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Management and treatment of produced water laden with organic polymers

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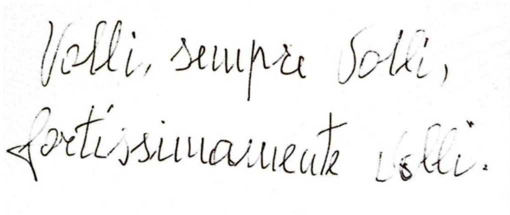

Volli, sempre volli,
fortissimamente volli.

SUMMARY

Abstract

Enhanced oil recovery refers to the process of producing liquid hydrocarbons by increasing the mobility of the displacing phase. Conventional recovery methods such as water and gas injection can extract less than half of the initial amount of oil in place, the remaining oil is a large and attractive target for enhanced oil recovery methods. Partially Hydrolyzed Polyacrylamide (HPAM) is a long-chain polymer added to the injecting fluid to increase the viscosity and the mobility of the displacing phase in a process called polymer flooding. As the HPAM usage for EOR increases due to the gradual depletion of oil resource, the challenge of produced-water management is also raised because residual HPAM in produced water increases unwanted viscosity in discharging or reinjecting the water.

In this work, the physico-chemical properties of the HPAM have been investigated with the target to identify suitable separation processes. The effectiveness of the flocculation enhanced by divalent ions additions was evaluated and compared with other conventional technologies such as membrane ultrafiltration in optimized conditions. Flocculation and ultrafiltration were compared in a representative range of HPAM and TDS concentration observed when this EOR technique is used in real application.

1 Introduction

1.1 General Context: Oil and Gas extraction

The development of oil and gas extraction techniques in the 19th century represented an important step through the industrial revolution and the modern era. However, the energy demand is growing with the increased population and improved lifestyle causing an inexorable depletion of this energy resource. According to the International Energy Outlook (IEO) 2019 published by the Energy Information Administration (EIA) “world energy consumption will grow by nearly 50% between 2018 and 2050”. A detailed picture of this prediction is shown in Figure 1 (a), which shown how most of this growth comes from countries not included in the Organization for Economic Cooperation and Development (OECD)[1] but from country where strong economic growth is driving demand, particularly Asia.

Although renewables will have the fastest growth, oil consumption will also increase, reaching almost 250 quadrillion British Thermal Units (BTU)[2] in 2050. In the period between 2018 and 2050 there will be an increase in energy consumption of approximately 300 quadrillion BTU, reaching an annual consumption of over 900 quadrillion BTU. This annual energy demand will be supplied for a third by oil, as depicted Figure 1 (b) [1].

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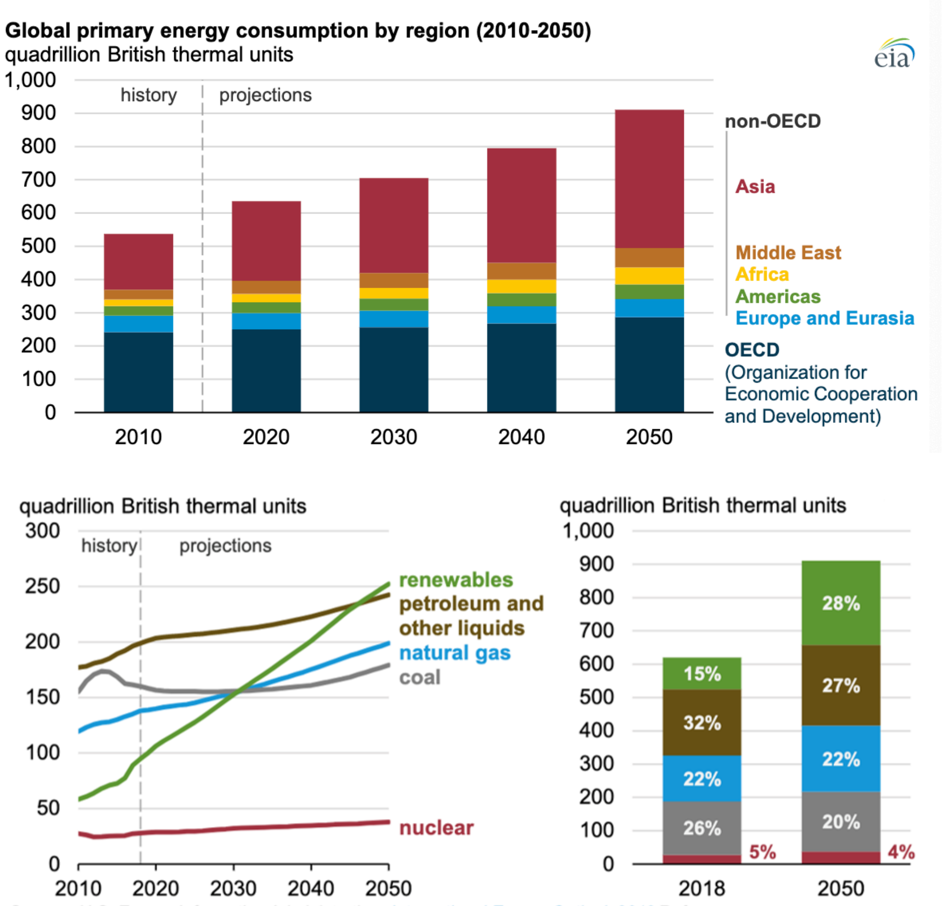
[1] OECD is a forum of countries describing themselves as committed to democracy and the market economy, providing a platform to compare policy experiences, seek answers to common problems, identify good practices and coordinate domestic and international policies of its members.

[2] A British thermal unit (Btu) is a measure of the heat content of fuels or energy sources. It is the quantity of heat required to raise the temperature of one pound of liquid water by 1 degree Fahrenheit at the temperature that water has its greatest density (approximately 39 degrees Fahrenheit).



Source: U.S. Energy Information Administration, *International Energy Outlook 2019* Reference case

(a)

(b)

Figure 1: *Global Primary energy consumption by region from 2010 with projection to 2050 described in British Thermal Units divided for (a) countries in the Organization for Economic Cooperation and Development (OECD) and non-OECD, (b, left) energy resources with (b, right) relative fraction on the total consumption in 2018 and projection in 2050 [1].*

1.2 Oil and gas extraction: Techniques and regulations for produced water

Petroleum and natural gas production occur through extraction wells. The process generates wastewater coming from the geological formation, these are contaminated by chemicals that are added into the extraction water, drilling fluids, oil and greases [2].

Oil and natural gas extraction process can be divided in the following steps:

1. Site preparation and drilling: after having put in place all the necessary infrastructures, the well is drilled to the depth of the reservoir [3].
2. Production: after completing the well, production begins and oil and natural gas are extracted from the reservoir.

The production phase can take place using three different techniques:

- Primary recovery: it is based only on natural forces, that is the strong difference in pressure that pushes the oil upwards [4], and it is used generally as a first stage of oil extraction [5].
- Secondary recovery: it is used as a second stage of oil production, generally it uses water flooding processes, increasing the extraction from 15 to 40% of the oil in place [6].
- Tertiary recovery: or Enhanced Oil Recovery (EOR), generally uses gas injection, thermal or chemical methods, reaching an extraction efficiency of about 60% [7].

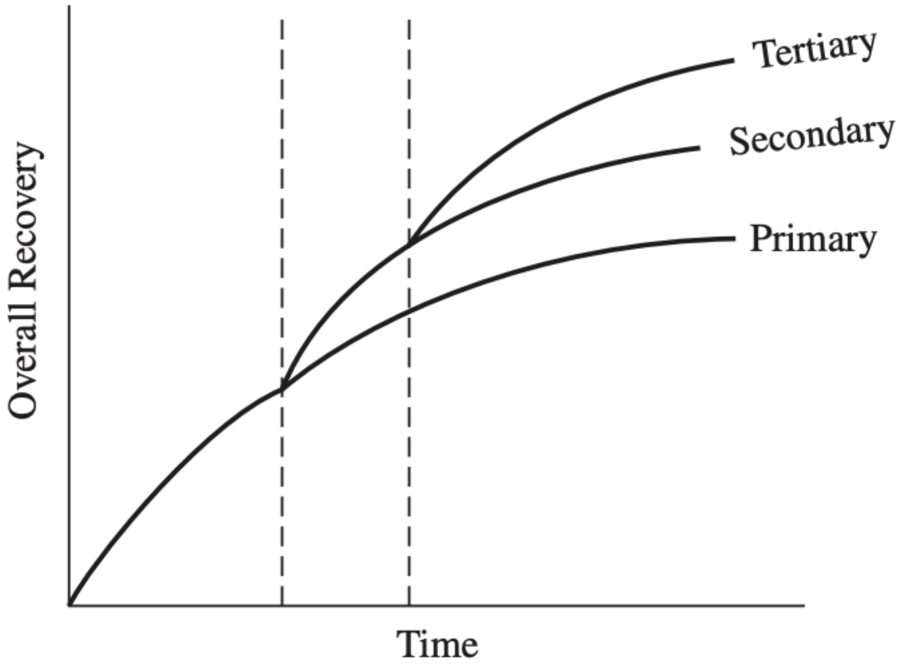


Figure 2: Overall Recovery as a function of time for oil extraction. To maximize the recovery, the oil must be kept under pressure and the extraction procedure is divided in stages: primary, secondary and tertiary recovery [8].

The oil extraction process is generally started with a first primary recovery phase, followed by the secondary and tertiary recovery stages. Indeed, the maximum overall recovery occurs if the three recovery methods are used in sequence, as shown in Figure 2 [8].

1.2.1 Enhanced Oil Recovery (EOR)

Although the demand for energy is increasing, the amount of oil produced by traditional methods (primary and secondary recovery) is running out. Classical methods of oil extraction can only extract part of the oil: a part of it remains trapped in the reserves due to capillary forces [9]. As already seen, oil extraction must take place in stages, to maximize the extraction efficiency.

The tertiary recovery, or Enhanced Oil Recovery (EOR) method, is an increasing technology for the extraction of trapped crude oil. EOR allows to extract 30 to 60% of a reservoir's original oil [10].

Figure 3 shows how EOR technique works: there is an injection well for gas, heat or chemicals and a production well for oil extraction [11]. There are three EOR techniques:

- Gas injection: uses gases (natural gas, CO_2 or nitrogen) that expand in the reservoir. The expansion allows to push up oil in the production well. Other gasses can be used that lower oil viscosity to increase its flow rate.
- Thermal injection: uses heat (in the form of steam) to lower oil viscosity and increase its flow rate through the production well.
- Chemical injection: uses various chemicals (as dilute solutions) to mobilize oil and reduce surface tension. Water-soluble polymers are generally used to increase the viscosity of water and oil production as a consequence.

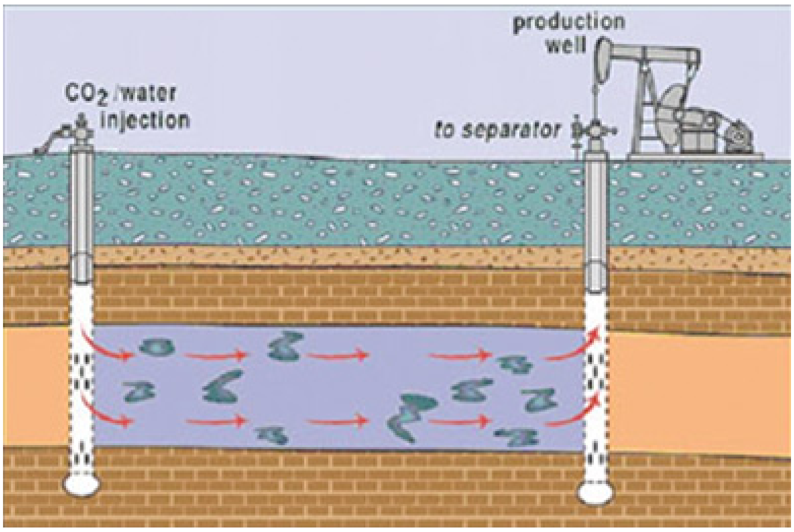


***Figure 3**: Scheme of EOR process: there is an injection well for gas, heat or chemicals and a production well for oil extraction. The injection elements cross the reservoir mobilizing trapped oil and gas and taking them to the extraction well [11].*

Chemical injection is a water flooding based process that is relatively low-cost. It can be used in high viscosity reservoirs if polymers are added to water. This last technique is called polymer flooding and it allows to bridge the difference in viscosity between water and oil. Polymer flooding increases the sweep efficiency with three mechanisms: it increases the viscosity of water, it minimize the permeability of water and it cover a larger area in the reservoir [12].

This process can be defined with the Mobility Ratio value, equal to:

$$\mathbf{Eq. 1} \quad M = \frac{mobility\ of\ displacing\ phase}{mobility\ of\ displaced\ phase} = \frac{K_w \mu_o}{K_o \mu_w}$$

Where:
- M represents the mobility ratio
- μ_w and μ_o represent the viscosity of water and of oil, respectively
- K_w and K_o represent the permeability of water and of oil.

To ensure a high sweep efficiency M must be lower or equal than 1, so the mobility of displaced phase must be higher than the mobility of displacing phase. Sweep efficiencies are a strong function of the mobility ratio. The phenomenon called viscous fingering can take place if the mobility of the displacing phase is much greater than the mobility of the displaced phase [13] as depicted in Figure 4 (a). The addiction of polymer is useful to retard this phenomenon, it acts reducing water mobility and producing a more stable displacement, as shown in Figure 4 (b) [14]. To increase water viscosity is then a good way to have a low value of M.

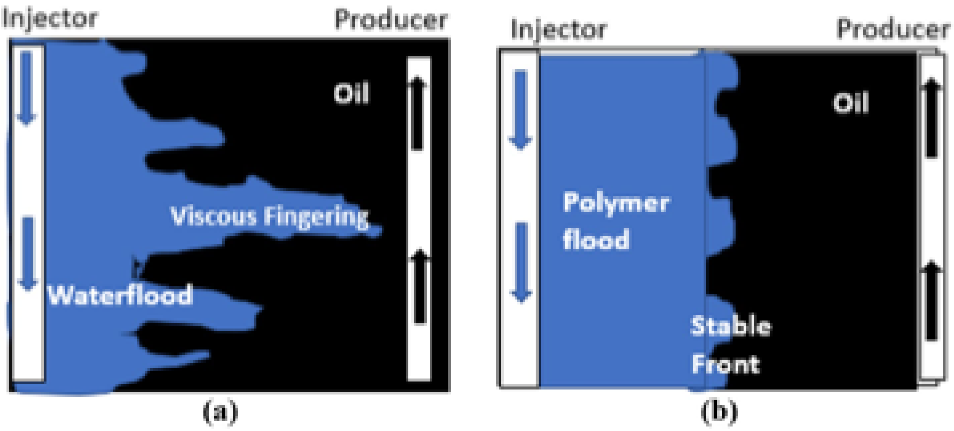


***Figure 4**: Scheme of oil displacement in Enhanced oil recovery:*
(a) Typical effect of mobility ratio M > 1 in water flooding: water is less viscous than oil and viscous fingering happens
(b) Typical effect of mobility ratio M < 1 in polymer flooding: the high viscosity of water leads to a stable front for the displacement of oil [14].

Polymer flooding is a widely used technology for oil recovery in mature reservoirs [15]. Generally, to improve oil recovery, long chain polymers are added to the injection water. Co-solvents or surfactants are also added to the solution to increase its stability and to reduce the surface tension between oil and water, this resulting in an increasing of efficiency [16], [17].

1.2.2 Produced water: regulation and treatment

The extraction procedures, particularly in the case of secondary and tertiary recovery require huge amounts of water.

The Environmental Protection Agency (EPA) has enacted the "Oil and Gas Extraction Effluent Guidelines and Standards" which regulates wastewater discharges from oil and gas extraction [2].

The type of hydrocarbon, the geology and the extraction method influence chemical and physical properties of the water leaving the reservoir [18].

An example of contaminated water is shown in Table 1. It contains mainly [19]:

- Total Dissolved Solids (TDS)
- Oil and Greases (O&G)
- BTEX[3]
- PAHs[4]
- Organic acids
- Phenols
- Inorganic compounds (e.g. heavy metals)
- Chemical additives used in the drilling operations and during fracturing.

Those listed contaminants are subject to strict limitations since the treated produced water could be either discharged into the environment or reused in extraction processes. Table 2 lists the limit parameters for reinjection.

The conventional treatment of produced water is divided in different stages. Firstly, the effluent passes through a two or three-phase separation system that generates an oil stream, a water stream and a gas stream. The water goes in primary treatments (such as hydro-cyclone or similar separators) and then in secondary treatments that are usually floaters. Tertiary water treatments (or polishing treatment) such as Carbon Adsorption, Air stripping, Chemical or Biological treatments or Membrane Filtration are usually required [18], especially when the produced water is either contaminated by high salinity and other volatile and small molecular weight contaminants.

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[3] BTEX is the acronym for benzene, toluene, ethylbenzene and xylene. These substances are part of the volatile organic compounds (VOCs) found in petroleum products.

[4] The acronym PAHs indicates polycyclic aromatic hydrocarbons. They contain two or more benzene rings joined in a single structure and are found naturally in coal and oil.

Table 1: *Produced Water quality from an oil extraction plant in Oman. The PW is contaminated by monovalent and divalent salts, sulfates, carbonates and heavy metals. It contains a huge amount of dissolved and suspended solids and it is characterized by high viscosity, due to the presence of HPAM.*

Parameter	Unit	Value
Sodium (Na)	mg/l	1,500
Calcium (Ca)	mg/l	50
Magnesium (Mg)	mg/l	10
Potassium	mg/l	25
Bromide	mg/l	9
Fluoride	mg/l	2.0
Chloride (Cl)	mg/l	2,000
Bicarbonate Alkalinity	mg/l as CaCO3	800
Carbonate Alkalinity	mg/l as CaCO3	<1.0
Sulfate (SO4)	mg/l	46
Carbonate (CO3)	mg/l	42
Silica (SiO2)	mg/l	24
Total Dissolved Solids (TDS)	mg/l	5,000
Suspended Solids (SS)	mg/l	5 to 7
pH		7.0 to 8.0
Turbidity	NTU	10 NTU
Hydrogen sulfide (H2S)	Not Reported	Not Reported
Aluminum	mg/l	0.03
Arsenic	mg/l	0.52
Barium	mg/l	0.39
Beryllium	mg/l	0.15
Boron	mg/l	1.69
Cadmium	mg/l	0.16
Chromium	mg/l	0.19
Cobalt	mg/l	0.1
Copper	mg/l	0.66
Lead	mg/l	0.21
Manganese	mg/l	0.13
Mercury	mg/l	<0.01
Molybdenum	mg/l	0.33
Nickel	mg/l	0.11
Selenium	mg/l	0.15
Strontium	mg/l	2.04
Vanadium	mg/l	0.15
Zinc	mg/l	1.350
Acetate	mg/l	2.0
Formate	mg/l	<1.0
Propinate	mg/l	<1.0
Ammonia as N	mg/l	<0.03
Nitrite + Nitrate as N	mg/l	<0.02
Total Phosphorous as P	mg/l	<0.05
OIW	ppm	50 – 100
Polymer (HPAM)	mg/l	70 – 1000
TSS	mg/l	<5
Viscosity	cP	Up to 12
H2S in water	ppm	50

***Table 2**: Limit parameters of Produced Water for the reinjection during the extraction of oil and gas from the reservoir. Viscosity must be reduced and also TSS content.*

Parameter	Unit	Limit
OIW	ppm	< 5.0
TSS	mg/l	< 2.0 (max. 10µm particle)
H_2S	ppm	< 10
Fe^{2+}	ppm	< 1.0
Dissolved Oxygen	ppb	< 10.0
Viscosity	cP	<1.5

In fact, as is shown in the water analysis of a real produced water stream (Table 1) Partially Hydrolyzed Polyacrylamide (HPAM), the added polymer in the EOR process, still loads the water stream in a concentration comprised between the 70 and 1000 mg/L, a considerable amount due to the rheological behavior exerted by this polymer, elevating the viscosity above 12 cP[5] at those concentration.

HPAM is one of the most widely used polymer for polymer flooding process [14], it is added to the injected water in high concentration (250 – 2000 ppm) to increase viscosity and then oil displacement efficiency. Because of the presence of HPAM in the water stream after the three-phase separation, the treatment processes must lower the viscosity at least 10 times to reach the limit values listed in Table 2.

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[5] Centipoise (cP) is the unit of measurement of dynamic viscosity in the CGS system and is equivalent to mPa·s in the International System.

1.3 Partially hydrolyzed polyacrylamide (HPAM): Chemical structure and influencing parameters in polymer flooding

Partially hydrolyzed polyacrylamide (HPAM) is a water-soluble polyelectrolyte characterized by negative charges on its chain.

Chemical structure of HPAM is shown in Figure 5: the left molecule is the amino group, the right molecule is the carboxyl functional group [15].

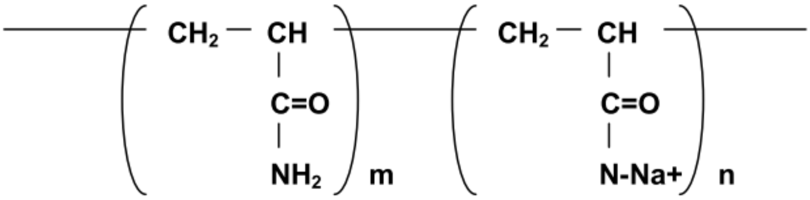


Figure 5*: Chemical structure of HPAM: on the left there is the amino group, on the right there is the carboxyl functional group which causes viscosity to increase if the polymer is brought into solution [15].*

Its high viscosity in solution is due to the negative carboxyl functional groups which cause electrostatic repulsion contributing to chain extension [15].

In particular, the viscosity of HPAM in solution relies on:

- pH: high pH causes deprotonation of carboxyl functional groups, increasing the electrostatic repulsion and resulting in an increase in viscosity
- Salinity: higher concentrations of monovalent and divalent cations lead to a decrease in viscosity due to a shield effect on the negative charge of the carboxyl functional groups
- Temperature: high temperature causes a reduction in viscosity, HPAM cannot be used in reservoirs with temperatures above 70 °C
- Molecular weight (MW): the higher is the MW, the higher is charge density of the polymer and viscosity increases

- Concentration: a higher concentration of HPAM leads to a higher viscosity of the solution [14].
- Degree of Hydrolysis: a chemical reaction in presence of water that allows polymer molecules to split into two or more parts, influencing its sensibility to pH variation. If the degree of hydrolysis increases, the pH sensitivity increases too.

Since polymer flooding strength relies on the higher viscosity of the injected fluid, those parameters need to be considered together to avoid viscosity reduction during the extraction phase.

Indeed, salinity can lower the stability of the emulsion, this phenomenon can be even enhanced by temperature increasing. The stability can be reduced to a critical point, called Cloud Point, that is the temperature from which the particle aggregation is induced causing plugging of porous media. Therefore, a polymer solution is potentially useful in EOR applications only below its cloud-point temperature [8], [10], [12].

On the other hand, these phenomena could be induced to separate the polymer in a flocculation-filtration treatment step at the head of a possible produced water treatment line.

1.4 HPAM separation from Produced Water in Polymer flooding

As mentioned in the previous chapter, the addition of HPAM in water has usually a range from 250 to 2000 ppm (parts per million) [24]. Leaving the reservoir, the Produced Water will certainly have a lower HPAM content, generally 70 – 1000 mg/L, as it interacts with the subsoil and a part of it precipitates, but especially due to the primary treatment of the produced water (i.e. Three-phase separation). However, specific steps are required during the water treatment to remove HPAM, especially when the target is water reinjection. Low viscosity limits of the reinjected fluids are usually met by HPAM degradation. However, degradation processes require high investment and operative costs, moreover, the oil extraction plants are generally located in remote areas involving high costs in chemicals transport and management. From this prospective, new technologies for HPAM separation in the produced water might be interesting.

In this work, preliminary tests for produced water treatment were made: an innovative flocculation-filtration method was tested, using divalent ions that are often already present in water and varying influence parameters such as temperature and pH. These parameters influence the Cloud Point, allowing the removal of the polymer. This method was then compared with other more established methods, such as membrane Microfiltration/Ultrafiltration technologies.

2 Materials and methods

2.1 Chemicals and membranes

The polymer (HPAM) and salts (NaCl, $MgCl_2$, $CaCl_2$) were purchased from Sigma-Aldrich. Ultrapure water was used as solvent for solution preparations and the pH was adjusted through NaOH and HCl (purchased from Carlo Erba, Italy). Five ceramic membranes made of TiO_2 were selected for this study (namely 1, 5, 15, 150 KDal and 0.45 μm with 6 mm inner diameter and 250 mm length) ranging from tight UF to MF. All the membranes have been purchased from TAMI Industries.

2.2 Flocculation-Filtration experiments

The flocculation experiments of HPAM were conducted under different conditions of salinity, pH and temperatures. Before flocculation, the solution was carried out at room temperature (25 °C) in sterile glass volumetric flasks and mixed with a magnetic stirrer for at least 24 h to ensure a complete solubilization of the polymer in the brine solution. During tests, pH was varied through controlled additions from concentrated stocks of soda and hydrochloric acid while temperature was regulated by a thermostatic bath. Target values were reached and kept as constant through the use of a pH-meter and a thermometer, respectively.

To induce flocculation, the target content of divalent cations was reached by controlled additions of concentrated stocks of $MgCl_2$ and $CaCl_2$.

A set of preliminary tests were conducted in very controlled conditions to assess the role of temperature, pH and divalent ions in the flocculation process. Those tests were performed with a high concentrated brine solution in term of monovalent ions and low operating volumes of 40 mL. The flocculation efficiency was retrieved by TOC analysis difference between the pre-flocculated solution and of the permeate obtained from the filtrate of 2 μm mesh filters.

2.3 MF/UF experiments

The microfiltration/ultrafiltration (MF/UF) experiments were performed in a lab-plant (Figure 6) composed by an isolated tank containing a heat exchanger which was used to heat up the 2 L of feed solution to the target operative temperature of 50 °C. The heating fluid was carried through a thermostatic bath and a thermometer inside the tank was used to monitor the effective feed temperature during filtration tests. A tangential flow rate of 200 L/h (Cross Flow Velocity, CFV, of 2 m/s) and 1 bar of applied pressure were set through an inverter controlling-volumetric pump and a back pressure valve. Ceramic membranes were used to treat the stream (feed) and the permeate flux was monitored during the test through a computer-interfaced balance system.

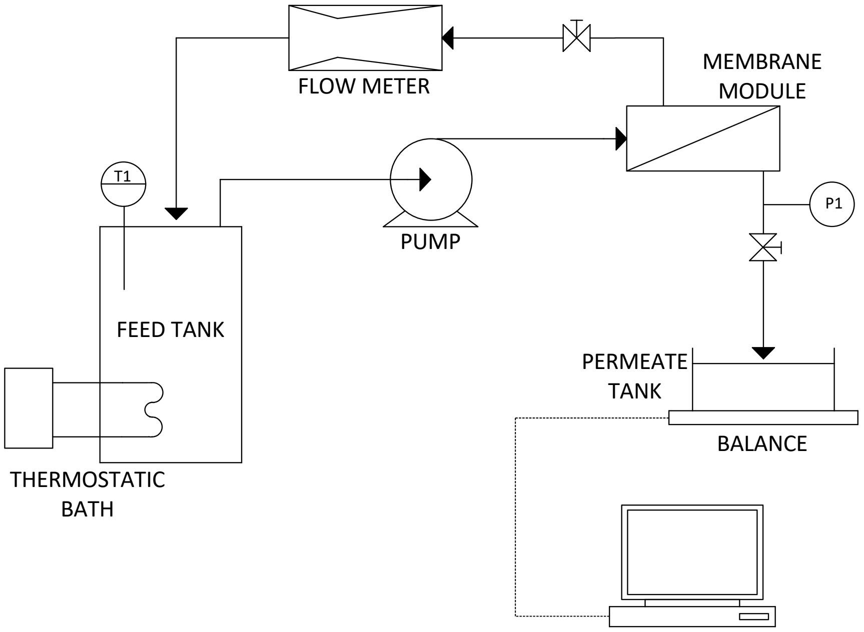


***Figure 6**: Pilot plant for MF/UF experiments. The Feed it is pumped in the membrane module through volumetric pump. The temperature is kept as constant by a thermostatic bath which heat exchanger was located in the tank.*
Cross flow velocity (CFV) and pressure are regulated by flowmeter and a valve.
The exerted pressure on the feed in the membrane module allows permeate collection which mass is weighed with a computer interfaced balance.

2.4 Analysis

2.4.1 TOC analysis

For the TOC analysis a TOC-L, Total Organic Carbon analyzer purchased by Shimadzu was used, showed in Figure 7 (a). The total organic carbon content measure is retrieved by the amount of CO_2 produced by its oxidation in the combustion chamber.

TOC-L analyzes 40 mL samples in series and was used to calculate the HPAM removal after the investigated treatment processes (i.e. flocculation-separation and membrane filtration). The removal of TOC was obtained from the difference between the organic carbon content before and after the treatment through the **Eq. *2***.

$$\textbf{Eq. 2} \quad TOC\ removal = 1 - \frac{C_{treated}}{C_{stream}}$$

Where:

- C_{stream} is the concentration before the treatment
- $C_{treated}$ is the concentration after the treatment.

2.4.2 Viscosity measurements

Viscosity measurements was made using a viscosimeter purchased by Anton Paar showed in Figure 7 (b). The viscosity was measured under different shear rate conditions, ranged from 1 to 100 s^{-1}. Viscosity measurements were made to derive rheological properties of HPAM solution, by varying all the parameters of influence.

40 mL samples were prepared at room temperature with progressive additions of chemicals (salts, NaOH or HCl) and then mixed with a magnetic stirrer for 24h.

The samples were then placed in 15 mL sterile laboratory tubes and analyzed with the viscosimeter.

2.4.3 Zpot analysis

The Z potential for different solutions was measured using a Zetasizer Nano analyzer purchased by Malvern, Figure 7 (c), that uses Light Scattering techniques to derive the superficial charge of samples, which affects the flocculation process. Samples were prepared through the same process explained above, by varying progressively salts content and pH.

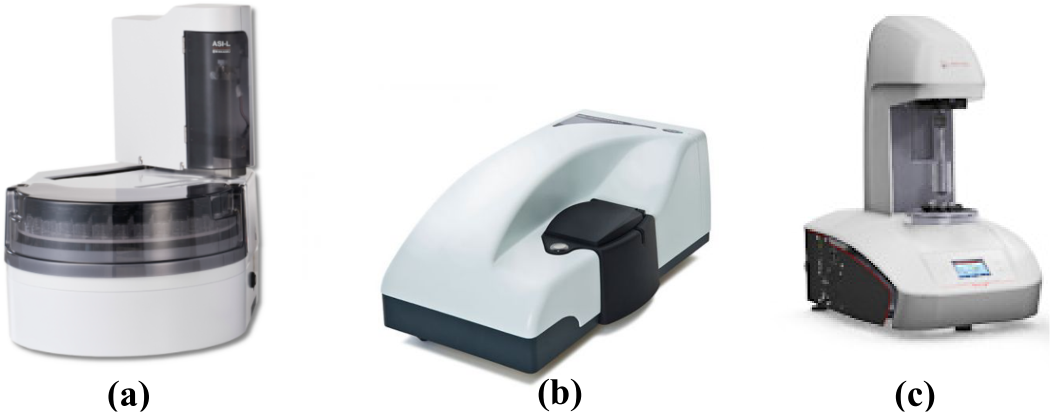

(a) **(b)** **(c)**

Figure *7: (a) TOC analyzer (b) viscosimeter (c) Zpotential analyzer.*

3 Results and discussion

3.1 Physico-chemical behavior of HPAM

Partially Hydrolyzed Polyacrylamide (HPAM) is widely used in polymer flooding because of its suitable solubility in water and its low cost [13].

The physico-chemical characteristics of the polymer was analyzed to understand how to remove it from the produced water: its dimension in solution was studied for membrane processes purposes, its charge and its response to pH variation was studied for flocculation purposes. Viscosity is also a very important parameter since it influences the complexity of treatment and management of the produced water: indeed, very viscous water is more difficult to treat.

3.1.1 Size of the polymer in solution and titration

As depicted in Figure 8, the polymer size increases with the concentration, reaching a clear asymptote to 1.5 µm above 100 mg/L HPAM. For the investigated range of concentration this value can be assumed as the main dimension of the polymer in water solution. For membrane processes purposes, the dimensions of the polymer in solution suggests to conservatively work in a range that goes from the tight UF to MF.

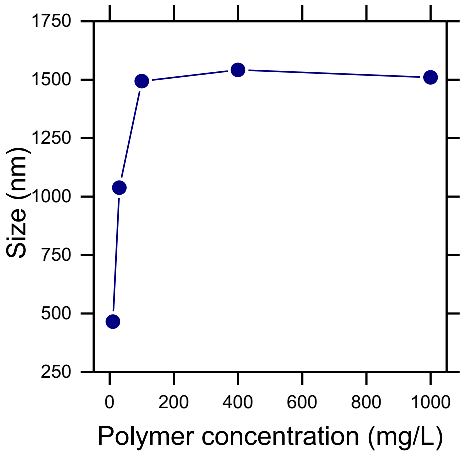


***Figure 8**: Polymer size. the polymer size increases with the concentration, reaching a clear asymptote to 1.5 µm after 100 mg/L HPAM.*

Titration was carried out to study the behavior with pH variation of the polymer in solution. Titration is a technique that consists in adding a solution that contains a known titre of a reagent (titolaite) into a known volume of solution with an unknown titre containing the analyte (titrating). Knowing the volume of titrant used and the reaction stoichiometry, it is possible to trace the concentration of the analyte. Titration can be acid-base, useful for determining the unknown concentration of an acid or base. The pH value initially varies very slowly and then has a sharp surge at the equivalence point, that is, the point where the moles of the titrant are stoichiometrically equal to those of the analyte. From the results of titration, it seems that HPAM itself can act as a buffer (Figure 9), therefore, a flocculation process carried out at high pH could have high soda dosage costs.

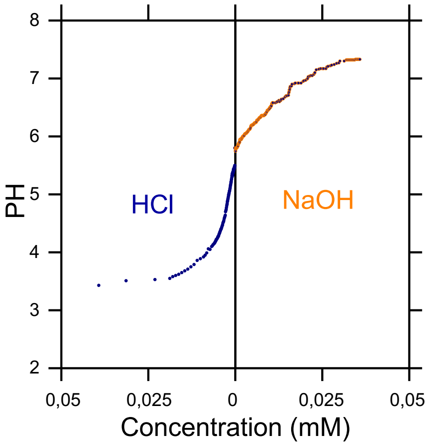


***Figure 9**: Titration of HPAM solution. HPAM can act as a buffer.*

3.2 Rheological behavior of HPAM

HPAM acts increases the viscosity of the solution and this behavior is advantageous to achieve good sweep efficiency during extraction. Viscosity is a function of different parameters, depending on shear rate, temperature, molecular weight (generally in the order of 10^{-7}), polymer concentration, pH, salinity (particularly divalent ions concentration [25]).

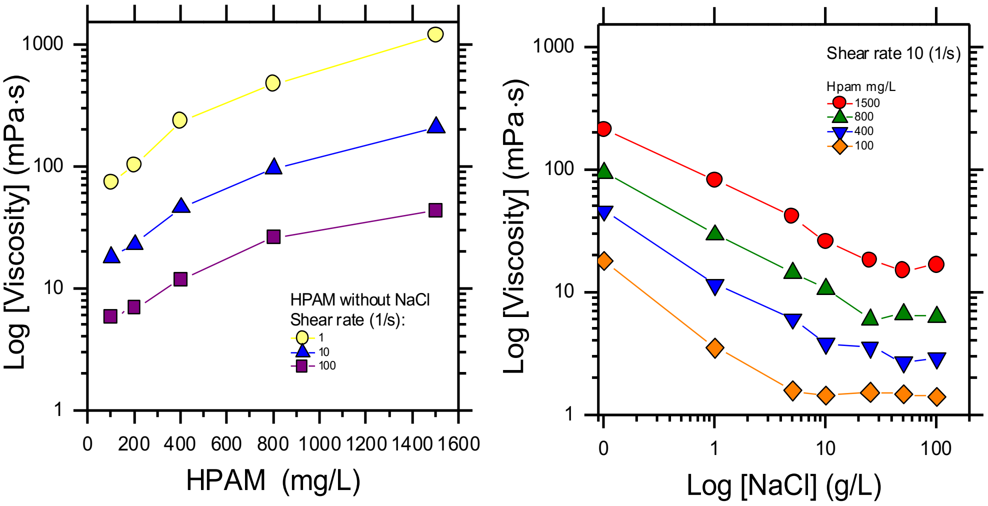
In general, during the oil extraction procedures, an attempt is made to control and predict these values so as not to decrease the viscosity of the solution during its use. However, these parameters could also be exploited during the Produced Water (PW) treatment train, to have a treatment step aimed at removing the polymer from the solution. A study of all the parameters of influence was made to verify if it is possible to use them to remove the polymer from the PW: Table 3 schematically shows the effects of the parameters on viscosity. To perform a deep insight in the rheology behavior, the combined effect of the most important parameters was investigated in this study.

***Table 3**: Influence parameters in a solution with HPAM and effects on its viscosity.*

parameters		effect on viscosity
shear rate	1/s	inversly proportional
salinity	g/L	
divalent ions	g/L	
pH	-	directly proportional
polymer concentration	mg/L	

3.2.1 Concentration, shear rate and salinity

The tested concentrations were 100-200-400-800 and 1500 mg/L HPAM, since produced water usually has HPAM content between 70 and 1000 ppm.



(a) (b)

Figure 10: (a) Dependence of HPAM solution from shear rate: the viscosity decreases if the shear rate increases (b) Dependence of HPAM solution from salt content: Viscosity decreases in NaCl concentration increases.

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Figure 10 (a) shows clearly the dependence of viscosity on polymer concentration: viscosity increases as HPAM concentration increases. This is due to the fact that, with high concentrations, the number of polymer molecules in the solution increases and more interaction between molecules can be seen. .

Figure 10 (a) shows also that HPAM in solution has a shear-thinning behavior [13], [25], [26]: the viscosity decreases if the shear rate increases. This is due to the fact that the high shear rate deforms and aligns the molecules along the flow direction. The size of the molecules (influenced by the pH), therefore, will minimally affect the viscosity of the solution.

The shear thinning behavior (non-Newtonian behavior) of HPAM is observed also in literature, where it is regulated by the following equation [13]:

$$\textbf{Eq. 3} \quad \mu = k\gamma^{n}$$

Where:

- μ represent the viscosity
- k is the consistency index
- γ represent the shear rate (1/s)
- n represent the flow behavior index.

If k and n are determined, the viscosity can be obtained under any shear rate but unfortunately it is still very difficult to predict HPAM viscosity under shearing degradation. For this reason, the dependence of viscosity on shear rate's value was studied using a rheometer.

So, as shown in Eq. 2, a fluid with shear thinning behavior has a negative exponential qualitative trend of viscosity for different shear rate values, as depicted in Figure 11 [27].

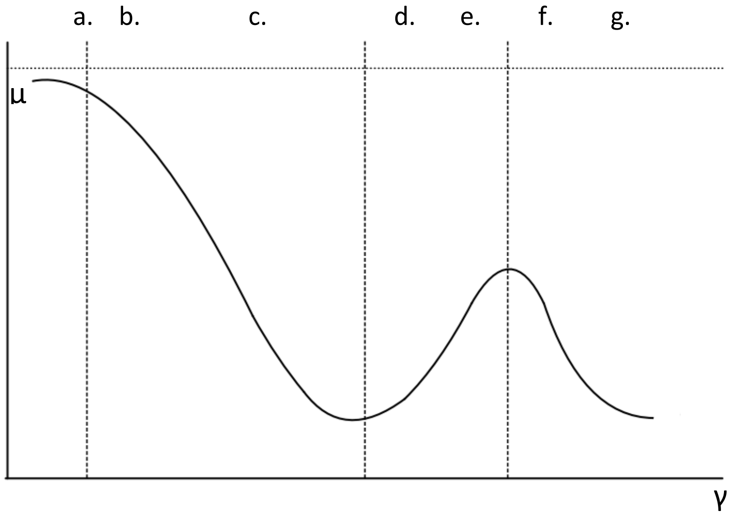

***Figure 11**: qualitative relationship between viscosity μ and shear rate γ. (a) zero shear rate (b) (c) shear thinning area, the viscosity drops as the shear rate increases (d) (f) extensional flow region (f) polymer destruction (g) brine viscosity reached [25].*

Figure 11 [27] shows the qualitative relationship between viscosity and shear rate:

- at zero shear rate the viscosity is the highest and constant

- (b) (c) increasing the shear rate, the fluid has a non-Newtonian behavior (shear thinning area), the viscosity drops as the shear rate increases
- (d) (f) extensional flow region causes an increase in viscosity
- (f) the polymer is destroyed and its length reduces
- (g) brine viscosity is reached.

For our purposes, the optimal shear rate for the interpretation is 10 1/s:

- 1 1/s is too close to measurement inferior limit
- 100 1/s have a masking effect on other parameters.

Keeping fix the shear rate to 10 1/s, the effect of salinity on viscosity was also studied.

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Figure 10 (b) shows the effect of salt (NaCl) on the viscosity of the solution for different concentration of HPAM. As the salt concentration increases, viscosity decreases until an asymptote is reached: the concentration of NaCl at which an asymptote is reached is proportional to the concentration of HPAM (if the concentration of HPAM increases the asymptote is reached for higher values of NaCl concentration) but never higher than 30 g/L NaCl for each case.
This behavior, called “buffering effect”, occurs because, once in solution, the polymer chain of HPAM interact with negative charges, the polymer chains lengthen repelling each other. However, if electrolytes are added, the repulsion between negative charges of carboxyl groups is shielded [21], reducing the viscosity of the solution because of the shrinkage of the molecule [25] as depicted in Figure 12.

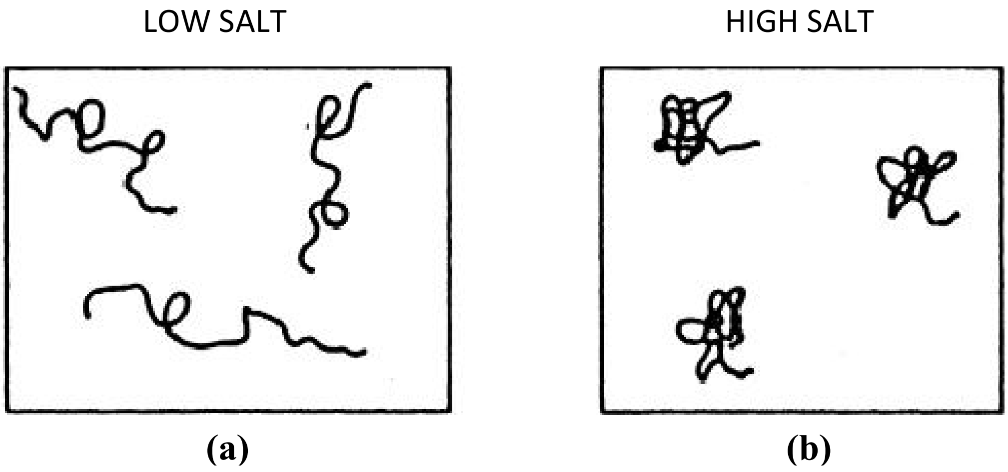

***Figure 12**: (a) HPAM in solution stretches its chain because of the repulsion between negative charges on the carboxyl groups.*
(b) In presence of salts, the negative charges are shielded, the shrinkage of the molecule happens [25].

3.2.2 Divalent ions at different salt content

A higher reduction of viscosity than those obtained for NaCl can be observed if divalent ions are added to the solution. This phenomenon is illustrated in Figure 13 for different concentrations of NaCl. It can be seen that the decrease in viscosity is less pronounced if enough NaCl is already present in solution, this happen because, once the divalent cations are added, they found the polymer already shielded by salt. However, for low concentration on NaCl, the effect of divalent ions (in the form of $MgCl_2$ and $CaCl_2$) is very pronounced: because of their higher polarizability and charge, the divalent ions bind on anions on the molecule chain, contracting the molecule to its minimum charge as described in the next chapter.

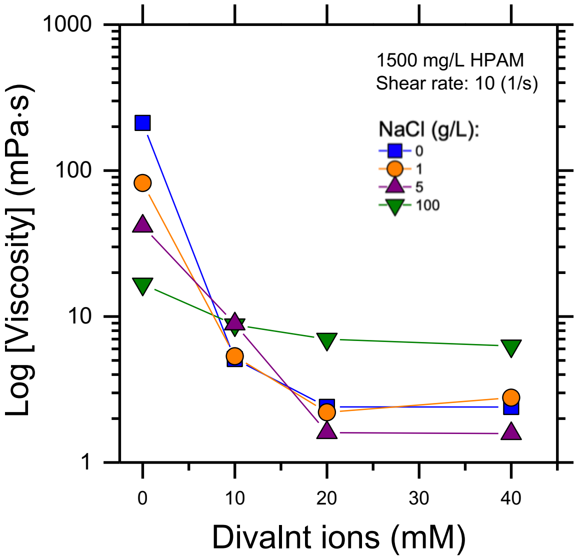

***Figure 13**: effect on divalent ions on viscosity for a solution 1500 mg/L HPAM. All the samples reach a clear asymptote in viscosity after 20 mM of divalent ions. The effect of divalent ions is less pronounced if high amount of NaCl is present.*

3.2.3 PH

As already mentioned, HPAM has two functional groups: the carboxyl group that control the pH sensitive rheological properties and the amino group. Depending on pH conditions, the carboxyl group exchanges protons with dissolved salts.

At high PH, the carboxyl groups dissociate, they are negatively charged and have a strong electrostatic repulsion that makes the molecule stretch. This leads to an increase in the viscosity of the solution [20]. The increase of viscosity ended at pH 6, as shown in Figure 14, because at this value the molecules reach their maximum extension [15].

On the contrary, at low pH, the carboxyl groups are protonated with hydrogen ions this leads to no charges on the polymer chains.

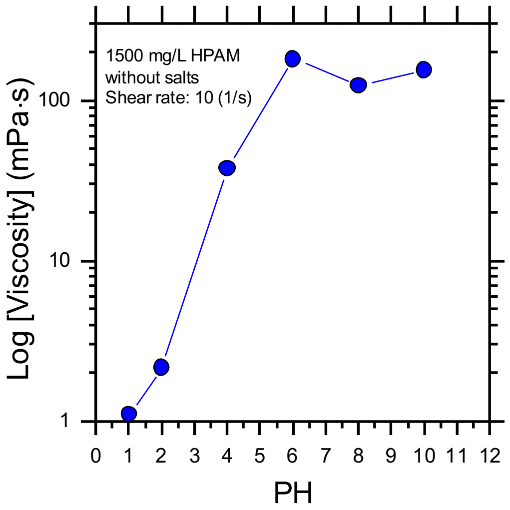

***Figure 14**: Viscosity as function of pH. Viscosity increases, reaching its maximum at pH 6 because at this value the molecule reaches its maximum extension.*

To deeply investigate the charge shielding effect provided by salts, causing the viscosity reduction, Z potential measurements were also performed. The Z potential, or electrokinetic potential, is responsible for the stability of the solution: high values for Z potential give high stability to the solution, because of the electrostatic repulsion that avoid the aggregation of the disperse particles, instead, if the Z potential is low, attractive forces prevail over the repulsive ones and therefore coagulation and flocculation phenomena can take place.

In this study the Z potential for different solutions and for different values of pH was measured using the dynamic light scattering, that allows to measure the mobility of suspended particles in a liquid, directly proportional to the Z potential.

Figure 15 shows the following experimental results:

- The effect of pH is negligible for high values of monovalent ions. Indeed, salt shields the polymer charge [21]

- Without TDS[6], pH plays a key role in the electrokinetic potential, increasing the pH, Z potential also increases, reaching a good stability at pH 10. This is due to the deprotonation of carboxyl functional groups
- With divalent ions pH influences the stability of the solution. By adding divalent salts, the solution is more stable because the charge is shielded more effectively than with the monovalent salts. Also, with divalent salts crosslinking phenomena could occur between carboxylate groups of different HPAM molecules. After a certain pH, then, flocculation occurs (Z potential decreases dramatically in absolute values): At higher pH deprotonation is enhanced and the free carboxylate groups can more easily be crosslinked by magnesium allowing flocculation to occur.

  For this reason, magnesium is much more effective in the flocculation and coagulation process than NaCl, and, even below the flocculation point, $MgCl_2$ has larger effect on the polymer charge even at a much lower concentration compared to NaCl.

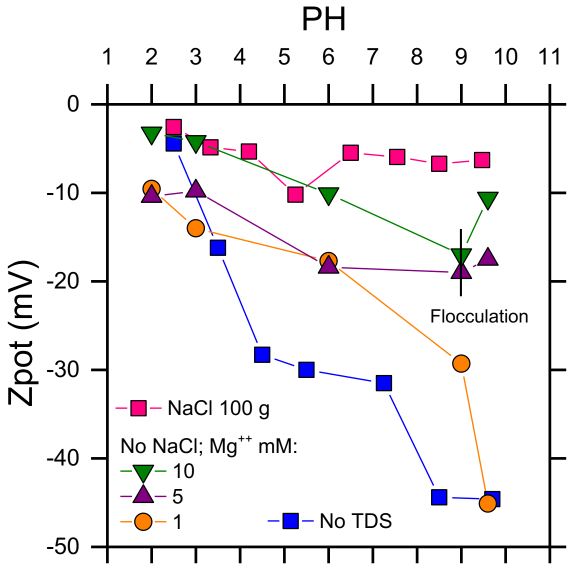

Figure 15*: The effect of pH is negligible for high values of monovalent ions. With divalent ions pH influences the stability of the solution. Without TDS, increasing the pH, Z potential also increases.*

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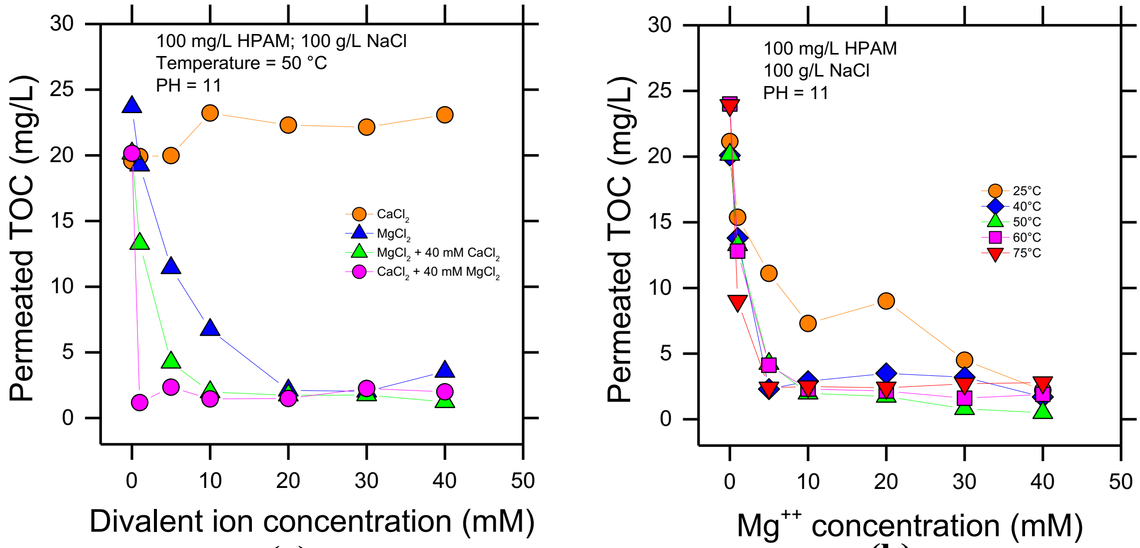
[6] TDS is the acronym for Total Dissolved Solids. In this case it can be assumed equal to the concentration of monovalent and divalent salts because the solution was prepared with demineralized water.

Overall, from the data obtained from the study of rheology and electrokinetic potential, it is clear that divalent ions and pH play an important role in the destabilization process, therefore they may be used for the flocculation process. On the other hand, the size of the polymer gave an indication that MF/UF processes might be used for polymer separation when still solubilized in the stream with regard in monitoring these parameters in order not to induce unwanted flocculation and pore-clogging during membrane operation with possible consecutive impairment of the process.

In the next chapters, flocculation and membrane separation techniques are tested and compared with careful attention to the investigated and influencing parameters described in this chapter.

3.3 Flocculation experiments results

The results obtained above confirms that divalent cations (particularly Ca^{2+}, Mg^{2+}) and pH can be used to promote the precipitation of HPAM.



(a) **(b)**

Figure 16*: The TOC content indicates the presence of HPAM in solution.*
(a) influence of different divalent ions on flocculation process: Calcium seems not to have any effect, instead Magnesium strongly influences the flakes formation
(b) effect of temperature on the permeated TOC: the increase of divalent ions causes thermal instability.

Figure 16 (a) shows the effect of divalent cations on the stability of the solution. The temperature was set on 50 °C because it is the temperature at which Produced Water is in general.

As expected, multivalent cations in solution cause instability: they are chelated by HPAM, forming stable cross-linking[7] complexes [28] and then precipitate complexes. Therefore, the physical and rheological properties of the solution are modified as describe in previous chapters [22].

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[7] Cross-linking is a process of chemical join between two molecules. Crosslinking reagents are molecule with reactive ends that are capable of attaching to functional groups on other molecules.

In the investigated conditions, calcium seems not to have a strong influence on the flocculation process, instead magnesium strongly influences it. At 100 mg/L of HPAM, the great removal efficiency happens at 10 mM Mg^{2+}. Hence, magnesium plays a predominant role in removing the polymer under these conditions, however a substantial increase in pH is required for flocculation (below pH 11 no precipitation was observed) and this could lead to high treatment costs, according with the results obtained from the titration (Figure 9).

In Figure 16 (b), instead, the effect of temperature on the stability of the solution was studied. The figure shows that temperature has a marginal role on the flocculation process [29]. It was made to vary from room temperature to 75 °C, because HPAM can be used only in low temperature reservoir and removing it at high temperatures would be very costly.

For all the tests, except for those conducted at room temperature (i.e. 25 °C), an asymptote was reached after a Mg^{2+} concentration greater than 10 mM, as expected. In this condition, 10 mM of divalent ions was enough to remove almost completely the 100 mg/L HPAM by filtering the stream with a 2 μm filter after flocculation. The temperature was then set at 50°C. This can be considered as the average temperature at which the Produced Water leaves the reservoir. Moreover, the process has an optimum at 50°C because, from direct observation of the flocculated samples, at lower temperature flocculation is weakly induced while higher temperatures seem to compromise the flakes integrity.

3.4 Membrane experiments results

3.4.1 Basic principles of membranes

Flocculation-filtration processes have limits because of the costs of the necessary chemicals for the flocculation processes, moreover, this kind of process requires a lot of space, which is often not present near the field, especially in offshore fields. As all the techniques currently used in wastewater treatment plant have limitations for the removal of particles with diameters lower than 20 µm [30], membrane separation could be used as a competitive technology as tertiary treatment removing solubilized particles in the dimensions range of the investigated polymer (see Figure 8).

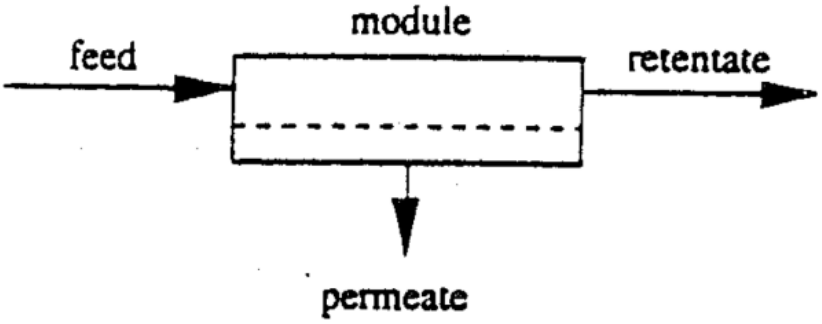


Figure 17: Filtration process: the feed enters in the module; the presence of a selective barrier (the membrane, represented with a dashed line) allows only some substances to pass through (permeate) and retain other substances (retentate or concentrate) [31].

Apart from the cleaning step, membrane process usually does not require chemical additives, the separation between water and HPAM happened because of the presence of a selective barrier, represented in Figure 17 with a dashed line. The membrane allows only some substances to pass through while it is not very permeable to other substances. The fluid that passes through the pores of the membrane is called permeate, what is retained is called retentate or concentrate.

In this work ceramic membranes were used because of their capability to be used in aggressive environment such as acid conditions or high temperature [32]. As already mentioned, the separation processes used in this work are microfiltration and ultrafiltration. The permeate transport mechanism in the MF/UF process can be described by the “pore-flow model”, in which solvents, generally water, passes through tiny pores, transported in a pressure driven convective flow [33]. The pore-flow model follows the Darcy’s law in Eq. 3.

$$\textbf{Eq. 4}\quad J = Kc\frac{dp}{dx}$$

Where:

- J represents the rate of transfer or water flux (g/cm^2·s)
- K is a coefficient that reflect the nature of the medium
- c represents the concentration (g/cm^3)
- dp/dx represent the pressure gradient in the porous medium

The general apparatus containing the membrane is called “vessel”. In Figure 18 that one used for this study is shown with two out of five of the relative used ceramic membranes.

Figure 18*: ceramic membranes (on the right) with their steal support structure (on the left).*

Tubular ceramic membranes which carry out crossflow filtration were therefore used, making a section of the membrane it is possible to see the qualitative behavior of the membrane, as shown in Figure 19.

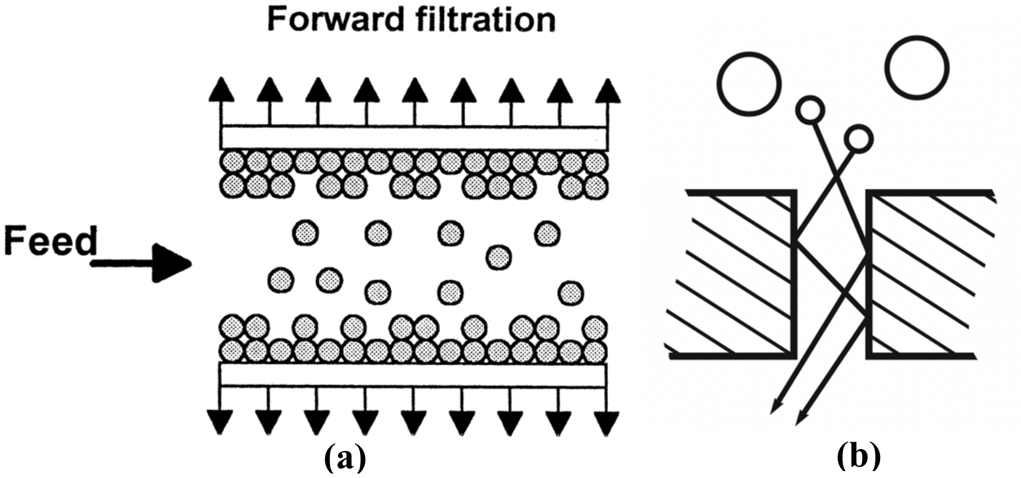
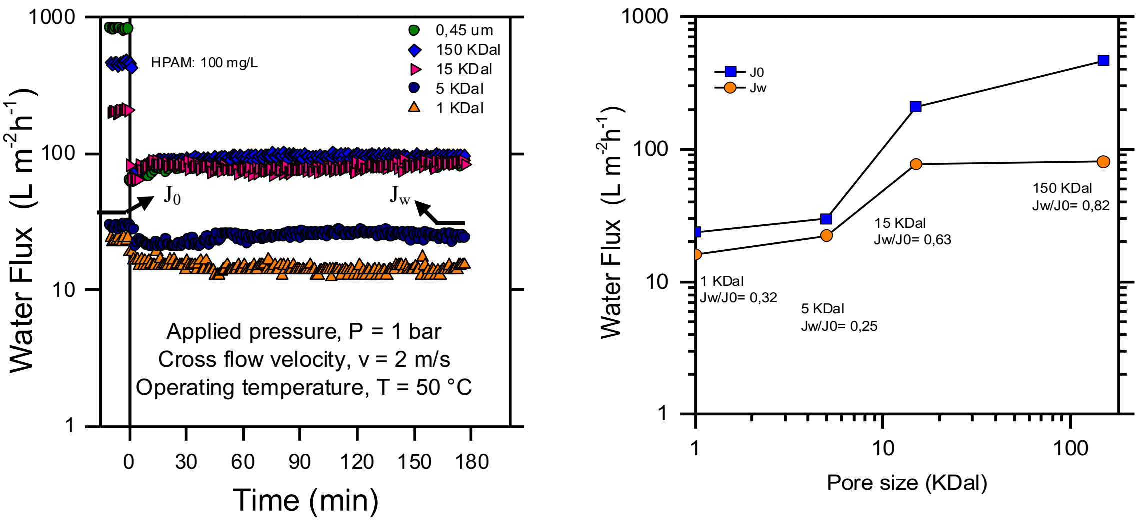


Figure 19: *ceramic tubular membrane: (a) qualitative behavior for the crossflow filtration: The Feed passes in the membrane, most of the particles remain trapped inside it because they are larger than the pores of the membrane (b) [33].*

3.4.2 Results of the membrane filtration experiments

Ceramic membranes with different pore size (i.e. 1, 5, 15, 150 KDal and 0.45 µm) were tested to find the most efficient one in terms of selectivity and permeability. When membranes are used, the main problem to be evaluated is the membrane fouling [31], due to the deposition of solute on the membrane, that causes changes in its structure and surface chemistry.

These effects cause the decrease of the permeate flux, with a loss of removal efficiency and time.



(a) **(b)**

Figure 20: (a) membrane permeability as a function of time. For negative times there is the stable flux phase: J_0 is the water flux through the membrane using DW. With HPAM injection an instantaneous decrease in the permeate flux is observed (J_w). (b) graphic representation of the flow loss for the 5 kDa and the 15 kDa membrane. The 5 kDal has a low water flux but also a low flow's loss; the 15 kDal has a higher water flux with respect the previous one.

Figure 21 (a) shows the water flux in the membrane against time. Negative time indicate the water flux before polymer addition and it is called J_0 in Figure 21 (a) and (b), it is the water flux through different membranes if demineralized water is used, it is called stable flux phase [34]. At time zero, the concentrated stock of polymer was added to reach 100 mg/L in the feed solution after addition. For all the tested membrane, a decrease in the water flux was immediately observed. The mean of the last values of the test is called J_w. In MF/UF process, HPAM induced an instantaneous decrease in the permeate flux, apparently proportional to the applied pore size of the membrane. From this point, the permeate flow remains constant without any direct observation or effect of fouling [30] when working at constant HPAM concentration in the feed (the permeate was continuously recirculated in the feed tank to not considered any effect imputable to polymer concentration). From the figure, two membranes are selected (the 5 kDal and the 15 kDal) as potentially usable membranes. **Figure 21** (b) can be used to select the best one.

The selection of the best membrane was basically based on two parameters:

- There must be the minimum flow loss, basing on Eq. 4.

$$\textbf{Eq. 5} \quad flow\ loss = 1 - \frac{J_0}{J_w}$$

- The flow must not be too low because of excessive treatment times and costs.

Based on these two factors, the two best membranes are confirmed to be:

- The 5 kDal membrane, due to its low flow loss with respect to the others
- The 15 kDal membrane, because it has a low flow loss with a higher value of flux with respect the 5 kDa one.

For the 5 kDal and 15 kDal membranes, recovery tests were also made for a feed composed by 100 mg/L HPAM and 1 g/L NaCl, to prevent the presence of salt from affecting the viscosity of the solution.

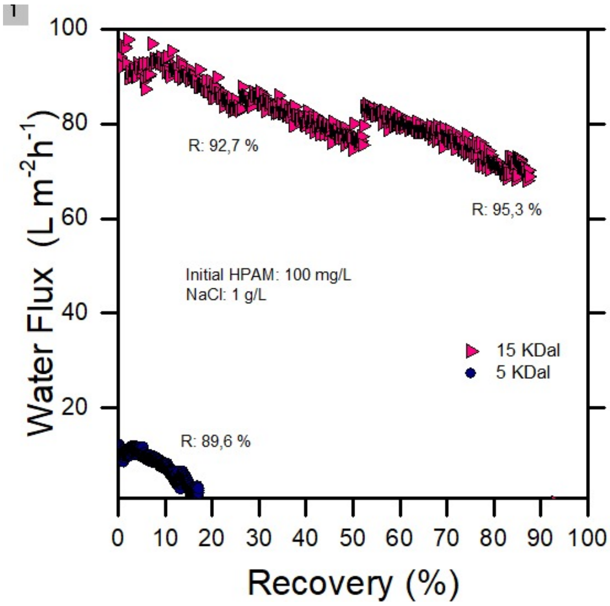


Figure 21*: Comparation between 5 and 15 kDal membranes.*
The 5 kDal one is not suitable for HPAM removal because of its too low water flux; instead, the 15 kDal membrane is promising because it has a low drop in water flux and high recovery and rejection (R) values.

The selected membranes have been then tested in two recovery experiments to assess the validity of the method to extract a clean permeate that could be used for reinjection purpose, while concentrating the polymer in a lower volume of stream that could be more easily managed. Figure 21 compares the two membranes in terms of water flux, recovery and rejection (R).

When the feed water passes across the membrane, only a part of it is converted to permeate. This parameter is the recovery rate (%) that can be expressed with the following Eq. 5:

$$\textbf{Eq. 6} \quad Recovery\ (\%) = \frac{Permeated\ volume}{Initial\ feed\ volume}$$

Instead, rejection term (R) represents the number of particles removed from the feed water and it can be expressed with the following equation:

$$\textbf{Eq. 7} \quad R = \left(1 - \frac{C_p}{C_f}\right) \cdot 100\ \%$$

Where c_p is the permeate concentration and c_f is the feed concentration.

Rejection is a measure of the capability of the membrane to separate substances from the feed solution.

Therefore, from Figure 21 it can be seen that the 5 kDa membrane shows a water flux below 10 LMH, which can be considered as too low for economical application. Moreover, maximum recovery achievable in those conditions was below 20%. For this reason, the 5 KDal membrane it is not suitable for removing HPAM under these conditions.

On the other hand, the 15 kDal membrane, allowed 80% recovery with still an economically feasible value of flux, above 60 LMH and a high and quite constant rejection above 92% during all process. Moreover, it has a good water flux and the flow drop is not too high, this allows for shorter treatment times. The water flux drop may be due to the formation of a cake layer on the surface of the membrane that causes fouling.

Therefore the 15 kDal membrane appears to be promising for the removal of HPAM from the feed.

Furthermore in terms of process costs the 15 kDal membrane is certainly less expensive than the 5 one.

4 Conclusions

HPAM is a long-chain polymer widely used in oil extraction during Enhanced Oil Recovery processes. It acts by increasing the viscosity of water in polymer flooding processes, increasing the displacement efficiency. Viscosity depends on different parameters, such as the applied shear rate, temperature, molecular weight, polymer concentration, pH, monovalent and divalent ions concentration. These parameters could either be exploited with the purpose to treat the target produced water limiting viscosity related criticality in managing the stream itself downstream in the treatment train.

In this work, the physico-chemical properties of HPAM were investigated to identify suitable separation processes before evaluating their effectiveness at the laboratory scale. Subsequently, two possible treatments were identified: flocculation followed by sedimentation or macrofiltration, and membrane processes.

In case of flocculation, the governing parameters were identified as: divalent ions concentration, temperature, and pH. In particular, divalent ions such as $MgCl_2$ dramatically decreased the viscosity of the solution for low concentration HPAM streams: because of their high polarizability and charge, the divalent ions bind on anions on the molecule chain, contracting the molecule and causing flakes formation. This process is strongly influenced by the pH of the solution. In fact, for high values of pH the carboxylate groups of the molecules undergo deprotonation and they can bind to divalent ions, allowing flocculation.

The obtained results in flocculation suggested that the optimal flocculation process can be obtained for a magnesium concentration equal to 10 mM and for a pH equal to 11, at 50 °C when treating a concentration of 100 mg/L of polymer in the stream. In these operating conditions, in fact, the removal of HPAM, conducted with 2 µm filters, reached an efficiency higher than 95%.

However, these operating conditions would lead to high soda dosage costs due to the "buffering effect" of HPAM.

The flocculation process was then compared with membrane filtration processes. Polymers dimension in water solution was measured by light scattering analysis, resulting below 1.5 μm in the typical range of concentration in a produced water stream. Based on this result, a filtration range comprised between tight UF and MF was selected. Ceramic membranes with different pore size distribution were used because of their capability to be used in aggressive environment as usually faced by produced waters treatment plants. The choice between the different membranes was made on the basis of efficiency: the membrane must be the most selective one but it must still maintain a high permeate flux. From the results of the preliminary tests, two potentially effective membranes have been identified: the 5 kDal and the 15 kDal ones. However, the 5 kDal membrane did not well performed the recovery tests due to infeasible permeate flux and low maximum recovery reached. This result could be impaired by the high selectivity exploited by this membrane. On the other hand, the 15 kDal membrane performed a high recovery, above 80 %, with high and constant rejection during the whole duration of the test. The water flux was high enough during operation, always above 60 LMH thus reducing treatment times and possible investment cost in case of scale up in real application. It was therefore concluded that the 15 kDal could be the suitable membrane for HPAM removal.

In conclusion, both processes analyzed can be used for the removal of HPAM from water. In particular, flocculation has the limits of the high costs of the reagents and the high footprint, important factors especially in offshore application. On the other hand, membranes seem a good alternative to flocculation for HPAM removal, especially with 15 KDal pore size and opens prospective for further experimentation on fouling phenomenon and regeneration procedures, especially under the wide range of different conditions that can be observed when treating produced water in real application.

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