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Impact of polymer molecular weight on the efficiency of temperature swing solvent extraction for desalination of concentrated brines

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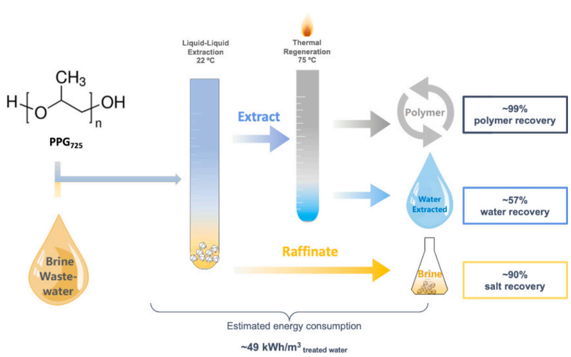
HIGHLIGHTS

- Polymer molecular weight (Mn) affects salt and water recovery in Temperature Swing Solvent Extraction (TSSE) desalination.
- An intermediate Mn (725 g/mol) polypropylene glycol provided the best overall water and salt recovery.
- TSSE was more efficient using a field derived concentrated brine than a model concentrated NaCl brine.
- Better separation in the thermal regeneration step will further improve water recovery in the TSSE process.

GRAPHICAL ABSTRACT



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ABSTRACT

Thermally-responsive non-ionic polymers can be used for temperature swing solvent extraction to desalinate concentrated brines. We determined how polypropylene glycols [PPG] with number average molecular weights (Mn) of 425, 725 or 1000 g/mol affected the quantity and quality of the extracted water, and overall process energy requirements using model 10 wt% NaCl (~100 g/L TDS) and field derived (82.1 g/L TDS) concentrated brines. The amount of water recovered and its salinity was highest for PPG_{425} (lowest Mn) and lowest for PPG_{1000} (highest Mn). PPG_{725} (intermediate Mn) provided the best balance between water recovery and salt rejection. PPG_{725} produced a water with low salinity (<1.6 wt% NaCl) from a field derived brine using a 20:1 Solvent:Feed ratio, with an overall energy consumption of 49 ± 13 $kWh/m^3_{treatedwater}$. This is comparable with mechanical vapor compression crystallizers (>50 $kWh/m^3_{treatedwater}$). The influent feed salinity at 20:1 S:F did not affect the water extraction efficiency, and $NaCl_{(s)}$ forms in the raffinate, suggesting the potential for near zero liquid discharge desalination in this process. Overall, PPG_{725} is a promising polymer for desalination of highly concentrated brines. Improving the efficiency of the water-polymer separation during thermal regeneration would further improve the attractiveness of this approach.

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1. Introduction

Concentrated brines (70–358 g/L total dissolved solids -TDS) [1] are ubiquitous and generally difficult to manage. These brines can be generated by many industrial processes, including brackish water desalination, landfill leachate treatment, and flowback and produced water from oil and gas extraction [2–4]. Oil and gas production alone produced an estimated 1 trillion U.S. gallons of produced water in 2017 [5]. The primary brine management strategies like evaporation ponds and deep well injection have inherent constraints (e.g., absence of required infrastructure at remote locations, need for long distance transport of brines, or land use restrictions) [5,6]. Treatment alternatives that avoid these constraints and enable on-site treatment and re-use of the concentrated brines for other applications (e.g., industrial, resource extraction, agriculture, and municipal) are needed.

Conventional desalination treatment for concentrated brines includes various thermal strategies like flash evaporation, distillation, and mechanical vapor compression [6,7], which are integrated into industrial brine concentrators or crystallizers. The former produces freshwater and a highly saturated brine, which can be further concentrated in crystallizers, ultimately providing zero-liquid discharge. However, there is no ideal desalination strategy for concentrated brines because each strategy works best within a specific range of feed salinities and has unique operational constraints (e.g., corrosion or formation of scales/precipitates [6]). High salinity also introduces thermodynamic constraints such as an increase in minimum energy required and an increase in specific work necessary to separate water and dissolved salts [6,8–10]. Additionally, conventional desalination technologies have technical water recovery limits that decrease with increasing feed salinity, particularly at high salinities (15–26 wt% NaCl) [6,10]. A technology in which water recovery and salt precipitation are less dependent on the feed salinity is desired to overcome such thermodynamic challenges.

Temperature swing solvent extraction (TSSE) is a desalination strategy that is relatively inexpensive, simple, and versatile [11–14]. The TSSE method uses a solvent to selectively extract water from the brine at ambient temperature, thereby producing a more concentrated brine (Fig. 1). The water extracted into the solvent is then recovered by increasing the solvent temperature, which decreases its water solubility, and the two phases separate. The ideal solvent maximizes water extraction, minimizes co-extraction of the salt, and has a low solubility in the brine. The ideal solvent should also have a low heat capacity and promote phase separation at a relatively low temperature to minimize the energy requirements for water recovery [8,13] (Fig. 1). Finally, the solvent must be reusable over many regeneration cycles [15,16], i.e., its temperature dependent solubility in water must remain consistent over many TSSE cycles.

Recently, the solvent diisopropylamine (DIPA) was shown to efficiently recover water (~91 % recovery) and to precipitate salt from a concentrated brine (TDS ~292 g/L, ~30 wt% NaCl) [12]. However, amine based solvents are prone to degradation (e.g., oxidative and thermal degradation) [17], with potential formation of the carcinogens nitrosamines and nitramines, which pose environmental and safety concerns [18]. Non-ionic, thermo-responsive polymers, namely the homopolymer polypropylene glycol (PPG, Mn 425 and 1000 g/mol), have also been suggested as potential solvents for TSSE of concentrated brines [19,20]. These polymers may be more desirable over amines in field applications because they have low or negligible toxicity to humans and various marine life, are non-flammable, and can be biodegradable [21–23]. The efficiency and energy requirements of a TSSE strategy [15,16] compared to other brine treatment strategies is rarely reported.

Hydrophobic properties, molecular size, surface area, and polymer conformation are among the driving forces of partitioning in aqueous two-phase systems like those used in TSSE [24]. PPG is a thermally-responsive polymer, with an aqueous solubility that decreases with increasing temperature [25,26] and increasing molecular weight [27,28] due to entropic constraints, i.e., hydration of a larger polymer (high Mn) requires more water molecules, which is entropically unfavorable [29]. When the number of PPG monomers in the polymer increases (i.e., molecular weight increases), polymer hydrophobicity increases and phase-separation occurs at a lower temperature (i.e., polymer water solubility decreases) [30]. Therefore, the molecular weight should affect the range of operating temperatures of the TSSE, and hence, energy requirements. To determine the magnitude of this

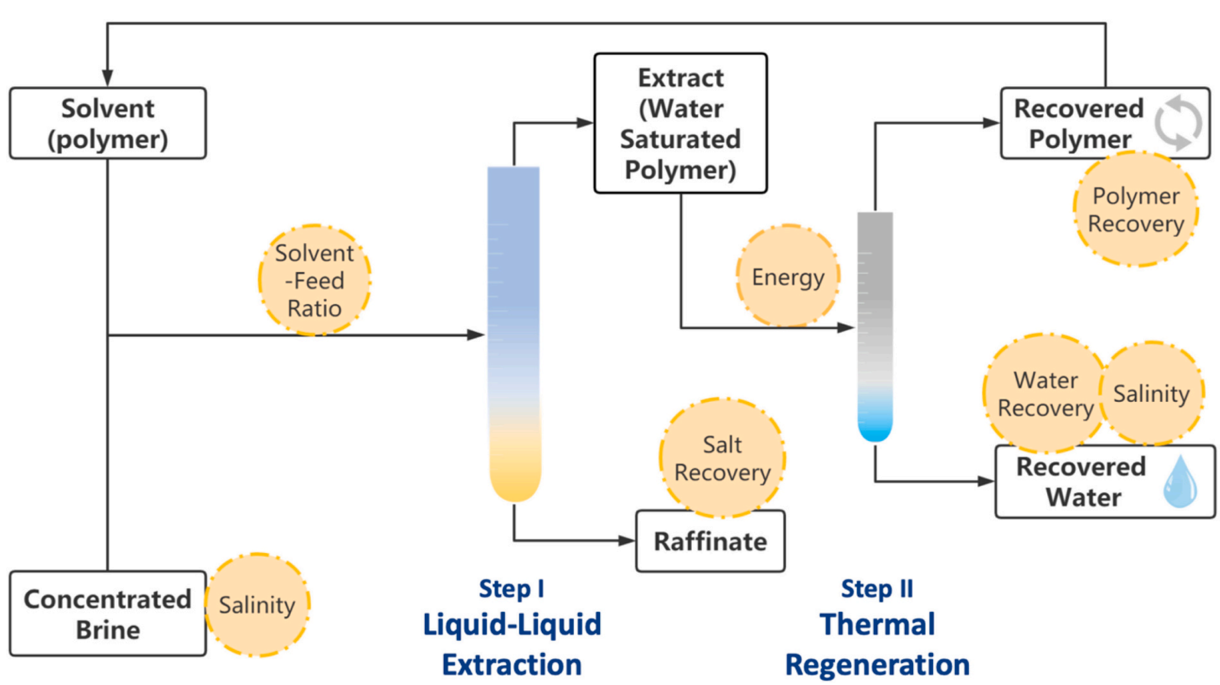

Fig. 1. Scheme of the complete TSSE process and important parameters (in yellow dashed circles) considered in the process energy calculation.

effect, we evaluated the performance of PPGs with molecular weights of 425, 725 and 1000 g/mol in a TSSE desalination strategy. The goals of the present study were to 1) assess the ability of thermo-responsive non-ionic polymers to recover water from concentrated brines using a TSSE approach, 2) evaluate the critical points affecting efficiency, and 3) estimate the energy requirements and resulting water quality compared to other approaches. Specifically, we evaluated the salt recovery, yield and quality of extracted water, and the ability to recover and reuse the polymer after the thermal regeneration step, at the best conditions determined for each polymer. We determined that PPG_{725} (intermediate Mn) can efficiently desalinate concentrated brines with energy inputs that are comparable to crystallizers used in industrial operations.

2. Material and methods

2.1. Chemicals

Linear PPG homopolymers (PPG_{425}, PPG $_{725}$ and PPG_{1000}, ≥99.5 w/w% purity) were purchased from Sigma Aldrich. All were used as received. Model brines - feed solutions (i.e., solutions with salinities between 7 and 20 wt% NaCl) were prepared by dissolving sodium chloride (ACS NaCl, ≥99 %) in Milli-Q water (IQ7000, EMD Millipore, Germany). Drill tailings were used to make a field derived concentrated brine for evaluation as described below (Section 2.3).

2.2. TSSE experimental procedure

2.2.1. Step I – liquid-liquid extraction to extract water from brine

The liquid-liquid extraction (LLE) step extracts water from the brine into the extract (i.e., water saturated polymer phase) (Fig. 1). This step was performed in 50 mL centrifuge polypropylene tubes containing a specified mixture of feed (e.g., 10 wt% NaCl solution) and polymer (either PPG_{425}, PPG_{725} or PPG_{1000}). Two grams of feed was added to different polymer masses to evaluate specific Solvent-to-feed (S:F) ratios. All masses were weighed and the S:F ratios were calculated and presented as mass ratios ($w_{polymer}$:w_{feed}). The mixtures were capped and agitated using an Eberbach, E6010.00 reciprocating shaker at 280 rpm for 120 min at 22 °C (lab temperature). After agitation, the extract (i.e., water saturated polymer) and the raffinate (Fig. 1) were separated by centrifugation for 6 min at 2000*g* (Avanti J-E, Beckman Coulter). The volume of each phase was determined and aliquots of extract and raffinate were collected by pipette or syringe, respectively. The volume and mass of each aliquot were recorded. The salt, water, and polymer mass in each phase was determined as described below (Section 2.4).

2.2.2. Step II – thermal regeneration to recover water from the water saturated polymer

After the LLE step, the water saturated polymers were heated to recover the water. Ten grams of the water saturated polymer was vortexed for 30 s, and then immersed in an oil bath at 75 °C (for PPG_{725} and PPG_{1000}) or 85 °C (for PPG_{425}) to promote the separation of the water and polymer phases. These temperatures represent the lowest temperatures at which the highest decrease in polymer water content was observed following thermal extraction, for the studied polymers. The polymer rich phase (top) was then collected by pipette. The bottom phase (recovered water) was collected using a syringe. The volume and mass of each phase was recorded, and the thermal extraction efficiency (TEE) was calculated using Eq. (1),

$$\text{TEE (\%water removal)} = \left(1 - \frac{\text{Polymer water content}_{\text{ATE}}}{\text{Polymer water content}_{\text{BTE}}}\right)*100 \quad (1)$$

where polymer water content is given by water % (w/w) in the polymer before thermal extraction (BTE) and after thermal extraction (ATE), respectively. To evaluate the effect of time on the water recovery, aliquots were collected at 24 and 48 h for all the polymers.

2.2.3. Polymer recycling efficiency

The recovered polymer collected in the thermal regeneration step was reused over three complete TSSE cycles to evaluate the ability to reuse the polymer. The first cycle was performed with the pure polymer that contained very low water content as determined by Karl Fisher titration (Section 2.4). Subsequent cycles were performed with reused thermally regenerated polymers and with new brines. At each regeneration cycle, to avoid recycling product water into the process, we excluded the lowermost layer of the recovered polymer.

For all the polymers the separation time was 24 h and the S:F ratios used for the recycling assessment corresponded to the ratio where a salt precipitate was obtained in the raffinate following LLE, i.e., with the highest water recovery (PPG_{425} and PPG_{725} with 15:1 and 20:1, respectively). Due to material constraints and absence of salt precipitation with the highest tested S:F ratio (20:1), the reusability of the PPG_{1000} was evaluated with a 10:1 S:F ratio. Although, PPG_{1000} was not evaluated at its optimal conditions, the reuse experiment will determine how reusing affects PPG_{425}, PPG_{725} and PPG_{1000} ability to extract water, and how these effects relate to polymer Mn.

2.3. TSSE experiments using field derived concentrated brine as feed

A concentrated brine from a field site was also tested to determine how a complex environmental matrix, that contains various dissolved ionic species and organic matter, affected the TSSE performance. This field derived concentrated brine was produced by leaching drilling tailings collected from an oil and gas site, which are highly saline solids requiring treatment to remove salt prior to disposal. The high salinity water recovered (2.0 wt% Cl^-) was evaporated at 70 °C to further concentrate the brine to approximately 5.0 wt% Cl^- for testing. Solids that precipitated during evaporation were removed by centrifugation (6000*g*, 6 min). The resulting concentrated brine had a pH = 6.6, 82.1 g/L TDS, 0.7 mg/L total organic carbon (TOC), 5.0 wt% Cl^-, and 0.55 wt% SO_4^{2-}. Note that the sulfate concentration was approximately 10 times lower than chloride. Although we only quantified the Cl^- in the brine, we present the salinity of the field derived concentrated brine on a mass based (wt% NaCl). Using the measured chloride data and assuming Na^+ as the dominant cation, the estimated TDS is 85 g/L (8.5 wt% salinity), consistent with the measured TDS value of 82.1 g/L. Thus, the TDS in this brine is NaCl dominated, which is typical for oil and gas produced water [10,31]. Four cycles of TSSE were performed as described above (Section 2.2.3), using PPG_{725} at a 20:1 S:F ratio.

2.4. Distribution of salt, water, and polymer in the two-phase system

Water content in the extract (i.e., water saturated polymer) and raffinate was evaluated by Karl Fischer volumetric titration (Eco KF Titrator, Metrohm, Switzerland) following the manufacturer's protocol. The dissolved NaCl content in both phases was estimated from chloride measurement by Ionic Chromatography (DIONEX AS-AP, ICS 5000 + DC, ICS 5000 + EG, Thermo Scientific). The polymer content in both phases was determined using a TOC analyzer (Laboratory TOC Analyzer, Sievers InnovOx). The distribution coefficients (D_i) of the species in the extract and raffinate phases, as well as recovery (η_i) of extraction were calculated on a mass basis [19] (Eqs. (2)–(3)).

$$D_i = \frac{(X_i)_E}{(X_i)_R}, \tag{2}$$

i = p,w,s, where p = polymer, w = water and s = salt, E (extract) and R (raffinate), $(X_i)_E$ = mass$_i$E/mass E and $(X_i)_R$ = mass$_i$R/mass R ;

$$\eta_i = \frac{(m_i)_{Rec}}{(m_i)_F} \tag{3}$$

i = w,s, where w = water and s = salt, m (mass), Rec (Recovered in extracted water and final brine, for water and salt, respectively) and F (feed).

2.5. Assessment of energy requirements for the separation

Following liquid-liquid extraction at lab temperature, thermal energy is required to raise the temperature of the water-saturated polymer (extract) to recover the water and dehydrate the polymer for the next cycle. A temperature of 75 °C was used for PPG_{725} or PPG_{1000} and 85 °C was used for PPG_{425}. The energy required to treat a cubic meter of feed water using the TSSE process was determined for each polymer based on the thermal energy required in the laboratory batch separation process described above (Section 2.2.3), assuming a thermal recovery efficiency of 90% [11]. The energy required (E) was calculated using Eqs. (4) and (5).

$$E\left(\mathrm{kWh/m^3}_{treated\ feed\ water}\right) = \left[\left(C_{pp}m_p + C_{pw}m_w\right)(T_{II} - T_I)k\right] / V_{treated\ water} \tag{4}$$

$$E\left(\mathrm{kWh/m^3}_{produced\ water}\right) = \left[\left(C_{pp}m_p + C_{pw}m_w\right)(T_{II} - T_I)k\right] / V_{produced\ water} \tag{5}$$

where C_{pp} is the polymer specific heat capacity (1.9 kJ/kgK, http://polymerdatabase.com/ and [32]), C_{pw} is the water specific heat capacity (4.20 kJ/kgK), m_p is the polymer mass, and m_w is the water mass, T_I and T_{II}, represent the temperature at which step I and step II occurred (Fig. 1), k is a constant (0.00028) required to convert kJ to kWh, $V_{treated\ water}$ is the volume of feed (brine) water that is treated under the tested conditions. Because most of the salt is retained in the raffinate in step I (Fig. 1), its effect on the water heat capacity and on the overall energy is negleted [12,33]. For Eq. (4), $V_{produced\ water}$ is the final volume of produced water obtained under the tested conditions. For more detailed information see Supplementary material.

3. Results and discussion

The first step in the process is water extraction from the brine by the polymers, resulting in a water saturated polymer and a more concentrated brine. The ability of the polymers to extract water and concentrate the brine without significant partitioning of polymer into the raffinate was determined by measuring the distribution of salt, water and polymer in the raffinate (i.e., bottom phase-concentrated brine) and extract (i.e., top phase-water saturated polymer) following liquid-liquid extraction at lab temperature (Fig. 1).

3.1.1. Influence of polypropylene glycol homopolymer molecular weight (PPG_{425}, PPG_{725} and PPG_{1000}) on the LLE step

We evaluated the effect of Mn on water extraction and salt recovery for three different molecular weight PPG's at different S:F ratios. For PPG_{425} (Fig. 2A), the lowest Mn polymer evaluated, S:F ratios of 4:1, 6:1, and 15:1, were used. As the S:F ratio increased from 4:1 to 15:1, a higher mass of water was transferred into the extract (Fig. 2A). The 15:1 S:F ratio extracted 100 ± 1 % of the water from the brine, precipitating $NaCl_{(s)}$ in the raffinate. The lower S:F feed ratios (i.e., 4:1 and 6:1) did not extract enough water to precipitate the salt in the raffinate. Despite the precipitation of salt, the highest S:F ratio (i.e., 15:1) resulted in lower

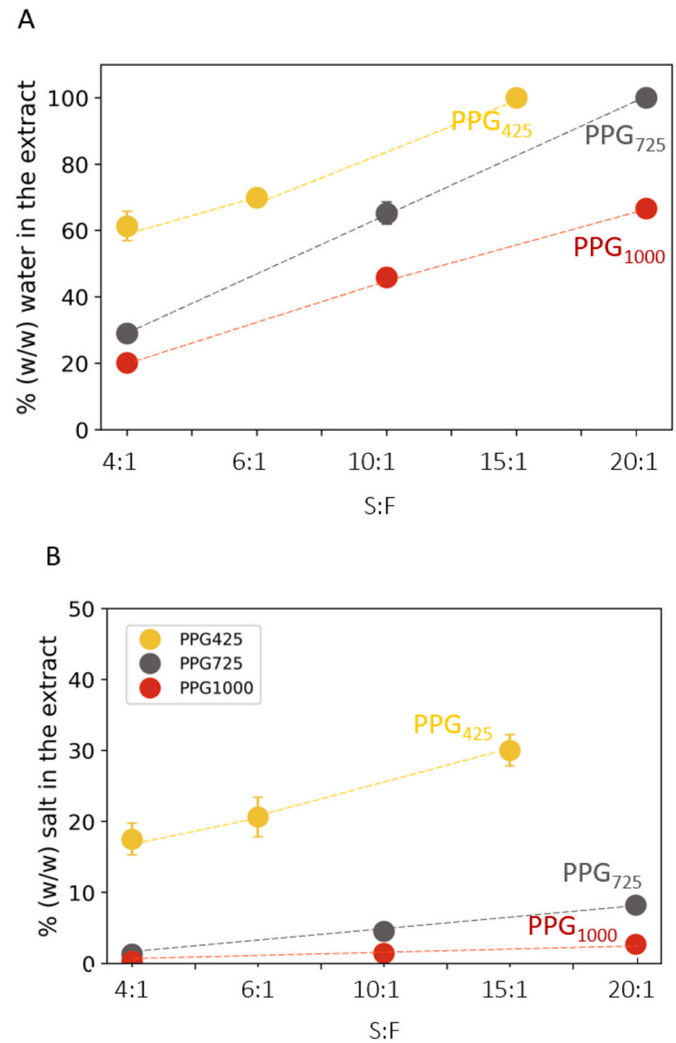

Fig. 2. Effect of S:F ratio on the distribution of the initial salt and water in the extract (% w/w) following the first step in the TSSE process, using fresh and fully dehydrated PPG_{425}, PPG_{725} and PPG_{1000}, respectively, with a 10 wt% NaCl model concentrated brine A) Percentage of the initial water in the extract following LLE. B) Percentage of the initial salt in the extract following LLE. Data points without error bars indicate that the standard deviation was too small to be visible in the graph (n = 3, except for the 4:1 S:F ratio with PPG_{725} and PPG_{1000}, n = 1).

salt recovery (calculated using Eq. (2)) in the raffinate because salt also partitioned into the PPG_{425} polymer along with the water. Salt recovery was 70 ± 2.2 % using a 15:1 S:F ratio.

For the intermediate Mn PPG_{725}, water extraction increased from 29 at the S:F ratio of 4:1, then from 65 ± 3.3 % at the S:F ratio of 10:1 to nearly 100 ± 8 % at the S:F ratio of 20:1 (Fig. 2B). The high water extraction into the polymer (%) at a S:F ratio of 20:1 led to $NaCl_{(s)}$ precipitation. Note that the very high salt recovery cases were difficult to quantify precisely because of the salt precipitate and the lack of a clear phase separation given that nearly all of the water partitions into the polymer. Salt recovery decreased from 96 ± 0.4 % to 92 ± 0.8 % for S:F ratios of 10:1 and 20:1, respectively. PPG_{1000}, the highest Mn polymer evaluated, had the lowest capacity to extract water from feed (Fig. 2C). This polymer extracted 67 ± 1.8 % of the water at a 20:1 S:F ratio due to its higher hydrophobicity and corresponding lower affinity for water, and the amount of polymer loss in the raffinate was low (<0.05 %) (Supplementary data Table S1). PPG_{1000} did not extract enough water to precipitate salt in the raffinate at all S:F ratios tested. However, it extracted the least salt and had the highest salt recovery in the raffinate (97.3 ± 1.0 %) for the analyzed polymers.

Overall, in the LLE step, increasing the Mn of the PPG polymer from 425 g/mol to 1000 g/mol decreased uptake of both water and salt into the extract (i.e., water saturated polymer), increasing the polymer water/salt selectivity (better salt recovery in the raffinate). This is consistent with the lower ability of the high Mn PPGs to solubilize small hydrophilic molecules like water compared to the low Mn PPGs, due to the increase in the miscibility gap with increasing Mn [29]. The dielectric constant of the hydrated polymer system may also play a role in the inverse relationship between water/salt sorption selectivity and polymer hydrophobicity in non-charged polymer membrane-based desalination strategies [34]. More hydrophilic polymers take up more water, and the dielectric constant of a hydrated polymer increases with increasing water uptake. Salts dissolve better in a medium with a higher dielectric constant due to its ability to polarize and stabilize the dissociated ion's electrostatic charge compared to a medium with a lower dielectric constant. Therefore, salt partitioning is less energetically favored in polymers with low water uptake (more hydrophobic), resulting in better selectivity. So the intermediate Mn polymer (i.e., PPG_{725}) appears to be the most promising polymer, as it provides both good water extraction and good salt recovery in the raffinate (both >90 %, respectively). Hence, this polymer was further investigated to determine the impact of feed salinity on the separation.

3.1.2. Effect of feed salinity on the PPG_{725} ability to extract water using a S:F ratio of 20:1

A previous study [19] found that feed salinity significantly affected water uptake by PPG_{425}, and less so for PPG_{1000} at a S:F ratio of 1:1. This indicates an effect of polymer MW on the sensitivity of water uptake on the results. These authors did not evaluate the performance of PPG_{725}. Hence, we evaluated the response of PPG_{725} for a wide range of feed salinity (i.e., 7–20 wt% NaCl, model concentrated brines) using a 20:1 S:F ratio.

Under the tested conditions (S:F ratio of 20:1), the feed salinity had little effect on the yield of extracted water as all the tested salinities extracted nearly 100 ± 9 % of the initial feed water (Fig. 3). We note that at a 1:1 S:F ratio there was a small effect of salinity on performance, consistent with prior reports [19] (Supplementary data Fig. S1). It is worth noting that water recovery and energy requirements in many desalination technologies used for brine management (e.g., mechanical vapor compression, multi-effect distillation, forward osmosis, and humidification–dehumidification) typically become less efficient as salinity of the feed increases, particularly in the high feed salinity range (15–26 wt% NaCl) [6,10]. Hence, the limited impact of salinity on performance (i.e., water recover) of PPG_{725}, using a high solvent to feed ratio (20:1) suggests the potential to be applicable over a range of brine concentrations, and potentially be more energy efficient than other desalination technologies in the high salinity range.

3.2. Efficiency of the thermal regeneration to recover water and regenerate the polymer

3.2.1. Effect of polypropylene glycol homopolymer molecular weight (PPG_{425}, PPG_{725} and PPG_{1000}) on the thermal regeneration step

The thermal regeneration step of the TSSE process produced a dehydrated polymer for reuse. It is a critical step because it affects the amount of water recovered per cycle and the capacity of the polymer to extract water from brine in the next cycle. A more complete dehydration of the polymer in the thermal regeneration step results in more water recovery in both the current and next cycle. The efficiency of this critical step in the process is commonly not reported [13,20].

Despite their different transition temperatures (>60 °C, 52–57 °C, and 40–47 °C for PPG_{425}, PPG_{725} and PPG_{1000}, respectively, as previously determined [35]), a minimum of 85 °C for PPG_{425} and 75 °C for both PPG_{725} and PPG_{1000} was needed to achieve phase separation and to maximize the water recovery. Thermal regeneration of PPG_{425} lowered the water content of the polymer from 6 % to 3.2 ± 0.5 % (52 ± 4.4 % removal) after 24 h of incubation at 85 °C (Fig. 4A). Thermal regeneration of PPG_{725} and PPG_{1000} lowered the water content from 4.2 % to 2.3 ± 0.9 % (41 ± 5.3 % removal) and from 4.5 % to 2.6 ± 0.2 % (47 ± 11 % removal), respectively, after 24 h of incubation at 75 °C (Fig. 4B and C, respectively).

3.3. Stability of the polymers over successive TSSE cycles

The polymer must be reusable over many cycles to be economically viable. However, its properties may degrade over each TSSE cycle. The performance of PPG_{425} was observed over four full TSSE cycles. Water recovery decreased from 60 ± 0.0 % during the first cycle with pure dehydrated polymer to 43 ± 0.0 % in the second cycle using the partially dehydrated regenerated polymer. Water recovery continued to decline with each cycle (Fig. 5A) reaching the lowest value (23.4 ± 0.2 %) in the last cycle. Salt recovery in the raffinate also dropped from 70 ± 2 % in the first cycle to 40 ± 1 % in the last cycle (Fig. 5B). These results suggest that the PPG_{425} water/salt selectivity decreased with reuse. The higher polymer hydration when reused (>2 wt% initial water content) compared to the pure polymer (<0.7 wt% initial water content). Because the composition of the polymer-rich and water-rich phases is non-linear in a three component (salt-water-polymer) system, the higher initial water content likely contributed to the higher amount of salt partitioning into the polymer rich phase, and the subsequent higher salt content of the recovered water after the TE step, increasing from 2.0 ±

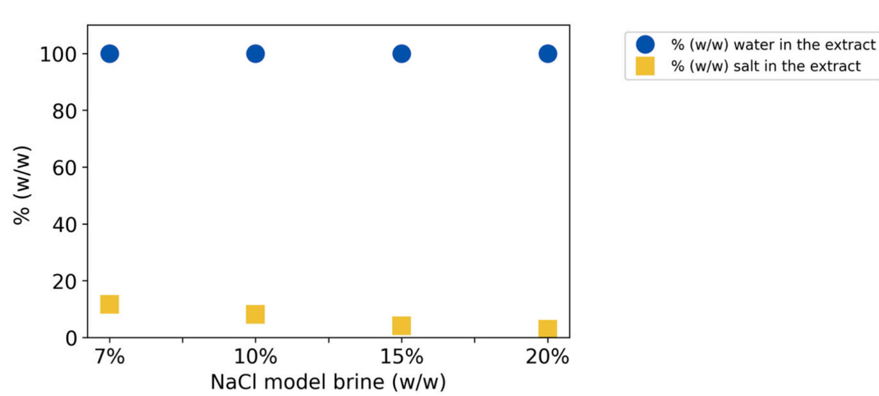

Fig. 3. Effect of feed salinity (7–20 wt% NaCl model concentrated brine) on the distribution of the initial salt and water in the extract (% w/w), following the first step in the TSSE process, for fully dehydrated PPG_{725}, using a 20:1 S:F ratio. Data point without error bars indicate that the standard deviation was too small to be visible in the graph (n = 2, except for 10 % salinity where n = 3).

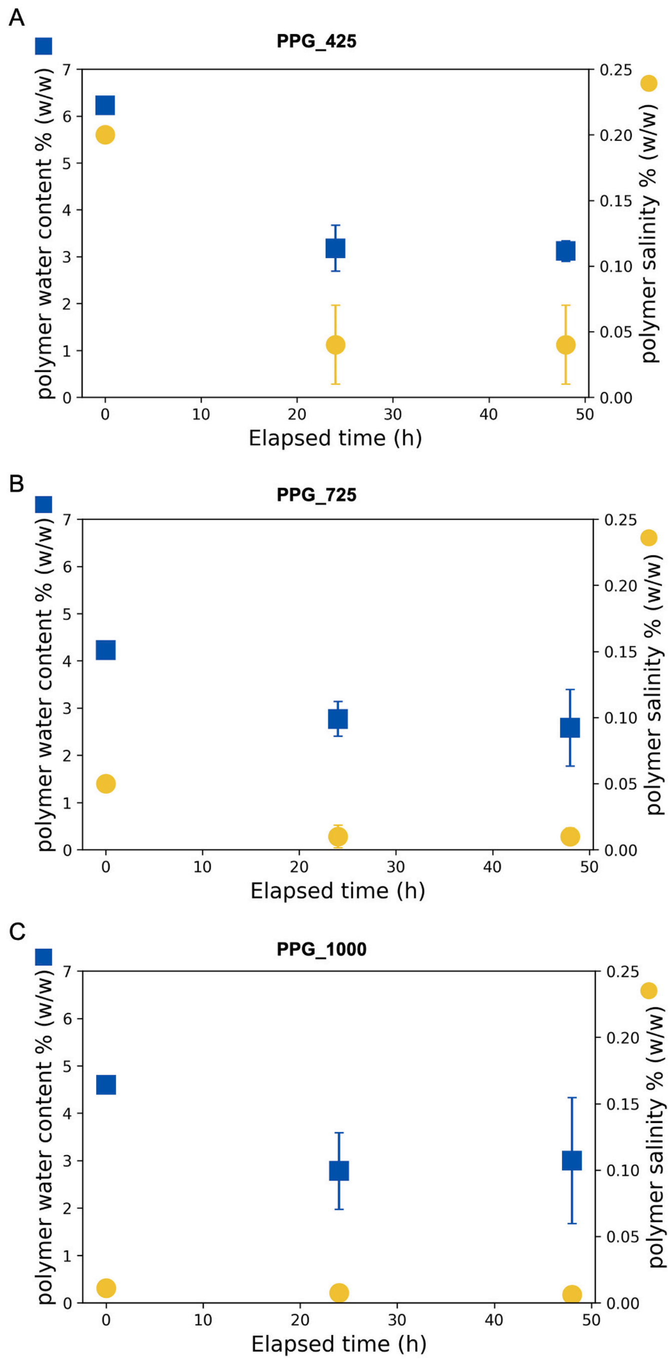

Fig. 4. Water (blue-left axis) and salinity (gold) (%) in the regenerated polymer following the thermal regeneration step at 75 °C ($PPG_{725/1000}$) and 85 °C (PG_{425}), over time, are shown in plot A, B, and C. The mixture composition (mass based) before the thermal regeneration step was 0.2 % NaCl, 6 % water and 94 % polymer for PPG_{425}, 0.05 % NaCl, 4 % water and 96 % polymer for PPG_{725}, and 0.01 % NaCl, 4 % water and 96 % polymer for PPG_{1000}. Data point without error bars indicate that the standard deviation was too small to be visible in the graph (n = 2, except for PPG_{425} with n = 3).

2.2 to >7.3 ± 0.1 %) (Fig. 5C). These results suggest that PPG_{425} is not effective in extracting water and separating it from the salt with reuse, and therefore is not a practical solvent for a TSSE desalination. Besides the produced water had a polymer content ranging from 15.9 ± 0.0 to 17.6 ± 0.2 % (Fig. 5D).

Different from PPG_{425}, the water recovery by PPG_{725} decreased from 69.8 ± 0 % in the first cycle (corresponding to the pure polymer) to an average of 46 ± 2 % in the later 3 cycles (Fig. 5A). In contrast to PPG_{425}, salt recovery for PPG_{725} remained constant at 91 ± 1 % over the analyzed cycles (Fig. 5B). The final extracted water also had a lower salinity (0.5–1.2 wt% NaCl) and lower polymer content (4.5–9.8 wt% polymer) than for PPG_{425} (Fig. 5C, D). Again, the lower water extraction observed for the thermally regenerated polymer is likely due to the inability to fully dehydrate the polymer in the thermal extraction step, resulting in a slightly different system (salt-water-polymer) composition than for the previous step.

PPG_{1000} had the lowest water recovery (ranged between 8 and 25 %) (Fig. 5A), but the highest recovery of salt in the brine (average 99 ± 0.4 %) (Fig. 5B), resulting in an extracted water with a salinity <0.6 % (wt% NaCl) (Fig. 5C) and polymer content <7 % (wt% polymer) except for the first extraction (Fig. 5D). Although this polymer has a lower water recovery, it can produce a water with the lowest salinity. A multi-stage approach, where the brine would be extracted multiple times could increase the amount of water recovered and decrease the mass/volume of final brine for disposal. Such strategies are currently applied to humidification–dehumidification, where brine recirculation is required due the low recovery obtained in a single step. A multi-stage approach using PPG_{1000} could be feasible, particularly when low salinity water is the goal, because PPG_{1000} extraction efficiency appears to be relatively independent of feed salinity [19] and PPG_{1000} also had a consistent efficiency over multiple re-use cycles.

While generally promising, the inefficient thermal regeneration of the polymers in the lab setup affects overall process efficiency. This includes lowering the water recovery during thermal regeneration and lowering the amount of water that can be extracted in the liquid-liquid extraction step in subsequent cycles. The use of these polymers in multiple cycles, and the impact of inefficient thermal regeneration, has not been reported in previous studies on this topic. Yet, we observed that over the reuse cycles, the water recovery capacity of polymer PPG_{425} decreases at each cycle, whereas the PPG_{1000} data suggests that its water recovery capacity improves over time, yet it is always below 30 % water recovery. Only PPG_{725} showed a water recovery above 40 % over multiple cycles. Thus, the PPG_{725} appears most promising for use in TSSE because it has a higher water recovery than PPG_{1000} and a lower salinity in extracted water than PPG_{425}. It also had a consistent efficiency over multiple re-use cycles. The ability of PPG_{725} to perform well using real brines and the energy requirements for the process relative to alternative processes are discussed next.

3.4. Treatment of a field derived concentrated brine from oil & gas operations

We evaluated the ability of PPG_{725} (20:1 S:F ratio) to concentrate a field derived concentrated brine (82.1 g/L TDS) generated from an oil & gas operations pit material. The water recovery using the field derived brine ranged between 53 and 61 % (Fig. 5A), higher than for the model (100 g/L TDS) NaCl brine (Fig. 5A). Although the chemical complexity of the real brine hampers a clear identification of the forces driving the observed differences, and because a stronger salting out effect is expected for sulfate than for chloride in three component systems (polymer+salt+water) [19,20], the presence of sulfate (0.55 wt%) might have contributed to these differences, by inducing a change in water partitioning in the TSSE.

Moreover, the extracted water salinity was <1.6 % (wt% NaCl) throughout the four extraction cycles and <7 wt% polymer (Fig. 5C, D), making it suitable for some reuse applications, e.g., reuse in soil washing to extract salt from brine impacted soil and drill tailings or resource extraction (e.g., gas, minerals). Coupling the TSSE with reverse osmosis (RO) could be a possibility, if other reuses requiring additional treatment are envisioned for the produced water. If this is required, the RO energy costs would be similar to those reported to desalinate brackish water (0.4–3.5 kWh/m^3 [36,37]). We note that the entrained polymer in the water is a result of imprecise separation of the water and polymer phase in a small-scale laboratory setting. An industrial process could

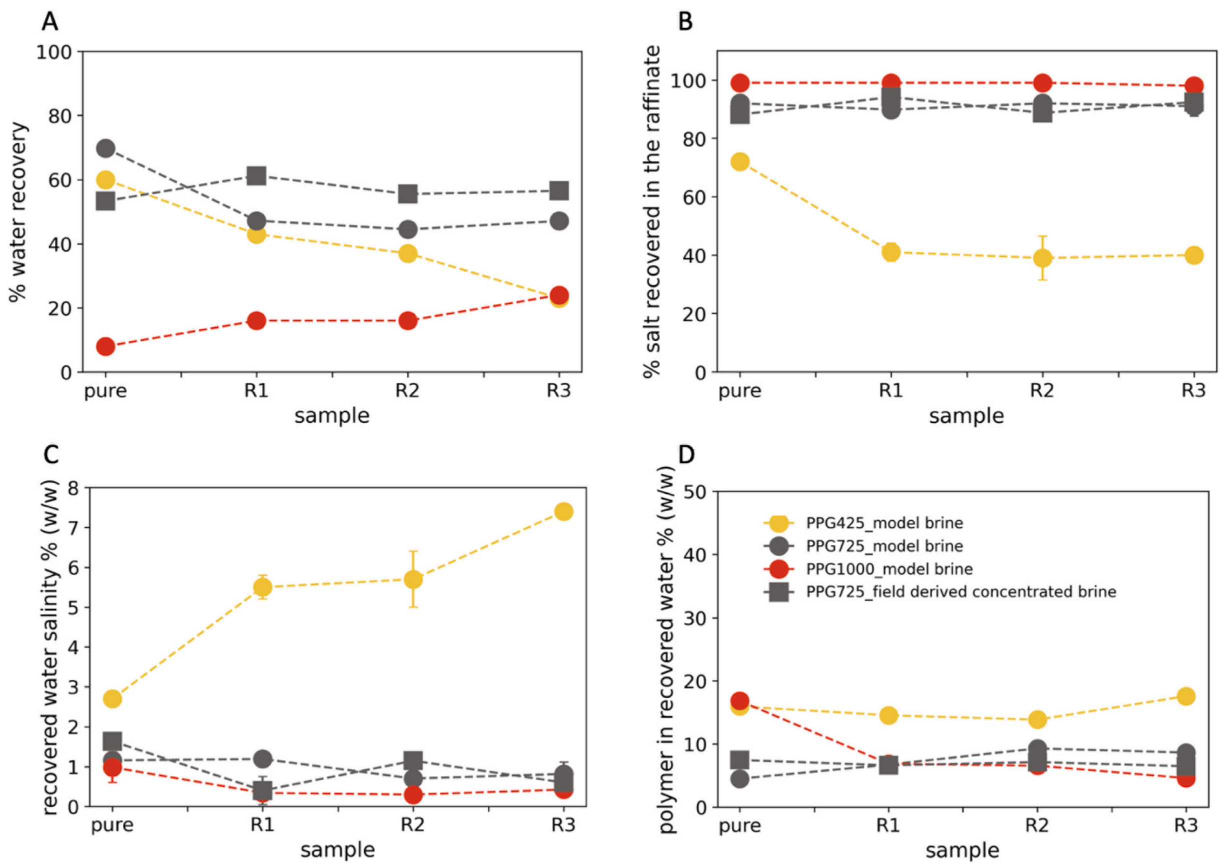

Fig. 5. PPG_{425}, PPG_{725} and PPG_{1000} performance over four TSSE cycles with a model concentrated brine (10 wt% NaCl, ~100 g/L TDS) and PPG_{725} performance over four TSSE cycles with a field derived concentrated brine (82.1 g/L TDS). (A) Percentage of water recovered following each TSSE cycle. (B) Percentage of salt recovered in the raffinate following each TSSE cycle. (C) Salt content in the recovered water following each TSSE cycle. (D) Polymer content in the recovered water following each TSSE cycle. Data points without error bars indicate that the standard deviation was too small to be visible in the graph, (n = 2, except for pure n = 3).

likely achieve better separation. The efficacy of that separation would also affect reuse opportunities and may impact the energy requirements of the process as described below.

3.5. Estimated energy costs associated with the TSSE

Desalination strategies are typically energy intensive and energy costs can be a significant fraction of the overall cost of treatment [8,9]. Therefore, preferred desalination treatments will likely be ones that minimizes energy costs, while providing a water quality that is fit for purpose. Here, we estimated the energy cost for brine treatment using PPG_{725} on the field derived concentrated brine and compare our estimates to other competing processes for the same purpose.

Using the field derived concentrated brine as feed, PPG_{725} had a water recovery of 53–61 %, using TSSE with a S:F ratio (w:w) of 20:1. The estimated required energy, which depends on the mass of polymer, mass of extracted water, initial and final temperature for the TSSE, and volume of treated water, was 49 ± 13 $kWh/m^3_{treated\ water}$ (81 ± 24 $kWh/m^3_{produced\ water}$) (Fig. 6A, B). This assumes a thermal recovery efficiency of 90% [11] for the process. Under the analyzed conditions, the extracted water salinity was <1.6 %. Interestingly, for a 20:1 S:F ratio the water extraction efficiency of PPG_{725} was found to be independent of feed salinity over a wide range of salinities (i.e., 7–20 wt% NaCl) (Fig. 3). Based on these data, and assuming that water extraction efficiency remained independent of feed composition up to saturated feeds (i.e., 26 % NaCl), the energy required to treat feeds with salinities ranging between 7 and 26 wt% NaCl, using a constant 20:1 S:F ratio with a water recovery of 60 %, ranged from 68 to 82 $kWh/m^3_{treated\ water}$ (76–87 $kWh/m^3_{produced\ water}$) (Fig. 6C, D). This indicates that the energy consumption increases slightly with influent feed salinity, but less so than reported for other desalination strategies (e.g., mechanical vapor compression, multi-effect distillation, forward osmosis, and humidification–dehumidification) [6,10]. This is primarily because the water extraction efficiency was not affected by the influent salinity, using the tested 20:1 S:F ratio. While, the estimated values are higher than the energy consumption reported for crystallizers using mechanical vapor compression (54–68 $kWh/m^3_{treated\ water}$, with feed salinities ranging between 60 and 450 g/L) [1], they are lower than reported for TSSE using diisopropylamine (DIPA) (172 $kWh/m^3_{treated\ water}$) for a 26 % salinity feed and 41:1 S:F ratio. It should be noted that the DIPA achieved 90 % water recovery and the treated water had a salinity of ~1.7 % [12].

As discussed above, the inability to fully dehydrate the polymer in the thermal regeneration step limits the overall process water recovery. A multi-stage thermal regeneration could increase water recovery, as occurs with MED (multi-effect distillation) [6,7,10], which will not greatly affect the estimated energy consumption for this desalination approach (Fig. 5A), and would still be comparable to the energy consumption reported for crystallizers using mechanical vapor compression (>50 kWh/m^3) [1]. It is worth noting that polymer lost to the recovered water would increase the energy demand of a process. If an industrial process provides efficient separation, the amount of polymer lost in the extracted water could be approximated by its solubility in the recovered water at its salt concentration of that water. The embodied energy of lost polymer would need to be added to the energy requirements of the process.

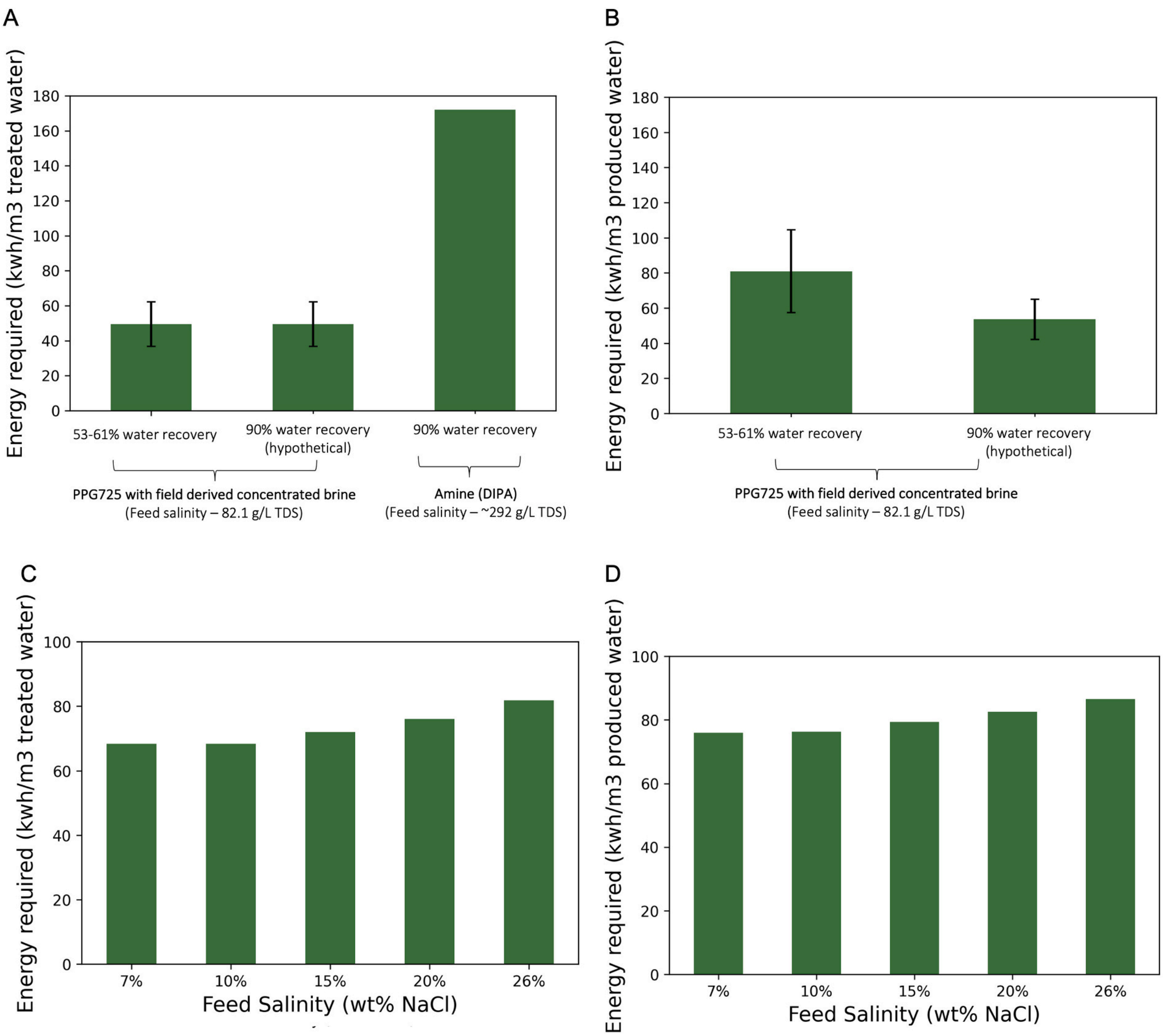

Fig. 6. Energy estimations for TSSE desalination process using PPG_{725}. Thermal energy requirement to desalinate a field derived concentrated brine using PPG_{725} (average value considering the data from 4 TSSE cycles) for the obtained water recovery (53–61 %) and for a hypothetical water recovery (90 %) assuming that the thermal regeneration step can be optimized to achieve this level, in comparison to an amine solvent (DIPA) previously reported [12]. A) ($kWh/m^3_{treated\ water}$). B) ($kWh/m^3_{produced\ water}$) Estimated thermal energy consumption in the TSSE using the polymer PPG_{725} as solvent, with different feed salinities (7–26 wt% NaCl), for the measured final water recovery of 60 %. C) ($kWh/m^3_{treated\ water}$). D) ($kWh/m^3_{produced\ water}$).

4. Conclusions

In summary, the polymer molecular weight affected the salt and water recovery in a TSSE process for concentrated brine treatment. An increase in Mn increased salt recovery but decreased water recovery due to higher polymer hydrophobicity. The best overall balance of water and salt recovery (i.e., 70 and 92 %, respectively) was obtained for dehydrated pure PPG_{725}, and the water extraction efficiency was independent of the feed salinity, for the evaluated S:F ratio (20:1). This polymer demonstrated the ability to be reused and to continue to recover ~60 % of the water from a field derived concentrated brine, recovering ~90 % of the salt in the initial feed (82.1 mg/L TDS initial concentration). Further optimization of the thermal regeneration step of the polymer can improve the efficiency of the polymer based TSSE process for desalination of concentrated brines, potentially making it competitive with existing treatment strategies.

CRediT authorship contribution statement

A. Rita Lopes: Conceptualization, laboratory experiments and analysis, Writing - Review & Editing. **Hairong Wang:** Conceptualization, laboratory experiments and analysis, and review & editing. **Jialin Dong:** Laboratory experiments and analysis. **Joonkyoung Han:** Conceptualization, Project administration, data analysis, Writing - Review & Editing. **Evan S. Hatakeyama:** Conceptualization, Project administration, data analysis, Writing - Review & Editing. **Thomas P. Hoelen:** Writing - Review & Editing. **Gregory V. Lowry:** Conceptualization, Project administration, data analysis, Writing - Review & Editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Gregory V. Lowry reports financial support was provided by Chevron Technical Center. Gregory V. Lowry reports a relationship with Chevron Technical Center that includes: funding grants.

Data availability

Data will be made available on request.

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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.2022.116104.

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