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Electrodialysis-based desalination and reuse of sea and brackish polymerflooding produced water



DESALINATION

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GRAPHICAL ABSTRACT



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ABSTRACT

The reuse of polymer flooding produced water (PFPW) generated in oil and gas industry is limited by its salt content, making desalination by electrodialysis a promising treatment option. Therefore, this study aimed to 1) assess the technical feasibility of employing electrodialysis to desalinate PFPW generated in assorted scenarios, and 2) evaluate the reuse of the electrodialysis-desalted water to confect polymer-flooding solution. The experimental work involved desalting two kinds of synthetic PFPW solutions, one with relatively low salinity (TDS = 5000 mg/L, brackish PFPW), and another with high salinity (TDS = 32,000 mg/L, sea PFPW), at two different temperatures, and later reusing the desalted solution to prepare viscous solutions. For the electrodialysis runs, the effects of feed composition and temperature on water transport, energy consumption and current efficiency were analyzed. It was found that the presence of polymer did not significantly influence the water transport rate or the specific energy consumption for the seawater cases, but had a measurable effect when desalting brackish PFPW. Still, both kinds of reused PFPW probed adequate to be employed as a basis for preparing n polymer solution.

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1. Introduction

1.1. Polymer flooding produced water

Polymer flooding is a method for chemical enhanced oil recovery (cEOR) that relies on the use of polymeric solutions to increase the recovery of hydrocarbons from existing oil fields. It is currently applied in several projects around the world –including countries like China, India, Oman, Angola, USA, Canada, United Kingdom, and Brazil– and its use is predicted to increase since both energy and oil demand will keep growing during the following decades, while finding new oil fields becomes increasingly challenging and costly [1–4].

Polymer flooding consists in employing displacing fluids with high viscosity, which consequently reduces the mobility of the aqueous phase and the water/oil mobility ratio, and finally leads to an increase in the macroscopic displacement efficiency [5]. In practice, this means that large volumes of water viscosified with polymers are pumped through an injector well in order to sweep the remaining oil and increase its recovery. The produced stream is later recovered in a production well and split in a gas, an oil and a water stream; the latter better called polymer-flooding produced water (PFPW) so to distinguish it from other produced water without polymers.

Depending on the geographic location of each project, the water for preparing the polymeric solution can be taken from different sources, therefore varying extremely in composition and salinity. As a rule, offshore projects rely on seawater as main water source, while onshore projects can have access to a variety of water sources. Recently, Henthorne et al. [6] published a survey about the source of injection water for over fifty EOR projects, including besides polymer addition, other chemical and thermal methods: most common source of water used was produced water itself (over 50% of the cases) followed by seawater (40%). The authors also reported that the salinity range of the water employed (57% of cases) was between 10.000 and 50.000 total dissolved solids (TDS), followed by lower salinity waters in the range of 1000 to 10,000 TDS (23%). For the specific case of polymer flooding projects, Standnes & Skjevrak [7] summarized the characteristics and results of 72 polymer flooding projects implemented around the world. Considering only the projects for which the polymer injection water quality is clearly stated, > 50% reported employing fresh water for the polymer preparation, 22% reported using produced water and 15% made use of high salinity water. Even though fresh water appeared as the preferred option, it must be considered that many of the evaluated projects were carried on during the 1960's to 1980's, but in contemporary conditions of growing water-scarcity and increasingly stringent legislation, it is foreseen that present and future EOR projects will become more dependent on produced water as a main supply source for their daily operation, including the make-up of polymer solutions. For example, state regulation in Oman forbids oil and gas companies to use fresh water reservoirs (including shallow aquifers) for oilfield development, so the operators in the country currently rely on deep groundwater and produced water as supply sources [8,9].

Legislation and environmental concerns do not only play an increasingly important role in the accessibility to water sources, but also in the selection of disposal methods for EOR produced water. Even in non-water-stressed regions, the discharge of PFPW has to adhere to progressively stringent regulations, making reuse a more and more appealing option [10]. For example, according to the United Kingdom law, the most commonly employed EOR polymer does not pass the standard biodegradation test, so the base case for any polymer flooding project in the country is currently that water that potentially contains traces of polymers cannot be disposed of and needs to be re-injected [11]. With more stringent regulations, it could be even possible that the practice of EOR produced water discharge may be phased out, forcing closed loop recycling [1]. Consequently, the reuse of produced water and PFPW in different EOR applications is being assiduously evaluated [1,12].



Fig. 1. Partially hydrolyzed polyacrylamide (HPAM) molecule.

Among the different reuse options, the use of PFPW to confect new polymer solution results threefold beneficial since it would minimize fresh water consumption, reduce the pollution caused by PFPW discharge and guarantee a reliable supply of water for the EOR projects [13]. In order to serve for reuse purposes, produced water is required to go through a series of operations to remove reuse hindering contaminants. Compared with the conventional produced water, PFPW contains not only crude oil, minerals, and bacteria, but also residual polymer. This makes treatment with commonly used methods difficult. Even after treatments such as flotation, coagulation, sedimentation, sand filtration and ultrafiltration, PFPW still contains residual organics and relatively high salinity (ranging from 2000 to 150,000 ppm), the latter making the mixture inadequate for reuse in EOR [14,15]. This is because the most employed viscosifying polymers are high molecularweight polyelectrolytes - like partially hydrolyzed polyacrylamide (HPAM, Fig. 1) and its derivatives - which are sensitive to the presence of ionic species in solution – salt, alkali, or ionic surfactants. These ionic species have the effect of shielding the natural repulsion between the negative charges of the carboxylate groups of the HPAM, reducing the hydrodynamic size of the polymer molecule [16], and consequently lowering the viscosity of the solution. Thus, for produced water to be reused to confect polymeric solution, reduction of the salinity is highly desirable. Indeed, it has been suggested that the ideal water salinity for this purpose is in the range of 500 to 1000 ppm, due to potential swelling and incompatibility with the reservoir formation [17].

1.2. Electrodialysis to desalinate PFPW

Currently, two types of processes are relevant for the desalination of produced water: thermally-driven processes - that include multistage flash evaporation, multiple-effect distillation and vapor compression evaporation,- and pressure-driven processes such as reverse osmosis (RO) and nanofiltration [18–20]. While each method possesses its own advantages and drawbacks, in this particular case they all share one inconvenience: production of a water stream very low in TDS, and a rejected stream concentrated in salts and organic matter. While the latter is problematic because it still poses disposal issues, the former does not have the adequate salinity to be reused in EOR, as previously explained.

This explains why electrodialysis (ED), a salt selective technology, has been recently proposed to reduce the salinity of the PFPW stream [21]. In the reuse scheme, this would have the highly desirable effect of reducing the amount of fresh polymer and chemicals required to reach the target injection viscosity. Other potential benefits of including a partial desalination step are the reduction of scaling along the injection system, a decreased risk of reservoir souring, and a diminished polymer contamination in the produced streams [22].

As stated before, the application of electrodialysis to desalinate PFPW is relatively recent (first documented ten years ago), and has been focused in PFPW from the Daqing field in China [21,23]. Until now results seem promising, leading to the construction of a 9600 t/d water treatment ED setup [24] and further studies addressing fouling of the ED membranes [24,25]. However, as EOR and polymer flooding are being applied in increasingly diverse scenarios, the variety of the generated PFPW is therefore also growing. For example, PFPW of salinities between 5000 TDS and seawater levels are abundant streams whose treatment with ED has not been reported. Therefore the reuse of these

new varieties of PFPW also needs to be considered as a genuine option over the traditional injection and discharge practices. This requires having actual experimental data and understanding of both: the ED desalination process of PFPW and the factors that control the quality of the reclaimed solution, leading to the objectives of this study.

1.3. Objectives

Accordingly, the two objectives of this work are the following:

- To assess the technical and energetic feasibility of employing electrodialysis to desalinate PFPW generated in assorted and relevant cEOR scenarios, i.e. with different compositions and temperatures. The assessment is to be performed in a way that allows identifying opportunity areas as well as potential implementation issues.
- To evaluate the reuse of the electrodialysis-desalted water to confect polymer flooding solution.

The variables, salinity and temperature, were specifically chosen because they are an obvious and unavoidable consequence of the variety of locations on which polymer-flooding is being implemented. Still, both can have important repercussions on the performance of ED and the characteristics of the treated water.

2. Materials and methods

2.1. Materials

2.1.1. Solutions for ED runs

Two different PFPW solutions were selected for this study, one with relatively low salinity (TDS = 5000 mg/L, from now on referred as brackish PFPW), and another with high salinity (TDS = 32,000 mg/L, referred as sea PFPW). Their compositions are specified in Table 1.

Brackish and sea PFPW synthetic solutions were prepared at a concentration of 1.0 g/L of HPAM with MW = 5-8 million Da. The size and concentration of the polymer were chosen considering reported values of polymer being back-produced with 50% of its original molecular size [26] and at a lower concentration of what originally injected.

For preparing the back-produced polymer solution the procedure was the following. First, 500 mL of previously prepared salt solution were poured in a glass bottle containing a magnetic stirrer. Then, 500 mg of commercial HPAM with MW = 5-8 million Da were weighted in an analytical balance and slowly poured in the vortex formed in the salt solution stirred at 600 rpm by a magnetic stirrer. Once all the polymer was poured in, the agitation was reduced to 150 rpm and the bottle was sealed. Each polymer solution was left stirring overnight in order to assure complete hydration [27], and was employed within 72 h of its preparation.

Analytical grade salts (NaCl, $CaCl_2 \cdot 2H_2O$, $MgCl_2 \cdot 6H_2O$, $NaHCO_3$, KCl, and Na_2SO_4) were purchased from VWR and employed without further purification. Two kinds of HPAM were employed, Flopaam

Table 1

Measured composition of solutions. Prepared based on values reported by [10,28].

	Sea water (SW)	Brackish water (BW)			
	g/L	g/L			
Na ⁺	9.500	1.761			
K ⁺	0.331	0.021			
Ca ²⁺	0.350	0.014			
Mg ²⁺	0.952	0.013			
Cl ⁻	17.407	2.009			
HCO ₃ ⁻	0.447	0.864			
SO4 ²⁻	3.051	0.207			

Desalination 447 (2018) 120-132

Table 2

Sets of viscous solution prepared to evaluate the viscosity as function of the concentration of HPAM 20 M Da.

Set	Basis for stock solution	Diluted with		
SW or BW no ED	Sea or brackish water	Sea or brackish water (no residual polymer)		
Diluate PFPW	Final diluate without polymer	Final diluate with residual polymer		
Diluate SW or BW	Final diluate without	Final diluate without		
pH = 8.0	polymer, pH adjusted to 8.0	polymer, pH adjusted to 8.0		
Diluate PFPW pH = 8.0	Final diluate without polymer, pH adjusted to 8.0	Final diluate with residual polymer, pH adjusted to 8.0		

3230S (MW = 5-8 million Da, 30% hydrolyzed), and Flopaam 3630S (MW = 20 million Da, 30% hydrolyzed), both kindly provided by SNF (France). All the solutions were prepared with Demi water.

2.1.2. Solutions for viscosity measurement as a function of polymer concentration

In order to evaluate the effect of reusing desalted PFPW on the amount of polymer required to attain the desired injection viscosity, a total of eight sets of solutions were prepared, four for each water case. One set of solutions was prepared with the original sea water (TDS \sim 32,000 mg/L), another with the original brackish water (TDS \sim 5000 mg/L), and the other six sets employed the reused diluates of the ED runs (TDS \sim 500 mg/L). Before preparing some of the viscous solutions, the pH of the ED diluates were adjusted to 8.0 by adding 1.0 M NaOH (Table 2).

Imitating the field procedure in which a concentrated (stock) polymer solution is prepared and then diluted to the desired injection viscosity, each of the eight sets of solutions was prepared from a stock HPAM solution (5.0 g/L). In order to assure proper polymer hydration, all stock solutions were prepared in a basis without residual polymer. The preparation method was similar to that described in Section 3.1.1, but with the necessary adjustments to achieve the design concentration of 5.0 g/L of the MW = 20 million Da HPAM.

After keeping the stock solutions under slow agitation for 24 h, volumetric dilutions were performed so to obtain solutions with 20 million Da HPAM concentrations ranging between 0.2 and 2.0 g/L. The water employed for diluting some solutions was the diluate of the ED experiments containing residual HPAM (5–8 million Da). The viscosity of these solutions was measured employing the rheometer and settings specified in Section 2.2.2.

2.1.3. Electrodialysis setup

Experiments were performed in an ED stack containing five repeating cells, each consisting of a cation and an anion exchange membrane. The CEM and AEM employed were Neosepta CMX and Neosepta ANX (Tokuyama Co., Japan), respectively, and had a working area of 104 cm^2 . An additional CEM was placed at the beginning of the stack to close the first cell. The intermembrane distance was fixed by using woven ETFE fabric spacers (Fluortex 09–590/47, Sefar, Switzerland), with reported thickness of 485 µm. Gaskets made of silicone rubber with a thickness similar to the spacer thickness were used to seal all the compartments and to form the alternated flow channels for the diluate and the concentrate. On both sides of the stack, squared titanium electrodes (mesh 1.7, area 96.04 cm²) with a mixed metal oxide coating of Ru/Ir (Magneto Special Anodes BV, The Netherlands) were employed as cathode and anode. The stack was closed with plates made of PMMA (poly(methyl methacrylate)) and 8 bolts (Fig. 2).

A potentiostat/galvanostat (Ivium Technologies, The Netherlands) was employed to control electrical current and to measure the potential difference. The potential difference over the membrane stack is measured using two references Ag/AgCl gel electrodes (QM711X, QIS, the



Fig. 2. Scheme of the electrodialysis stack employed, which was composed of six cation exchange membranes (CEM) and five anion exchange membranes (AEM). Adapted from Vermaas et al. [29].

Netherlands) placed at the inlet of each electrode compartment.

Conductivities of the diluate and concentrate were measured in line with two conductivity probes (Orion DuraProbe 4-electrode conductivity cell 013005MD) directly before the ED stack. The probes were connected to a dedicated transmitter box (Orion Versastar Pro), which corrected the measured values to the reference value at 25 °C, and this last to a computer, where conductivity data was recorded every 5 s. pH of the diluate and concentrate were also measured inline, after the ED cell, with two pH probes (MemoSENS Endress + Hauser, pH range 1 to 12), connected through a transmitter box (P862, QIS) with a data logger (Memograph M RSG30, Endress + Hauser).

The solutions were pumped through the stack with peristaltic pumps (Cole-Parmer, Masterflex L/S Digital drive, USA). Temperature control during the experiments was achieved by employing 1.0 L glass jacketed vessels to store the diluate and concentrate solutions. On the external part of the vessels, water coming from a temperature-controlling recirculation bath was circulated. Fig. 3 illustrates the setup configuration.

2.2. Methods

2.2.1. Electrodialysis runs

ED experiments were carried out in a batch operation mode at fixed working temperatures (20 °C and 40 °C). The diluate and concentrate containing vessels were pre-conditioned to the desired temperature by circulating water supplied by the temperature-controlling bath. Later, 500 mL of the diluate and concentrate solutions were poured in their corresponding vessels. For all experiments, the initial concentrate consisted on 5.0 g/L of sodium chloride solutions. As diluate, four different kinds of solutions were employed: sea and brackish PFPW with and without HPAM added. Runs with and without polymer were always performed in an alternate pattern.

The electrode rinse solution (2.0 L of sodium sulfate 20 g/L) was conditioned to the experiment working temperature by using another temperature-controlling bath. The concentrate and the diluate were recirculated through the corresponding compartments of the ED stack at a constant flow rate of 120 mL/min, while the electrode solution was re-circulated at a flow rate of 100 mL/min. The solutions were circulated in their correspondent circuits during 10 min before starting the experiment, allowing them to stabilize at the desired working temperature.

The experiments were run in constant current mode, at a fixed current density of 24 A/m^2 , and switched to constant voltage mode when the limit value of 8.6 V was reached over the work electrodes. All experiments were stopped when the diluate's conductivity dropped to 1.0 mS/cm. During all experiments, stack voltage and current, as well

as pH and conductivity were monitored for each circuit. Samples of 1.0 mL were taken periodically from the diluate and concentrate compartments.

During the experiments, the mass of the diluate was monitored by means of a mass balance placed under its vessel. The volume of the solution at each data point was calculated from the mass data using a density value corresponding to the composition of the solution at a reference temperature of 25 °C (1.0075 g/L for the experiments with sea PFPW and 1.00 g/L for the experiments with brackish PFPW). These density values were calculated as the average of measured densities of the solutions before and after being desalinated.

After each experiment with HPAM involved, the membrane stack was cleaned in-place. The procedure consisted in pumping a series of solutions in both the diluate and the concentrate compartments, each solution for a period of 10 min. The sequence of solutions was: sodium chloride solution (15 g/L), sodium hydroxide solution (0.1 M), fresh sodium chloride solution (15 g/L), hydrochloric acid solution (0.1 M), and finally fresh sodium chloride solution (15 g/L) [30].

All the experiments were performed by triplicate, and the results shown are the average of the values obtained for each of them.

2.2.2. Viscosity measurements

The dynamic viscosities of the polymer solutions were measured with a Discovery HR-3 rheometer (TA instruments) with a bob and cup configuration. The cup had an internal diameter of 30.43 mm and the bob an external one of 28.04 mm. The temperature of the solution was controlled by a heating jacket and the viscosity measured at \pm 0.1 °C of the specified temperature. The measurements were performed at constant shear rate, starting from 1 s⁻¹ to 100 s⁻¹.

2.2.3. Analytical methods

Samples taken during the ED runs were analyzed to determine their cation and anion content. Cations (Na⁺, K⁺, Ca²⁺, Mg²⁺) were measured by inductive-coupled plasma optical emission spectroscopy (ICP-OES, Optima 5300DV, Perkin Elmer) and anions (Cl⁻ and SO₄²⁻) by ion chromatography (IC, 761 Compact IC, Metrohm). For all the runs with HPAM involved and selected samples without it, both diluate and concentrate samples were analyzed for total carbon (TC) and total organic carbon (TOC) using a TOC analyzer (Shimadzu TOC-VCPH). With this method, besides monitoring the polymer concentration, it was possible to quantify the inorganic carbon as the difference between the detected TC and the TOC. The inorganic carbon detected was considered to be in the bicarbonate form (HCO₃⁻) as long as the pH of solution was above the pK_a of the carbonic acid/bicarbonate pair (pK_a = 6.4). Additionally, the diluate samples were analyzed utilizing liquid chromatography followed by an organic carbon detector (LC-



Fig. 3. Scheme of the setup configuration. The electrodialysis stack was connected to a potentiostat/galvanostat to control the electrical current and measure the potential difference between two reference Ag/AgCl gel electrodes. The temperature of the solutions during the experiments was controlled by two controlling baths.

OCD) (Doc-Labor, Germany) to get further size and nature information of the organic matter fractions of the polymer [31].

The total dissolved solids (TDS) content of each sample was calculated by adding the obtained concentrations of cations and anions, including the bicarbonate.

3. Results and discussion

3.1. Electrodialysis performance

ED experiments were carried out at two different temperatures, 20 and 40 °C, at a fixed current density of 24 A/m^2 , and stopped when the diluate's conductivity reached 1.0 mS/cm. The initial conductivity of the solutions circulating in the diluate circuit was, on average, $49.20 \pm 0.6 \text{ mS/cm}$ for the sea PFPW and $8.4 \pm 0.1 \text{ mS/cm}$ for the brackish PFPW, with no significant difference for the solutions with polymer and without polymer. Thus, all experiments performed with seawater had approximately the same duration -400 min- despite the presence of polymer, the same happening with all the experiments performed with brackish water, which lasted approximately 56 min (see Fig. A1 on supporting material).

As explained in Section 2.2.3, the TDS of each sample was calculated by adding up the measured concentrations of cations and anions. The values obtained are also represented in Fig. A1, which shows the decrease in remaining TDS as a function of the measured conductivity. For the case of sea PFPW, the samples taken at the end of the experiment contained in average 405 mg/L of TDS – a removal percentage of 98.7%. This TDS value is slightly below the suggested minimal 500 mg/L to prepare the polymer solution for EOR [17], so it is advisable for

future experiments to target a final conductivity above 1.0 mS/cm. Additionally, it was found that at the end of the desalination, the only ions still present in the diluate were Na⁺, Cl⁻, SO₄²⁻ and HCO₃⁻, with a respective mass percentage of 38, 30, 30 and 2%.

Regarding the brackish PFPW, the average TDS of the diluates at the end of the desalination was 450 mg/L. From the initial TDS content of 5000 mg/L, the percentage of removal is approximately 90.7%. Again, the only ions detected in the final diluate were only Na⁺, Cl⁻, SO₄²⁻ and HCO₃⁻, in this case with a respective mass percentage of 38, 28, 13 and 20%. These results are in agreement with those presented by Jing et al., who reported faster removal of Ca²⁺ and Cl⁻ compared to the removal of Na⁺ and HCO₃⁻ when desalting Daqing PFPW [21].

Since all the experiments were performed at constant current and only switched to constant voltage for the last minutes, the desalination time ought to be proportional to the amount of salts removed, or more accurately, to the number of molar equivalents that were transferred. In the case of sea PFPW, the average removal rate was 157.8 \pm 1.3 meq/ h, while in the case of brackish PFPW, a removal rate of 150.2 \pm 2.3 meq/h was attained. When statistically compared, both removal rates differ insignificantly (p > 0.05).

3.1.1. Water transport

Together with the ions, water is also transported, consequently influencing the efficiency of the separation process [32–34]. Thus, it is of great interest to understand the implications of water transport when desalting PFPW.

During electrodialysis, water transport can occur either as free or as bound water. Free water transport (osmosis) will take place due to the difference in concentration between the diluate and the concentrate [35]. The relationship between this driving force and the flux of water transported by osmosis $J_{osm} \pmod{m^{-2} s^{-1}}$ can be characterized by the water transfer or diffusion coefficient $D_w \pmod{m^2/s}$, as expressed in the Eq. (1) [33,35]:

$$J_{osm} = D_w \frac{(c_c - c_d)}{\delta} = \frac{\Delta m}{A \cdot t}$$
(1)

where c_c and c_d are, respectively, the molar concentrations in the concentrate and diluate (mol/m³), δ is the membrane thickness (m), Δm is the amount of water transported (mol), *A* is the membrane area (m²), and *t* is the time (s).

Transport of water bound to ions, known as electro-osmosis, will take place whenever ions are passing through the membrane, and has a minimum corresponding to the water in the primary hydration sphere of the ions [32,36]. The amount of water transported by electro-osmosis is highly related to the membrane structure and properties, to the nature of the electrolyte solution and its concentration, and to the current density [33,34,37–39]. The water flux due to electro-osmosis is proportional to the flux of ions as expressed by:

$$J_{eosm} = t_w \sum_i J_i \tag{2}$$

Here, J_{eosm} is the electro-osmotic water flux (mol m⁻² s⁻¹), t_w is the average water transport number for a specific membrane pair (-), and J_i is the flux of positive and negative ions (mol m⁻² s⁻¹). It is important to notice that t_w is calculated as the average water transport number across a membrane pair, thus comprising the water carried by anions and cations combined [40].

As can be inferred, water transport through ion-exchange membranes is a complex topic which can be addressed at many detail levels. For our study, the main interest is to have a general outlook of the impact of the chosen variables - salinity, temperature and polymer presence - on the observed water transport and finally on the overall process efficiency. Of particular interest is the assessment of the effect of viscosifying polymer in the diluate stream. After all, the osmotic water transport is thermodynamically defined as a function of the difference in water activities across the membrane [41], and it is known that the addition of a solute to water always lowers its thermodynamic activity [42]. From this perspective, lower water transport could be expected for the viscosified solutions. And although electrodialysis has been widely employed to desalinate multicomponent solutions with viscosities higher than water - like meat extract [43], maple sap [44] and crude glycerol [45], - the impact of the viscous component regarding the observed water transport was not quantified.

During our study, the diluate's mass was recorded and from this data, the volume of solution was calculated (Section 2.2.1). The

computed volume decrease for all the studied PFPWs is presented in Fig. 4. The conductivity of the diluate is presented in the *x* axis instead of time to facilitate the comparison of the amount of salts present at a given moment in the sea and brackish cases. For the sea water PFPW, the water transport profile of all the studied cases was quite similar, showing only a larger volume drop in the last two data points of the experiments without polymer running at 40 °C. Thus, at the end of the desalination, the largest water transport was recorded for the referred set of experiments, from which the recovered volume was $81.3 \pm 0.3\%$ of the initial one. In contrast, for the runs at the same temperature but with polymer, the water loss was slightly less severe ($83.4 \pm 0.9\%$ recovered volume).

Although with a smaller volume decrease, the experiments performed with brackish water showed a tendency like the one observed in the seawater ones. In the brackish case, the highest volume recovery was registered in the runs with polymer at 20 °C. Meanwhile, the runs at 40 °C without polymer showed again the smallest volumetric recovery (94.9 \pm 0.8%), while for the runs with polymer at the same temperature the recovery was 96.6 \pm 0.6%. Although the statistical analysis showed that neither the differences in the sea water nor in the brackish water cases are significant (p > 0.05), the potential recovery of an extra 2.0% volume of water could be large enough to draw the attention towards the differences when desalting solutions in the presence or absence of viscosifying polymer.

In order to assess the role of osmotic and electro-osmotic water transport in the observed volume reductions, Eqs. (1) and (2) were employed to calculate the projected volume changes as a function of t_w and D_w . Since the values of these parameters may vary depending on the actual experimental conditions, they were calculated by performing a regression analysis of the experimental data obtained at 20 °C and without HPAM. By setting a target to minimize the difference between the calculated and the measured diluate volumes, an optimal combination of $t_w = 8.0$ and $D_w = 2.0 \times 10^{-10} \text{ m}^2/\text{s}$ was found. Both parameters are in agreement with other values reported in the literature, where t_w values of 8.2 and 8.0 for the same membrane pair have been recently reported [40,46]. In a similar way, the calculated transfer coefficient D_w is in the same order of magnitude that the value reported by Galama for a similar membrane pair [33]. Finally, these t_w and D_w values reveal that the electro-osmotic water transport had the largest influence in the total amount of transported water. It was calculated that, respectively, 94 and 95% of the effective water transport in the sea and brackish cases, was attributable to the electro-osmotic mechanism.



3.1.2. Energy use and current efficiency

Since the desalination experiments were run at constant current and stopped at similar desalination degrees, the effects of the presence of

Fig. 4. Remaining volume in the diluate as function of the measured conductivity. Experimental data points are represented by markers and modelled results by continuous dashed lines. Model calculated employing process efficiency of 90% (see Section 3.1.2), $t_w = 8$, and $D_w = 2.0 \times 10^{-10} \text{ m}^2/\text{s}$.



Fig. 5. Measured voltages over the 5-cell pair stack. For the sea cases, there was a slow and steady increase in potential until reaching approximately the minute 340. when most likely the limiting current was reached, and from there on the voltage increases rapidly. For the brackish case, the sharp increase in voltage occurred around the minute 30 for the solutions at 40 °C and before for the solutions at 20 °C. In general, it is observed that the lower voltages were recorded for the sea cases (when compared to the brackish ones); for the experiments running at 40 °C (over those running at 20 °C); and for the experiments running without HPAM (especially for the brackish case).

polymer and the variation in temperature were reflected in the energy use. The first indication of energy consumption tendencies are the voltages supplied to the cell during the runs, shown in Fig. 5. In the case of sea PFPW, the initial voltages are around 0.5 V, and all of them increase slowly and steady as the desalination progress. They all show a sharp increase around the minute 360, the time at which the diluate's conductivity had decreased to approximately 5.0 mS/cm. It is also noteworthy that the experiments running at the same temperature behave in similar way, despite the presence or absence of HPAM. On contrary, in the case of the brackish PFPW results, there were larger differences between the experiments with and without polymer, especially for the runs at 20 °C. These differences again can be explained as the result of the different viscosities of the solutions, which affect the diffusion rate of the ions and influence the thickness of the ion depletion layer.

Furthermore, to assess the energy costs of desalting the different types of water studied, and to compare the results with available data, the energy requirement per unit of diluate volume (*W*) was calculated. For that, the following equation can be employed [33]:

$$W_{desalination} = \frac{\int I \cdot E_{stack} \, dt}{V_d} \tag{3}$$

where *I* is the current (A), E_{stack} is the measured voltage in the stack (V), *t* is the time period (s), and V_{d} is the measured diluate volume (m³). It is important to notice that this equation only accounts for the stack's energy use; electrode losses and pumping energy are not included.

Since it has been mentioned that the required desalination degree of PFPW would depend of the location and reservoir, Eq. (3) was employed to calculate the energy necessary to reach two different TDS concentrations: 1000 and 500 mg/L (Fig. 6). As expected, the specific energy consumption for desalting seawater was larger than for desalting brackish water, experiments running at 40 °C consumed less

energy than the ones running at 20 °C, and the presence of polymer also increased the energy use, most notoriously for the desalinations reaching 500 TDS and the runs at lower temperature. It should be emphasized that although the process parameters were not optimized, the energy consumption for the seawater case falls within the values reported by other authors [47].

As in all desalination processes, not all energy supplied to an ED system is used effectively. In a large extent, the efficiency of electrodialysis is determined by the properties of the membranes. Phenomena like back-diffusion of ions or co-ion transport can occur due to their non-perfect selectivity [33]. Additionally, electrodialysis efficiency is also affected by the process and system design, which determine the limiting current density, the current utilization, the concentration polarization, etc. In order to quantify the effectiveness of current utilization, the coulombic efficiency is extensively used, defined as the total amount of electric charge transported by ions, divided by the electric charge applied to the system [33,48]. This is shown in Eqs. (4)–(6).

$$\eta = \frac{Q_{transported}}{Q_{applied}} \times 100 \tag{4}$$

$$Q_{transported} = F \sum_{i} z_i \Delta n_i \tag{5}$$

$$Q_{applied} = N_{cell} \int_0^t I dt \tag{6}$$

Where η is the coulombic efficiency (%), Q the electric charge (C), F is Faraday constant (C/eq), z_i is the valence of the ion (eq/mol), Δn_i , the moles of ions transported (mol), and N_{cell} the number of cell pairs (–). It must be noted that Eq. (5) can be employed either for the cations or for the anions, but not both simultaneously. Thus, the efficiency for each experiment was reported as the average of the efficiencies



Fig. 6. Specific energy consumption for desalting sea and brackish PFPW in kWh per m^3 of desalted product.





calculated independently for the cations and for the anions.

In general, the calculated current efficiencies were higher for the brackish water experiments, ranging between 89 and 97%, while for the seawater ones it was found to in the range of 84 to 90% (Fig. 7). The most surprising finding is that in 3 of the 4 cases, the runs without polymer presented a lower current efficiency than the same run with polymer. This can possibly be explained as an effect of the lower diffusivity of the ions when the viscosity of the solvent increases, which causes the back-diffusion phenomena to happen at a lower rate.

3.2. Evaluation of the PFPW solutions

As explained, the final goal of desalting the PFPW is to reuse it to confect fresh polymer solution. Thus, as important as analysing the process feasibility in energetic terms, it is to make sure that the desalted stream can be reused in the polymer-flooding process. Of special attention is its readiness to confect viscous solutions, as it will be further studied in this section.

It has been stated that in polymer flooding, the oil recovery is increased by lowering the mobility of the displacing phase (water) compared to the mobility of the displaced phase (oil). This mobility reduction of the water phase is achieved by increasing its viscosity through the addition of water-soluble polymers [4,5]. The type of polymers employed and their concentration vary for each reservoir and project, but in general it is preferred to use polymers with high molecular weight, and in concentrations between 1000 ppm and 3000 ppm [5]. The viscosity of the polymer solution must be evaluated at least at two temperatures, reservoir and environmental, to ensure that the fluid viscosity remains within the desired range at downhole conditions, but that it is also reasonably viscous to be pumped at surface conditions [5]. And even though steady and dynamic rheological properties of the polymer solution are important for cEOR applications [5,49,50], the initial evaluation of a solution consists on performing a viscosity curve at different shear rates, with special attention given to the viscosity obtained at a shear rate of 7.3 s^{-1} or similar.

Accordingly, this study relied on steady shear measurements to characterize the polymer solutions. The viscosities of the synthetic sea and brackish PFPW solutions were measured before and after the desalination, at 20 and 40 $^{\circ}$ C at various shear rates (Section 2.2.2). To

facilitate the analysis, the viscosities recorded at shear rate of 6.3 s^{-1} are summarized in Table 3, but the complete set of measurements is available in the Supplementary material (Fig. A3).

Focusing on the values before the desalination, it is possible to notice that the sea and brackish PFPW had, respectively, viscosities 3 to 9 times higher than same solutions without polymer. It is also apparent that the viscosity of the solutions at 40 °C is approximately 30% lower compared to that of the same solution at 20 °C, which is also normally observed in HPAM solutions [52]. Finally, when comparing the viscosities of the different PFPW's, the values measured for sea PFPW were found to be 2 to 3 times lower than those for the brackish PFPW, something that was expected due to the differences in salinity. Indeed, this difference in viscosity as a function of salinity is similar to the one reported by Levitt for solutions of the same polymer, Flopaam 3230S, although his measurements were performed with higher polymer concentration and only using NaCl [27].

Then, after desalting the sea and brackish PFPW to a similar TDS content and composition, one might expect the viscosity values to be higher and alike. Remarkably, this was not the case. As presented in Table 3 (and in Fig. A3) both, sea and brackish PFPW, showed an increase in viscosity after treated with ED. However, the change in the sea PFPW was moderate, while for the brackish case it was much more substantial. The viscosity of the sea PFPW at 40 °C increased almost twofold, from 2.23 to $4.17 \text{ mPa} \cdot \text{s}$, while the viscosity of the brackish PFPW measured at the same temperature increased nearly four times, from 6.08 to 22.93 mPa \cdot \text{s}. This meant that even after the desalination, the properties of both solutions still differ. Thus, before trying to reuse them to prepare fresh polymer-flooding solution, the cause(s) of these differences in viscosity were further scrutinized.

3.2.1. HPAM content during the electrodialysis runs

Viscosity is highly dependent of the polymer concentration. Thus, the actual polymer content of the solutions during the desalination process was monitored through TOC analyses, which were carried on for both the diluate and the concentrate compartments. Initially, the sea and brackish PFPW solutions registered an average of 381 and 360 mg/L TOC, respectively, while the analysis of the concentrate solution showed zero TOC content. For all the subsequent concentrate measurements, the TOC measurement always resulted below the detection limits (1.0 mg/L), indicating that the polymer was not able to pass through the IEMs.

The TOC measurements for the diluate sides of the sea and the brackish PFPW are shown in Fig. 8. In the case of the sea PFPW, it is observed that the TOC values are practically constant since the beginning of the desalination process until the conductivity reached 20 mS/ cm, decreasing slightly in the three last measurements. For the case of the brackish PFPW, it results noticeable that there is a larger decrease of the TOC values in a much shorter desalination time. Furthermore, since water was being transported from the diluate to the concentrate and the polymer was not passing through the membranes, it was expected to detect an increase in the polymer concentration in the diluate as the desalination occurred. This was not observed, as shown with the dashed lines in the aforementioned graphs, which represent the expected TOC concentration when considering the water transported during the

Table 3

Viceesities	of 000		huo alviah		a lutiona	(:	m De e	`
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	Sea water	Sea water		Sea PFPW (HPAM) ^c		Brackish water		Brackish PFPW (HPAM) ^c	
	20 °C	40 °C	20 °C	40 °C	20 °C	40 °C	20 °C	40 °C	
Before desalination After desalination	1.059 ^a 1.002	0.694 ^a 0.653	3.331 6.033	2.233 4.172	1.010 ^b 1.002	0.659 ^b 0.653	9.027 32.01	6.080 22.93	

^a Viscosity of solutions of salinity 30 g/kg [51].

^b Calculated as the average viscosity of water with 10 g salt/kg solution [51] and the viscosity of pure water.

 $^{\rm c}\,$ Viscosities of solutions with HPAM reported at a shear rate of $6.30\,s^{-1}$



Fig. 8. Measured and calculated TOC (top) and DOC (bottom) in the diluate's of desalted solutions. The TOC quantifies all the polymers present in solution, while the DOC can be regarded as the concentration of small polymer particles which could pass through a 0.45 µm PES filter. Each data point indicates the average concentrations of samples taken from at least three different experiments. The dashed lines represent the expected TOC and DOC concentrations considering volume reduction due to water transport.

process. Since organic carbon was never detected in the concentrate solution, the only explanation would be that the missing polymer got adsorbed and/or precipitated on the IEMs and spacers and stayed in the stack. This is a plausible explanation since it is known that the charged polymer has affinity for the ion-exchange membranes, as already reported in previous studies [24,25]. Additionally, when performing the cleaning protocol, it was possible to observe some polymer and small solids precipitating in the solutions, mainly in the basic one.

Considering the recovered volumes of the diluates and the measured TOC concentrations, it is possible to quantify the amount of polymer remaining in the stack. For the sea PFPW desalination runs at 40 and 20 °C, it was calculated that 28.2 and 21.6%, respectively, of the initial mass of polymer in solution was left behind. This represents a 14% (40 °C) and 6% (20 °C) reduction in the polymer concentration measured by TOC. In the case of the brackish PFPW, 25.5 and 30.1% of the HPAM remained in the stack during the runs at 40 and 20 °C, respectively. This was reflected as 22% (40 $^\circ\text{C})$ and 28% (20 $^\circ\text{C})$ reduction in the polymer concentration. Thus, despite both kinds of water suffered similar polymer losses in terms of mass, for the brackish case the loss occurred in a much shorter period of time. This observation, together to the accelerated decrease rate on the sea PFPW when reaching a conductivity of 10 mS/cm, suggests that the polymer loss is closely related with the ionic strength (salinity) of the solution. It seems that this variable affected the polymer loss more than the temperature or processing time. As measured in the sea cases, the polymer tends to remain in solution while the salinity is high, but once the salinity reaches a certain level its attachment on the stack increases. This can be explained by the shielding of the charges on the polymer. When the stream has high salinity, the charges on the polymer are effectively covered, so it is not substantially affected by the electric forces on the stack. However, as the salinity decreases its intrinsic charges become less shielded, making it more susceptible to have electrostatic interactions with the stack elements.

Additional to the TOC analysis, all the diluate samples were also analyzed with LC-OCD. One of the parameters that can be evaluated by this technique is the concentration of dissolved organic carbon (DOC), which is all the organic carbon still in solution after filtering the sample through a 0.45 µm PES filter. The results for the sea PFPW (Fig. 8, bottom left), show initial DOC values for both temperatures around 240 mg/L, which is approximately 60% of the initial TOC concentrations, meaning that 40% of the polymer particles in solution were large enough to be retained by the filter. At this point it is important to emphasize that when filtering an HPAM or any other polymeric solution, the hydrodynamic radius of the particles in solution plays a significant role in their filter retention. The hydrodynamic radius of a HPAM molecule depends not only on its molecular weight and hydrolysis degree [53], but it is also highly sensitive to the ionic strength of the solution [27], pH [53,54], polymer concentration [54], and to the presence of multivalent cations [55]. Regarding this last point, it has been demonstrated that when calcium ions are present in the solution, intrachain and interchain complexes are formed, so a particle is not a single polymer molecule, but a cluster of molecules [55].

Further on, it is interesting that the two subsequent data points of the sea PFPW analysis showed a small increase in DOC, and still the samples taken at 20 mS/cm contained nearly the expected DOC concentration given the volume change of the solution (dashed line). Since this tendency was not observed in the TOC analysis, a plausible explanation is that while larger polymer molecules get adsorbed as soon as the desalination starts, the smaller polymer molecules remain in solution for a longer time. However, the initial tendency reverts and, from the 10 mS/cm reading until the end of the desalination, the DOC values decrease proportionally to the TOC values, suggesting that there was no more distinction between small and big particles. Still, the final ratio of DOC to TOC was around 0.65, slightly larger than the initial one.

Meanwhile, the DOC analysis of the brackish PFPW experiments and its comparison with the TOC evolution (Fig. 8, right) suggests that, for this case, the temperature plays a more significant role than for seawater. Although the overall DOC tendency seems similar to the one of TOC, when closely examining it results clear that while the DOC to TOC ratio is practically the same before and after the 40 °C runs (0.67), it increases from 0.72 up to 0.85 for the ones at 20 °C. At first glance this result is counter-intuitive: as the viscosity of the solution increased, one would expect small particles to uncoil during the process, thus reducing the ratio of DOC to TOC. Apparently, this effect was small compared to the larger loss of the bigger HPAM particles in solution, as can be understood from the decrease in TOC.

It must be added that although the LCD-OCD analysis also included the chromatographic separation of the dissolved organics, the results only indicated that all the organics remaining in solution had an estimated molecular weight above 20,000 Da.

Another variable that was analyzed to explain the viscosity change during the process was the pressure difference in the diluate stream. Although the analysis was not conclusive, it is included as Appendix B.

In summary, the results presented in this section gave a good insight into the differences when desalting sea and brackish PFPW, but some questions remain. Why after removing 31,500 mg/L TDS, the viscosity of the sea PFPW only had a light increase, especially when compared against the change in the brackish PFPW? And why does a solution with less polymer concentration show a higher viscosity? A logical explanation for both questions would be that since the sea PFPW was desalted for a longer time, the polymer in solution suffered more degradation (chain breaking), which was not possible to detect with the TOC/DOC analyses. However, yet another parameter might also be playing an important role in the observed behaviour: the pH.

3.2.2. The role of pH

One of the key parameters to consider when evaluating HPAM solutions is their pH. The carboxyl groups along the backbone chain of the molecule are pH-sensitive, so the viscosity of HPAM solutions is strongly dependent on the hydrolysis degree (content of carboxyl groups) and the variation of pH. These carboxyl groups can exchange protons with dissolved salts in water, depending on pH conditions. At high pH, the carboxyl groups dissociate and are negatively charged. Still, counter-ions balance most of the charge inside the coil, so their osmotic pressure makes the chain expand to larger sizes, resulting in the increased solution viscosity. On the other hand, low pH causes all carboxyl groups to be protonated with hydrogen ions, resulting in no charges on the polymer chain. The polymer molecules are now in a coiled state which decreases viscosity [53]. Experimental results of this viscosity dependence on the pH of solution [52,53], as well as on the addition of hydroxide [52], have been previously reported.

Accordingly, the pH of the diluate solutions exiting the ED cell was constantly monitored. For the sea PFPW the initial pH was 7.9, slightly basic, due to the presence of bicarbonate ions in the solution. However, as the desalination progressed the pH decreased, reaching average values of 4.5 and 3.8 for the runs at 40 and 20 °C, respectively (Fig. 9). It was also noted that there was a large pH variability among the runs, especially in the readings between 20 and 5 mS/cm.

On the other hand, the brackish PFPW had an initial pH of 8.4, consequence of a higher bicarbonate concentration (Table 1). The pH of these solutions also decreased during the desalination, but in a less extent and with almost no variability, consistently reaching a final pH of 6 regardless of the temperature.

These observations can be explained as combination of several factors. First, it must be recalled that the bicarbonate ion is removed from the diluate together with the other anions, so its concentration was decreasing over time. This is apparent from the inorganic carbon results, which are also presented in Fig. 9. It must be noticed that the inorganic carbon value encompasses several inorganic molecules, including carbonate, bicarbonate, carbonic acid, and carbon dioxide. Initially, the main component of both kinds of solutions was bicarbonate. since their pH was higher than the pK_a of the carbonic acid/bicarbonate pair ($pK_a = 6.4$). However, as the desalination progressed, the bicarbonate was removed, so the solution had less buffering capacity. This made the solutions more sensitive to any H⁺ entering the diluate, which can be coming from the anode reactions and/or from water splitting happening within the cell. It is worth to notice that, although the numeric change in pH appears to be very large, actually the concentration of protons went from $0.01 \,\mu mol/L$ (pH = 8) to about $100 \,\mu mol/L$ (pH = 4). Seen from this point of view, the net increase of protons in the diluate becomes less outstanding. In case that most of the extra protons were originated in the anode, it is considered that an increase in the number of cell pairs and in the flow rate of the electrode rinse would be sufficient to minimize the pH variation.

However, there is evidence suggesting that the pH change was also enhanced by water splitting within the membrane stack. When comparing the pH evolution of the solutions with HPAM (Fig. 9) and without it (data not shown), it was noted that the HPAM containing solutions had a faster pH decrease, and their final pH value was slightly lower than for the solutions without polymer. Since the relation diluate/electrode rinse was the same in all cases, the most feasible explanation is that water splitting was occurring as consequence of membrane fouling. It is known that water splitting occurs when the concentration in charged species is not sufficient to ensure the current transport at the membrane interface in the electrodialysis cell [29]. When this limiting current density is reached, water dissociation occurs in the interface of the AEMs [36,37,56]. The phenomenon causes the generation of H⁺ at the AEM diluate interface and OH⁻ at the AEM concentrate interface. From this study (Section 3.2.1) and from others before it is known that HPAM tends to foul the ion exchange membranes [24,25]. And when fouling occurs, the conditions for splitting water become more ideal, which may even keep triggering the fouling formation [5,30,31]. Indeed, from the fast voltage increase in the last minutes of the desalination (Fig. 5), it can be deduced that the limiting current density was reached during this part of the ED treatment.

Since the desalted sea PFPW had higher polymer concentrations and even less ions than the brackish PFPW one might, at least partially,

gmg

[Inorganic carbon]



Fig. 9. pH (open symbols) and inorganic carbon (filled symbols) evolution in the diluate solution. The largest pH drop (from approximately 8 to 4) was observed for the sea PFPW, which had a low initial inorganic carbon content (derived from a low bicarbonate content). Meanwhile, the brackish PFPW had a moderate pH change (from 8.4 to 6), which could be related to a higher initial inorganic carbon content.



Fig. 10. Comparison of the viscosities of polymeric solution as a function of HPAM 20 M Da concentration and the type of water employed for their preparation. A hypothetical viscosity goal of 20 mPas is represented by the horizontal black line. All values reported were measured at 40 °C and shear rate of 7.3 s^{-1} .

attribute the minimal change in viscosity of the former to its lower pH. In that case, the restoration to (nearly) neutral pH might result useful to uncover the viscosifying potential of the remaining HPAM in solution.

3.3. Preparation of viscous flooding water with desalted solution

Finally, the desalted solutions were employed together with 20 million Da HPAM to prepare polymer flooding viscous solutions with different polymer concentrations (Section 2.1.2). For comparison purposes, two sets of viscous solutions were also prepared with original sea and brackish water. The viscosities were evaluated at 40 °C, close to the median temperature of 46 °C of many polymer flooding projects [4].

All the measured curves confirm that the viscosity of the viscous solution is highly dependent of the concentration of polymer (Fig. 10). For both studied cases, sea and brackish, the desalted solutions showed higher viscosities than the non-desalted for same added polymer concentration.

As elucidated in the previous section, the low pH of the seawater diluates was probed to be partially responsible for their lower viscosity compared to the desalted brackish PFPW. In Fig. 10 it is shown that, by adjusting the pH of the PFPW diluate from its final value of 4.9 to 8.0, the viscosity increased from 4 to 10 mPa·s. However, the effect of correcting the pH of the reused solutions is only noticeable at low HPAM concentrations (below 1.5 g/L for the sea case and under 1.0 g/L for the brackish case). This occurs because the addition of fresh HPAM also has the outcome of increasing the pH of the solution, so even without initial pH control, the PFPW diluates with 2.0 g/L HPAM reached a pH close to neutral. When the salinity and pH are similar, the viscosities of the sea and brackish PFPW diluates should be alike, as found in the measurements for the 2.0 g/L HPAM concentration.

It is also interesting to compare the viscosities achieved by reusing PFPW with residual polymer vs using desalted water, both being in neutral pH conditions. In the sea case, the presence of residual polymer made the reused PFPW up to four times more viscous that its equivalent, diluate SW, without residual polymer. In the case of brackish water, the viscosity differences were smaller, but still 50% larger when residual polymer is present. For both kinds of water, the viscosifying effect of the residual polymer is noticeable only when the fresh HPAM concentration was below 1.5 g/L.

To finalize with the discussion about the differences in viscosity between the desalted sea and brackish water, it can be pointed out that although the restoration to neutral pH duplicated the viscosity of the sea PFPW diluate, it did not equalize it to the one of the desalinated brackish PFPW. Since it has already been established and explained that the sea diluate contained even a higher concentration of polymer, it can be concluded that the polymer suffered some form of degradation. This could be attributed to two factors, shear degradation due to the relatively long pumping time, and chemical degradation due to the acidic conditions. The validation of these hypotheses would need to be addressed in further studies.

Lastly, a hypothetic polymer flooding design with desired viscosity of 20 mPa·s at 40 °C was considered (Fig. 10). For the sea water case, the use of desalted water would mean polymer savings of approximately 75%, while the use of desalted PFPW with residual polymer and pH = 8 could use less 10 times less polymer. These results fully agree with the estimations of Ayirala et al., who indicate 5–10 times lower consumption of polymer in low salinity water compared to seawater [17]. Regarding the brackish case, it is estimated that 60 to 100% less fresh polymer would be needed, depending on the presence of residual polymer. Riethmuller et al. projected a slightly lower (50%) reduction in the consumption of polymer and associated stabilizing agents for brackish water desalted to 1000 ppm, but when considering a viscosity goal of 55 mPa·s [9].

4. Conclusions

Electrodialysis is a suitable desalination process to treat PFPW of different salinities and compositions. It was possible to reduce the salinity of synthetic PFPW (containing 1.0 g/L of commercial 5–8 million Da HPAM) with two different salinity levels (32,000 and 5000 TDS in ppm) to approximately 500 ppm, the optimal salinity to confect new polymer solution.

Water transport during the desalination was substantial, especially for the sea water cases, for which only 81–83% of the initial volume was recovered. Slightly lower water transport rates were measured for the runs with polymer at 20 °C, but the differences were not significant. The volume decrease was a consequence of osmotic and electro-osmotic transport, the last being the most prominent. Yet, since osmotic transport is a function of process time, lower volume losses could be attained by employing higher current densities, at least for the initial part of the desalination, with its consequent lower process time.

In terms of energy use, it was found that the presence of polymer did not significantly influence the specific energy consumption for the desalination runs on seawater or brackish water at 40 °C, but indeed it had a measurable effect when desalting brackish water at 20 °C. These results are thought to be related to the higher viscosity of the latter stream, which restricts the movement of ions and results in an accelerated arrival to the limiting current. It is noticeable that despite the process conditions are not yet optimized, the energy consumption for the sea case at 40 °C was approximately 4.0 kWh/m³ if the desalination is stopped when 1000 ppm are still in solution. Regarding the energy efficiency, the presence of polymer seemed to have a beneficial effect for achieving higher energy efficiencies, most likely due to hampering the back-diffusion of ions.

Concerning the analysis of the desalted PFPW, it was found that 20 to 30% of the initial mass of polymer in the diluate stream remained on the stack, most likely adsorbed/precipitated on the membranes and spacers. The polymer loss was faster on the brackish cases than on the sea ones, and for the latter the decrease rate accelerated when reaching certain salinities. Thus, the decrease was associated to the ionic strength of the solution. This variable seems to be more critical than temperature or processing time regarding polymer adsorption/precipitation, an observation that may result valuable when studying fouling (and associated loss and degradation processes in the stack) for this type of polymers.

The desalted solutions presented an immediate and moderate increase in viscosity. Even though the final salinity in all studied cases was similar, the final viscosities of the sea and brackish PFPW differed significantly. It was verified that this was partially due to the pH decrease during the desalination, and most likely also due to partial degradation of the residual polymer. However, when fresh polymer was added, all desalted solutions showed higher viscosities compared to the non-desalted ones. The viscosifying effect of the residual polymer is also tangible, so it has been demonstrated that by reusing PFPW the consumption of fresh polymer could be reduced, resulting beneficial in environmental and economic terms.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.desal.2018.09.012.

References

- [1] J.A. Herschell, Water and Wastewater Treatment for Enhanced Oil Recovery, Mahon, Cork, Ireland, (2016).
- [2] Internacional Energy Agency (IEA), World Energy Outlook 2016, Paris, http:// www.iea.org/publications/freepublications/publication/WEB_ WorldEnergyOutlook2015ExecutiveSummaryEnglishFinal.pdf, (2016).
- [3] A. Muggeridge, A. Cockin, K. Webb, H. Frampton, I. Collins, T. Moulds, P. Salino, Recovery rates, enhanced oil recovery and technological limits, Philos. Trans. R. Soc. A Math. Phys. Eng. Sci. 372 (2013) 20120320, https://doi.org/10.1098/rsta. 2012.0320.
- [4] J.J. Sheng, B. Leonhardt, N. Azri, Status of polymer-flooding technology, J. Can. Pet. Technol. 54 (2015) 116–126, https://doi.org/10.2118/174541-PA.
- [5] M.S. Kamal, A.S. Sultan, U.A. Al-Mubaiyedh, I.A. Hussein, Review on polymer flooding: rheology, adsorption, stability, and field applications of various polymer systems, Polym. Rev. 55 (2015) 491–530, https://doi.org/10.1080/15583724. 2014.982821.
- [6] L. Henthorne, G.A. Pope, U. Weerasooriya, V. Llano, Impact of Water Softening on Chemical Enhanced Oil Recovery, (2014).
- [7] D.C. Standnes, I. Skjevrak, Literature review of implemented polymer field projects, J. Pet. Sci. Eng. 122 (2014) 761–775, https://doi.org/10.1016/j.petrol.2014.08. 024.

- [8] S. of O. Ministry of Oil & Gas, Oil & Gas Law, http://www.oman.om/wps/wcm/ connect/f5b459d2-584d-42a9-b766-f8f555567763/10Oil + and + Gas + Law + %28Royal + Decree + No. + 4274%29.pdf?MOD = AJPERES, (2011).
- [9] G. Riethmuller, A. Abri, N. Al Azri, G. Stapel, S. Nijman, W. Subhi, R. Mehdi, Opportunities and challenges of polymer flooding in heavy oil reservoir in south of Oman, SPE EOR Conf. Oil Gas West Asia. 2014, https://doi.org/10.2118/ 169737-MS.
- [10] A. Fakhru'l-Razi, A. Pendashteh, L.C. Abdullah, D.R.A. Biak, S.S. Madaeni, Z.Z. Abidin, Review of technologies for oil and gas produced water treatment, J. Hazard. Mater. 170 (2009) 530–551, https://doi.org/10.1016/j.jhazmat.2009.05. 044.
- [11] Oil & Gas Authority United Kingdom, Polymer Enhanced Oil Recovery, London, (2017).
- [12] Y. Liu, E.B. Kujawinski, Chemical composition and potential environmental impacts of water-soluble polar crude oil components inferred from esi FT-ICR MS, PLoS One 10 (2015) 1–18, https://doi.org/10.1371/journal.pone.0136376.
- [13] G. Jing, L. Xing, S. Li, C. Han, Reclaiming polymer-flooding produced water for beneficial use: salt removal via electrodialysis, Desalin. Water Treat. 25 (2011) 71–77, https://doi.org/10.5004/dwt.2011.1766.
- [14] E. Drioli, A. Ali, Y.M. Lee, S.F. Al-Sharif, M. Al-Beirutty, F. Macedonio, Membrane operations for produced water treatment, Desalin. Water Treat. 3994 (2015) 1–19, https://doi.org/10.1080/19443994.2015.1072585.
- [15] R. Zhang, W. Shi, S. Yu, W. Wang, Z. Zhang, B. Zhang, L. Li, X. Bao, Influence of salts, anion polyacrylamide and crude oil on nanofiltration membrane fouling during desalination process of polymer flooding produced water, Desalination 373 (2015) 27–37, https://doi.org/10.1016/j.desal.2015.07.006.
- [16] A. Samanta, A. Bera, K. Ojha, A. Mandal, Effects of alkali, salts, and surfactant on rheological behavior of partially hydrolyzed polyacrylamide solutions, J. Chem. Eng. Data 55 (2010) 4315–4322, https://doi.org/10.1021/je100458a.
- [17] S.C. Ayirala, E. Uehara-Nagamine, A.N. Matzakos, R.W. Chin, P.H. Doe, P.J. van den Hoek, A designer water process for offshore low salinity and polymer flooding applications, SPE Improv. Oil Recover. Symp. 2013, https://doi.org/10.2118/ 129926-MS.
- [18] C. Murray-Gulde, J.E. Heatley, T. Karanfil, J.H. Rodgers, J.E. Myers, Performance of a hybrid reverse osmosis-constructed wetland treatment system for brackish oil field produced water, Water Res. 37 (2003) 705–713, https://doi.org/10.1016/ S0043-1354(02)00353-6.
- [19] E.T. Igunnu, G.Z. Chen, Produced water treatment technologies, Int. J. Low Carbon Technol. 9 (2014) 157–177, https://doi.org/10.1093/ijlct/cts049.
- [20] S. Munirasu, M.A. Haija, F. Banat, Use of membrane technology for oil field and refinery produced water treatment—a review, Process. Saf. Environ. Prot. 100 (2016) 183–202, https://doi.org/10.1016/j.psep.2016.01.010.
- [21] G. Jing, X. Wang, H. Zhao, Study on TDS removal from polymer-flooding wastewater in crude oil: extraction by electrodialysis, Desalination 244 (2009) 90–96, https://doi.org/10.1016/j.desal.2008.04.039.
- [22] E.C.M. Vermolen, M. Pingo-Almada, B.M. Wassing, D.J. Ligthelm, S.K. Masalmeh, H. Mohammadi, G.R. Jerauld, M. Pancharoen, IPTC 17342 low-salinity polymer flooding: improving polymer flooding technical feasibility and economics by using low-salinity make-up brine, SPE Imroved Oil Recover. Symp. 15 2014, https://doi. org/10.2118/153161-MS.
- [23] G. Jing, Y. Liu, T. Zhao, C. Han, Reclamation of the polymer-flooding produced water, 2nd Int. Conf. Bioinforma. Biomed. Eng. iCBBE 2008, 2008, pp. 3240–3243, , https://doi.org/10.1109/ICBBE.2008.1138.
- [24] T. Wang, S. Yu, L-an Hou, Impacts of HPAM molecular weights on desalination performance of ion exchange membranes and fouling mechanism, Desalination 404 (2017) 50–58, https://doi.org/10.1016/j.desal.2016.10.007.
- [25] H. Guo, L. Xiao, S. Yu, H. Yang, J. Hu, G. Liu, Y. Tang, Analysis of anion exchange membrane fouling mechanism caused by anion polyacrylamide in electrodialysis, Desalination 346 (2014) 46–53, https://doi.org/10.1016/j.desal.2014.05.010.
- [26] H. Al Kalbani, M.S. Mandhari, H. Al-Hadhrami, G. Philip, J. Nesbit, L. Gil, N. Gaillard, Treating Back Produced Polymer To Enable Use Of Conventional Water Treatment Technologies, (2014), https://doi.org/10.2118/169719-MS.
- [27] D.B. Levitt, The Optimal Use of Enhanced Oil Recovery Polymers Under Hostile Conditions, The University of Texas at Austin, 2009.
- [28] J. Zheng, B. Chen, W. Thanyamanta, K. Hawboldt, B. Zhang, B. Liu, Offshore produced water management: a review of current practice and challenges in harsh/ Arctic environments, Mar. Pollut. Bull. 104 (2016) 7–19, https://doi.org/10.1016/ j.marpolbul.2016.01.004.
- [29] D.A. Vermaas, M. Saakes, K. Nijmeijer, Doubled power density from salinity gradients at reduced intermembrane distance, Environ. Sci. Technol. 45 (2011) 7089–7095, https://doi.org/10.1021/es2012758.
- [30] H. Guo, F. You, S. Yu, L. Li, D. Zhao, Mechanisms of chemical cleaning of ion exchange membranes: a case study of plant-scale electrodialysis for oily wastewater treatment, J. Membr. Sci. 496 (2015) 310–317, https://doi.org/10.1016/j.memsci. 2015.09.005.
- [31] S.A. Huber, A. Balz, M. Abert, W. Pronk, Characterisation of aquatic humic and nonhumic matter with size-exclusion chromatography - organic carbon detection - organic nitrogen detection (LC-OCD-OND), Water Res. 45 (2011) 879–885, https:// doi.org/10.1016/j.watres.2010.09.023.
- [32] H. Strathmann, Electromembrane processes: basic aspects and applications, Compr. Membr. Sci. Eng. (2010) 391–429, https://doi.org/10.1016/B978-0-08-093250-7. 00048-7.
- [33] A.H. Galama, M. Saakes, H. Bruning, H.H.M. Rijnaarts, J.W. Post, Seawater predesalination with electrodialysis, Desalination 342 (2014) 61–69, https://doi.org/ 10.1016/j.desal.2013.07.012.
- [34] C. Jiang, Q. Wang, Y. Li, Y. Wang, T. Xu, Water electro-transport with hydrated

cations in electrodialysis, Desalination 365 (2015) 204–212, https://doi.org/10.1016/j.desal.2015.03.007.

- [35] T. Sata, Ion Exchange Membranes: Preparation, Characterization, Modification and Application, Royal Society of Chemistry, 2004.
- [36] V.K. Indusekhar, N. Krishnaswamy, Water transport studies on interpolymer ionexchange membranes, Desalination 52 (1985) 309–316, https://doi.org/10.1016/ 0011-9164(85)80040-0.
- [37] A.G. Winger, R. Ferguson, R. Kunin, The electroosmotic transport of water across permselective membranes, J. Phys. Chem. 60 (1956) 556–558, https://doi.org/10. 1021/j150539a010.
- [38] N. Berezina, N. Gnusin, O. Dyomina, S. Timofeyev, Water electrotransport in membrane systems. Experiment and model description, J. Membr. Sci. 86 (1994) 207–229, https://doi.org/10.1016/0376-7388(93)E0075-U.
- [39] L. Han, S. Galier, H. Roux-de Balmann, Ion hydration number and electro-osmosis during electrodialysis of mixed salt solution, Desalination 373 (2015) 38–46, https://doi.org/10.1016/j.desal.2015.06.023.
- [40] S. Porada, W.J. van Egmond, J.W. Post, M. Saakes, H.V.M. Hamelers, Tailoring ion exchange membranes to enable low osmotic water transport and energy efficient electrodialysis, J. Membr. Sci. 552 (2018) 22–30, https://doi.org/10.1016/j. memsci.2018.01.050.
- [41] G.M. Geise, D.R. Paul, B.D. Freeman, Fundamental water and salt transport properties of polymeric materials, Prog. Polym. Sci. 39 (2014) 1–24, https://doi.org/10. 1016/j.progpolymsci.2013.07.001.
- [42] M.J. Blandamer, J.B.F.N. Engberts, P.T. Gleeson, J.C.R. Reis, Activity of water in aqueous systems; a frequently neglected property, Chem. Soc. Rev. 34 (2005) 440, https://doi.org/10.1039/b400473f.
- [43] S. Shi, S. Cho, Y. Lee, S. Yun, J. Woo, S. Moon, Desalination of Fish Meat Extract by Electrodialysis and Characterization of Membrane Fouling, 28 (2011), pp. 575–582, https://doi.org/10.1007/s11814-010-0375-4.
- [44] L. Bazinet, D. Lavigne, N. Martin, Partial Demineralization of Maple Sap by Electrodialysis: Impact on Syrup Sensory and Physicochemical Characteristics, 1698 (2007), pp. 1691–1698, https://doi.org/10.1002/jsfa.
- [45] P. Vadthya, A. Kumari, C. Sumana, S. Sridhar, Electrodialysis aided desalination of crude glycerol in the production of biodiesel from oil feed stock, Desalination 362

(2015) 133-140, https://doi.org/10.1016/j.desal.2015.02.001.

- [46] W.J. van Egmond, U.K. Starke, M. Saakes, C.J.N. Buisman, H.V.M. Hamelers, Energy efficiency of a concentration gradient flow battery at elevated temperatures, J. Power Sources 340 (2017) 71–79, https://doi.org/10.1016/j.jpowsour.2016.11. 043.
- [47] Y. Ghalavand, M.S. Hatamipour, A. Rahimi, A review on energy consumption of desalination processes, Desalin. Water Treat. 54 (2015) 1526–1541, https://doi. org/10.1080/19443994.2014.892837.
- [48] H. Strathmann, Ion-Exchange Membrane Processes in Water Treatment, Elsevier, 2010, https://doi.org/10.1016/S1871-2711(09)00206-2.
- [49] D. Wang, J. Cheng, Q. Yang, G. Wenchao, L. Qun, F. Chen, Viscous-Elastic Polymer Can Increase Microscale Displacement Efficiency in Cores, (2000), https://doi.org/ 10.2118/63227-MS.
- [50] R. Zhang, X. He, S. Cai, K. Liu, Rheology of diluted and semi-diluted partially hydrolyzed polyacrylamide solutions under shear: experimental studies, Petroleum (2016) 1–10, https://doi.org/10.1016/j.petlm.2016.08.001.
- [51] J.D. Isdale, C.M. Spence, J.S. Tudhope, Physical properties of sea water solutions: viscosity, Desalination 10 (1972) 319–328, https://doi.org/10.1016/S0011-9164(00)80002-8.
- [52] J.C. Jung, K. Zhang, B.H. Chon, H.J. Choi, Rheology and polymer flooding characteristics of partially hydrolyzed polyacrylamide for enhanced heavy oil recovery, J. Appl. Polym. Sci. 127 (2013) 4833–4839, https://doi.org/10.1002/app.38070.
- [53] S. Choi, pH Sensitive Polymers for Novel Conformance Control and Polymer Flooding Applications, The University of Texas at Austin, 2008.
- [54] M.P.S. Gomes, M. Costa, Determination of the critical concentration of partially hydrolyzed polyacrylamide by potentiometry in an acidic medium, J. Appl. Polym. Sci. 128 (2013) 2167–2172, https://doi.org/10.1002/app.38310.
- [55] S. Peng, C. Wu, Light scattering study of the formation and structure of partially hydrolyzed poly(acrylamide)/calcium(II) complexes, Macromolecules 32 (1999) 585–589.
- [56] Y. Tanaka, Concentration polarization in ion-exchange membrane electrodialysis: the events arising in an unforced flowing solution in a desalting cell, J. Membr. Sci. 244 (2004) 1–16, https://doi.org/10.1016/j.memsci.2004.02.041.