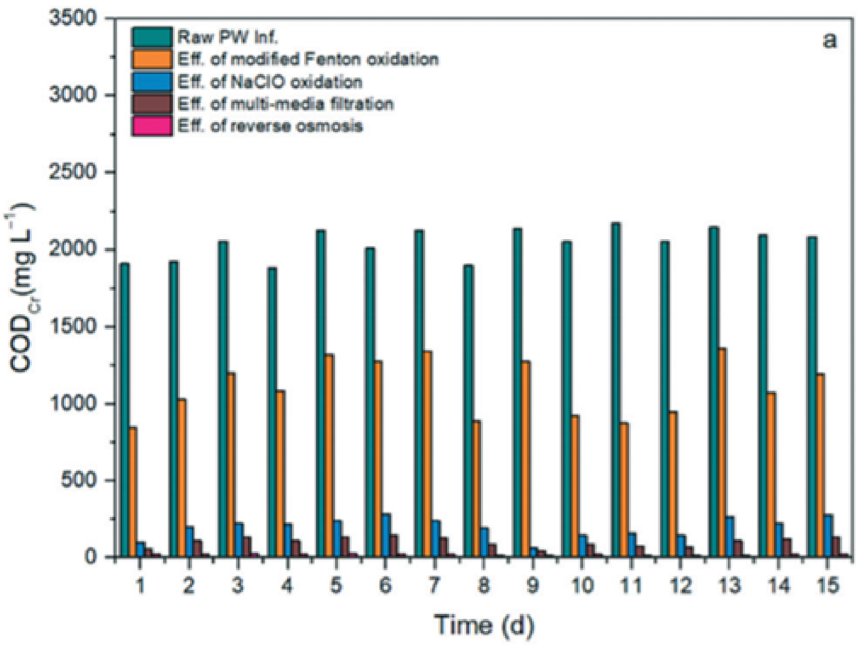

Figure 4.4: Removal profile of COD removal at the pilot scale experiment with samples from 15 days of real production. (Zhang et al., 2019)

The results from laboratory and on-site scale showed that mineralization and desalination of produced water in this field was technically feasible, allowing for discharge on surface water under the legislation of China. The authors focus on the important factor that the correct pre-treatment steps play in the alleviation of fouling on RO, which has still to be tested on the long-term for real cases.

The chlor-alkali factory near the PW treatment plant requires a large volume of brine as a raw material to produce sodium hydroxide. The reverse osmosis concentrates, which are nearly half the volume of raw produced water, were treated and evaporative concentrated to a salinity of above 23% with solid pollutant concentrations well below the brine quality standard limits. The advanced oxidation to remove degrading refractory organic compounds was the main challenge in the recycling. An O3-H2O2 oxidation process exhibited an effective TOC removal, with a residual TOC of 1.6 [mg/L]. Overall, the quality of the concentrated brine satisfied the requirements of the factory. This external reuse for RO waste helps make the process more sustainable, as management and recycling of this effluent is one of the major drawbacks of RO technology. Other technologies used for the management of concentrates include thermal and membrane-based technologies, but the authors indicate this technique results less energy intensive, although it depends on the availability of reuse options.

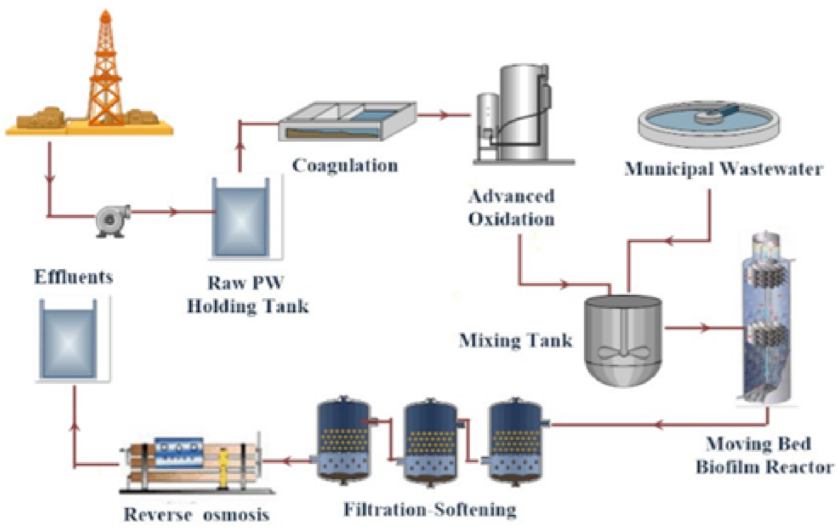

Figure 4.5: Laboratory-scale co-treatment of PW and municipal wastewater by a biofilm reactor.

The last evaluation was to assess if the co-treatment of produced water with domestic sewage wastewater through biological treatment was a feasible option. In a first trial, untreated PW was mixed with sewage and tested. Results showed that the lack of treatment inhibited the process performance significatively, even with a PW-to-sewage ratio of below 15%. Due to this, water was pretreated with advanced oxidation processes and then co-treated for 108 days with different mixing ratios, showing different removal efficiencies for different compounds by increasing or decreasing the ratio. The authors concluded that the effects of high salinity and recalcitrating organic compounds affects the feasibility of the long-term implementation of this method, additional to the lack of research into modified or advanced co-treatment processes, necessary pre-treatments, or configurations to reduce toxicity and increase biodegradability of produced water. Nevertheless, this configuration is certainly a potential cost-effective treatment technique to be developed. Additionally, Zhang et al. (2019) presented an economic evaluation for the PW desalination and RO concentrate recycling in a full-scale centralized shale gas PW treatment plant. The total treatment and recycling of 1 cubic meter of produced water from the field was $12.114. The most significant cost included the advanced oxidation processes, brine evaporation and sludge disposal, as seen in Tables 4.4 and 4.5. Operation costs for desalination is high although PW from this field is similar to seawater in terms of salinity. High additional cost is required to remove hydrophobic organics and colloidal particles to achieve low fouling rates.

TABLE 4.4: Costs in USD for treating 1 cubic meter of PW in a plant with a capacity of 1500 [m3/d] for PW desalination

Cost (USD/m^3)	**Coagulation**	**Fenton oxidation**	**Multi-media filtration**	**Ultrafiltration-RO**
Electricity	0.005	0.034	0.028	1.11
Chemicals	0.039	0.854	0.05	0.03
Sludge	0.625	1.25	-	-
Labor	0.034	0.034	0.034	0.034
Total	0.7	2.169	0.109	1.171

TABLE 4.5: Costs in USD for treating 1 cubic meter of PW in a plant with a capacity of 1500 [m3/d] RO concentrate recycling

Cost (USD/m^3)	**Pre-treatment**	**Oxidation**	**Filtration**	**Evaporation**	**Brine Recycling**
Electricity	0.011	0.612	0.022	5.98	0.015
Chemicals	0.092	0.145	0.095	0.05	-
Sludge	0.773	-	-	-	-
Labor	0.034	0.034	0.034	0.034	0.034
Total	0.91	0.791	0.151	6.064	0.049

Therefore, further studies must optimize pretreatment efficiency and reduce sludge production, as well as the optimization of evaporative systems to reduce the operational cost of this step, which composes the largest expense in the concentrate recycling.
Zhang et al. (2019) mention that although research on PW alternative management due to increasing environmental criteria, the feasibility of integral treatment processes has

not been extensively evaluated and is important for it to develop in the next years, understanding that an applicable treatment process is not merely a combination of processing units, but an optimized result of all technical, environmental an economic factors. Additionally, they indicate that Chinese regulation in terms of unconventional oil and gas industry-specific regulation is lacking and must be developed in order to include toxicity and NORM content, as well as new standards for industrial salts or brine.

4.5 Cost and energy efficiency evaluations for different strategies of treatment for Produced water

As mentioned before, it is a fact that economical rentability is a major factor for the selection of technologies applied in any operation in an oil and gas field. This is true also for waste management techniques, which includes produced water. This means it is necessary to identify the management strategy for this effluent that will give the most benefit at a feasible cost. In the following section, multiple economic evaluations from different researchers were studied in order to obtain a descriptive framework of the operational costs of the most effective produced water management technologies applicable to oil and gas fields.

As stated before, desalination and removal of organic content are usually the main objectives of treatment in order to provide an effluent fit for applicable regulations. Oil and grease removal is the most essential step in produced water treatment, and it is always present at any operation. However, soluble organic compounds are often not characterized for most disposal options but are very important to remove in case reuse is intended. Desalination is another difficult step in water treatment, especially in produced water with much higher salinities than those of seawater. However, desalination is an essential step in order to consider reuse in applications outside the energy sector.

Different factors define the capital and operational costs associated with treatment technologies, such as energy consumption, equipment required, maintenance, and chemical agents required. Desalination especially has high energy consumption overall, where the recently researched reverse osmosis has been proved to have the least energy requirement compared to thermal or membrane processes.

Cost assessment for each available technology varies on a site-to-site basis, as every specific location will present different issues associated with logistics, energy prices, civil work costs, brine composition, taxes, among many other factors.

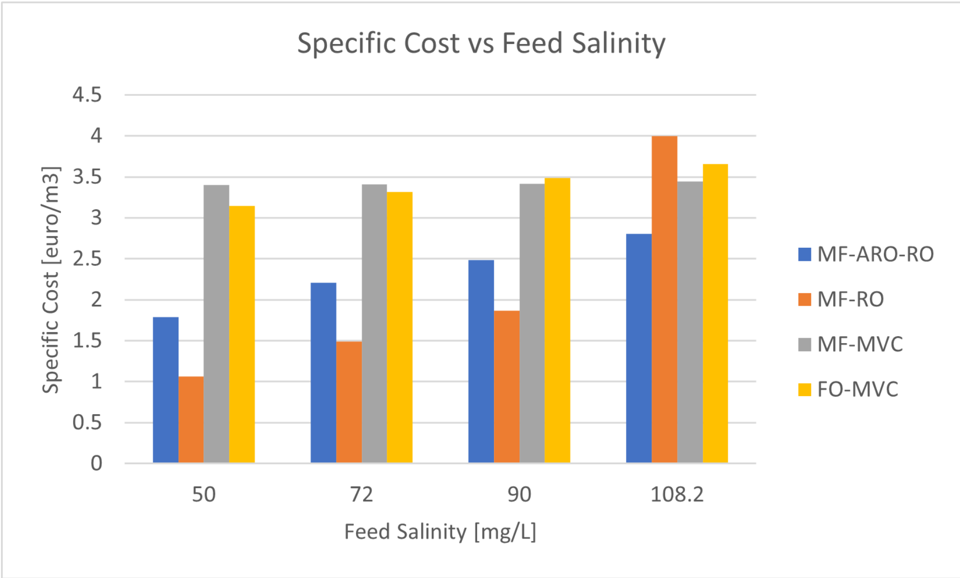

FIGURE 4.6: Specific price for the desalination of 1 cubic meter of water with different feed salinities through different setups: 1) microfiltration-assisted reverse osmosis-reverse osmosis, 2) microfiltration-reverse osmosis, 3) microfiltration-mechanical vapor compression, 4) forward osmosis-mechanical vapor compression.

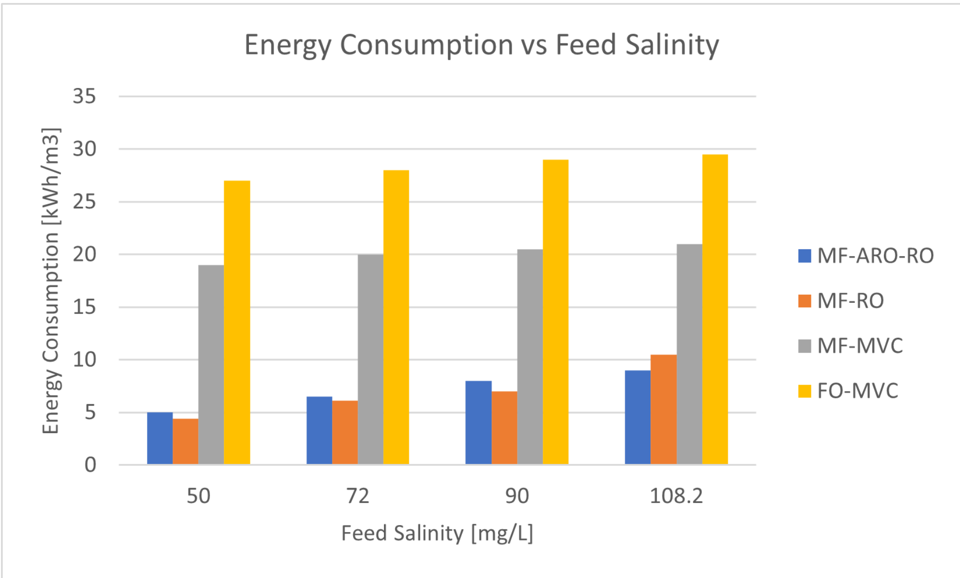

FIGURE 4.7: Energy Consumption in kWh/m^3 for the desalination of 1 cubic meter of water with different feed salinities through different setups: 1) microfiltration-assisted reverse osmosis- reverse osmosis, 2) microfiltration-reverse osmosis, 3) microfiltration-mechanical vapor compression, 4) forward osmosis-mechanical vapor compression.

Osipi et al. (2018) made a cost assessment of different combinations of desalination technologies for onshore treatment, involving forward osmosis (FO), reverse osmosis (RO), assisted reverse osmosis (ARO), microfiltration (MF), mechanical vapor compression (MVC) and membrane distillation (MD). This assessment was run through simulations and optimized for different reuse destinations (focusing on irrigation, with final streams

with 2000 [mg/L] NaCl and 0% oil and grease), with different initial salinity; their results showed that the cheapest combination for salinities lower than 90 [g/L] was the MF-RO, while FO-RO had the highest cost; for higher salt contents, MF-ARO-RO was the cheapest alternative.
Speaking about energy consumption, it depends mainly on the initial composition of produced water; for a 26% initial salinity, a single effect mechanical vapor compression unit have been calculated to consume from 23-42 [kWh/m3] depending on system size and compression efficiency, where a two effect MVC system can require as little as 20 [kWh/m3] . For the same conditions, with a forward osmosis with thermal regeneration, an input of 25-150 [kWh/m3] is required, depending on the site of the unit and its efficiency, although most of energy consumption comes again from the thermal effect. An RO system requires energy inputs of about 4-16[kWh/m3] at moderate recovery ratios. However, lower energy consumption does not necessarily mean lower cost, as systems run primarily on thermal energy may benefit from lower cost energy, and solutions with lower energy consumption require more pre-treatment steps, which varies from system to system and is required for assessment. (**?**).
Membrane distillation evaluated for approximately 2000 [m3/day] with an average salinity of 100,000 [g/L] with a resulting brine of 300,000 [g/L] meaning a recovery factor of 66.7% in the Marcellus shale gas play in USA was calculated to have a total cost of €4.85 per cubic meter, which can be significatively reduced to €0.63 if a source of waste heat can be integrated that, although it requires a higher capital cost for the heat exchangers utilized, would mean total savings that would compensate additional capital cost in few months of operation. The total cost of this water treatment plant was also compared to the business-as-usual (BAU) strategy of USA operators by the use of disposal wells. Considering feed and output water transportation and treatment, the total cost of produced water treatment for membrane distillation is €56.1 per cubic meter, reduced to €51.8 with thermal waste integration. In comparison, the continuation of BAU strategy sums to a total of €112.3 per cubic meter considering trucking and injection in disposal wells. (Osipi et al., 2018).

4.6 Discussion

As interest in environmental protection increases and stricter limits are imposed by regulatory agencies around the world, research on emission reduction advances on every industry. The case of produced water is the same, as research on optimization of advanced treatment strategies is fairly recent and will continue to develop over the years. The main problematic when trying to make a general comparison between all strategies available is that produced water composition is completely different from site to site, even among wells located in the same reservoir. This is important because the efficiency of every treatment technology varies greatly with the initial contents of the water to be treated, especially in terms of dissolved solids and dissolved organic compounds, as well as with the volumes to be treated, and the rates at which they are produced. Additionally, site-to-site differences include also logistic-associated costs, such as the availability of treatment plants, or the rentability of creating them, and transportation costs, space availability, maintenance required, storage costs and final disposition options. These depend heavily on the geographical location of each specific operation, which means a complete techno-economic assessment must be done at every site in order to select and optimize the best solutions possible.
Overall, in literature available, certain treatment technologies are mentioned as the best option, but this varies greatly depending on the factors mentioned. For example, reverse osmosis membrane filtering is constantly referred to as the most energetically and economically efficient technology for water treatment, resulting in very high removal efficiencies. However, they are only applicable for streams with salinities lower than 40 [g/L] which means their application might require different pre-treatment steps, which would increase costs and energy consumption.
Alternatives, such as thermal distillation or mechanical vapor compression are very good at treating water from all sources, but the power requirement associated with heat generation is significatively larger than membrane technologies, which increases operating costs greatly. However, research for optimization includes these conventional technologies with modern approaches, such as the utilization of renewable sources for on-site energy production, or the creation of new designs with the objective of heat recycling within processes to minimize the energy requirements for feed heating, as in the cases of mechanical vapor compression (described before) or even more operation specific set-ups such as the treatment of water produced through steam assisted gravity drainage (a thermal technology for heavy oil and bitumen extraction through the injection of steam) by the use of thermal membrane distillation, which requires extensive amounts of energy for feed heating, but results rentable when using the water produced from this operation as it is already initially at very high temperatures, with costs ranging from 0.25 to 3.8

euros per cubic meter (Elsayed et al., 2015).
This applies also to final-destination strategies, where conventional disposal strategies will remain the most economically feasible approach in most places, unless regulation or logistics change this. In many site-specific assessments available in literature, produced water reuse has proven to be significatively more rentable than disposal, but this depends largely on the demand for such water volumes, such as irrigation fields or chemical plants requiring brine, and the treatment required to minimize risks which, as said before, require extensive assessment for every operation.
Another large problem with feasibility evaluation of emerging treatment technologies is that most of them have been tested only at the laboratory scale; even when some have been tried on pilot tests, most of them remain unproven in real operations, which means more experimentation and real application must be developed in future years in order to point them as best available technologies.

Chapter 5

Conclusions

Every operator in charge of hydrocarbon production activities in the world needs to deal with effluent planification. Reservoir water is the largest of this effluents overall, and current operations have all their own strategies to deal with them based on cost and logistical efficiency. Nevertheless, as environmental damage awareness increases in the world as a whole and the possibility to continue with conventional disposal methods becomes more limited in certain areas as the time goes by, researchers and operators have gained interest in evaluating new methods to dispose of the large volumes of water they are responsible for, and treatment technologies that allow for them to represent the lowest possible environmental damage and human health risks.

Research on technologies begin usually with those that have been successfully applied before at other industrial sectors which have to deal with similar volumes of water, like municipal waste, chemical industries, potabilization of saltwater among others. The difference with produced water comes with the composition of the effluent, where produced water has hydrocarbon, solids and salt contents that surpass by much those contained in water volumes treated in other industries. This includes the presence of dissolved organic matter that is difficult to characterize, and naturally occurring radioactive agents which, even if the concentration is small, can cause environmental problems in the long term when they are not correctly monitored.

Although the treatment required for complying with limits applicable to the industry has been researched for a very long time, some of its long-term effects have been only observable in relatively recent experiments. The main conclusions of current research point at the importance of the availability in the near future for effective characterization methods and requirements that allow for a complete knowledge of the complex composition of every produced water stream to correctly design their final fate.

This final fate conventionally meant being discharged into oceanic bodies, or being injected in disposal wells for underground storage. However, the pondering of the possibility to use this volume for other activities which require large quantities of water creates the option to transform this waste effluent into an actual resource which over time could help fight water scarcity, which is an important issue in some areas of the world. Research until now seems to prove that the highest potential in this area falls into the reuse of water for hydraulic fracturing and other techniques for the enhancement of production within the same industry. This already means a relief on the environment by the reduction of the volumes of water for these activities that need to be drawn from other sources. However, these same activities produce their own effluents which in time must be disposed of, and options for their use as sources for other activities are continuously being evaluated. Even though assessments show that produced water represents a very little percentage of the total volume required for other activities like crop irrigation, this still represents a solid way to dispose of this water in a relatively more useful way than when it is stored underground. However, the further these final use options are from the hydrocarbon industry, the more exposure they mean for humans and the environment, which requires for the action of researchers, regulators and stakeholders to develop chains of supply that allow for the economical feasibility, the environmental safety, and the monitoring of such operations in areas where it results possible. This evolution, however, will be restricted by multiple external factors in the future, such as market prices for hydrocarbon products.

Available technology increases by the year, and current efforts are dedicated at the evaluation of possible applications that produce the most optimal treatment for every specific case, evaluating sensibility to water composition, recovery rates, costs, energy requirements, among numerous other factors. However, most of the research available until this point is based only on laboratory-scale experiments, which are not enough to prove the effectiveness of these novel configurations at real scale, where logistics are complex and operations need to be continuous and efficient during many years. In order to be able to actually prove and standardize methods for certain similar operations, large-scale experiments should be the focus of researchers of produced water treatment optimization.

The petroleum industry will remain an essential part of the economy and the energy generation of the world in years to come, and as international efforts unite to reduce damages caused to the planet to satisfy our needs, it is important for stakeholders of oil and gas production to make their part in order to continue the development of these essential tasks while minimizing their risks for human health and the environment as much as possible.

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