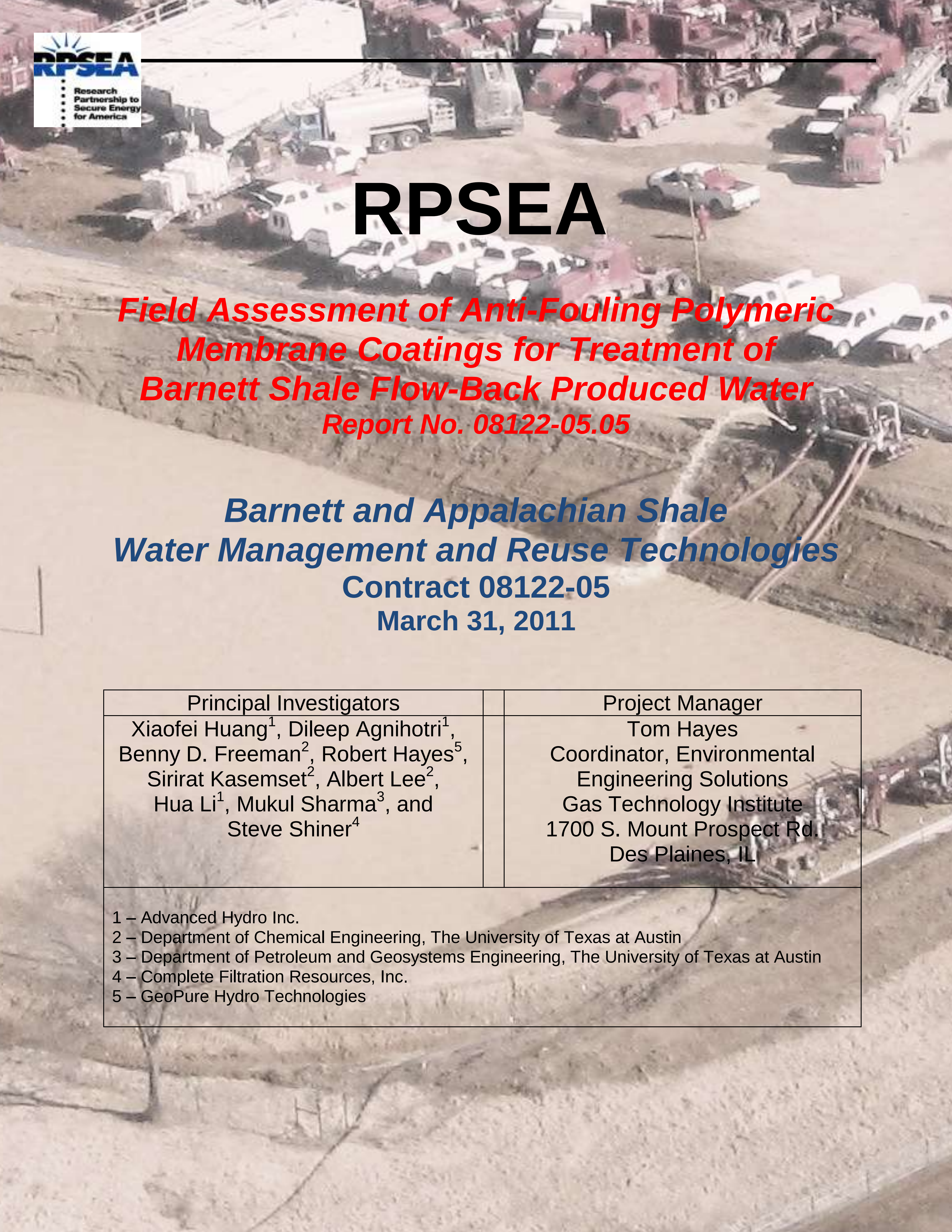

RPSEA

Field Assessment of Anti-Fouling Polymeric Membrane Coatings for Treatment of Barnett Shale Flow-Back Produced Water

Report No. 08122-05.05

Barnett and Appalachian Shale Water Management and Reuse Technologies

Contract 08122-05

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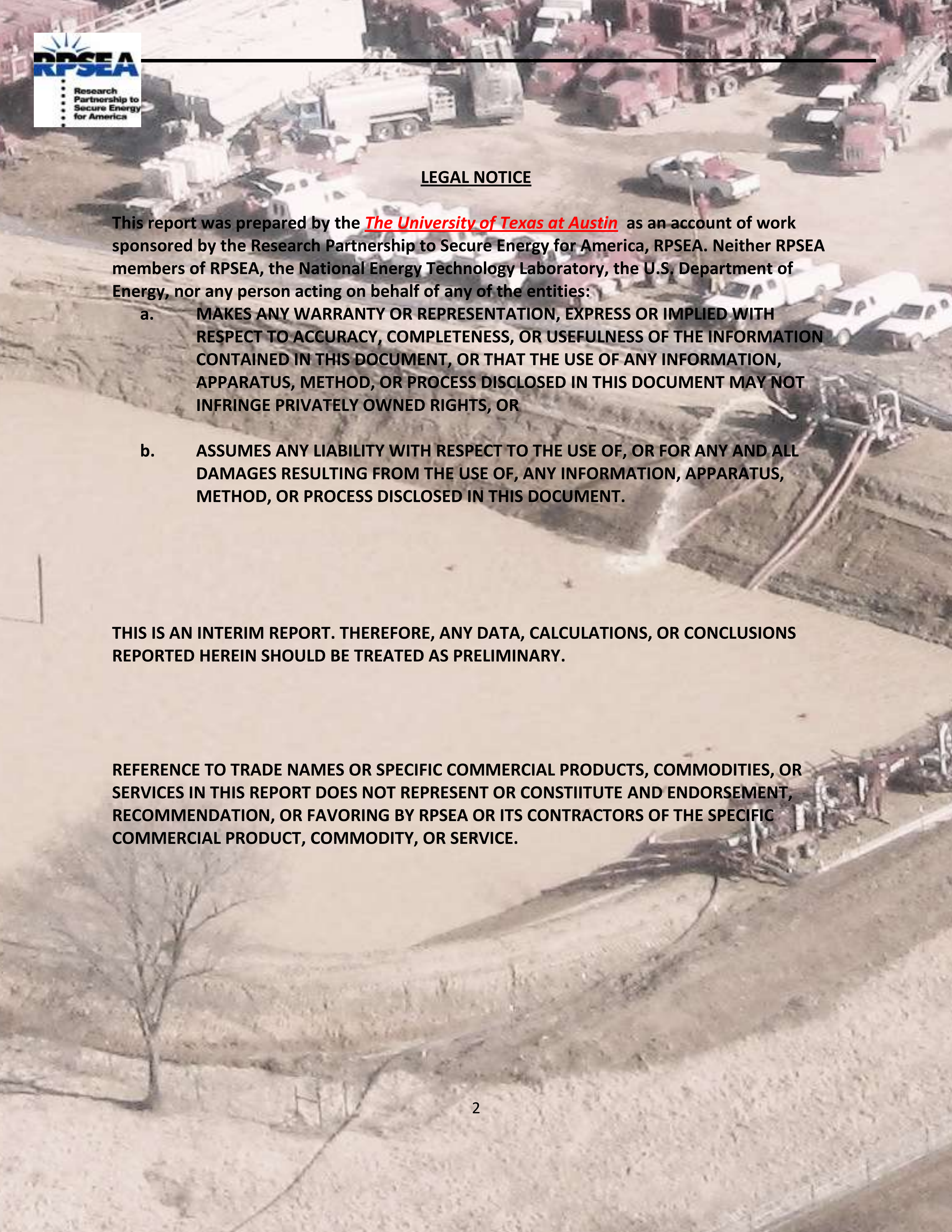

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Summary

This report summarizes results of a brief (30 day) test of Anti-fouling Polymeric Membrane Coatings developed at the University of Texas at Austin (licensed and marketed by Advanced Hydro, Inc.) for treatment of shale flow-back “frac” produced water. Flow-back water collected from various shale wells in the Barnett Shale area was processed with ultra-filtration (UF) and reverse osmosis (RO) membranes. Membranes coated with polydopamine and PEG-amine were tested for their resistance to fouling due to organic and inorganic foulants in the feed water. Non-coated membranes were used as control for performance comparison.

Polyvinylidene Fluoride **(**PVDF) based spiral wound flat-sheet and polyacrylo nitrile (PAN) based outside-in hollow-fiber UF membranes were used in this pilot for pre-filtration for feed water prior to desalination using Polyamide RO membranes. Coated hollow-fiber UF elements outperformed non-coated elements, in terms of better cleaning efficacy (recovery) and higher flux, by almost 50%. In addition, coated spiral wound UF elements were easily maintained with daily chemical enhanced clean and fully recovered with regular acid-base cleaning operation. The coated spiral elements achieved 106 hours run time without using a strong oxidant. The autopsy study revealed that UF membranes were fouled with organic substances, which could be mainly removed by acid/base clean. No significant flux loss was observed for both coated and non-coated seawater RO membranes during the pilot. Coated RO membrane demonstrated much better salt rejection than non-coated under high salinity conditions. This brief project provided validation of the coatings technology and its benefit for produced water purification. In addition, with improved salt rejection during desalination, a two stage nanofiltration or nano/RO membrane system with an optimized ultra-filtration (UF) or micro-filtration (MF) membrane is expected to enable membrane based purification of produced water while maximizing water productivity and minimizing maintenance and energy costs.

Contents

1. Introduction

1.1 Background and Challenges of Shale Water Treatment and Reuse

The Barnett and Appalachian shale are among the largest and most active natural gas plays in the U.S. that geographically covers all or part of 20 counties in North Texas and large areas of Pennsylvania, West Virginia, Ohio and New York. The Barnett and the Marcellus are among a number of natural gas shale basins in the U.S. The Barnett area is proven to have approximately 2.5 trillion cubic feet (59 km^3) of natural gas reserves and is widely estimated to contain up to 27 trillion cubic feet (700 km^3) of technically recoverable natural gas [1,2]. The Marcellus play in the Appalachian basin is considered to be larger in size and capacity in comparison to the Barnett. Both shale plays are considered to be unconventional gas formations and require hydraulic fracturing to make them productive. Hydraulic fracturing is a process in which large volumes of water, sand and chemicals are injected at high pressures into underground rock formations. The process creates fractures in the shale rock, allowing natural gas or oil to escape into the wellbore and be recovered.

Hydraulic fracturing (fracing), a necessary step for economic well performance, requires between 1 and 4 million gallons (3,800 and 15,200 m^3) of water for successful well completion. Vertical wells require approximately 1 million gallons (3,800 m^3) and horizontal wells require 3-4 million gallons (11,400 to 15,200 m^3) according to a recent survey among Barnett Shale Producers [3]. The same per well water use is found in Appalachian shales. Of the total water used by the industry, frac jobs represent about 89 % and drilling represents 10 % [3]. This level of water demand poses a number of challenges for industry in the course of developing the Barnett and Appalachian shales for natural gas production. The industry must procure large volumes of water from regions where water may not be readily available. The typical shale gas well is a horizontal well that requires over 3.5 million gallons of water for completion (>80,000 bbls) requiring over 750 trucks to transport the water to the well site. This water is stored in a lined impoundment and stored there until the day the well is completed; during the well completion process, water from the impoundment is pumped down the well to achieve hydraulic fracturing of the shale rock. Following completion, about 1 million gallons of water is collected; this water contains elevated concentrations of salts, oils & greases, polyacrylamid polymers (added to reduce friction of the water along the well bore and in the cracks in the shale) and other soluble organics (such as volatile acids). Because well completion requires significant volumes of water within relatively narrow period of time (within a few days), water conservation has become an important element of water management for the shale gas industry.

Economics and stakeholder demands of water management are driving the oil and gas industry to consider water reuse as a means to reduce the cost of transportation and to reduce the industry's demand for fresh water supplies. One approach to achieving this goal is through the reuse of flowback and produced water; these water streams contain extreme levels of hardness, high scale formation potential, substantial presence of oils and greases, bacteria and polymers and other chemicals that can cause fouling on equipment involved in water storage, handling and treatment. If demineralization is required to meet the specifications for water reuse, challenges will include the control of factors that affect water processing.

1.2 Water Demineralization Technologies

An important approach for decreasing shale gas industry water demand is to direct the flowback and produced waters collected from each completed well toward reuse in performing future well completions. The "reuse" option has the advantage of reducing the amount of freshwater required for each completion; other environmental benefits include reduced trucking requirements, easing of traffic congestion, reduced road wear, and decreased emissions and carbon footprint over the development life of the play. Generally, in the Barnett and Appalachian Shale Regions, the amounts of flowback water collected is usually in the range of 10 to 30 percent of the original water volume required for hydraulic fracturing. Some energy developers have treated flowback and produced water for the partial removal of suspended solids, oils and greases and scale forming constituents (e.g. calcium and barium) and blended these streams with freshwater for hydraulic fracturing at a ratio of more than 4:1; this practice can result in a blended water with a salt concentration of more than 10,000 mg/l which may require added expense for storage system integrity. Among some shale gas developers, concern still lingers over the potential effects of high dissolved solids in water on increased demands for friction reducers (though a new generation of friction reducers exhibits a higher tolerance for salt concentrations) and some operators are concerned over the long-term effects of high-TDS-water-mediated completions on shale gas well performance. For these reasons, many energy developers have been interested in the evaluation of technologies capable of an efficient recovery of demineralized water from brines for purposes of reuse.

The main families of technologies capable of demineralization of brines include thermal processing and membrane treatment. One of the most reliable of separation technologies is the thermal distillation/condensation process which is a well proven water separations technology used in seawater desalination and in water management of many industries such as food processing (sugar), beverage, automotive, textile and commercial chemicals production. In the evaluation of this technology for water recovery from produced waters, the most commonly used evaporative treatment design has been the mechanical vapor recompression (MVR) system. This particular design is capable of handling a wide range of produced water salt concentrations from freshwater quality to above 200,000 mg/l, while achieving water recoveries of greater than 70%; recovered water is of distilled water quality, well suited for blending with freshwater supplies and suitable for storage in impoundments normally designed for holding freshwater. Design improvements have enabled modern MVR processes to operate at far higher energy efficiencies due to equipment features that efficiently recover heat from the condenser for transfer to the influent brines entering the evaporation chamber. This has enabled the process to operate with energy inputs as low as 0.11 mmBtu/barrel. The compelling advantage of MVR is its reliable performance under highly varied field conditions as evidenced by its ability to process brine streams of highly varied strength and quality over extended periods of time while generating a stream of distillate water for reuse and a concentrated brine containing nearly all of the salts that reduced in volume by more than 65%.

Efficient demineralization of can also be achieved using membrane-based processes. Some energy companies have explored the use of reverse osmosis (RO) as a means of achieving brine volume reduction for shale gas waters and for conventional gas well produced water. For both types of produced water, pilot tests have shown that although a 3:1 reduction of brine volume could be achieved, and although a deionized product stream of good quality water (approaching distilled water quality) could be produced, there has been a practical limitation of RO to demineralize brines that exceed 40,000 mg/l TDS under the usual operating pressure drops of the RO process. Another challenge to membrane processes tested on produced waters in the past has been membrane fouling which has been among the typical operational problems noted in previous attempts to deploy the technology under actual field conditions. Fouling problems arise from the complex composition of the produced water and the effects of certain constituents on the membrane material. Free and dissolved oils collect on RO membranes causing them to lose their permeability and the presence of soluble hydrocarbons including volatile acids and BTEX can promote the growth of microbial films on ultrafiltration (UF) and RO membrane surfaces causing them to lose separation performance. These fouling problems are largely responsible for the lack of deployment success of RO in the oil and gas industry. Recent advances in applying rigorous preprocessing of produced water to remove fine suspended solids, oils & greases, and scale forming constituents show potential of reducing fouling problems, but extending membrane life is still a complex and site-specific problem.

The development of a new generation of UF and RO membranes that could resist fouling while achieving energy savings in the demineralization would open even more opportunities to use low-energy-input membrane processes to recover a demineralized water stream from large volumes of moderately concentrated brines. In addition to providing a another tool for the recovery of product water from flowback waters that are of moderate strength (<50,000 mg/l TDS), membrane processing could provide a method of preconcentrating brines before feeding them into a thermal processor (such as an MVR) for further brine volume reduction and distilled water recovery. Whether used independently or together in a hybrid treatment system (as shown in Figure 1), the membrane treatment system and thermal processing represent important complimentary tools in the arsenal of water management for the shale gas industry.

With regard to the improvement of membrane technology, recent research conducted under RPSEA support at the University of Texas has resulted in the identification and testing of polymeric coatings that, when applied to UF and RO membrane surfaces, enhance resistance to fouling and improve performance in salt separations in the treatment of synthetic mixtures designed to simulate shale gas flowback waters. Specifically, pPolydopamine (PDOPA) was found to be an effective anti-fouling surface coating for UF, NF, and RO membranes. The surface deposition of PDOPA improved the permeate flux for all types of membranes studied during oil/water emulsion filtration. For UF membranes, additional grafting by using poly(ethylene glycol) (PEG) further enhanced the fouling resistance. Significantly, the coated membranes exhibited substantially improved performance in terms of flux rates achieved when pressure drop across the UF and RO processes were kept constant. Potential energy savings of greater than 27% were estimated on the basis of these higher observed membrane flux rates as measured in the laboratory.

On the basis of these results, a decision was made to initiate a field experiment to evaluate the effectiveness of the coatings technology to improve fouling resistance and performance in UF and RO treatment units under actual field conditions. To conduct this work, GTI has assembled a team including GeoPure (the owner of the UF/RO test skid), the University of Texas (owner of the coatings IP), and Advanced Hydro (membrane coatings deployment) to conduct a field evaluation of novel coated membranes with the cooperation of Devon Energy (the host for the demonstration). The purpose of this report is to document the field trials and results of this cooperative effort.

1.3 Innovative Anti-fouling Polydopamine Membrane Coating Technology

Polydopamine is a polymer of dopamine (DOPA), which is a naturally-occurring hormone and neurotransmitter. Messersmith et al. [10] reported that dopamine solution will undergo polymerization under slightly alkaline conditions to form a polymer that mimics the properties of mussel adhesive proteins (specifically, *M. edulis* foot protein 5 (Mefp-5)). The mechanism of polymerization has been studied and elucidated elsewhere [11]. Messersmith's suggested structure of polymerized dopamine or polydopamine (PDOPA) is shown in Figure 1. Polydopamine can non-selectively deposit onto virtually any surface. The deposition is on the order of 1-100 nanometers in thickness depending on contact time. The polydopamine layer exhibits excellent adhesion properties as it cannot be removed under sonication at extreme acidic conditions.

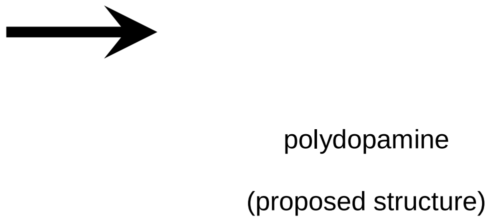
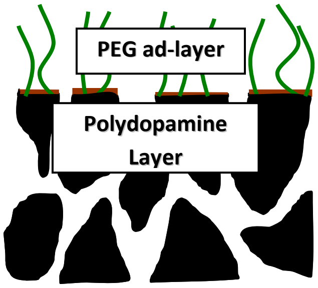


Figure 1: Dopamine and polydopamine structure. The exact structure of polydopamine is currently unknown; this structure was proposed by Messersmith et al. [10]

Polymerized dopamine coating for membranes has been developed for UF/MF, RO, and forward osmosis membranes by Freeman's research group [12, 13]. Now this patent pending membrane coating technology is licensed through Advanced Hydro Inc. for commercialization. A PDOPA-coated membrane shows two advantages over a non-coated membrane: (1) The polydopamine layer is uncharged and hydrophilic, which should reduce oil/grease and protein/bacterial adhesion. (2)Polydopamine, under alkaline conditions, rearranges to form a quinone-like structure, providing a mean of further conjugation of other organic compounds.

The free hydroxyl groups on polydopamine can be used to covalently bind other molecules to the PDOPA-coated surface. McCloskey et al. [13] reported that amine-terminated poly(ethylene glycol) (PEG-NH_2) can be grafted to a PDOPA-modified surface to improve the surface hydrophilicity without drastically altering the surface charge. Many other molecules could be grafted to the surface by a similar technique. Coating membranes with a thin layer of polydopamine should improve their resistance to fouling and provide a versatile starting point for further surface modification to a wide variety of membranes due to its nonspecific properties. Because the deposited polydopamine layer is so thin, the effect of the coating on membrane flux should be minimal.

PDOPA-PEG coating has been performed previously on finished UF and MF elements. Field pilot test results demonstrated superior permeation performance and fouling resisting property when used as seawater desalination pretreatment and waste water treatment. As shown by Figure 2, the attached PEG chain forms hair-structured layer, which is believed to be able to lock a water layer on membrane surface due to its super hydrophilic nature. Consequently, foulants cannot easily get close to membrane surface to form resilient fouling layer. Fouling layer would be more readily ripped off during cleaning operation.



polydopamine

(proposed structure)

PDOPA-g-PEG

Figure 2: Cross-sectional structure of polydopamine and PEG coated membrane; conjugation of PEG-NH_2 to polydopamine surface at pH 8.8.

Strong oxidants ($NaOCl$, H_2O_2, ClO_2, NH_2Cl) are common cleaning reagents recommended by membrane manufacturers. With the PDOPA-PEG coating protection, membrane water productivity can be easily recovered by regular acid/base clean, even daily hot water clean can sustain the filtration performance for long period of time. This largely minimizes membrane operation and maintenance costs. Through coating treatment, membrane life can be extended by 30 percent, and 50 percent of cleaning chemicals can be saved. For the coated microfiltration and ultrafiltration membranes, energy saving is estimated to be 40 percent, and 10 percent reduction on labor cost as well as a 50 percent reduction in the cost of cleaning chemicals.

1.4 Pilot Study Objective and Overview

1.4.1 Objective

The overall objective of this pilot study was to evaluate the polydopamine treated membrane separation technology in the application of shale oil and gas produced water treatment and reuse. The scope of work included the following elements: (1) Evaluate the effectiveness of UF and RO membrane technology in treating oil and gas produced water; (2) Identify the improvements polydopamine coating technology can benefit the membrane procedure in terms of water productivity (flux-gallons per square foot per day) and fouling control; (3) Consolidate preliminary pilot experience, and propose an optimized future work plan.

1.4.2 Pilot Overview

The pilot was planned as a 30 day trial to recover shale flowback waters using ultrafiltration (UF) and reverse osmosis (RO) processes. This short-term pilot was located in the Barnett Shale region near Fort Worth, TX, and co-existed with a vapor compression evaporation (VCE) treatment plant. Flowback water and produced water were transported from various production sites to the treatment facility and the treated demineralized water was trucked back to the fields to perform frac jobs. Raw water was treated by coagulation and sedimentation prior to processing by the membrane systems. Two types of ultrafiltration membranes were used in this pilot – the first set included two hollow fiber UF elements and the second set used two spiral wound UF elements. For the two hollow fiber UF elements, one was treated with polydopamine and PEG, the other was not treated and used as "control" element for comparison purposes. Both elements were run in parallel simultaneously during the pilot. In addition, two spiral wound UF elements were treated with polydopamine and PEG and used in series inside a single pressure vessel. UF effluents from both systems were blended in a storage tank that was subsequently fed to the RO system. Two trains of RO membranes, each with three elements in series, desalinated the water processed by ultrafiltration. Elements in one of the RO train were treated with polydopamine. The two trains of the RO system were run alternately every 12 hours.

Due to safety concerns, filtration systems were operated only during daylight hours. The pilot was also shut down during the Thanksgiving holidays for four days. During the normal running days, filtration was stopped for several times due to deficiency in raw water supply availability. As a result, the total accumulative filtration duration for spiral UF was 106 hours, hollow fiber UF was 58 hours, and about 50 hours for each RO train. Pilot started from Nov. 17, 2010 and ended on Dec. 18, 2010.

2. Methods and Approaches

2.1 Pilot Site Location

The pilot system was located at the Maggie Spain Water Reclamation Facility operated under the support of Devon Energy in the Barnett Shale region near Fort Worth, TX. Raw produced water was trucked from different production locations and discharged into a lined storage pond before treatment. Raw produced water was primarily treated by coagulation and sedimentation before it flowed into compression evaporation facility. The pretreated water was pumped to a working buffer tank as supply to both filtration pilot systems. The reject from the UF and RO systems was pumped to the VCE treatment facility's concentrate tank for off-site disposal. The permeate from the RO system was discharged to the VCE treatment facility's condensate (finished water) lined pond. Figure 3 below demonstrates a layout of pilot facilities.

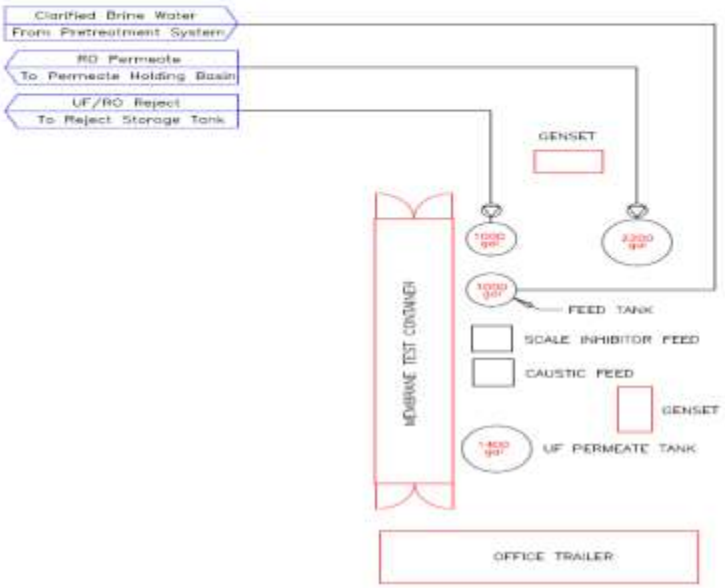


Figure 3: Layout of the pilot and collocated treatment facilities.

2.2 Filtration Facility and System Design

Two sets of UF filtration systems were used in this pilot – the first one being a hollow-fiber, PLC controlled ultrafiltration system with two hollow fiber UF elements in parallel. This system was designed and built by Advanced Hydro Inc. Due to high fouling potential of the produced feed water, hollow fiber modules were back-flushed every 15 minutes interval with air-scour for 30 seconds. To maintain the membrane performance, daily hot water clean (110 F) was also performed on hollow fiber modules at the beginning or end of each day's operation. Among two hollow fiber modules, one was coated with polydopamine and PEG, while the other one was kept untreated as a control membrane. Filtered water from this system was stored in a common buffer tank before being fed to the RO system. Fully automated real-time flow and pressure data were recorded every minute by the PLC program. See Figure 4 for the layout of the filtration system.

The second UF system facilitated running of two spiral wound UF elements in series inside a stainless steel vessel. The second UF system also included two RO vessels; one vessel housed three dopamine-coated elements, with the other vessel containing three untreated RO elements. Both spiral wound UF elements were treated with polydopamine and PEG. This combined UF and RO system was designed and fabricated by Complete Filtration Resources and provided by GeoPure HydroTechnologies and required manual operation and data logging. Membrane performance data and operation parameters were recorded manually every 20 minutes. Permeate from UF system was stored in a common buffer tank for feeding the RO system. UF vessel was flushed every 4 hours with heated caustic solution to maintain sustainable performance. A set of 5 micron cartridge filters were installed in front of UF segment to prevent large particles entering spiral wound membranes. These filters were removed after the first few days of the pilot study in order to allow the spiral and dead-end UF membranes to see the same "unfiltered" feedstock. A schematic drawing was illustrated in Figure 4 for the filtration system design.

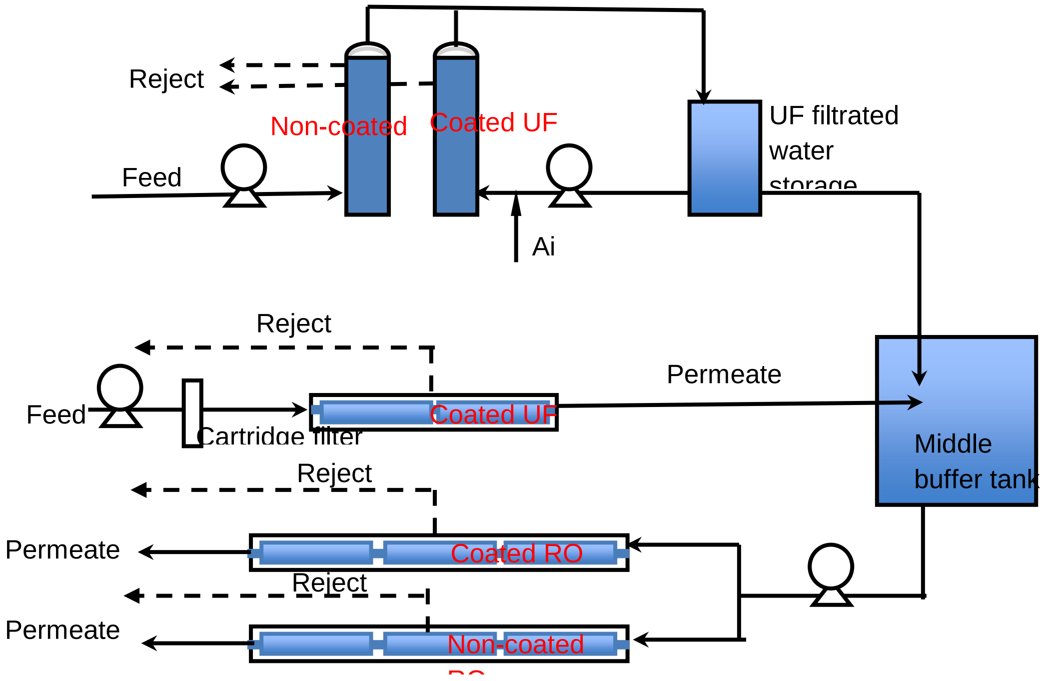


Figure 4: Schematic of membrane filtration design

Figure 5: Picture of the hollow fiber, spiral wound and RO filtration systems

After a few days of test runs, the optimal operating conditions were determined. Hollow fiber UF elements were operated dead end filtration mode with an initial feed flow rate of 5.8 GPM for each module. The backflush frequency was set to 15 minutes and its duration was 30 seconds. Spiral UF elements were operated in cross flow mode. The initial feed flow rate was set at 50 GPM for two elements, 45% of flow was recycled back to the feed tank to enhance the recovery, and 16% of flow was bled off as concentrate. The average feed pressure was about 55 PSI at the beginning, and initial permeate flow rate was set to about 20 GPM. When the permeation rate decreased to 10 GPM, caustic enhanced hot water cleaning was performed to recover flux. RO elements were run at feed flow rate of 15 GPM per vessel. The recovery (ratio of permeate to feed) of the RO system was kept low both to control operating pressures to less than 1,000 psi and to minimize scaling due to high feed hardness concentrations. The UF permeate buffer tank was used to maintain feedstock to the RO while cleaning was performed on the UF system.

Membrane Specifications

a. Hollow fiber UF membrane: Ultra-Flo U630C (Ultra-Flo Pte Ltd, Singapore) was chosen as the demonstration UF membrane. The original membrane fibers are made out of hydrophilic modified PAN (poly(acrylonitrile)). The fiber outer diameter is 1 mm, and the inner diameter is 0.5 mm. The membrane surface area is 323 ft^2. Recommended feed water turbidity is less than 5 NTU. Typical product turbidity is below 0.1 NTU. It is an outside-in capillary style membrane. The pore sizes of this membrane ranged between 0.1 to 0.01 microns. This system was brought in with last minute changes because the Geopure skid did not support side-by-side testing for UF. This limited our selection of membranes available at the time, with the selected membrane not optimum for use on produced water. However, we used the opportunity to generate data with side-by-side coated and non-coated control elements.
b. Spiral wound UF membrane: Sanitary ultrafiltration spiral membrane 8038 HFM-100 (Koch, Massachusetts, USA) was selected as another demonstration UF membrane. This membrane is

fabricated from PVDF (poly(vinylidene difluoride)). The molecular weight cut-off of HFM-100 is 50,000 daltons. The surface area of this membrane is 319 ft^2.

c. RO membrane: Seawater RO (SWRO) membrane SWC3+ (Hydranautics, California, USA) was selected as demonstration RO membrane. This membrane is a typical interfacial composite polyamide RO membrane with a nominal surface area of 400 ft^2. Maximum feed water turbidity is required to be less than 1 NTU, and maximum cross flow must be less than 75 GPM.

2.3 Membrane Cleaning Procedures

Two types of membrane cleaning methods were employed to recover UF membrane performance: chemical enhanced hot water clean (HWC) and standard chemical clean-in-place (CIP).

HWC was performed daily to recover ultrafiltration membrane flux. For this procedure, RO filtered water was used as the cleaning solution. The membrane elements were first flushed with RO water to dilute the feed solution (produced/flow-back water) retained in the module. The water was heated to 125 ^{o}F. Caustic or citric acid was used to enhance the cleaning efficiency. Solution pH was adjusted to 11.0 with caustic during alkaline cleaning for organic foulant removal, and adjusted to a pH of 2.0 with citric acid during acid cleaning for scale removal. This water was circulated through the membranes for 30 minutes. After the HWC, membrane modules were fully flushed with RO water to remove the residue chemicals. Spiral membranes were flushed through the feed side, while backflushing was performed on hollow fiber membranes to remove foulants and residual chemical.

CIP was occasionally performed on ultrafiltration membranes as a more intensive cleaning procedure. During CIP cleaning, caustic clean with NaOH (1% wt) was performed first for 2 hours and followed with citric acid (2%) cleaning for 1.5 hours. Cleaning solutions were also maintained at 125 ^{o}F during circulation. The membranes were fully flushed with RO water between each solution change.

2.4 Water Quality Analysis

Water samples were collected and sent on different days to the UT-Austin laboratories for analysis where TOC and major component ions were analyzed. Water quality information related to feed water turbidity, RO feed, permeate conductivity, pH, temperature were collected in real-time at 20 minute intervals during membrane operation. In addition, alkalinity, hardness, calcium and chloride concentrations were tested on- site frequently using portable drop count titration test kits from Hach, Colorado, USA.

Metal and non-metal elements (i.e. B, Na, Mg, Si, P, K, Ca, Fe, Sr, and Ba) in the water were also analyzed using inductively coupled plasma mass spectrometry (ICP-MS) (Agilent, model 7500ce) at Quadrupole ICP-MS Laboratory in Jackson School of Geosciences, University of Texas at Austin. Prior to testing by ICP-MS, the water samples were filtered with 5 um particle filters to remove any particulates in the water. Subsequently, each sample was diluted to 1:100 and 1:500 in 2% HNO_3 to ensure repeatability and to match with an operating range and a matrix of standard solutions.

Anions (i.e. Cl^-, NO_3^-, SO_4^{2-}, and PO_4^{3-}) were analyzed by ion chromatography (IC). The water samples were diluted to 1:2000 in deionized water to ensure that the concentrations fell within the detection limit of the equipment.

Total organic carbon (TOC) analyzer (Shimadzu, model TOC-VCSH) was used to analyze the organic carbon present in the water samples. In this analysis, non-purgeable organic carbon (NPOC) method was used for analysis of the TOC content.

Total petroleum hydrocarbon (TPH) concentrations were analyzed using a silica gel treated n-hexane extractable material (SGT-HEM) method of extraction and gravimetry (EPA 1664A). The TPH test was performed by TestAmerica Lab, an environmental testing firm in Pittsburgh.

2.5 Evaluation of Membrane Filtration Effectiveness

Ultrafiltration membrane efficacy was evaluated through membrane permeation flux, applied pressure, and cleaning frequency. These data and parameters were recorded during the filtration operation. Coated membrane performances were tracked and compared to their non-coated control twins and results are summarized in section 3.

Reverse osmosis membrane performance was assessed based on salt rejection and permeation flux. Since it is a pressure-driven procedure, besides the permeation flux data, the overall productivity was also evaluated in terms of recovery and net driving pressure. Salt rejection and temperature corrected permeate flux were calculated using an Excel based “RO data normalization utility” provided by membrane manufacturer Hydranautics. Calculation equations and conversion methods are discussed in the technical manual from manufacturer’s website [14].

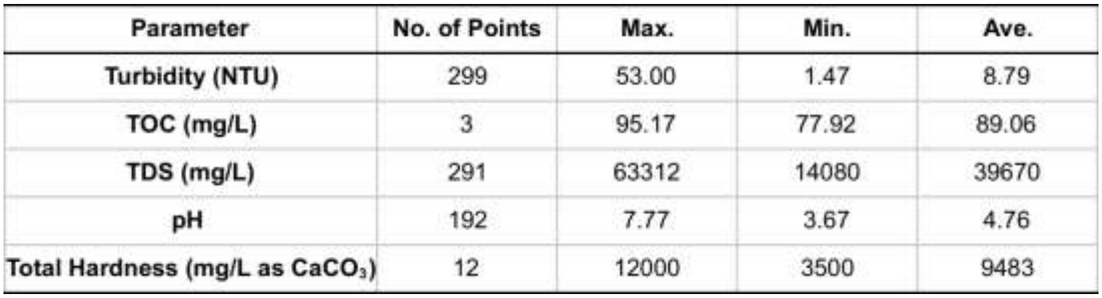
2.6 Investigation of Membrane Fouling

Used elements were autopsied to investigate fouling following the 30 days of pilot work. Leading spiral UF membrane, tail RO membranes and both hollow fiber UF elements were dissected for further examination. Multiple membrane samples were extracted and examined for foulants. Control samples were prepared by acid and base cleaning and served as reference for clean membrane surface. ATR-FTIR and SEM measurements were performed at the UT-Austin to study the presence of foulants.

3. Results and Discussion

3.1 Water Quality Analysis

Raw water quality data is summarized in Table 1. Turbidity, TDS, temperature, and pH parameters were tracked and recorded during the entire pilot and are presented at charts below. Few water samples for feed and permeates were collected for TOC and TPH tests. Alkalinity and hardness were analyzed.



Parameter	No. of Points	Max.	Min.	Ave.
Turbidity (NTU)	299	53.00	1.47	8.79
TOC (mg/L)	3	95.17	77.92	89.06
TDS (mg/L)	291	63312	14080	39670
pH	192	7.77	3.67	4.76
Total Hardness (mg/L as $CaCO_3$)	12	12000	3500	9483

Table 1: Summary of feed water quality

A wide variation in feed water quality was observed during the short pilot duration. This included feed turbidity ranging from 1.5 to 53 NTU with an average of 8.8. TOC varied from 77 to 95 mg/L with an average of 89 mg/L. TDS had a significant variation that directly impacted RO productivity. The overall TDS varied from 14,000 to 63,000 mg/L with an average of 40,000 mg/L. Since the water went through pretreatment, its pH remained mostly acidic (due to addition of HCl to reduce carbonate scaling) with an average pH of 4.8. Hardness measurements based on calcium carbonates also varied significantly with a range of 3,500 to 12,000 mg/L with an average of 9,500 mg/L. Since this pilot was run during November and December timeframe in Dallas area, temperature variations also showed trends with lowest in morning and generally increasing throughout the day.

All turbidity data (Figure 6), total dissolved solids (Figure 7) and temperature (Figure 8) are recorded in the figures below.

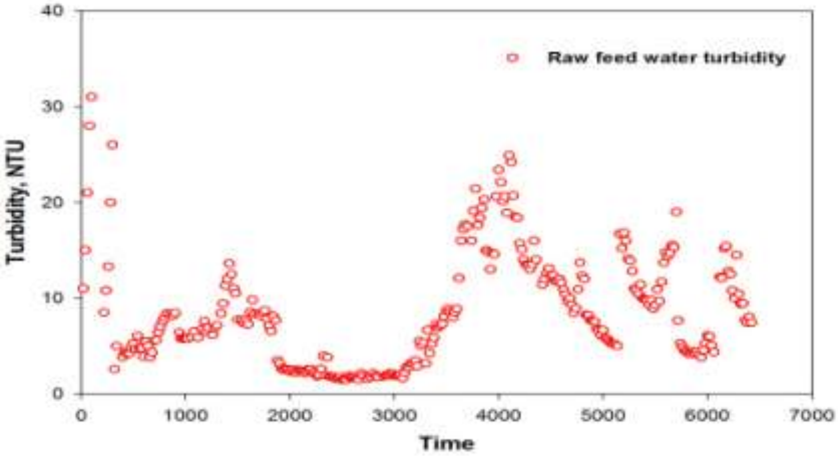


Figure 6: Feed water turbidity during the 30 day pilot

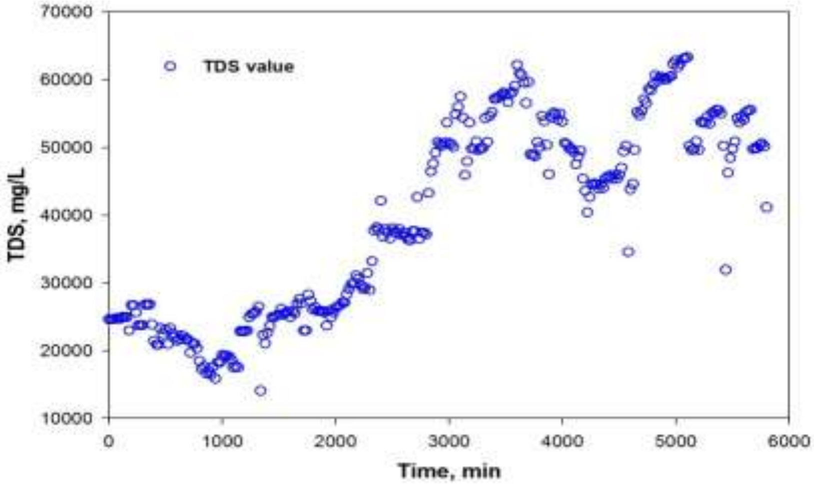


Figure 7: TDS variations for feed water during the 30 day pilot

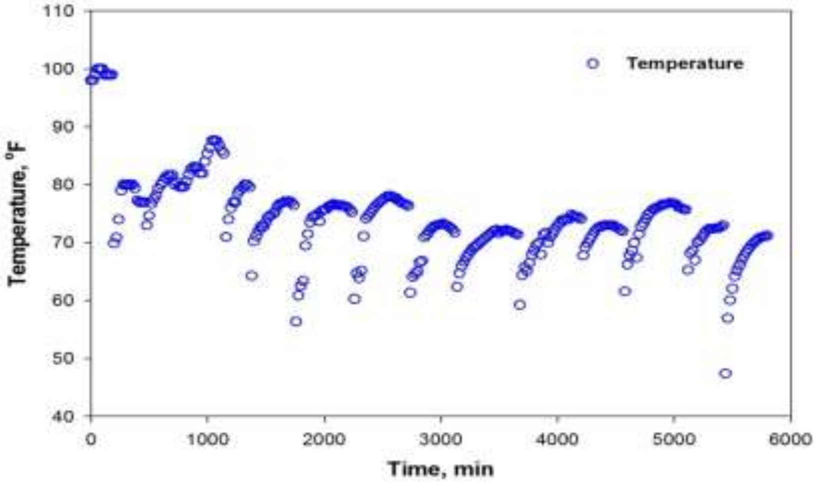


Figure 8: Temperature variations for feed water during the 30 day pilot

Major component ions of collected water samples were analyzed using IC and ICP-MS methods. Only one water sample was collected from each stage of the filtration process. Measured values of these ions are listed in Table 2. All the analyzed ions were retained in the UF permeates. There were gain and loss on the reduction percentage of UF permeate from the feed ionic concentrations, which was mainly due to the fluctuation of feed water quality. Rejection ratios for most tested ions were high above 99% on RO membrane. About 80% removal of Boron and 75% removal of nitrate achieved by this single stage SWRO membrane. Only uncoated RO permeate water was accepted full span ion analysis. The comparison data for ion rejections (mainly on hardness ions and chloride) for coated and non-coated RO membranes is discussed in section 3.4. No TPH was detected for the collected feed and permeate water samples. We suspect that water analysis for TPH was not accomplished within the required timeframe to get representative data.

		Feed		Spiral UF Permeate			Hollow fiber UF Permeate			Uncoated RO Permeate			Uncoated RO Concentrate	
Parameter	Units	No.of Points	Value	No.of Points	Value	Reduciton	No.of Points	Value	Reduction	No.of Points	Value	Reduction	No.of Points	Value
TPH	mg/L	1	ND	1	ND		1	ND		1	ND		1	ND
Boron	mg/L	1	23.56	1	31.23	-32.56%	1	24.27	-3.01%	1	6.218	80.09%	1	38.84
Sodium	mg/L	1	10435	1	9730	6.76%	1	9800	6.09%	1	94.85	99.03%	1	17012
Magnesium	mg/L	1	319.15	1	322.4	-1.02%	1	284.1	10.98%	1	1.434	99.56%	1	506.8
Silica	mg/L	1	51.415	1	55.02	-7.01%	1	37.88	26.33%	1	0.2308	99.58%	1	64.98
Phosphorus	mg/L	1	2.481	1	1.96	21.00%	1	2.076	16.32%	1	0.0049	99.75%	1	5.5
Potassium	mg/L	1	599.9	1	309.7	48.37%	1	197.8	67.03%	1	2.79	99.10%	1	401.38
Calcium	mg/L	1	3676.7	1	4390	-19.40%	1	4371.5	-18.90%	1	21.297	99.51%	1	7740.6
Iron	mg/L	1	9.029	1	11.485	-27.20%	1	6.97	22.80%	1	0.0234	99.80%	1	13.842
Strontium	mg/L	1	166.9	1	153	8.33%	1	151.85	9.02%	1	0.8182	99.47%	1	302.1
Barium	mg/L	1	5.04	1	4.58	9.13%	1	4.51	10.52%	1	0.0283	99.38%	1	8.484
Chloride	mg/L	1	16829.65	1	20272	-20.45%	1	23327	-38.61%	1	358.97	98.23%	1	42702
Nitrate	mg/L	1	4416.42	1	4566.23	-3.39%	1	4518.92	-2.32%	1	1145.5	74.91%	1	3566.8
Sulfate	mg/L	1	321											

Table 2: Ion analysis results for raw feed water, UF permeate, RO permeate, and RO concentrate.

3.2 PAN Hollow Fiber UF Membrane: Coated vs. Non-coated Test Results

Hollow fiber ultrafiltration membranes were tested in parallel for PDOPA/PEG coated and non-coated elements. All operating conditions and cleaning procedures were identical for both elements. During the 60 hour run, coated membranes demonstrated significantly better performance than non-coated membranes. Coated elements generated more permeate (higher flux) than non-coated elements. This advantage in water productivity became more significant in the latter stages of running as membranes fouled. Figure 9 shows the permeate water flux measured during the pilot. The membranes we used were available off-the-shelf and typically used for water treatment with a recommended maximum feed turbidity of less than 5 NTU. Such membranes are not optimum for produced water pre-treatment; however, these were the only membranes available for the side-by-side testing.

Pilot testing began with new membranes with the initial flux for both hollow fiber modules set at 25 gallons per square foot of membrane per day (GFD). Flux for both membranes dropped gradually over time. Although both coated and non-coated control membranes lost flux during the 60 hours of pilot operation, coated membrane provided nearly 50% higher flux compared to that of a non-coated control. Irreversible losses from 25 to 15 GFD are due to the fact that membrane module is not the optimum for high turbidity water and had a very tight fiber geometry to achieve higher surface area. We found corroborating evidence during membrane autopsy and there were significant amounts of large particulate residues retained inside the module that did not get removed during the backflush processes.

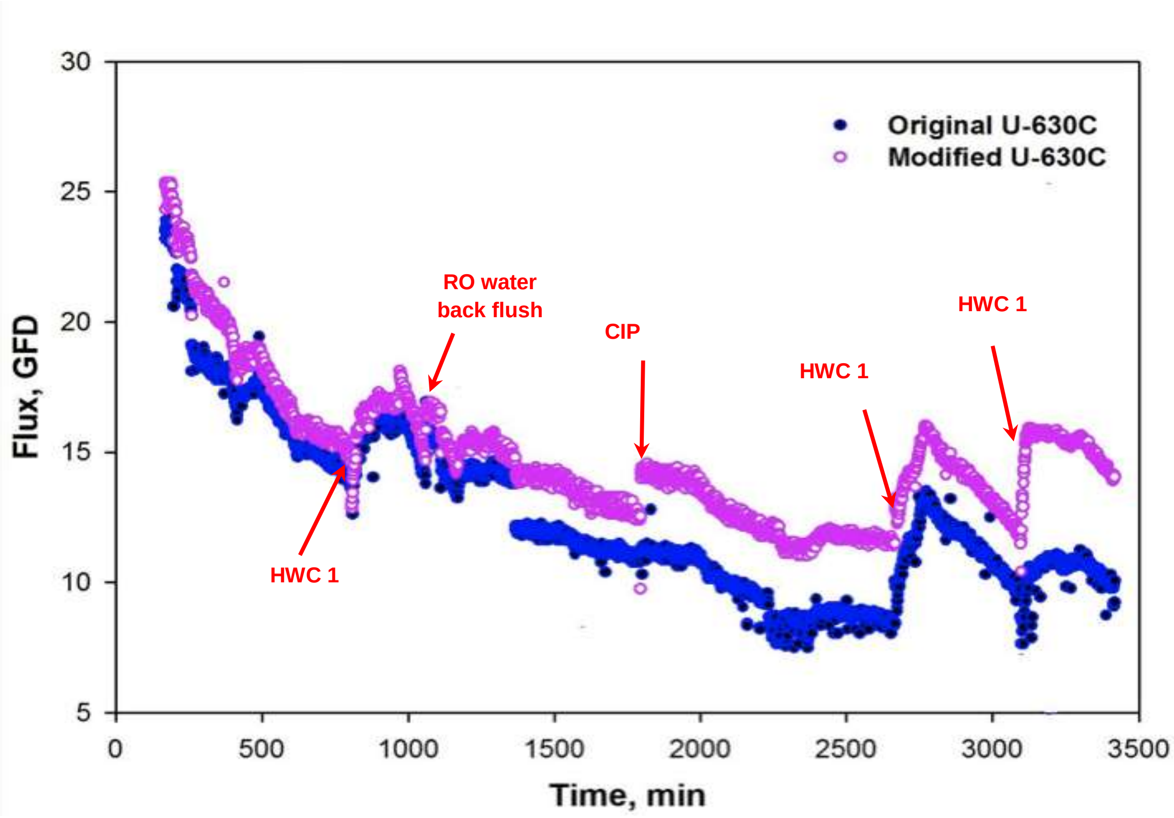


Figure 9: Ultrafiltration Membrane permeation flux for 3500 minutes; HWC1: caustic enhanced hot water clean, pH=11, 30 minutes circulation at 110 °F. CIP: clean-in-place, with caustic clean first, pH=11, 2 hours circulation at

110 ^{o}F; followed with citric acid clean, pH=2, 1.5 hours circulation at 110 ^{o}F. RO Water back flush: UF membranes were flushed using treated demineralized water from the RO process.

During the operation, we performed chemical cleaning on both elements as documented in Fig 9. Caustic enhanced hot water cleaning was found to be effective to recover flux, since organic fouling was the main issue for the feed water.

During the final days of pilot, the coated membrane was producing approximately 50% more water than the non-coated control. In addition, "hot water clean" (HWC) and "clean in place" (CIP) cleaning recovered coated membrane flux more effectively than the non-coated membrane. The typical flux for the coated membrane was maintained between 12-16 GFD using only daily caustic enhanced HWC. On the other side, caustic HWC and acid/base CIP barely retrieved flux on non-coated control membrane, suggesting formation of resilient fouling layer for acid and base cleaning chemistries. To remove such foulant, harsh chemicals (perhaps strong oxidants such as bleach or hydrogen peroxide) may be necessary to recover membrane performance. The typical flux for the non-coated UF membrane was maintained between 7-11 GFD.

Trans-membrane pressure (TMP) is a measure of the pressure difference between the feed side and the permeate side of the membrane during the filtration process. To create permeation across the membrane, TMP acts as the driving force for the filtration processes. It also directly relates to pore blocking (fouling) and energy consumption for the separation process. When a fouling layer is present, the membrane becomes less permeable, leading to an increase in TMP values. We measured TMP for both coated and non-coated membranes during the pilot side-by-side testing as represented in Figure 10. The non-coated membrane consistently showed higher TMP (about 25%) compared to the coated membrane. The typical differences are of the order of 4-5 psi. Such data is consistent with the earlier piloting of this technology in seawater desalination and laboratory development at laboratory scale. The lower TMP results from hydrophilic PDOPA + PEG coatings and their propensity to prevent adhesion of the foulants to the surface.

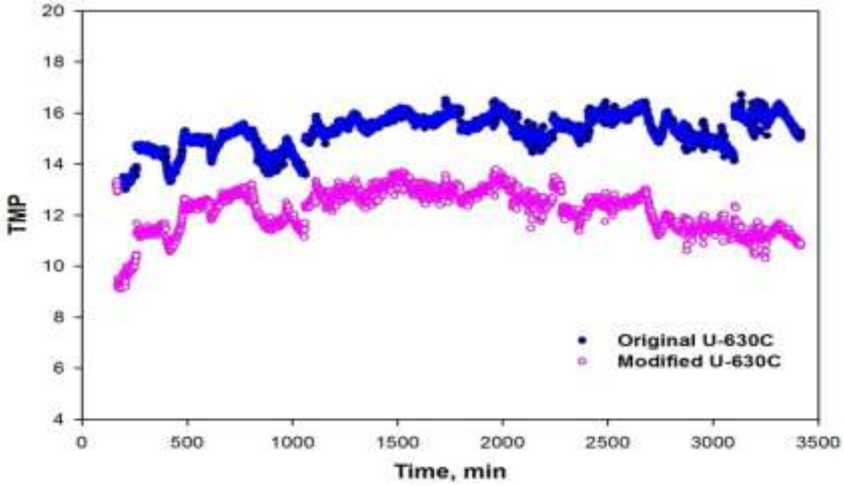


Figure 10: Trans-membrane pressure data for two side-by-side UF hollow-fiber elements. The red data represent the coated membrane and blue data represents non-coated control element.

Despite nearly 25% lower TMP across the coated filtration membrane, this membrane was generating about 40-50% higher flux during the second half of the pilot (post initial fouling). The combined effect of such data can be quantified as specific flux (GFD/psi). The ratios of flux and TMP (Specific flux) are plotted in Figure 11. This data represents a direct measurement of productivity and energy consumption for the filtration process. Notably, higher specific flux is obtained for the coated membrane. The coated membrane operated at about 1.5 GFD/psi specific flux compared to non-coated operating at 0.8 GFD/psi, nearly a factor of 2X higher. The coated module's performance increased over time.

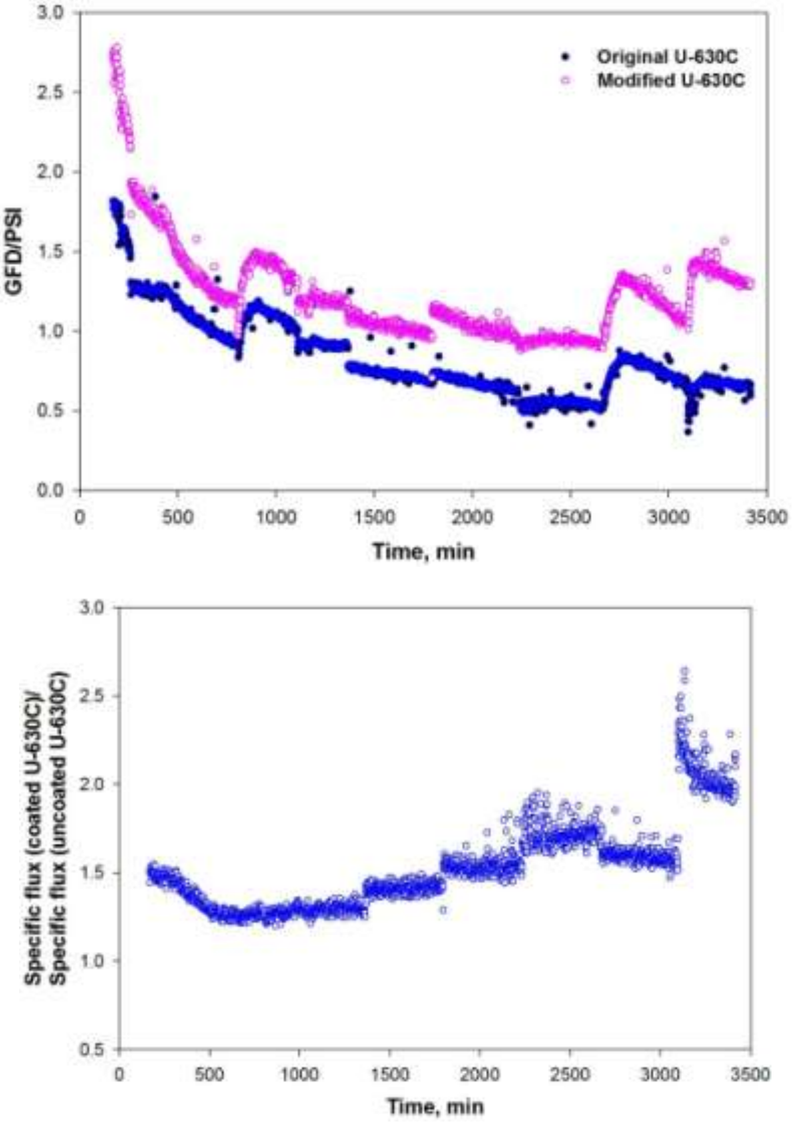
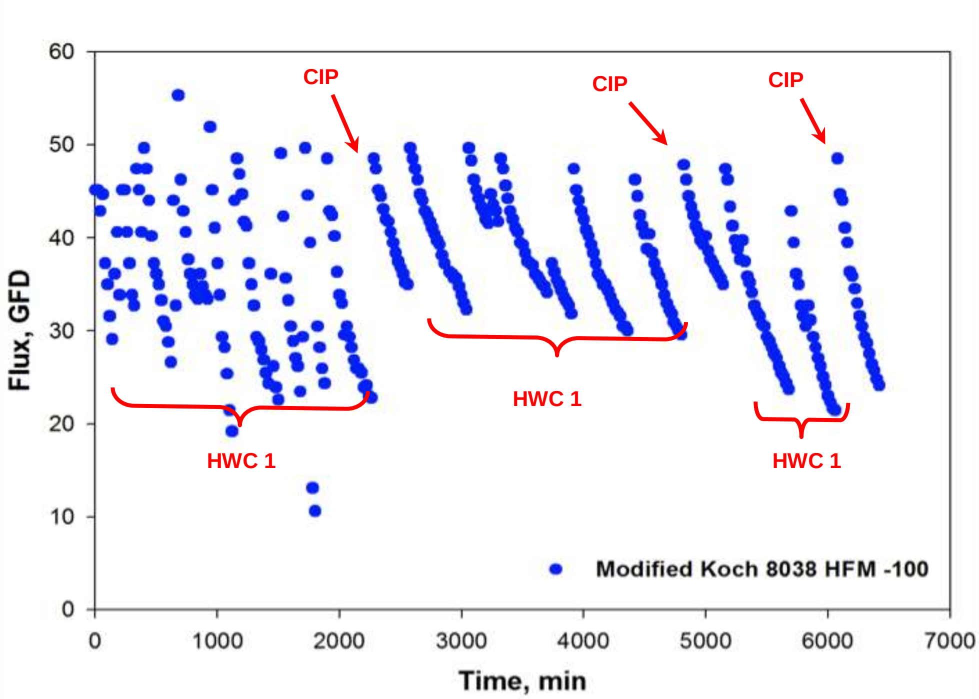


Figure 11: Specific flux data for two side-by-side UF hollow-fiber elements (top). The red data represent the coated membrane and blue data represents non-coated control element. A ratio of two specific fluxes comparing coated and non-coated is also plotted (bottom).

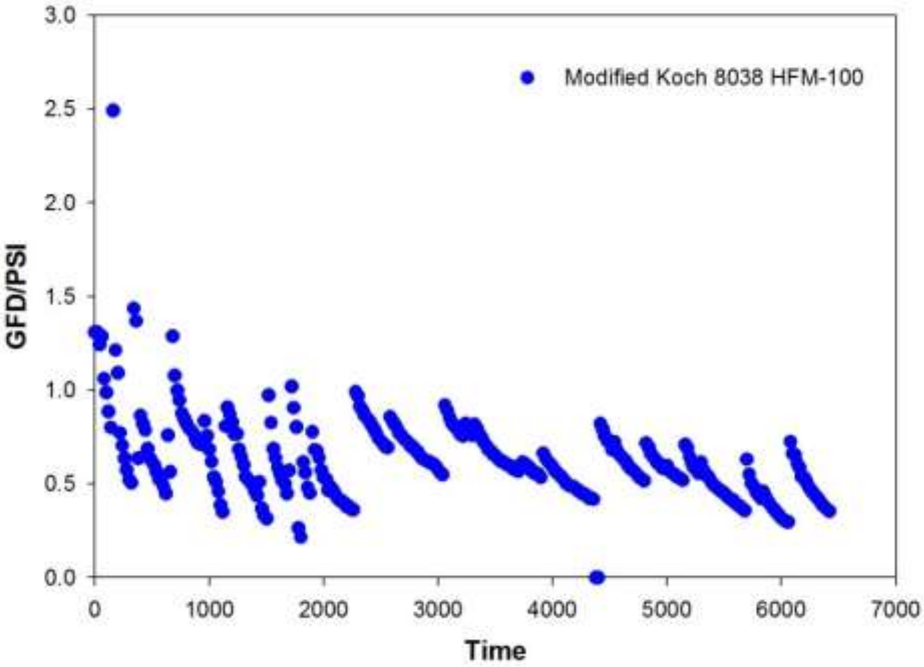
3.3 Koch Coated PVDF Spiral UF Membrane Test Results

Two spiral UF elements were coated with PDOPA/PEG and tested in this pilot for about 6500 minutes. During the initial test runs, we established a requirement for HWC cycle every 4 hours to maintain a sustainable flux for subsequent feed to the RO stage. However, at later stages, although the water was more turbid, after initial fouling, the membranes reached stable operation requiring HWC once or twice a day during 12 hours of operations. During the 30 day period, we performed a total of 3 CIP cycles for this set of membranes and nearly 20 HWC processes to manage fouling. We expect to improve this further with an optimized pre-filtration cartridge that can capture oily components (see discussion later).

After treated with polydopamine/PEG coating, Koch spiral 8038 HFM-100 membranes can sustainably treat shale produced water, although frequent caustic cleanings were required. The average filtration productivity was 35 GFD for the 106 hours of runtime, which is relatively large for a spiral UF module under this feed water condition. Trans-membrane pressure increased gradually over the test duration. Apparently, the cleaning could not fully restore the original separation performance in terms of energy consumption. Although the flux mostly recovered after each cleaning cycle, feed pressure kept increasing over time, which results in the 50% loss on specific flux from its original value. This indicates the adsorption of foulants on the membrane surface. However, permeate flux could be effectively recovered on coated membrane by caustic HWC. The cleaning temperature was found to be critical to restore the permeate flux. Cleaning temperatures around 120^{o}F provided an excellent recovery of the membrane flux during circulation of caustic solution, which is within the cleaning temperature range required by the membrane manufacturer (105-130^{o}F) [15]. The entire data set is plotted in Figure 12 below as flux (top), TMP (middle) and specific flux (bottom). For this set of membranes, we did not have a control element due to skid design limitations. Based on achieving a sustainable flux of over 35 GFD, we are clearly seeing a significant benefit due to the presence of the coating layer. For such challenging water, it may be difficult to achieve flux in the range of 25 GFD without the coating layer for this kind of membrane.



CIP
CIP
CIP
HWC 1
HWC 1
HWC 1
● Modified Koch 8038 HFM -100
Flux, GFD
0
10
20
30
40
50
60
0
1000
2000
3000
4000
5000
6000
7000
Time, min



● Modified Koch 8038 HFM-100
GFD/PSI
0.0
0.5
1.0
1.5
2.0
2.5
3.0
0
1000
2000
3000
4000
5000
6000
7000
Time

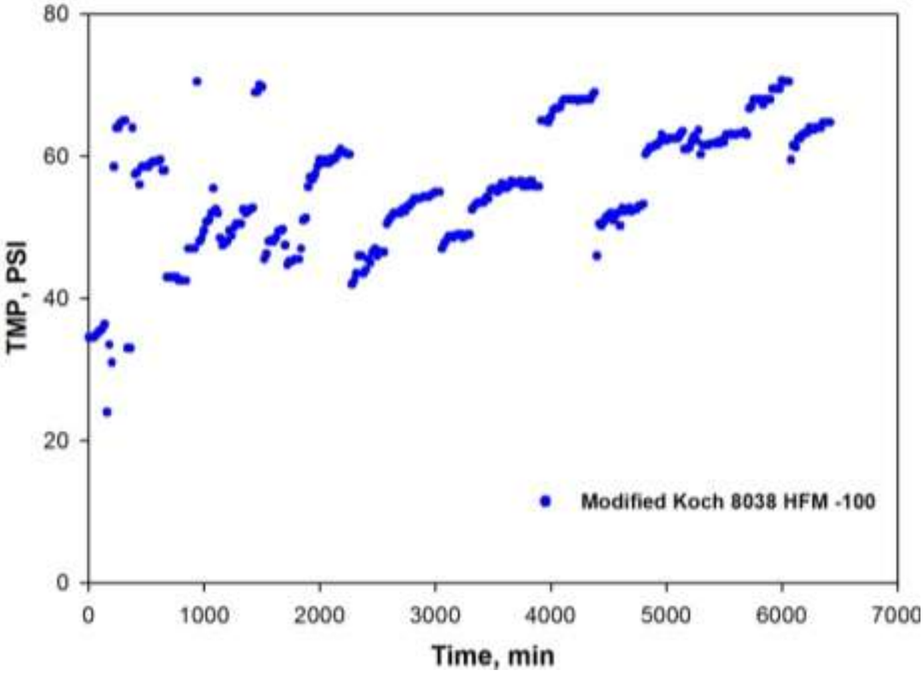


Figure 12: Spiral UF module pilot data. Top: membrane permeation flux for 6500 minutes; Middle: trans-membrane pressure for 6500 minutes; Bottom: specific flux (Flux/TMP) for 6500 minutes. HWC1: caustic enhanced hot water clean, pH=11, 30 minutes circulation at 110 ^{o}F. CIP: clean-in-place, which uses caustic clean first, pH=11, 2 hours circulation at 125 ^{o}F; followed with citric acid clean, pH=2, 1.5 hours circulation at 125 ^{o}F.

Since, there is no equivalent non-coated data we can be use to compare the performance, we studied some data from previous pilot tests to get basic ideas of how such membranes may perform without coating in treating produced water. However, it must be noted that the data we present below, corresponds to water that was very different and much better quality compared to the water in current pilot. Only basic raw water quality data is available from this old pilot. Table 3 below illustrates the difference between water quality for our pilot at the Maggie Spain Facility near Fort Worth (Fort Worth pilot) and the water handled by an old pilot system previously operated elsewhere (both pilot efforts utilized the same spiral UF membrane).

	Feed Turbidity, NTU	Average Feed Turbidity, NTU	TDS, mg/L	Temperature, °F
Fort Worth Pilot	1.47-53	8.79	14080-63312	56-100
Old Pilot	1.2-10	5.45	15000-20000	60-92

Table 3. Feed water qualities of Fort Worth pilot and a pilot conducted elsewhere using the same spiral UF membrane (Old pilot).

It is clear that in the Fort Worth pilot we had an average of 60% higher turbidity and nearly 2x higher TDS. The old pilot had better feed water quality than Fort Worth pilot. Five test runs were conducted during the old pilot, with each test run lasting for about 3 hours. Total running time was about 1000 minutes. In Figure 13, the first 1000 minutes operation results from Fort Worth pilot are plotted and compared with the other pilot data.

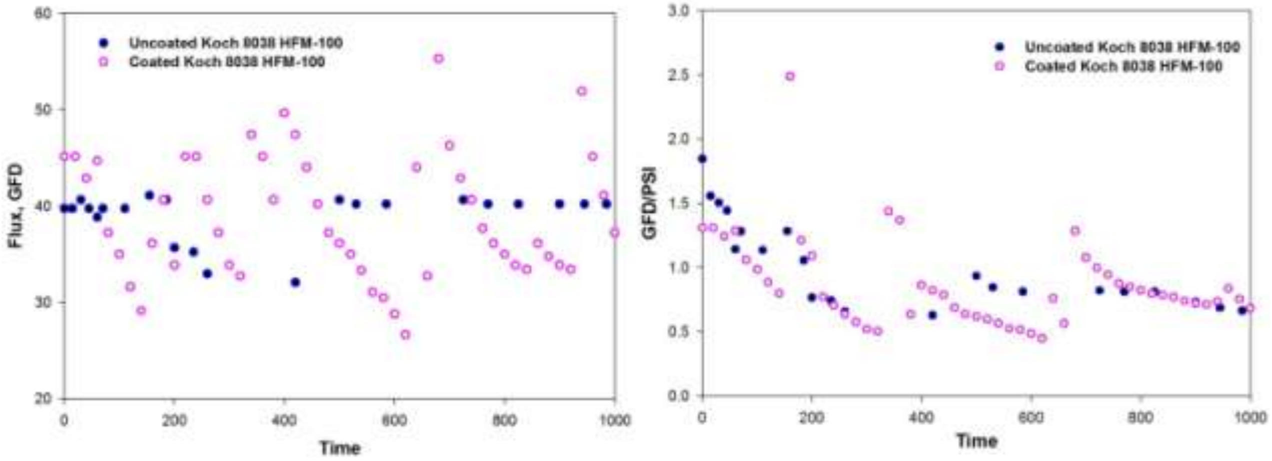


Figure 13: Pilot data of coated spiral UF membrane plotted with pilot data of non-coated spiral UF membrane. Left: Water flux for the first 1000 minutes run; Right: Specific flux (Flux/TMP) for the first 1000 minutes run.

As seen from Figure 13, non-coated Koch spiral UF membrane provided stable flux at around 40 GFD. This performance was also maintained by caustic enhanced HWC. It was reported that caustic clean was conducted in between each test run. Although the Fort Worth pilot featured feed water with more challenging features (higher suspended solids and higher salinity), the coated spiral UF membrane displayed comparable performance as a non-coated membrane treating less challenging water. The flux change was more dramatic for the Fort Worth pilot, but the coated membrane demonstrated a recoverable surface in the presence of a highly fouling feed stream.

Although this data is not a direct comparison, it is able to shed light on the fact that with a water that has nearly 2x higher TDS and 80-90 mg/L organics and 60% higher turbidity, coated membranes can achieve about 35 GFD flux over a nearly 6x longer pilot duration, exhibiting a very recoverable operation. We attribute such benefits to the use of the coating applied to the membranes.

During the CIP cleaning of Koch spiral UF membranes, significant amounts of oil emulsion residue were found in the circulated citric acid based cleaning solution (Figure 14, left) during the beginning of the cleaning cycle. However, this residue disappeared during the latter half of the circulation process. Whenever this happened, the feed pressure could not be effectively recovered by cleaning, suggesting the oil residue was being entrapped against the inside of the membrane (mostly inlet) during the cleaning circulation mode. To resolve this problem, a cartridge filter needs to be installed in-line before the cleaning solution goes back into the membrane vessel; this filter was not a component of the existing skid.

The reject solution from the caustic cleaning was very dirty and dark in color, which suggests that most foulants were organic substances and effectively removed during the caustic cleaning.

Figure 14: Oil residue/particulates collected during citric acid cleaning (left), and a dark solution collected during caustic cleaning (right) representing predominantly organic foulants adhering to the membrane.

3.4 Reverse Osmosis Membrane Performance

Water processed (permeate) from the ultrafiltration membranes was collected in a common tank and supplied to the RO as feed for subsequent removal of dissolved ions (desalination). The feed flow rate was fixed at 15 GPM with an initial recovery at 50%. Antiscalant Flocon 260 was added into the feed line to prevent scaling in the concentrate side of the RO elements. As discussed earlier in Figure 7, TDS values fluctuated greatly from day to day. The highest measured value for TDS reached about 63,000 mg/L. Since the maximum capacity of the RO feed pump was limited to 1000 PSI, during high TDS conditions, recovery could only be maintained at 10-15% due to the high salinity of the feed. Specific permeate flux and rejection were normalized by temperature and plotted in Figure 15, for which, all the flux and rejection data were temperature corrected to 25$^{\mathrm{o}}$C.

As seen below in Figure 15 (top), relatively, no significant specific permeate flux changes were noticed on both coated and non-coated SWC3+ membranes. The normalized specific flux data show significant random variations for later half of the pilot when feed TDS was more than 50,000 mg/L. This may appear unusual; however, such behavior is generally attributed to significant drop of net driving pressure across the RO membrane. ssociated with understood in terms of net driving. This reduced net driving pressure resulted from significantly increased TDS values. As seen in Figure 16, feed water TDS increased about 2.4-3 times in the latter half period of pilot run, which leads to the reduction on the membrane recovery as the net driving pressure dropped. The limited maximum feed pressure led to the loss of net driving pressure due to the increase on osmotic pressure of the higher saline feed. This membrane material gets more permeable at lower net driving pressure, which might be due to the less compacted structure of membrane sheet at low pressure range.

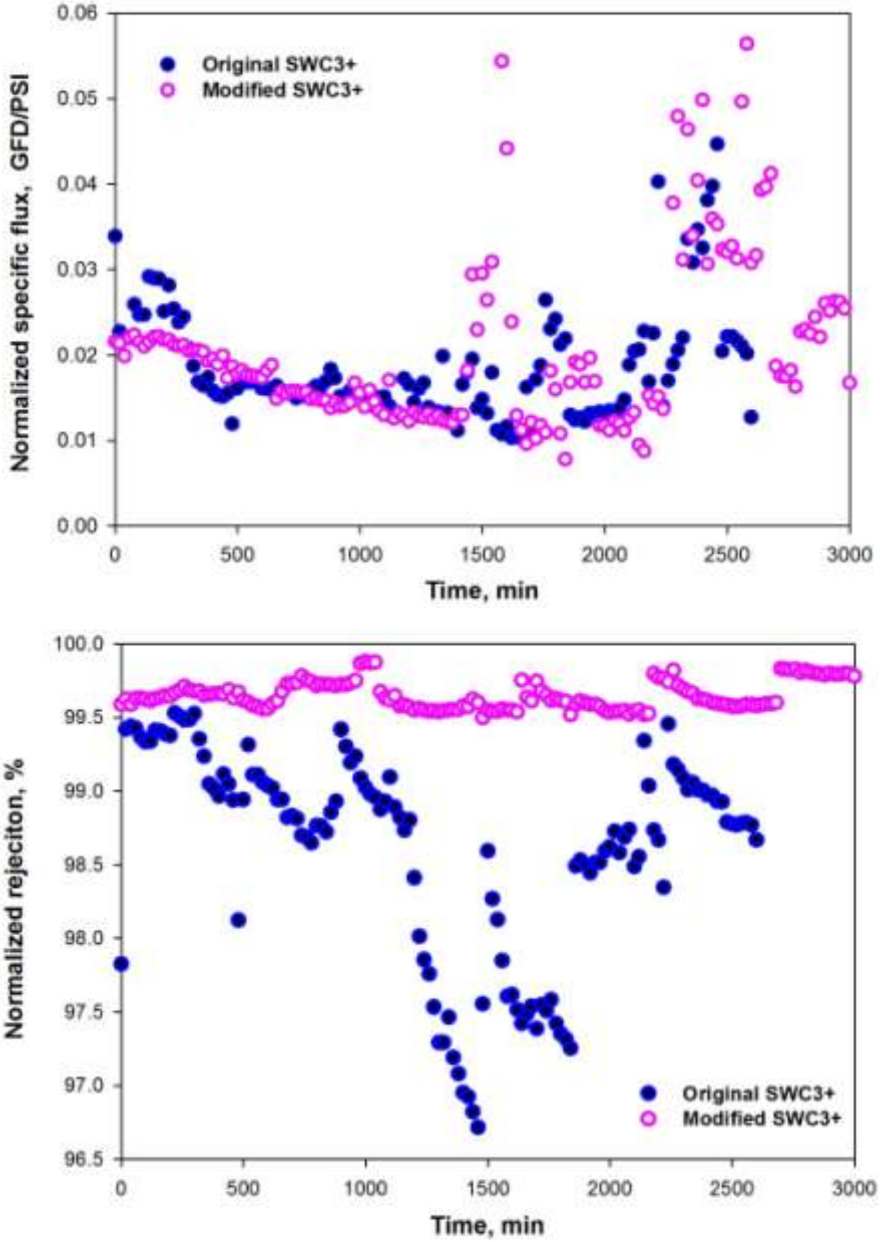


Figure 15: Coated and non-coated SWC3+ pilot test results. Top: Normalized flux; Bottom: Normalized rejection.

During our testing, we found higher and more stable salt rejection for coated membranes. The non-coated membranes experienced a significant decrease in rejection when the feed TDS increased. Rejection started for non-coated membranes at 99.5% and dropped to the lowest value of 96.6%. However, for coated membranes, rejection remained well maintained above 99.5% throughout the pilot. This is expected behavior for polydopamine coating on RO membranes. Based on this observation, we expect a system where nano-filtration membranes with polydopamine coating may perform very well for filtration of high TDS water streams and eventually enable either a NF-NF or NF-RO combination of desalination for a wide range of salinity streams. We recommend that such a study be performed in a full-scale pilot effort in the near future.

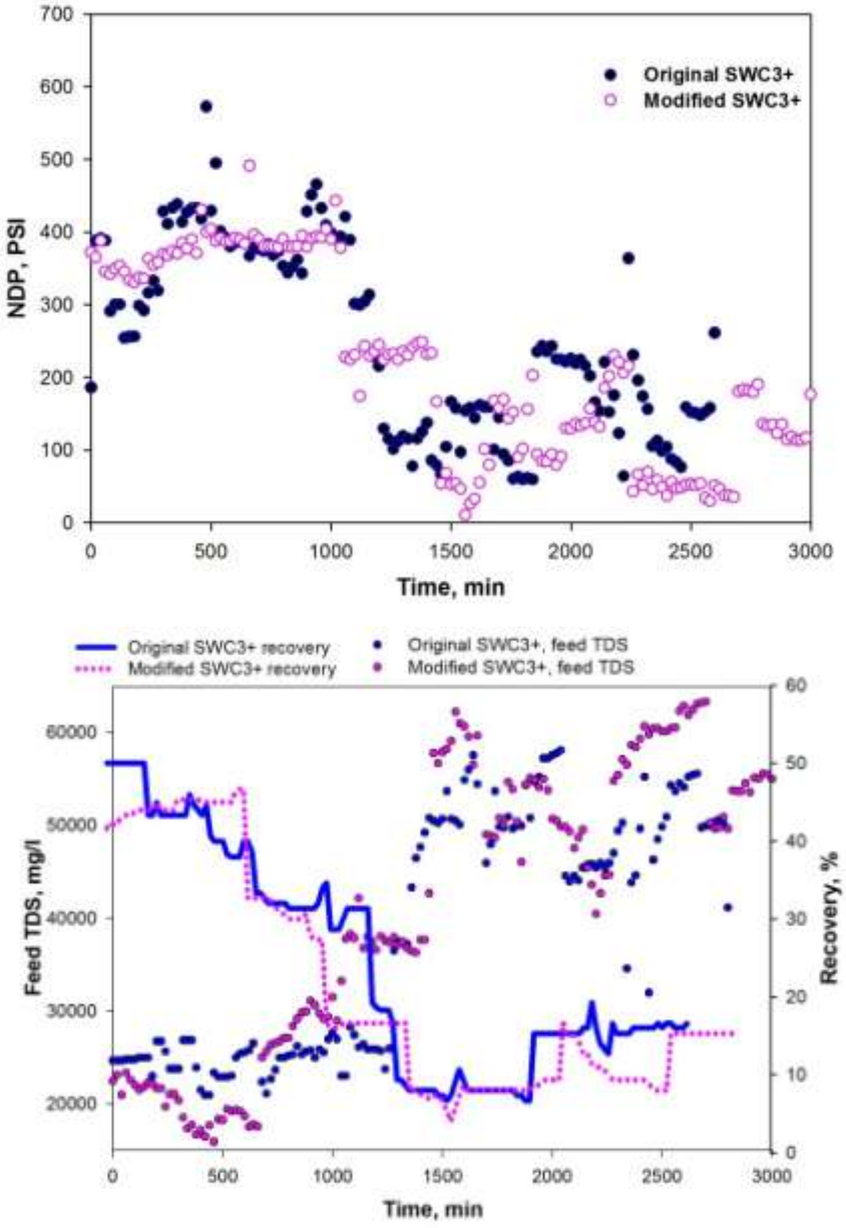
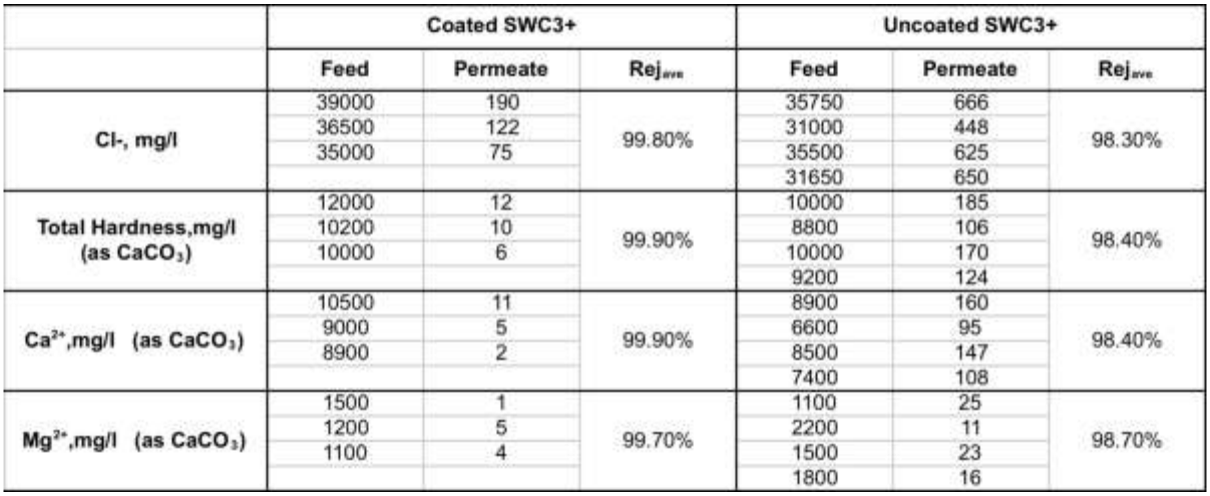


Figure 16: Top: Net driving pressure (NDP= ΔP-Δπ); Bottom: Feed water TDS values vs. membrane recovery during the RO pilot test.

Chloride and hardness (Ca^{2+}, Mg^{2+}) concentrations were measured using on-site titration for feed and permeate RO water to evaluate the individual rejection of specific ions. Results are presented in Table 4. Rejection of chloride and hardness ions was higher for the coated membrane than for the non-coated membrane. This observation is also in agreement with the rejection data presented in Figure 15 (bottom) earlier, which evaluated from the on-line conductivity measurement.



	Coated SWC3+			Uncoated SWC3+		
	Feed	Permeate	Rej_{ave}	Feed	Permeate	Rej_{ave}
Cl-, mg/l	39000	190	99.80%	35750	666	98.30%
	36500	122		31000	448	
	35000	75		35500	625	
				31650	650	
Total Hardness,mg/l (as $CaCO_3$)	12000	12	99.90%	10000	185	98.40%
	10200	10		8800	106	
	10000	6		10000	170	
				9200	124	
Ca^{2+},mg/l (as $CaCO_3$)	10500	11	99.90%	8900	160	98.40%
	9000	5		6600	95	
	8900	2		8500	147	
				7400	108	
Mg^{2+},mg/l (as $CaCO_3$)	1500	1	99.70%	1100	25	98.70%
	1200	5		2200	11	
	1100	4		1500	23	
				1800	16	

Table 4: Specific ion rejection by coated and non-coated SWC3+ membrane

3.5 Membrane Autopsy Analysis

Leading spiral UF elements, tail RO elements for coated and non-coated membranes, and two hollow fiber UF elements were opened for fouling evaluation. The resulting autopsy examination and analysis are discussed in the following sections.

3.5.1 Membrane Leaf Examination

During membrane autopsy, we made following observations (Figure 17 below) –

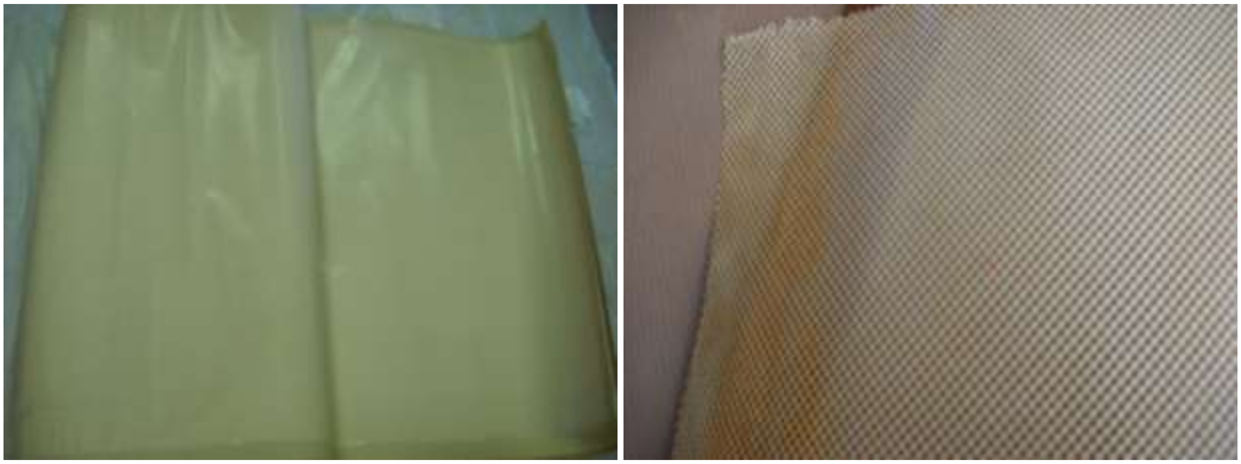
1. Coated Spiral UF: Membrane leaves were dark in color, and surface looks oily. Brown stains were found on brine spacer leaves.
2. Non-coated SWC3+: Membrane leaves were light pink in color, and surface looks clean.
3. Coated SWC3+: Membrane leaves were light brown in color, and surface looks clean.
4. Non-coated hollow fiber UF: Fibers were brown in color.
5. Coated hollow fiber UF: Fibers were dark brown in color.

Spiral UF before autopsy

RO Before autopsy

Spiral UF element leading edge RO element leading edge

Spiral UF membrane leaf Non-coated RO membrane leaf



Spiral UF brine spacer Coated RO membrane leaf

Figure 17: Opened elements leaf examination.

3.5.2 Hollow fiber UF Membrane Examination

Fibers were cut from the opened modules and studied. Sample fibers were cleaned with either acid/base (washed) or acid/based and bleach (washed and bleached) with sodium hypochlorite. Images of fibers as obtained from the elements without cleaning, post washed and post washed and bleach were taken and are shown in Figure 18. Coated fibers were brown in color as expected from the coating polymer. Fouled fibers in both coated and non-coated elements are slightly darker in color. The fiber color became lighter after cleaning (washed). Cleaning with a strong oxidant (bleach) restored the original color of the membrane fiber. After bleaching, coated fibers turned white in color, which suggests the removal of the polydopamine/PEG coating layer. In addition, coated fibers exposed native surface while uncoated fibers retained some color, most likely from unrecoverable fouling.

Figure 18: Coated and non-coated fibers treated with different cleaning reagents. Left: uncoated fiber, from bottom up: untreated, washed with acid /base, washed with acid/base and bleached; Right: coated fiber, from bottom up: untreated, washed with acid/base, washed with acid/base and bleached.

3.5.3 Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR) Examination of Membranes

Membrane samples taken from the opened elements were cleaned and compared with unclean raw samples using Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR). After cleaning, the virgin surface was mostly observed. Therefore, in Figure 19-22, cleaned membrane spectra should represent the pristine surface of either coated or uncoated membranes (probably mixed with a little foulants depending on how well the membrane was cleaned).

Figure 19 shows IR spectra of cleaned spiral UF membrane and fouled UF membrane. The 1500-650 cm^{-1} region contains characteristic peaks of PVDF [16]. Peaks in this region are attenuated in the fouled membrane, indicating that the original surface properties were masked by the fouling layer. The broad band centered at 3300 cm^{-1} is due to the overlapping of vibration of hydroxyl (-OH) groups from the coating layer and carboxylic groups from the fouling layer [17]. Small peaks in the range of 1550-1650 cm^{-1} of the fouled membrane are probably due to the contribution of amide (C=O or protonated amine), nitro (N=O or R-NO_2) groups and carboxylic functional groups [18, 19]. The increased absorbance at around 1000 cm^{-1} may suggest the presence of polysaccharide-like substances. The peak between 900-1100 cm^{-1} probably corresponds to a ketone group of polysaccharide in cellulose [20]. This peak overlapped with attenuated PVDF peaks close by and formed a region of increased absorption at around 1000 cm^{-1} in the fouled membrane spectra. The differences between the spectra of the fouled membrane and the cleaned membrane suggest that organic matter is the primary foulant on these spiral UF membranes.

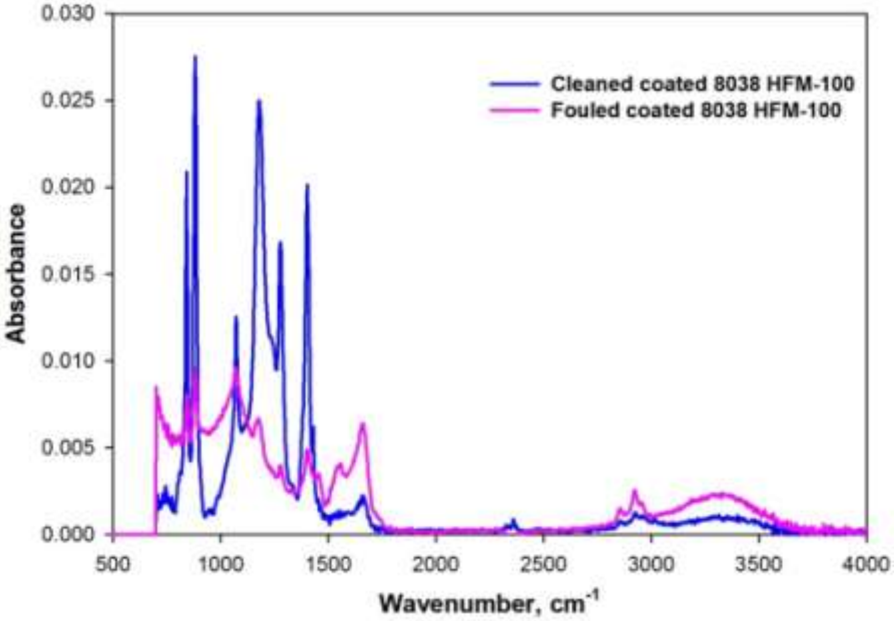


Figure 19: IR spectra for coated spiral UF membrane, cleaned versus fouled.

Figure 20 below presents IR spectra for cleaned coated and non-coated SWC3+ membranes. The peaks at 1540, 1610, and 1660 cm^{-1} correspond to C-N stretching (amide II), aromatic ring breathing, and C=O (amide I) functional groups which are associated with the presence of amide groups [21]. Membrane IR profiles are also characterized by a broad band centered at 3300 cm^{-1}, which corresponds to the presence of amide (N-H), carboxylic (COOH), and hydroxyl (-OH) functional groups. Theses polyamide characteristic peaks were all slightly attenuated for the coated SWC3+ spectrum, which indicates the presence of the coating layer on the top of the virgin surface.

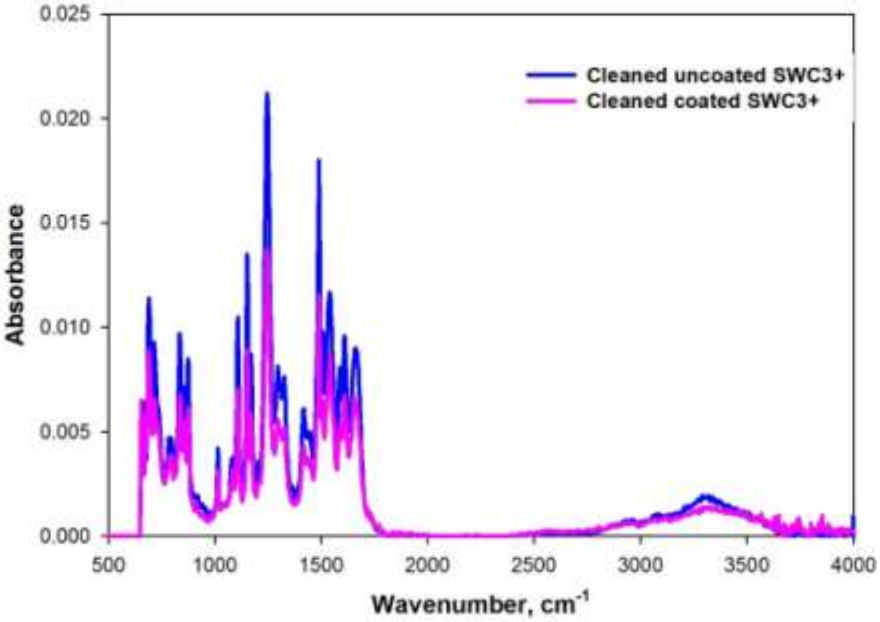


Figure 20: IR spectra for non-coated and coated RO membranes.

When comparing the fouled membrane with the clean membrane, as shown in Figure 21 for a non-coated membrane and in Figure 22 for a coated membrane, characteristic polyamide peaks in the spectrum were attenuated by various amounts compared to the spectrum of a clean membrane. This result implies a thin layer of bounded foulants or coating, which hindered the penetration of infrared radiation into the virgin polyamide layer. The extent of peak reduction semi-quantitatively suggests the thickness of fouling layer or coating layer.

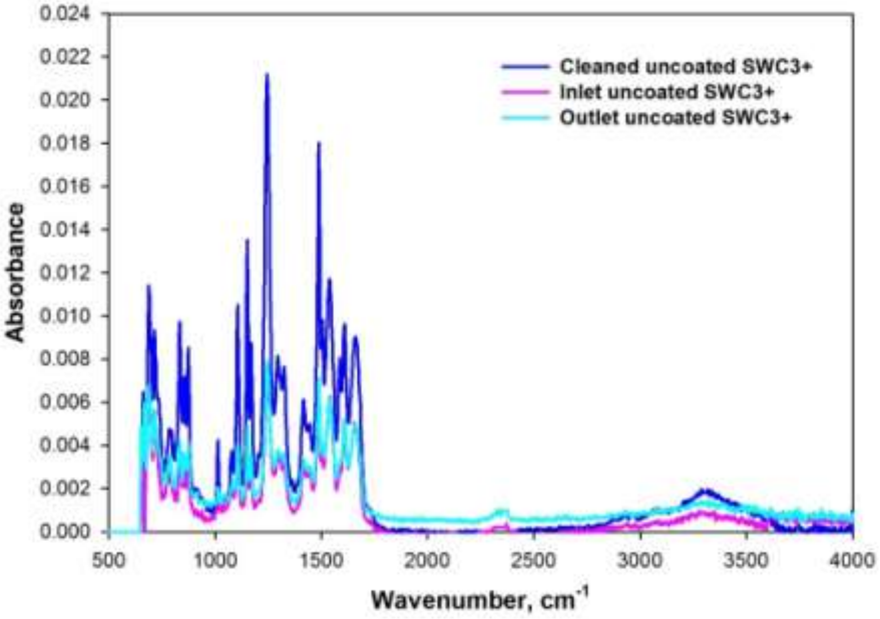


Figure 21: IR spectra for non-coated RO membrane, cleaned versus fouled.

As seen in Figure 21, uncoated membranes show attenuation due to the presence of the foulant layer. Although no noticeable performance decrease was observed with these membranes, the infrared results suggest early signatures of fouling; 30 days of service were apparently not enough to produce a strong impact of fouling on flux.

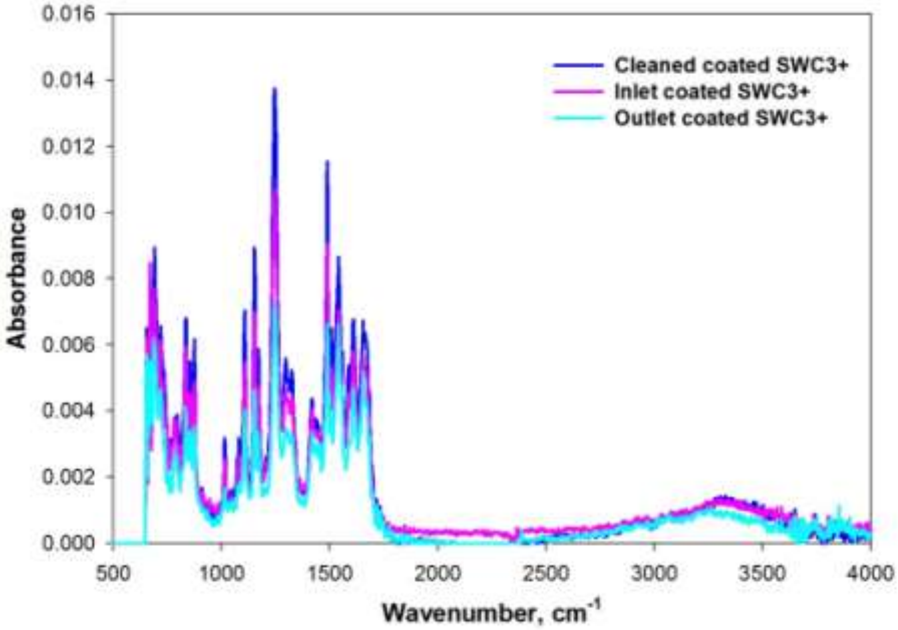
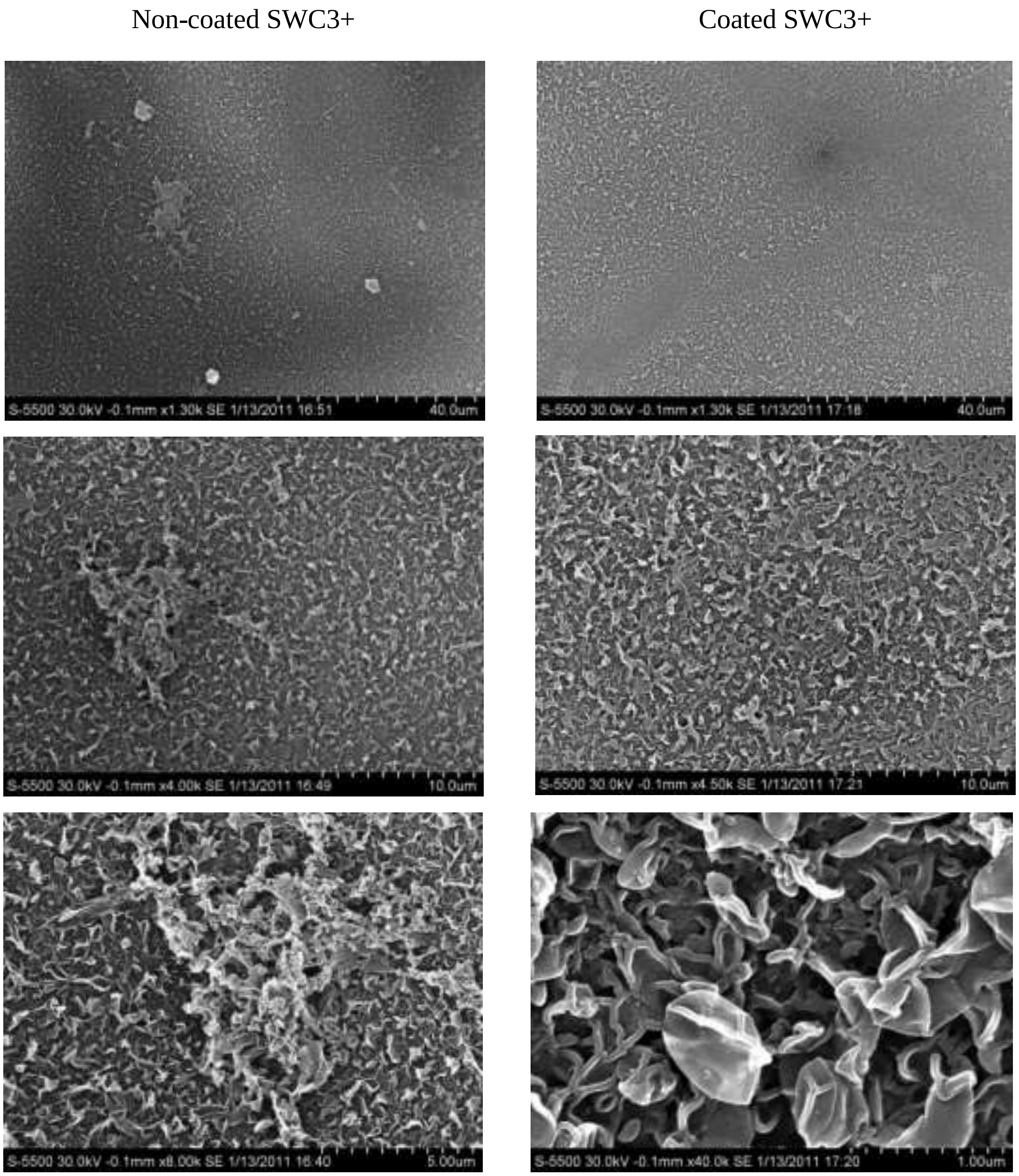


Figure 22: IR spectra for coated RO membrane, cleaned versus fouled.

As seen in Figure 22 above, there is very little change in FTIR intensities on coated membrane compared to that of the coated and cleaned membrane, suggesting evidence of a much thinner layer of adsorbed foulants. These intensity changes are significantly less than those of a non-coated membrane, suggesting that the coating has significant anti-fouling impact.

3.5.4 SEM Examination

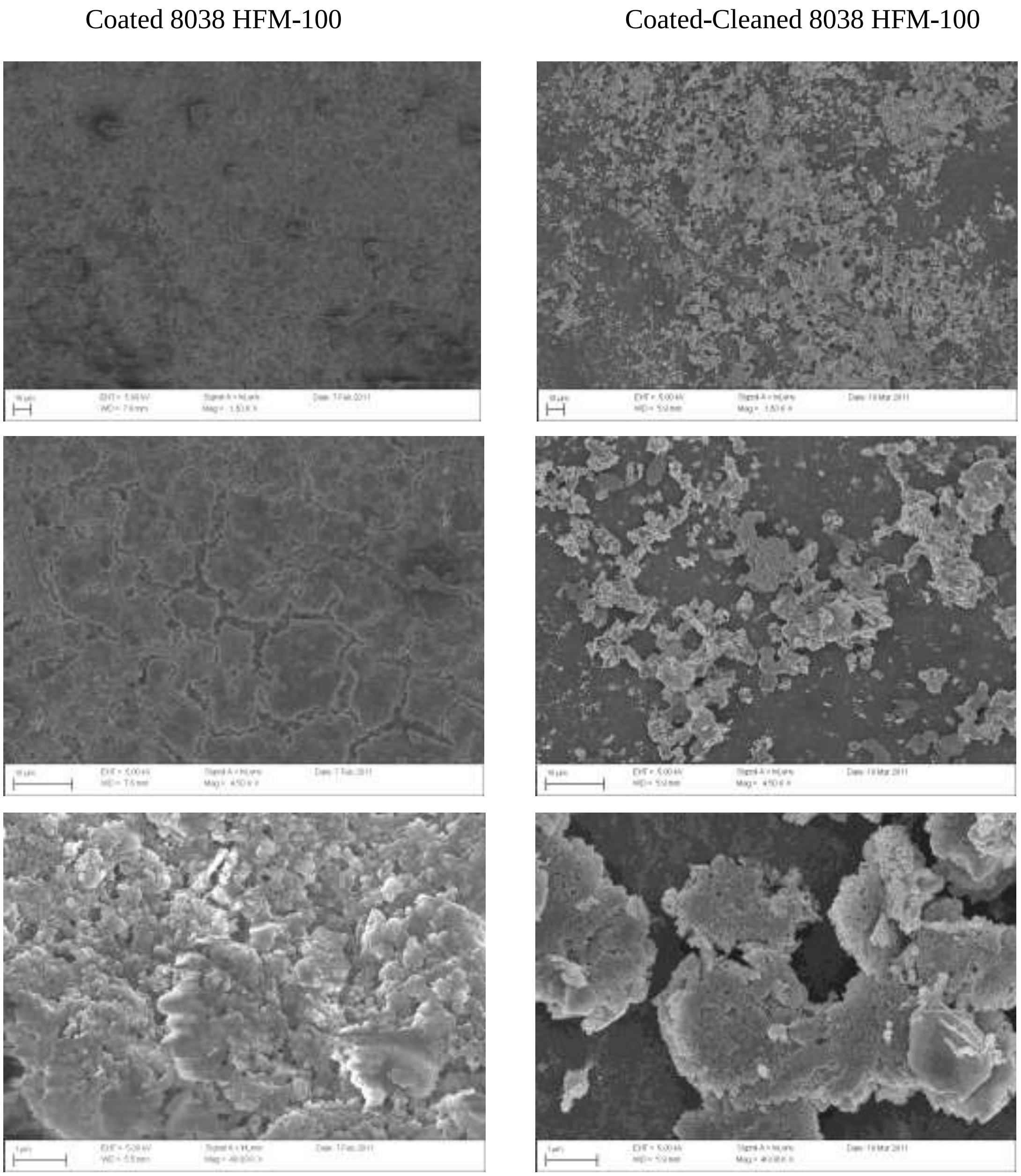
SEM images were taken for RO and spiral UF membranes obtained during the autopsy of the membrane elements. SEM pictures of smaller to larger magnification are arranged top down in Figure 23 and 24. Both coated and non-coated SWC3+ membranes retained their original surface morphology. The surface looks clean for these RO membranes. No specific deposits were found on the scanned samples. On the other hand, the coated spiral UF membrane (8038 HFM-100) surface was fully covered with colloidal clusters, which were composed of small nodular lumps about 100 nm in size. The original porous structure of the PVDF membrane was totally covered by the fouling layer. This fouling layer was mostly removed by CIP cleaning using caustic and citric cleaning mediums. The FTIR data very much corroborates the SEM examination.



Non-coated SWC3+

Coated SWC3+

Figure 23: SEM images for non-coated RO (left) and coated RO (right) at various magnification levels (1.3k, 4.5k, 40k, top down)



Coated 8038 HFM-100

Coated-Cleaned 8038 HFM-100

Figure 24: SEM images for coated 8038-HFM UF membrane. Left column represents fouled and non-clean membrane surface. Right column represent fouled membrane after a clean process that included several hours of wash with caustic and citric. Top down represent various magnification levels (1.3k, 4.5k, 40k).

4. Conclusions and Recommendations

4.1 Pilot Summary

PDOPA coating technology was tested on hollow fiber ultrafiltration PAN membranes (U630C, Ultra-Flo), spiral ultrafiltration PVDF membranes (8038 HFM-100, Koch), and seawater reverse osmosis membranes (SWC3+, Hydranautics) in the application of treating shale "frac" flowback water. Parallel tests were performed on hollow fiber UF membranes with coated and non-coated elements. Parallel tests for SWRO membranes were conducted by running coated and non-coated elements alternately. Only coated spiral UF membranes were tested in this pilot due to skid limitations.

Feed water supplied to the membrane systems was a blend of shale gas frac flow-back and produced water pretreated via coagulation/flocculation and gravitational settling. This water was rich in organic substances (soluble and insoluble), suspended solids, hardness, barium, sulfate, salinity, bacteria and was acidic in nature. Raw water quality fluctuated greatly during the entire pilot time span.

For the parallel tests on hollow fiber UF and SWRO, coated membranes demonstrated improved performances over their virgin non-coated counterparts without any loss of flux due to coating. Coated hollow fiber UF membranes gave about 50% more water productivity than the non-coated ones. Cleaning operations were more efficient in recovering flux and pressure for the coated membranes. Coated seawater RO membranes achieved better salt rejection than non-coated membranes. Under the circumstances of very high salt concentrations, non-coated SWC3+ membranes experienced significant decline in salt rejection, while coated SWC3+ membranes maintained salt rejection values above 99.5%. No noticeable flux decrease was observed on both coated and non-coated SWRO membranes for this pilot. However, FTIR spectra of the used membrane samples indicated a thin fouling layer on both coated and non-coated RO surfaces, while coated sample had less foulant deposition than the non-coated membrane sample. Therefore, in conclusion, dopamine coated SWC3+ outperformed the non-coated membrane with higher salt retention and lower fouling potential and higher flux for UF stage.

Coated spiral UF membranes achieved sustainable performance in treating this produced water, although they required chemical enhanced cleaning operations a few times a day to maintain high (35 GFD) flux. Simple acid and base enhanced hot water cleaning can efficiently recover the flux, while full standard CIP was occasionally needed. Foulants found on the membrane surfaces were mainly organic in nature. Considering the challenging raw water quality in this pilot test, this type of spiral UF membrane still demonstrated a relatively more easily cleaned surface property following application of a PDOPA/PEG coating.

4.2 Key Notes from the Pilot

(1) It is obvious that hollow fiber UF is a more efficient and easily maintained module than spiral wound configuration. Chemically enhanced HWC was only required every 12 hours for hollow fiber elements, while the cleaning frequency for spiral elements was every 4-6 hours. Routinely built-in backflush on the hollow fiber system maintained the flux in a more stable range than that of the spiral elements.

(2) The high salinity of this produced water hampered the productivity of the RO procedure. With feed TDS value at 25,000 mg/L, 580 PSI feed pressure can achieve 50% recovery on water production. When feed TDS went above 50,000 mg/L, 800 PSI feed pressure can only achieve 15% recovery. In this case, one stage RO process becomes very inefficient and highly energy consumable in treating shale produced water.

Nanofiltration (NF) membranes are widely used in brackish and seawater desalination. NF offers many advantages over RO in cases of high salinity feed, such as high flux with lower operating pressure, high retention of multivalent anions (Ca, Mg, Ba, Sr) and organic matter. Two-stage NF or using NF as RO pretreatment are frequently practiced in seawater desalination. Overall seawater TDS can be cut by 57 %, while 93% of total hardness can be removed by one time pass of NF. The permeate obtained with NF would be much easier to treat by RO or a second stage of NF. It was reported that this integrated desalination system reduces the seawater desalination cost by 20-30% compared to conventional SWRO [22, 23] and 70% water recovery is possible from NF pretreated SWRO [24].

Recognizing the enhanced salt retention property of dopamine coated RO membranes in this pilot, we expect this coating technology would boost NF membrane salt rejection by a considerable amount while the high permeation of the nanofiltration process could still be retained while simultaneously providing better anti-fouling characteristics for sustained, long term operation.

Two stages of dopamine coated nanofiltration or one stage of coated NF followed by another stage coated SWRO is highly recommended to optimize the membrane filtration productivity for shale produced water treatment.

4.3 Future Work Recommendation

Based on this short-term pilot study, future pilot studies and research should be considered:

(1) A relatively long-term pilot should be considered for further evaluating the UF/RO dopamine coating technology in the application of shale produced water treatment. A twelve months run time is recommended for this long-term pilot using a two stage NF + NF or NF + RO system. In addition, for optimum operation for pre-treatment, we recommend testing of both MF and UF prior to RO using outside-in membranes. RO membrane fouling is expected to occur during longer tests, and CIP recovery will provide more membrane cleaning efficacy for coating technology. Optimal membrane cleaning and system maintenance methods will also be resolved in such a pilot test. The cost of reclaimed water production from shale produced water can be accurately estimated from such pilot.

(2) Water quality needs to be routinely investigated for the next stage pilot test. Parameters like TOC and TPH should be more frequently monitored during the entire pilot test.

(3) Membrane filtration systems should be designed with the objectives set forth in bullet #1. We recommend that the future pilot test use hollow fiber ultrafiltration and microfiltration membranes, and add at least one stage of nanofiltration membranes as the pretreatment for reverse osmosis process. This change can maximize the productivity of the permeate to the maximum extent possible. Meanwhile, maintenance work will be significantly reduced. With the help of this

innovative anti-fouling coating technology, UF and multi-stage NF/RO or NF/NF membrane filtration, we expect to enable cost effective treatment of produced water to solve the water reuse problem in shale produced water.

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