Fouling-resistant membranes for the treatment of flowback water from hydraulic shale fracturing: A pilot study

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A B S T R A C T

Polyacrylonitrile hollow fiber ultrafiltration (UF) and polyamide spiral wound reverse osmosis (RO) membrane modules were surface-modified by contact with an aqueous solution containing dopamine to deposit polydopamine on the membrane surfaces and other wetted parts inside the modules. UF modules were further modified by grafting poly(ethylene glycol) (PEG) brushes to the polydopamine coating. Polydopamine and polydopamine-g-PEG coatings increase hydrophilicity of the membrane surfaces and have previously been shown to improve fouling resistance towards model oil/water emulsions in laboratory studies. In a pilot-scale test treating hydraulic fracturing flowback water from the Barnett Shale region of Texas, the fouling performance of modified UF and RO membrane modules was compared to that of unmodified analogs. UF modules were used to remove most of the highly fouling organic matter in the feed before desalination by a train of RO elements. Polydopamine-modified UF modules maintained higher flux, lower transmembrane pressure difference, and improved cleaning efficiency relative to unmodified modules. The polydopamine coating did not appear to improve RO fouling behavior, presumably because most of the organic foulants had been removed by UF pretreatment of the feedwater. However, higher and more stable salt rejection was observed in modified RO modules than in unmodified modules.

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1. Introduction

Hydraulic fracturing has been used to enhance the productivity of oil and gas wells since its introduction by Standard Oil in 1949 [1]. Its application, especially in the recovery of natural gas from shale fields in North America, has grown intensely over the past decade with the advent of horizontal drilling technology [2]. A map of major shale gas basins in the United States is shown in Fig. 1. Once a wellbore is created in a rock bed containing petroleum or gas reservoirs, fluid is pumped into the well at a pressure sufficient to fracture the rock, permitting extraction of the petroleum or gas. Hydraulic fracturing has dramatically increased in popularity over the past decade with some reports suggesting that 60% of all wells drilled today undergo fracking [1]. The substantial reduction in the price of natural gas, relative to oil, during the past few years has been attributed in large measure to the use of horizontal drilling coupled with hydraulic fracturing, which has greatly increased the estimated supply of accessible natural gas in the U.S. [3].

Water is, by far, the most common fracturing fluid—96% of all fractured wells employ an aqueous fluid. “Frac jobs” for shale gas production in the Marcellus basin, for example, require about 1 million gallons of water for vertical wells and 3–6 million gallons for horizontal wells [4]. The tremendous water requirement of hydraulic fracturing creates two problems: fresh water demand is high and used water disposal is expensive [2]. The location of wells in remote areas often means that water must be trucked to the sites. Transportation costs to wells in arid regions, such as North Dakota, Texas, and Colorado, are high enough that on-site water treatment is already being used [5]. About 10–30% of the fracking water returns to the surface as “flowback” water with the released oil or gas [5]. Disposal of used fracturing water in an injection well costs $1.50–$2.00/bbl, and the cost of transportation to the disposal site may add up to $4.00/bbl [5] to this expense. The substantial demand for fresh water to fracture wells and high disposal costs may both be addressed by reuse of flowback water. While no standards exist for fracturing water quality, flowback water is typically not suitable for direct reuse due to high salt

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Barium, iron, strontium, and sulfates contribute to scaling that may obstruct fractures, reducing well productivity. Additionally, certain injection water additives are not compatible with high salinity or other impurities commonly found in flowback water [5]. Desalination to remove the salts that interfere with these additives therefore is critical if flowback water is to be reused in more fracturing [6].

Typical composition ranges of flowback water from the Barnett (Texas) and Marcellus (Appalachian) shale plays are shown in Table 1.

The small footprint of membrane units makes them attractive for on-site flowback water purification systems. For example, many flowback water treatment scenarios require relatively short term (e.g., several weeks [7]) access to water purification due to the transitory nature of flowback water production. Having small footprint water purification systems, which allows them to be mobile, could be advantageous since the water purification system could be moved from site to site as new wells are completed [4]. Reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF) are all increasingly being used to treat oily produced water [8]. MF and UF membranes are typically used to remove oils and other organics while NF and RO membranes can remove dissolved solids such as salts. With mixtures as complex as hydraulic fracturing flowback water, membrane fouling becomes a significant hurdle to implementation of membrane-based purification systems. Mixtures of salt, oils, particulates, and other contaminants often cause significant and irreversible deterioration of permeate flux, requiring aggressive chemical cleaning that shortens membrane lifetime. Water purification membranes are typically made of hydrophobic polymers and, as a result, oil and grease tend to be highly fouling due to hydrophobic–hydrophobic interactions between the membrane surface and such foulants.

Membrane surface modification is a popular means of mitigating membrane fouling. Surface modifications that increase hydrophilicity tend to reduce membrane fouling by hydrophobic foulants [9]. Hydrophilic surfaces attract a layer of tightly bound water molecules, preventing direct interactions between the foulant and the membrane surface [10]. Recently, our laboratory has been exploring polydopamine (PD) as a membrane surface modification agent. Messersmith and co-workers reported that PD spontaneously and non-specifically deposited onto nearly any substrate from a buffered, alkaline aqueous solution containing dopamine [11]. PD layers are often deposited onto membranes under conditions where they form thin (e.g., tens of nm), hydrophilic layers, permitting application of fouling-resistant coatings from aqueous solution with little or no loss.

### Table 1

Composition ranges of Barnett and Marcellus flowback waters [13].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Barnett (5 locations)</th>
<th>Marcellus (19 locations)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Range</td>
<td>Median</td>
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<tr>
<td>pH</td>
<td>6.6–8.0</td>
<td>7.1</td>
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<tr>
<td>Total dissolved solids (mg/L)</td>
<td>23,600–98,900</td>
<td>36,100</td>
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<td>Alkalinity (mg/L CaCO₃)</td>
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<tr>
<td>Total suspended solids (mg/L)</td>
<td>36.8–253</td>
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<tr>
<td>Total organic carbon (mg/L)</td>
<td>9.5–99.3</td>
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<tr>
<td>Biochemical oxygen demand (mg/L)</td>
<td>92.6–1,480</td>
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<tr>
<td>Chloride (mg/L)</td>
<td>16,500–72,400</td>
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<tr>
<td>Bicarbonate (mg/L CaCO₃)</td>
<td>145–994</td>
<td>372</td>
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<td>Sulfate (mg/L)</td>
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<td>Calcium (mg/L)</td>
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<tr>
<td>Barium (mg/L)</td>
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<td>7420–25,300</td>
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</tr>
<tr>
<td>Magnesium (mg/L)</td>
<td>75.3–757</td>
<td>156</td>
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of water flux [12]. The application of PD to membranes of many compositions and architectures yielded improvements in fouling performance when challenged with oil/water emulsions [12–14]. PD may also be used as a platform for surface conjugation of other molecules. Messersmith showed that primary amines may be grafted to polydopamine-coated substrates via Shiff-base or Michael addition chemistries [11]. Poly(ethylene glycol) has historically found use in biomedical [15] and membrane [16] applications as a fouling-resistant material. PEG-NH₂ has been grafted to polydopamine-coated membranes [12], which further increased fouling resistance relative to polydopamine-only treated membranes [17].

The goal of this study was to extend laboratory tests of polydopamine-coated membranes to a relative to polydopamine-only treated membranes [17]. Ultrafiltration and reverse osmosis membrane modules were modified with polydopamine; ultrafiltration modules were further modified by grafting PEG to the polydopamine coating. Previous work has demonstrated improved UF fouling resistance when PEG was grafted to the PD coating [13]; in the case of RO, the grafted PEG layer contributed to significantly increased mass transfer resistance [12], so the RO modules were coated only with PD in this study. Modules were used to purify saline hydraulic fracturing flowback water from wells in the Barnett shale play in north Texas. The UF modules were used primarily to remove residual suspended solids and organics (especially emulsified oils) from the pretreated raw feed, and the RO modules were used mainly to desalinate the UF permeate. The fouling behavior of modified UF and RO modules was compared to that of unmodified modules.

2. Materials and methods

2.1. Membrane modules

Two ultrafiltration modules were obtained from Mann + Hummel Ultra-Flo Pte, Ltd. (Portage, MI) and contained hydrophilized polyacrylonitrile hollow fibers. Six reverse osmosis modules were obtained from Hydranautics (Oceanside, CA). These RO modules consisted of spiral-wound, flat sheet membranes based on interfacial composite polyamides. Manufacturer specifications for both module types are recorded in Table 2.

2.2. Module modification

Dopamine HCl (3-hydroxytyramine hydrochloride) and Trizma HCl were purchased from Sigma Aldrich (St. Louis, MO). Sodium hydroxide was obtained from Fisher Scientific (Pittsburgh, PA), and poly(ethylene glycol) monoamine (5000 Da) (PEG-NH₂) was purchased from JenKem Technology (Allen, TX). All chemicals were used as received.

One UF module and three RO modules were surface-modified with polydopamine using the following procedure. A module was flushed with ultrapure water overnight to fully wet the surfaces to be modified. Tris buffer (15 mM) was prepared first by dissolving Trizma HCl (5.875 g) in ultrapure water (2.5 L) and adjusting the pH of the resultant solution to 8.8 using sodium hydroxide pellets. Dopamine (5 g) was dissolved in the Tris buffer (2.5 L), and the resultant 2 g/L solution was poured into the feed side of a module. The modules were gently rolled back and forth for 60 min to ensure that the dopamine solution contacted all wetted surfaces on the membrane feed side. Every 10 min, the feed inlet was opened to introduce fresh oxygen, as dopamine polymerization requires the presence of dissolved oxygen [18]. Residual dopamine was flushed from the module with ultrapure water.

The UF module was further modified by grafting PEG to the polydopamine coating. Tris buffer (2.5 L, prepared as described above) was heated to 52 °C. PEG-NH₂ (1.25 g) was dissolved in the Tris buffer and this solution was poured into the feed end of the UF module. The module was gently rolled back and forth for 45 min to ensure that the PEG-NH₂ solution contacted all of the polydopamine-modified surfaces. After PEG grafting, the UF module was flushed with ultrapure water to remove residual PEG-NH₂ solution. PEG was not grafted to the polydopamine-treated RO modules because, as noted previously, grafted PEG creates a substantial mass transfer resistance on the surface of RO membranes, resulting in a flux loss that more than offsets any fouling-reducing benefit of the coating. After modification, the modules were filled with deionized water for storage until use.

2.3. Pilot study

The site of the pilot study was the Maggie Spain Water Reclamation Facility operated with the support of Devon Energy in the Barnett Shale region near Fort Worth, TX. Flowback water from hydraulically fractured natural gas wells in the Barnett Shale play was brought to the treatment facility by truck and stored in a lined pond before processing. Raw water was subjected to coagulation and sedimentation before treatment by the membrane systems. The feed water was pH-adjusted to a typical value of 5. Modified UF and RO modules were operated in parallel with unmodified, control modules. The RO reject was stored in a tank for off-site disposal. The RO permeate was collected in a finished water storage tank before being trucked back to the field for use in fracturing. A flowsheet of the pilot system is shown in Fig. 2.

Two UF modules were operated concurrently in parallel—one was surface modified as described above, and the second was an unmodified control. The UF units were operated continuously for a total of approximately 60 h. The UF permeate was mixed, collected in a buffer tank, and used to feed the reverse osmosis modules. The six RO membranes were divided into two trains consisting of three modules each—one train of PD-modified modules and one train of unmodified modules. Within each train, the three RO modules were connected through permeate core tubes in series, with concentrate from the first module feeding the second module, etc. The two RO trains were operated alternately for
Therefore, each train operated four times. The unmodified train was operated for the first 12-h block, followed by the modified train for the second 12-h block, then the unmodified train for the third 12-h block, the modified train in the fourth 12-h block, and so on until the total 100-h RO operating time had elapsed.

The UF modules were operated in dead-end mode with an initial feed flow of 21.9 L/min. The feed pump for the UF modules was run at a constant speed throughout the test; permeate flux and transmembrane pressure were allowed to vary as the membranes fouled. Permeate backwashing was performed for 30 s every 15 min due to the highly fouling nature of the UF feed. Two intensive cleaning procedures—chemically enhanced hot water cleaning (HWC), performed daily, and traditional clean-in-place (CIP), performed as needed, were used to recover UF permeate. All cleaning solutions were prepared using RO permeate as solvent. The chemically enhanced HWC step was a short version of the CIP procedure conducted to boost membrane performance. During the chemically enhanced HWC cleaning procedure, heated caustic and then acid solutions were introduced from the feed side of the membrane and circulated for a short period of time. Specifically, heated (52 °C) caustic cleaning solution, prepared by adjusting the pH of RO permeate water to 11.0 with sodium hydroxide, was first circulated through the UF modules for 15 min. Then, the cleaning solution pH was changed to 2.0 with citric acid and circulated for 15 more minutes. Finally, the modules were flushed with fresh RO permeate to remove the chemicals and dislodged foulants. During the traditional CIP process, a 1 wt.% sodium hydroxide solution was circulated throughout the modules at 52 °C for 2 h. The modules were then flushed with RO permeate. Next, a 2 wt.% citric acid solution (also heated to 52 °C) was circultated through the modules for 2 h. Finally, the modules were flushed with fresh RO permeate. During UF cleaning, feed flow to the reverse osmosis train was maintained using water stored in the buffer tank (see Fig. 2).

The reverse osmosis modules were operated in crossflow with a feed flow of 56.7 L/min. The RO feed pump was operated at constant speed, which resulted in some variation in permeate flux and transmembrane pressure. Because the permeate flux was not held constant, recovery varied throughout the pilot study. Recovery was initially set at 50%, but during periods of high feed TDS concentrations, recovery decreased to as low as 10%. No chemical cleaning was performed on the RO modules.

Feed water turbidity, temperature, and RO feed and permeate conductivities were measured at 20-min intervals. Turbidity was measured with an on-site nephelometer. Alkalinity, hardness, calcium concentration, and chloride concentration of the UF feed, UF permeate, RO feed, and RO permeate were measured frequently on-site using a drop-count titration test kit from Hach Company (Loveland, CO). RO membrane rejection is typically evaluated by measuring feed and permeate stream conductivity with in-line conductivity meters [19]. Conductivity meters, which had a maximum reading of 20,000 μS/cm, were calibrated using 18,000 μS/cm (10,264 mg/L) NaCl standard solution from Hach Company. Membrane rejection values were subsequently calculated from conductivity readings of feed and permeate streams.

3. Results and discussion

The performance of ultrafiltration and reverse osmosis modules was evaluated when challenged with hydraulic fracturing flowback water from natural gas wells in the Barnett Shale region of north Texas. An unmodified, hollow fiber, polyacrylonitrile UF module was operated simultaneously and in parallel with an identical module that was surface-modified with a polydopamine-PEG coating. Similarly, results from a train of three spiral wound, unmodified RO modules were compared with those from a train of three polydopamine modified modules. UF modules were cleaned regularly with periodic permeate backwashes and with typical chemically enhanced hot water cleaning and clean-in-place procedures. Autopsy of the modules at the conclusion of the study provided visual confirmation (by the characteristic brown color of polydopamine) that the coating was still in place on the membrane.

3.1. Ultrafiltration

In this two-stage pilot, the UF membranes removed suspended particles and highly fouling organic matter from the feed prior to desalination by the RO membranes. The feed turbidity was reported in Nephelometric Turbidity Units (NTU) and is shown in Fig. 3. Turbidity was highly variable, particularly after ~20 h of operation, suggesting that the feed became more highly fouling in the latter stages of the study. The turbidity exceeded the UF membrane manufacturer-recommended maximum feed turbidity of five NTU (Table 2) for much of the study. Application of a UF module with a more appropriate maximum recommended feed turbidity may have resulted in improved performance.

Permeate flux and transmembrane pressure difference of the ultrafiltration modules were recorded as a function of time. Fig. 4 compares the flux of unmodified and PD-g-PEG-modified modules over 60 h. Permeate backwash was performed every 15 min; other cleaning cycles (HWC and CIP) are indicated on the figure. At the start of the pilot test, the permeate flux of both modules was about 42.5 L/m²·h. Both modules exhibited similar flux deterioration as they fouled during the first 15 h. After 20 h of filtration, corresponding to the time that the feed turbidity increased sharply (Fig. 3), the flux of the modified module became higher than that of the unmodified module. Presumably, the hydrophilic PD-g-PEG coating reduced flux deterioration. The modified module had higher flux than the unmodified module for the remainder of the study. By the end of the pilot, the modified module flux was 50% higher than that of the unmodified module.

The PD-g-PEG modified module also showed improved recovery relative to the unmodified module upon cleaning, leading to higher ultimate productivity. Especially after the CIP at ~30 h and the HWC at ~52 h, the modified module recovered to a significantly higher flux than that of the unmodified module, so the hydrophilic coating appears to facilitate cleaning. Hydrophilic surface modifications have previously been reported to improve the efficacy of cleaning steps, as measured by flux recovery, in RO [20] and UF [21] membranes. According to literature reports, the thin water layer which is strongly bound to a hydrophilic coating...
reduces strong hydrophobic interactions between hydrophobic foulants and the hydrophobic surface of the native (i.e., uncoated) hydrophobic membrane [10], thereby permitting easier removal of foulants by in situ cleaning protocols such as those used in this study. Improved recovery following cleaning suggests that fouling of the modified membrane is more reversible than that of the unmodified membrane. The rate of flux decline between cleaning procedures was similar in the unmodified and modified modules, suggesting that the rate of fouling of the modules was similar. Therefore, the principle benefit of the PD-g-PEG modification appears to be improved flux recovery following cleaning protocols, particularly after periods where the module was exposed to aggressive fouling conditions, such as the high turbidity of the feed solution that occurred near the mid-point of this study (Fig. 3).

The transmembrane pressure differences of the unmodified and PD-g-PEG-modified modules are presented in Fig. 5. The TMP of the modified module was about 15% lower than that of the unmodified module at the beginning of the study. That is, the transmembrane pressure was approximately 100 kPa in the unmodified module and 70 kPa in the modified module. Based on this result, the UF membrane with the hydrophilic PD-g-PEG surface modification had lower mass transfer resistance relative to the unmodified membrane, since both the modified and unmodified membranes had similar initial fluxes (Fig. 4), but the modified membrane had a lower TMP. As the study progressed, the difference in TMP between the modified and unmodified modules increased, so that the modified module exhibited a TMP about 20% lower than that of the unmodified module by the conclusion of the study. This difference in TMP over the course of the study supported the hypothesis that the cleaning cycles were more effective on the modified module than on the unmodified module. Apparently irreversible fouling in the unmodified module caused its TMP to gradually increase, while the cleaning cycles were able to effectively maintain or reduce the TMP of the PD-g-PEG modified module. In the latter half of the pilot, the TMP of the modified module gradually decreased, suggesting that repeated, periodic cleanings could maintain the TMP near levels observed at the beginning of the study.

To compare the modified and unmodified UF membrane performance given that both flux and TMP varied during the test, it is useful to consider the membrane permeance (PM), which is the flux (J) divided by the transmembrane pressure (TMP) [22]

$$PM = \frac{J}{TMP}$$

The reciprocal of permeance is the mass transfer resistance of the membrane. As a membrane fouls, its mass transfer resistance increases, so permeance decreases. A higher permeance or lower

Fig. 3. UF feed turbidity as a function of operating time. Feed turbidity generally increased and was highly variable in the latter half of the study.

Fig. 4. Flux of PD-g-PEG-modified and unmodified UF modules. The modified module showed improved flux relative to the unmodified module after 20 h of filtration, when the feed turbidity increased. The modified module also recovered flux to a greater degree than the unmodified module after cleaning. HWC is chemically enhanced hot water cleaning, and CIP is clean-in-place.

Fig. 5. TMP evolution in PD-g-PEG-modified and unmodified UF modules. The modified module maintained a 15–20% lower TMP than the unmodified module during the entire study.
rate of decrease in permeance over time would indicate a lower fouling membrane, all other factors being equal. Fig. 6 compares the permeance values of the modified and unmodified UF membrane modules. The modified module exhibited 25–50% higher flux than the unmodified module at 15–20% lower TMP, resulting in a significantly higher permeance than that of the unmodified membrane. The ratio of modified module permeance to unmodified module permeance is shown in Fig. 7. By the conclusion of the pilot test, the modified membrane permeance was approximately two times higher than that of the unmodified membrane, suggesting that the modified module could process up to twice as much water at a given TMP as an unmodified module.

3.2. Reverse osmosis

The performance of two reverse osmosis trains was evaluated by monitoring their permeate fluxes and salt rejections throughout the pilot study. The permeate flux and salt rejection are sensitive to, among other things, feed pressure, feed temperature, and feed salt concentration [23]. Variations in feed temperature and feed salt concentration (measured as total dissolved solids) are shown in Figs. 8 and 9, respectively. The unmodified and PD modified trains were not run concurrently; instead, they were run

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**Fig. 6.** Permeances of PD-g-PEG-modified and unmodified UF modules. Permeance is a measure of the productivity of the module relative to its energy consumption. The Permeance of the modified module was higher than that of the unmodified module due to its higher flux and lower TMP.

**Fig. 7.** Ratio of PD-g-PEG modified UF module permeance to unmodified UF module permeance. The modified module was twice as productive as the unmodified module by the conclusion of the pilot study.

**Fig. 8.** Temperature variation in the feeds to PD modified and unmodified RO trains. Variations are the result of daily cycles in ambient temperature.

**Fig. 9.** Salt concentration (measured as total dissolved solids) of the feed to PD modified and unmodified reverse osmosis trains. A significant increase in feed-water salt concentration occurred approximately halfway through the study.
Alternately for 12 h each. Data were not collected during periods when a train was not operating. Variations in feed temperature reflected the daily cycles in ambient air temperature. Due to changing flowback water characteristics in the field, the feed salt concentration roughly doubled at the midpoint of the study, increasing from approximately 25,000 to more than 50,000 mg/L for some part of the latter half of the study.

The net driving pressure (NDP) is the average driving force available for water permeation through RO membranes [24]. It is calculated as the transmembrane pressure difference (TMP) minus the osmotic pressure difference ($\Delta \pi$) between the feed and permeate as described in Appendix A. The osmotic pressure of the feed is intrinsically linked to its salt content. Therefore, at a fixed feed pressure, the driving force available for water transport through the membrane varies with salt concentration. The NDP evolution of the two RO trains is shown in Fig. 10. The total dissolved solids concentration of the feed water increased significantly around 40 h into the study (Fig. 9), so the osmotic pressure of the feed also increased, and the NDP for both trains correspondingly decreased from about 2500 kPa to about 750 kPa. Osmotic pressures were calculated, as shown in Appendix A, from conductivity measurements of the feed and permeate. The conductivity meters were calibrated using standard NaCl solutions, so the calculated osmotic pressure is based on the assumption that all salt present is NaCl.

Because appreciable variations in feed temperature and salt concentration (and therefore net driving pressure) were observed, permeate flux and salt rejection values were normalized to a set of standard conditions as described in Appendix B. Normalization adjusts the measured flux and rejection for variations in temperature, feed pressure, and feed salt concentration, thereby permitting direct comparison of modified and unmodified trains despite changing feed conditions. In the following discussion, measured data collected under actual operating conditions will be compared to normalized data.

Fig. 11 presents the measured permeate fluxes of unmodified and PD-modified RO trains. The fluxes of both the modified and unmodified modules in the first few hours are about 13 L m$^{-2} \cdot$ h$^{-1}$. The fluxes of both trains decreased around 40 h due to the increase in feed salt concentration (and corresponding net driving pressure decrease, cf. Figs. 9 and 10). After 50 h, the fluxes of both trains fluctuated within a range of 2–5 L m$^{-2} \cdot$ h$^{-1}$, following the more minor variations observed in feed salt concentration and net driving pressure observed through the end of the study.

Normalized fluxes of the unmodified and PD-modified RO trains are shown in Fig. 12. The normalized fluxes of both trains ranged between 5 L m$^{-2} \cdot$ h$^{-1}$ and 25 L m$^{-2} \cdot$ h$^{-1}$ and were generally higher than the actual permeate fluxes (Fig. 11) at any time. Normalization according to ASTM standard protocols [25] did not eliminate variability in flux data due to changes in feed temperature, feed concentration, and net driving pressure. Instead,
the normalization exacerbated fluctuations, especially in data collected towards the end of the study (50–100 h). The introduction of such variability may be due to the large magnitude of the correction factors used to account for changes in temperature and net driving pressure. Additionally, the normalization procedure does not account for other influences on permeate flux, such as concentration polarization. Concentration polarization is well-known to affect the passage of water and salt across the membrane [26] and itself varies with permeate flux [27]. A similar result has been reported by Safar et al. [28], where normalization by the ASTM method results in higher variability than that observed in the measured data. Another possible reason for the variability of normalized data may be the ASTM assumption that all salt present is NaCl. Variations in the conductivity may not be properly reflected in the salt concentration (and, consequently, osmotic pressure) calculations if the feed and permeate streams are comprised of complex mixtures of monovalent and multivalent salts.

Unlike the UF results, the polydopamine-modified RO train did not exhibit systematically improved permeate flux relative to the unmodified train in either the measured data (Fig. 11) or after normalization (Fig. 12). While PD-coated RO membranes exhibited improved resistance to fouling by a simple oil/water emulsion in laboratory tests [13], the RO membrane feed water in this pilot study had already been treated by the ultrafiltration modules, so it was largely free of organic foulants. For this reason, the RO feed water was likely not highly fouling, and little benefit of a fouling resistant coating was realized with regard to permeate production.

A comparison of apparent salt rejection values between the modified and unmodified RO trains is made in Figs. 13 and 14. Fig. 13 presents the measured apparent salt rejections. No corrections were made for concentration polarization. Fig. 14 presents the normalized salt rejection calculated as described in Appendix B. Rejection normalization accounts for variations in feed salt concentration, permeate flow rate, and temperature [25]. The measured rejection of the unmodified train ranges from over 99.5% to below 96.5%, below the manufacturer-specified minimum salt rejection of 97%. Once normalized to the manufacturer-specified operating conditions, however, the unmodified train measured rejection varied between 99.85% and 99.95%, consistent with the manufacturer-specified minimum salt rejection. In both the measured and normalized salt rejections, the PD modified train exhibited higher and more stable rejection than the unmodified train. Previous studies have reported improved salt rejection of commercial membranes modified with hydrophilic surface coatings [16]. One possible hypothesis for such improvements is that the coating seals minor defects inherently present in the thin, selective polyamide layer. Other studies have noted the presence of defects in ultrathin polymeric separation layers, including Lonsdale, Merten, and Riley’s seminal publication describing the preparation of cellulose acetate RO membranes where lower-than-expected salt rejection was measured [29]. Sagle et al. observed improved salt rejection values upon coating polyamide RO membranes with PEG-based hydrogels and suggested that the highly permeable PEG layer could caulk defects in the separation layer [30]. The findings of this study, where the application of a PD coating to thin, interfacially polymerized polyamide RO membranes resulted in an improvement in salt rejection, are consistent with these other reports.

Table 3 records the average measured (i.e., not normalized to standard conditions) rejection of individual ions, including chloride, calcium, magnesium, and total hardness over the duration of the pilot test. Calcium, magnesium, and total hardness were measured by titration as CaCO$_3$. Calcium and magnesium

![Fig. 13](image1.png) Measured salt rejections of PD modified and unmodified RO trains. The modified train showed a higher and more stable rejection than the unmodified train.

![Fig. 14](image2.png) Normalized salt rejection of PD modified and unmodified RO trains. The modified train showed a higher and more stable rejection than the unmodified train.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Feed (mg/L)</th>
<th>Permeate (mg/L)</th>
<th>Rejection (%)</th>
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<td>Cl$^-$</td>
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<td>98.2</td>
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<tr>
<td>Ca$^{2+}$</td>
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<td>59</td>
<td>98.5</td>
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<tr>
<td>Mg$^{2+}$</td>
<td>1880</td>
<td>31</td>
<td>98.4</td>
</tr>
<tr>
<td>Total</td>
<td>1650</td>
<td>19</td>
<td>98.9</td>
</tr>
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Table 3: Measured rejection of chloride, calcium, magnesium, and total hardness, averaged over the entire pilot duration.
concentrations were subsequently calculated using their respective atomic masses. The coated modules showed improved rejection of all ions, corroborating the rejection results obtained with conductivity measurements (Figs. 13 and 14). Generally, reverse osmosis membranes reject multivalent ions more effectively than monovalent ions, as was the case here [23].

4. Conclusions
Polydopamine was used to modify commercial ultrafiltration and reverse osmosis membrane modules. Ultrafiltration modules were further modified by grafting PEG to the polydopamine coating. Modified and unmodified modules were employed in a pilot study where they were challenged with flowback water from hydraulic fracturing operations in the Barnett shale gas basin. Modified UF membranes showed improved flux and decreased transmembrane pressure and therefore higher permeances than their unmodified counterparts during the study. Furthermore, both modified and unmodified UF modules were cleaned regularly with typical chemical cleaning regimens; the modified module showed enhanced flux recovery after cleaning. The principle benefit of the PD-g-PEG coating in the UF modules therefore appears to be facilitated cleaning. The polydopamine-coated RO membranes did not show enhanced flux or depressed transmembrane pressure difference relative to the unmodified module, likely due to the cleanliness of the RO feed after UF pretreatment. Salt rejection, however, was both higher and more stable in the modified than in the unmodified modules, perhaps due in part to caulking of minor defects in the thin polyamide separation layer by polydopamine. Therefore, with UF pretreatment, the polydopamine coating need only be applied to RO modules if a salt rejection higher than that provided by the native membrane is desired. Previous studies on polydopamine membrane coatings focused on laboratory-scale experiments. This study demonstrated that polydopamine and PEG can be employed in the modification of industrial membrane modules and those modifications improved the fouling behavior of modules challenged with complex, highly fouling feedwater. Polydopamine and polydopamine-g-PEG modifications can improve the quantity and quality of permeate from membrane-based industrial water purification.

Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>membrane area (m²)</td>
</tr>
<tr>
<td>C_f</td>
<td>feed salt concentration (mg/L)</td>
</tr>
<tr>
<td>C_FB</td>
<td>feed-brine salt concentration (mg/L)</td>
</tr>
<tr>
<td>C_P</td>
<td>permeate salt concentration (mg/L)</td>
</tr>
<tr>
<td>EPF</td>
<td>element permeate volumetric flow (L h⁻¹)</td>
</tr>
<tr>
<td>J</td>
<td>flux (L m⁻² h⁻¹)</td>
</tr>
<tr>
<td>PM</td>
<td>permeance (L m⁻² h⁻¹ kPa⁻¹)</td>
</tr>
<tr>
<td>K_p</td>
<td>transport temperature correction coefficient (-)</td>
</tr>
<tr>
<td>MF</td>
<td>microfiltration (-)</td>
</tr>
<tr>
<td>NDP</td>
<td>net driving pressure (kPa)</td>
</tr>
<tr>
<td>NF</td>
<td>nanofiltration (-)</td>
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<td>P_B</td>
<td>brine pressure (kPa)</td>
</tr>
<tr>
<td>P_F</td>
<td>feed pressure (kPa)</td>
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<td>P_FB</td>
<td>feed-brine pressure drop (average of the feed and brine pressures) (kPa)</td>
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<td>PD</td>
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<td>Q_F</td>
<td>feed volumetric flow (L h⁻¹)</td>
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<td>Q_P</td>
<td>permeate volumetric flow (L h⁻¹)</td>
</tr>
<tr>
<td>R</td>
<td>permeate recovery (expressed as a decimal) (-)</td>
</tr>
<tr>
<td>Ρ</td>
<td>salt rejection (%)</td>
</tr>
<tr>
<td>RO</td>
<td>reverse osmosis (-)</td>
</tr>
<tr>
<td>SP</td>
<td>salt passage (-)</td>
</tr>
<tr>
<td>STCF</td>
<td>salt transport temperature correction factor (-)</td>
</tr>
<tr>
<td>T</td>
<td>temperature (°C)</td>
</tr>
<tr>
<td>TCF</td>
<td>temperature correction factor (-)</td>
</tr>
<tr>
<td>TMP</td>
<td>transmembrane pressure difference (kPa)</td>
</tr>
<tr>
<td>UF</td>
<td>ultrafiltration (-)</td>
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Greek

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<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>π_RB</td>
<td>feed-brine osmotic pressure (average of feed and brine osmotic pressures) (kPa)</td>
</tr>
<tr>
<td>π_P</td>
<td>permeate osmotic pressure (kPa)</td>
</tr>
</tbody>
</table>

Subscripts

<table>
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<th>Subscript</th>
<th>Description</th>
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<tr>
<td>a</td>
<td>at actual operating conditions</td>
</tr>
<tr>
<td>s</td>
<td>normalized to standard conditions</td>
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</table>

Acknowledgments

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Appendix A. Calculation of the reverse osmosis net driving pressure

The net driving pressure (NDP) is the average driving force available for water permeation through RO membranes [24]. It is calculated, as described in ASTM Standard D4516 [25], as the transmembrane pressure (TMP) minus the difference in osmotic pressure (Δπ) between the feed and permeate

$$\text{NDP} = \text{TMP} - \Delta \pi$$  \hspace{1cm} (2)

This equation may be expanded as follows:

$$\text{NDP} = \left( \frac{P_{F} + P_{FB}}{2} \right) - \left( \pi_{FB} - \pi_{P} \right)$$  \hspace{1cm} (3)

where \(P_F\) is the feed pressure, \(P_{FB}\) is the pressure drop along the feed-brine side of the module, \(P_P\) is the permeate pressure, \(\pi_{FB}\) is the feed-brine osmotic pressure, and \(\pi_P\) is the permeate osmotic pressure. The osmotic pressure (kPa) of the feed-brine is estimated...
using [25]

\[ \pi_{FB} = \frac{0.2654G_{FB}(T+273.15)}{1000 - \frac{C_{FB}}{C_{FB}}} \]  

(4)

where \( C_{FB} \) is the feed-brine salt concentration, and \( T \) is the feed temperature. The observed permeate

\[ R = \frac{Q_P}{Q_F} \]  

(6)

where \( C_F \) is the feed salt concentration, and \( R \) is the module permeate recovery. The recovery is calculated as the ratio of

The salt concentrations \( C_F \) and \( C_P \) are determined from measurements of the feed and permeate conductivities. Conductivity

The expression for permeate osmotic pressure is typically used for seawater applications, where the salt concentrations can range from 31,000–48,000 mg/L [31]. Hydraulic fracturing flowback water is often at least as highly saline as seawater [32], and the water used in this pilot study was no exception. The feed TDS concentration, initially around 20,000 mg/L for both trains, nearly
triples over the course of the pilot to values near 60,000 mg/L. The average feed salt concentration in this study was about 41,000 mg/L. The

Conductivity meters were calibrated with a standard salt solution, as described in the experimental section, to determine the actual concentrations. Finally, the ASTM standard recommends the following approximation for calculation of the permeate osmotic pressure

\[ \pi = 0.01 \pi_{FB} \]  

(7)

This expression for permeate osmotic pressure is sensitive to operating conditions. Unlike the calculation for normalization of the permeate flow, the normalization of salt passage presented in ASTM standard D4516 is not based on the solution-diffusion model and was likely developed empirically [33]. The salt passage (SP) at standard conditions is calculated by [25]

\[ SP = \frac{EPF_s \times STCF_s \times C_{FB} - C_{FB}}{EPF_s \times STCF_s \times C_{FB} - C_{FB}} \times SP_n \]  

(11)

where EPF is the element permeate volumetric flow rate and STCF is the salt passage temperature correction factor. EPF is not necessarily identical to \( Q_{PS} \) calculated above [25] and is, instead, the manufacturer-specified permeate flow shown in Table B1. \( C_{FB} \) is also taken from Table B1. Eq. (5) is used to calculate \( C_{FB} \) and \( C_{FB} \), in the case of \( C_{FB} \), the permeate recovery \( R \) is the manufacturer-specified permeate recovery under standard operating conditions (Table B1). Element manufacturers sometimes provide an expression for the salt transport temperature correction coefficient. Otherwise, the temperature correction factor (TCF, Eq. (9)) may be used, as was the case here. STCF was therefore equal to unity. The actual salt passage, expressed as a decimal, is given by

\[ SP = \frac{C_{FB}}{C_{FB}} \]  

(12)

Finally, the salt rejection (\( R \)) normalized to standard conditions may be calculated

\[ R = (1-SP) \times 100\% \]  

(13)

where \( SP \) is the salt passage.

### Appendix B. Normalization of reverse osmosis data

The permeate flux and rejection of reverse osmosis membrane modules are sensitive to feed pressure, feed temperature, and feed salt concentration [23]. RO performance data were normalized as described in ASTM Standard D4516 [25] which has been assessed in several literature reports [28,33,34]. The observed permeate flow and salt passage are normalized to a set of standard conditions; the conditions for which the manufacturer specifies nominal performance values are convenient for this purpose [28]. For the Hydranautics SWC3+ modules used here, these values are shown in Table B1, below.

Normalization of the permeate flow is based on the solution-diffusion model for water transport through a dense polymer film [33]. The permeate flow is normalized to a standard net driving

### Table B1

<table>
<thead>
<tr>
<th>Standard condition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed concentration</td>
<td>32,000 mg/L NaCl</td>
</tr>
<tr>
<td>Applied pressure</td>
<td>5515.8 kPa</td>
</tr>
<tr>
<td>Operating temperature</td>
<td>25 °C</td>
</tr>
<tr>
<td>Permeate recovery</td>
<td>0.1</td>
</tr>
<tr>
<td>Element permeate volumetric flow</td>
<td>1104 L/h</td>
</tr>
<tr>
<td>Element pressure drop</td>
<td>68.9 kPa</td>
</tr>
</tbody>
</table>

pressures and a standard feed temperature as follows [25]:

\[ Q_{PS} = \frac{(NDP_s \times TCF_s)}{(NDP_s \times TCF_s)} \times Q_{PS} \]  

(8)

where TCF is the temperature correction factor. The subscript \( s \) denotes the standard conditions to which data are normalized, and \( a \) denotes the actual experimental conditions. NDP is calculated as shown in Eq. (3) of Appendix A, with the applied pressure (the difference between the feed pressure, \( P_F \) and the permeate pressure, \( P_B \)) and the element pressure drop (\( P_{FB} \)) taken from Table B1. The temperature correction factor is derived from the Arrhenius response of water flux to temperature variations [35]

\[ TCF = \exp \left[ Ke \left( \frac{1}{T + 273.15} - \frac{1}{298.15} \right) \right] \]  

(9)

where the constant \( Ke \) is provided by the manufacturer (here, \( Ke = 2700 \)). Because the standard temperature is 25 °C (Table B1), TCF is equal to unity. Finally, the normalized flux is calculated by dividing the normalized permeate flow rate by the total membrane area (\( A \))

\[ J_s = \frac{Q_{PS}}{A} \]  

(10)

Like permeate flux, the salt passage of an RO membrane is also sensitive to operating conditions. Unlike the calculation for normalization of the permeate flow, the normalization of salt passage presented in ASTM standard D4516 is not based on the solution-diffusion model and was likely developed empirically [33]. The salt passage (SP) at standard conditions is calculated by [25]

### References


