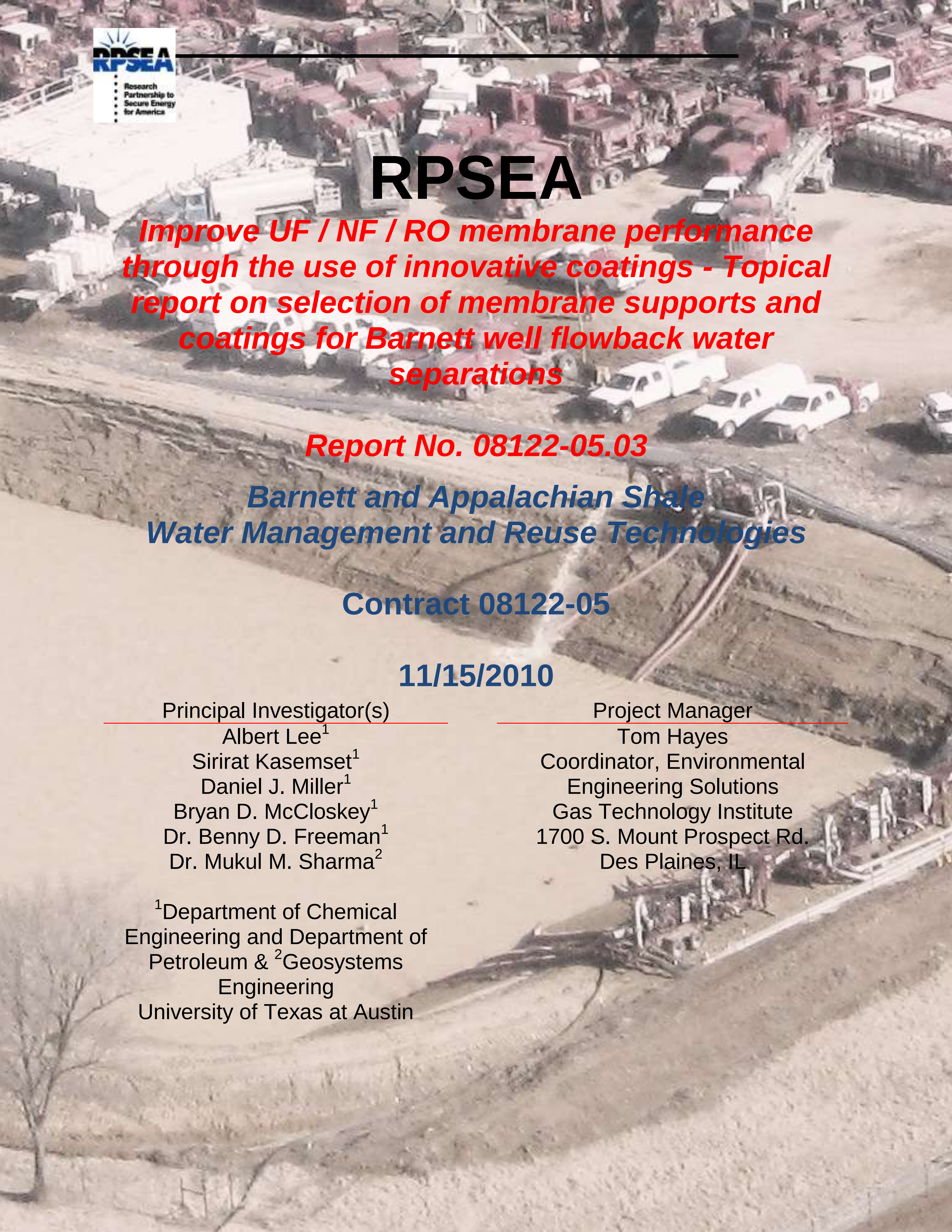

RPSEA

Improve UF / NF / RO membrane performance through the use of innovative coatings - Topical report on selection of membrane supports and coatings for Barnett well flowback water separations

Report No. 08122-05.03

Barnett and Appalachian Shale Water Management and Reuse Technologies

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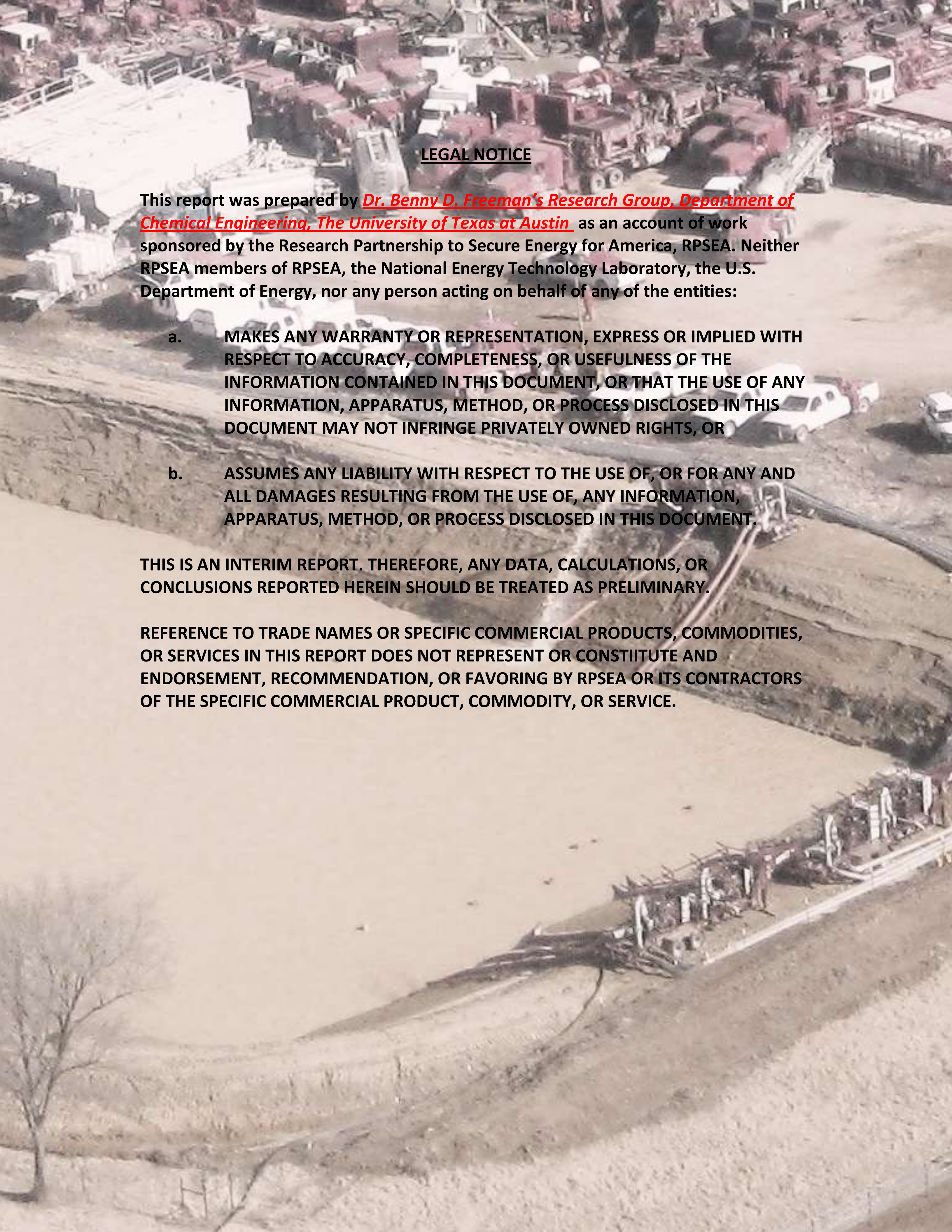

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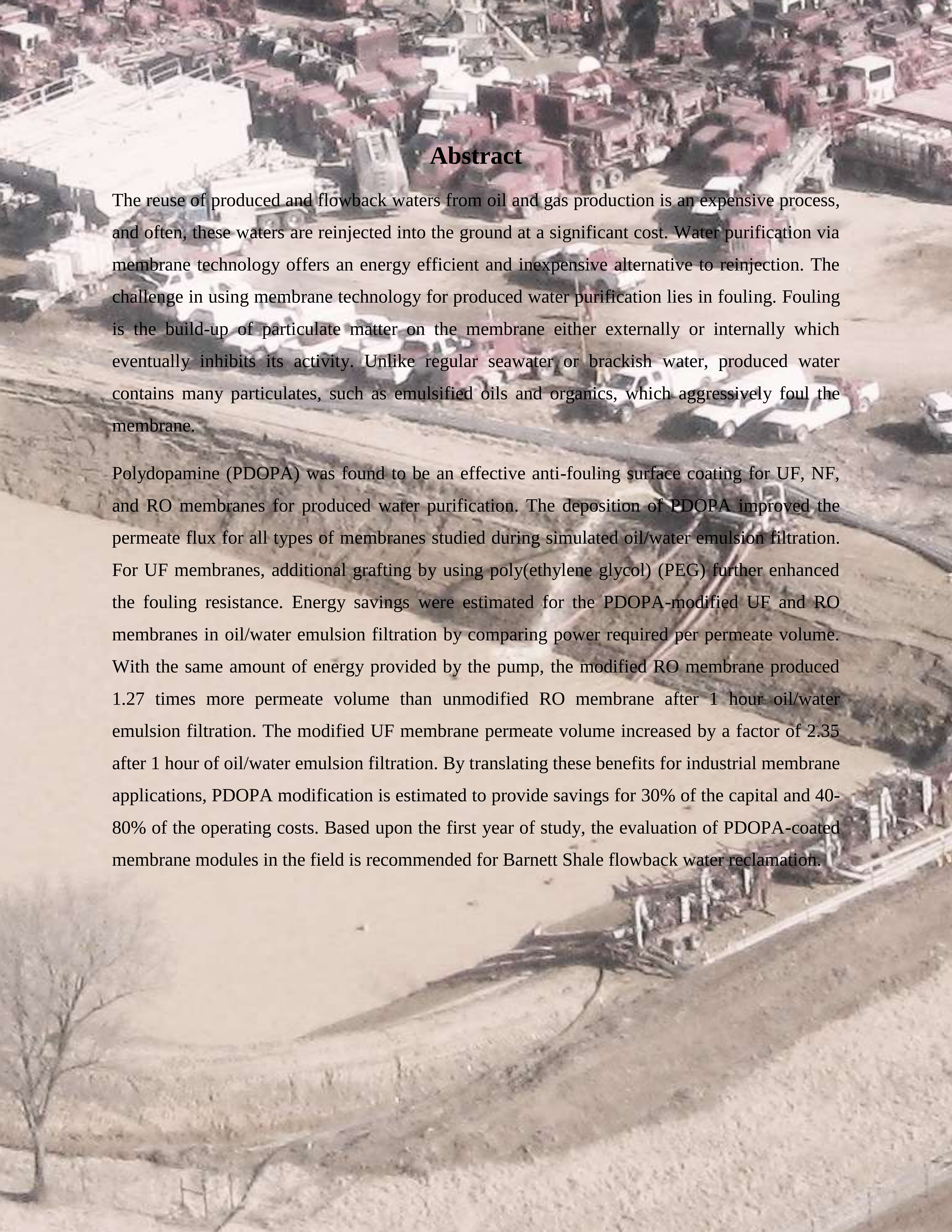
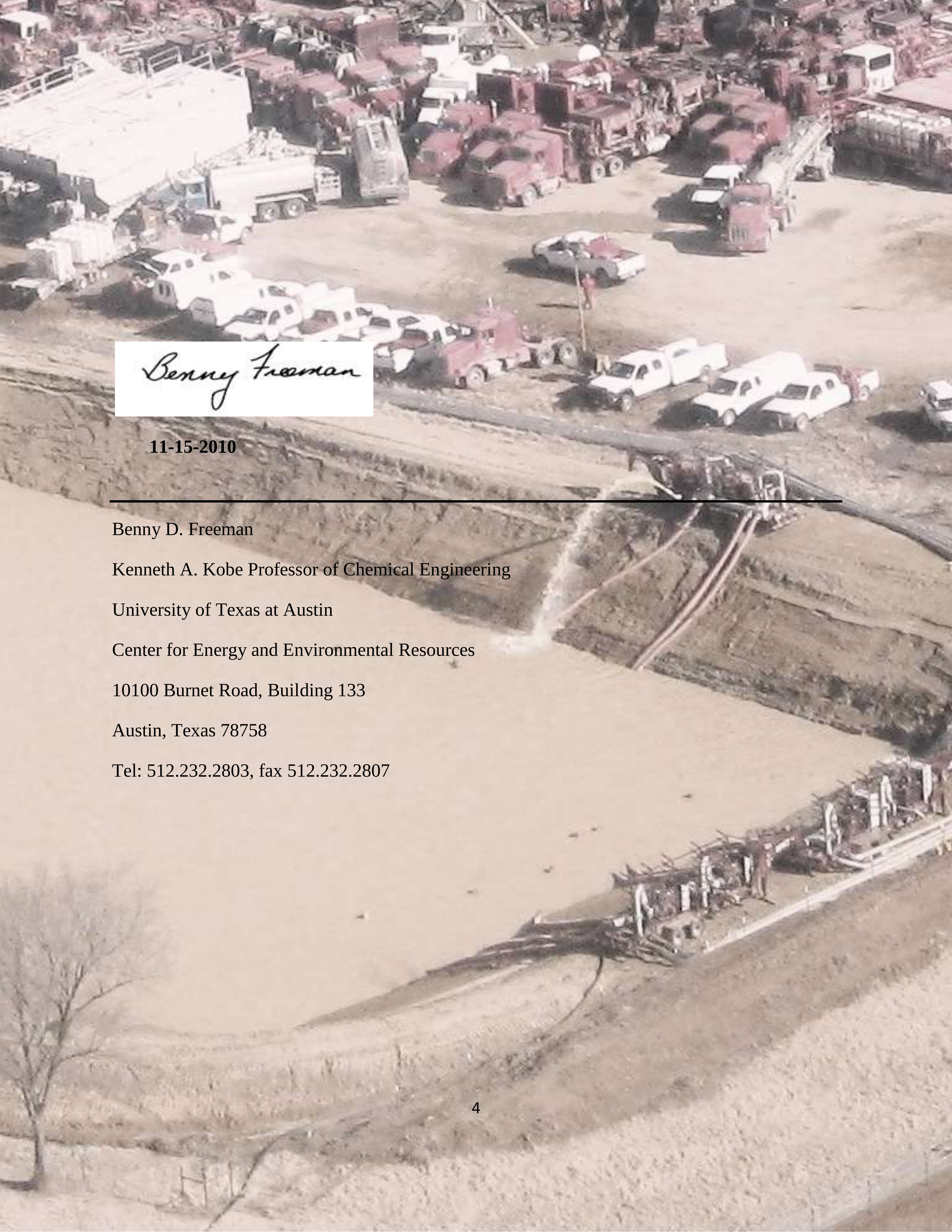


Abstract

The reuse of produced and flowback waters from oil and gas production is an expensive process, and often, these waters are reinjected into the ground at a significant cost. Water purification via membrane technology offers an energy efficient and inexpensive alternative to reinjection. The challenge in using membrane technology for produced water purification lies in fouling. Fouling is the build-up of particulate matter on the membrane either externally or internally which eventually inhibits its activity. Unlike regular seawater or brackish water, produced water contains many particulates, such as emulsified oils and organics, which aggressively foul the membrane.

Polydopamine (PDOPA) was found to be an effective anti-fouling surface coating for UF, NF, and RO membranes for produced water purification. The deposition of PDOPA improved the permeate flux for all types of membranes studied during simulated oil/water emulsion filtration. For UF membranes, additional grafting by using poly(ethylene glycol) (PEG) further enhanced the fouling resistance. Energy savings were estimated for the PDOPA-modified UF and RO membranes in oil/water emulsion filtration by comparing power required per permeate volume. With the same amount of energy provided by the pump, the modified RO membrane produced 1.27 times more permeate volume than unmodified RO membrane after 1 hour oil/water emulsion filtration. The modified UF membrane permeate volume increased by a factor of 2.35 after 1 hour of oil/water emulsion filtration. By translating these benefits for industrial membrane applications, PDOPA modification is estimated to provide savings for 30% of the capital and 40-80% of the operating costs. Based upon the first year of study, the evaluation of PDOPA-coated membrane modules in the field is recommended for Barnett Shale flowback water reclamation.



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11-15-2010

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Table of Contents

Chapter 1: Introduction

Water Scarcity

Covering over 70% of the Earth's surface, water is an abundant resource. However, with the oceans accounting for 97% of this water and much of the fresh water located far below ground or frozen in icecaps and glaciers, less than 1% of the world's water is readily accessible as fresh water for human consumption[1]. Today, according to the World Health Organization (WHO), over one billion people around the world do not have access to clean water, and this number is expected to grow exponentially[2]. To meet these additional demands for clean water, the challenge is finding an economic treatment method for water sources accessible in large quantities around the world such as seawater, brackish water, and produced water[1],[3].

Produced Water

With the rise of the oil and gas industry around the world, one water source has become readily available: produced water. Produced water is a byproduct of oil and gas production that is typically composed of dispersed oil, organics, salts, metals, treatment chemicals such as scale and corrosion inhibitors, coagulants to remove solids, and emulsion breakers[4]. In 1999 alone, over 77 billion barrels of produced water was created, about 7 times the production of oil[3]. This water is usually considered unfit for municipal use and is reinjected into the ground at significant cost. Moreover, since produced water varies in composition and is difficult to treat, the cost of purification is still higher than the cost of reinjection. Due to produced water's presence in especially in water stressed areas of the world, purification and reuse of this water would be a major step in solving water scarcity

Water Purification Technologies

In water purification, desalination to treat brackish water and seawater used to be dominated by thermal techniques: evaporating the water into vapor, thereby separating out the salt[4]. This method consumes a large amount of energy. Consequently, using such thermal techniques to achieve produced water purification is expensive. Oil and gas production companies often avoid this purification method and choose to reinject the water at a lower cost. Since the late 1990s, membrane-based desalination, which treats water by a selective membrane layer, has become the most economical choice for conventional desalination of, for example, brackish and seawater. These membranes for water purification can discriminate contaminants according to size, and their relatively low use of energy, around ten percent of thermal purification, makes them an economic choice over thermal desalination[2]. The majority of the desalination plants being constructed today employ membrane technology. By translating these economic benefits, membrane technology is an avenue worth exploring to produce water purification.

Fouling

The major challenge in purifying produced water with membranes is fouling. Fouling, as shown on Figure 1, is the build-up of particulate matter on the membrane either externally or internally which eventually inhibits its activity. Internal fouling occurs when foulants clog the pores of the membranes. External fouling occurs when foulants build up on the surface of the membrane. Unlike regular seawater or brackish water, produced water contains of many particulates, such as emulsified oils and organics, and the membrane surfaces in contact with such a mixture can undergo this process. This accumulation of foreign material on the membrane hinders the flow of water through the membrane, which in turn drives up the cost of operation[5].

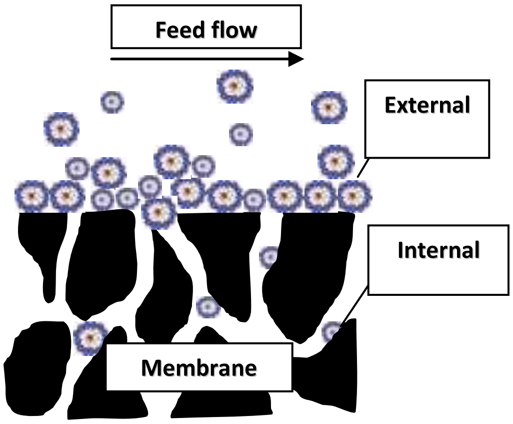

Figure 1. Particulate fouling in porous water purification membranes.

Membrane Selection

Liquid purification membranes are often categorized by their ability to discriminate particulate size. As shown in Figure 2, the four main categories of water purification are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO).

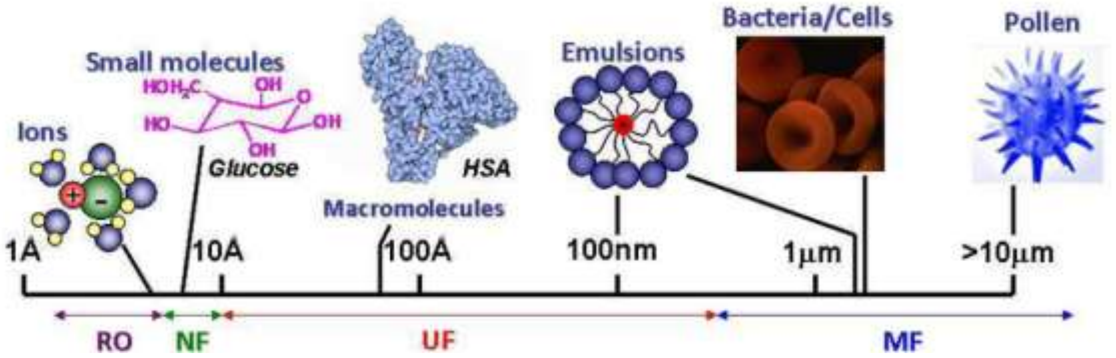

Figure 2. Membrane classification according to size-sieving ability.

Since the most cost effective purification would be to purify the water in one step (removing most of the organics and salts), the main type of membrane used in produced water purification is the reverse osmosis (RO) membrane, as is such in desalination. Highly size-sieving, RO membranes can purify many salts and organics that are present in produced water. Unfortunately, RO membranes suffer from heavy fouling when treating produced water for extended periods of time. Because of the nonporous nature of RO membranes, this fouling occurs mostly on the surface. Consequently, surface modification by changing the fouling characteristics on the surface of commercial RO membranes is a major focal point of this research.

Chapter 2: Background

Polydopamine (PDOPA)

A novel approach to improve fouling resistance of the membranes is surface coating by using polydopamine (PDOPA). Polydopamine is a polymer of dopamine (DOPA), which is a naturally-occurring hormone and neurotransmitter. The proposed structure of dopamine is shown in Figure 3. Messersmith et al.[6] 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 is not known. However, Messersmith's suggested structure of polymerized dopamine or polydopamine is shown in Figure 3.

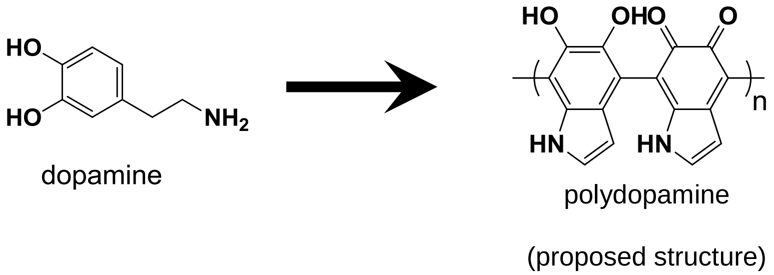

Figure 3. Dopamine and polydopamine structure. The exact structure of polydopamine is currently unknown; this structure was proposed by Messersmith et al.[6]

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.

Polydopamine Coated Membranes

A PDOPA-coated membrane shows two advantages over an uncoated 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.[7] 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.

Membrane Pretreatment

A UF membrane was prepared for PDOPA modification by immersing in isopropyl alcohol for 10 minutes to wet the membrane pores. After that, the membrane was immersed in deionized water for 30 minutes to completely replace the alcohol in the pores.

Similarly, NF and RO membranes were prepared by soaking in 25% (v/v) aqueous isopropyl alcohol solutions for 20 minutes to remove any extractable components (e.g., glycerin) and wet the membrane pores. Then the membranes were soaked in deionized water which was changed three times. Finally, they were stored in deionized water overnight (16-24 hours) prior to PDOPA modification.

Membrane Coating Procedure

The membranes were coated with PDOPA by immersing their active layers in an aqueous dopamine solution as shown in Figure 4. The coating process was performed by placing the membrane (with its active surface face up) on a glass plate and securing the membrane to a glass ring by applying vacuum grease on the outer edge. Then the dopamine (DOPA) solution was poured into the glass ring (in contact with the membrane surface) and the glass plate was placed on a rocking platform shaker to provide even coverage on the membrane. The dopamine solution was prepared from dopamine hydrochloride in 15 mM Tris-HCl buffer. Typically, a dopamine concentration of 2 mg/mL was used with a Tris-HCl buffer pH of 8.8 and the deposition lasted 45 and 30 minutes for UF and NF/RO membranes respectively. After that, the membrane was rinsed thoroughly with deionized water for 2-3 times and stored in deionized water before use.

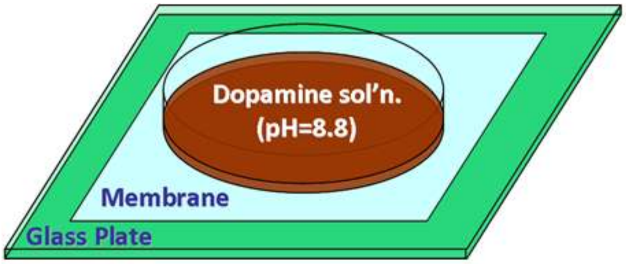

Figure 4. Polydopamine deposition technique.

To further enhance the hydrophilicity of the PDOPA-coated surface, a common fouling-resistant polymer, poly(ethylene glycol) was grafted to polydopamine by using methyl-terminated poly(ethylene glycol) amine (mPEG-NH_2, MW = 5 kDa) as shown in Figure 5. The grafting process was performed by immersing the PDOPA-coated membrane in 1 mg/mL solution of PEG-NH_2 at 60°C. The grafting time was 60 and 30 minutes for UF and NF/RO membranes respectively. The PEG-NH_2 solution was prepared from PEG-NH_2 in 15 mM Tris-HCl buffer at pH 8.8. The PDOPA-g-PEG-modified membrane was then rinsed and stored in deionized water until use.

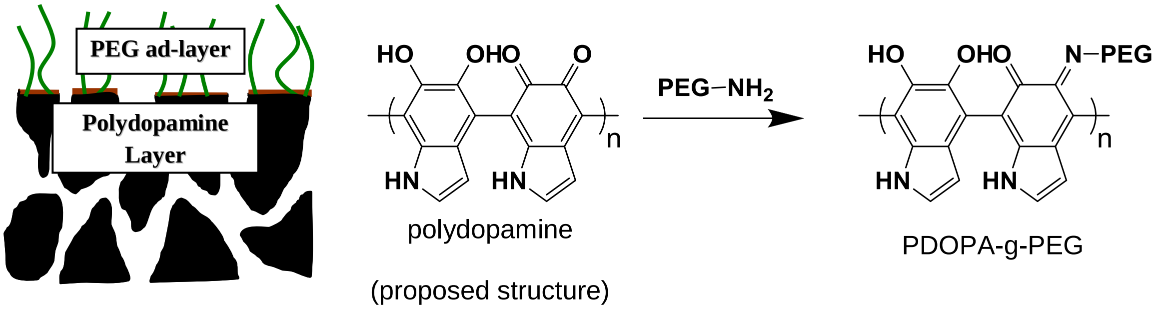

Figure 5. Conjugation of PEG-NH_2 to polydopamine surface at pH 8.8.

Effect of Surface Properties on Fouling

Membrane surface modification is an approach to improve anti-fouling properties. This method can help prevent irreversible internal membrane fouling which cannot be eliminated via cleaning processes or an optimization of operating conditions (i.e. adjusting fluid dynamics on the membrane surface). The factors identified in this research to influence surface fouling are hydrophilicity and roughness of the membrane surface[8].

Generally, the effect of hydrophilicity of the membrane on fouling depends on specific characteristics of the foulants. In the case of hydrophobic foulants (e.g. oil), the increase in membrane hydrophilicity helps reduce membrane fouling through a limitation in hydrophobic interactions on the surface. In addition, the surface hydrophilicity helps increase the affinity of water for the membrane and results in the higher water flux.

The surface roughness represents the peaks-and-valleys morphology of the membrane surface. Membranes with higher roughness tend to promote fouling because the foulants are easily accumulated in the valleys of the rough membrane. This valley clogging will block the surface area of the membrane, create mass transfer resistance, and reduce the permeate flux.

Chapter 3: Experimental Results

Constant transmembrane pressure (TMP) crossflow filtration

The fouling study was done via a constant transmembrane pressure (TMP), variable flux crossflow filtration system as shown in Figure 6. The model feed solution contained an oil/water emulsion of 1350 ppm soybean oil and 150 ppm DC193 non-ionic surfactant. In case of NF and RO membranes, 2000 ppm NaCl was added to the feed solution to study salt rejection of the membranes. The permeate flux was evaluated as a function of time to determine fouling characteristic of the membranes. Different crossflow rates, TMP, and filtration time were used for different types of membranes as tabulated in Table 1.

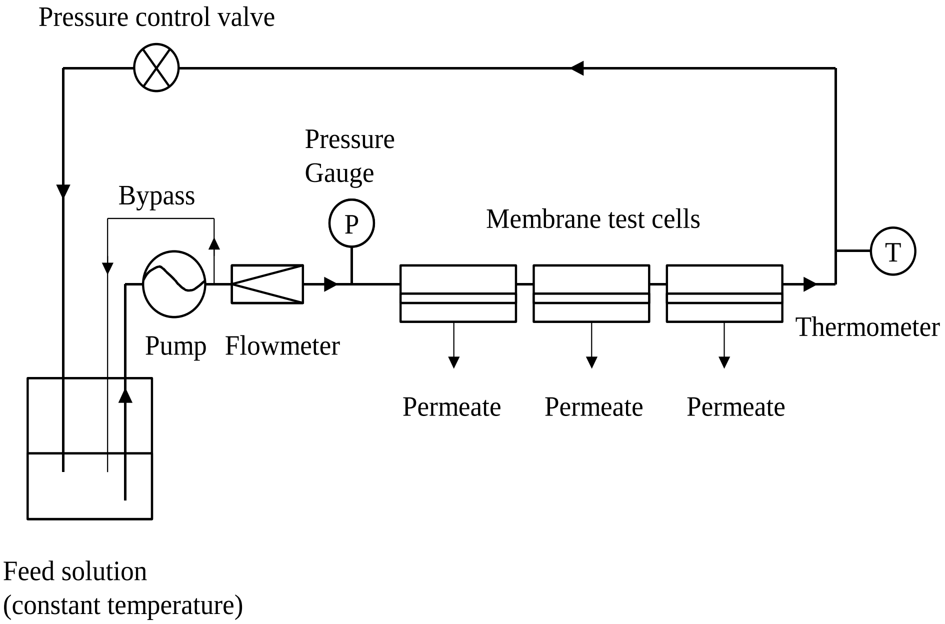

Figure 6. Constant TMP crossflow filtration system.

Table 1. Crossflow rates, TMP, and filtration time for each membrane type

Membrane type	**Crossflow rate (L/min)**	**TMP (atm)**	**Filtration time (hour)**
UF	0.8	2.1	1
NF/RO	3.8	10.2	24

Emulsified oil fouling measurements

Two classifications of membranes with different polymer types were selected in this experimental set as listed in Table 2. They were chosen according to their industrial relevance. McCloskey et al.[7] completed a number of crossflow experiments to determine the fouling resistance of PDOPA-modified membranes and PDOPA-g-PEG-modified membranes. The experimental results are shown in Figure 7.

Table 2. Commercial membranes used in this study

Classification	Membrane polymer	Manufacturer	Pore size	Flux [LMH/bar]	Study ID
UF	Polysulfone	Sepro (PS-20)	~20 kDa MWCO	1000	PS-20 UF
UF	Polyethersulfone	Sepro (PES-30)	~20 kDa MWCO	300	PES UF
NF	Polyamide	Dow (NF-90)	N/A	12.3	NF-90
RO	Polyamide	Dow (XLE RO)	N/A	7.7	XLE RO

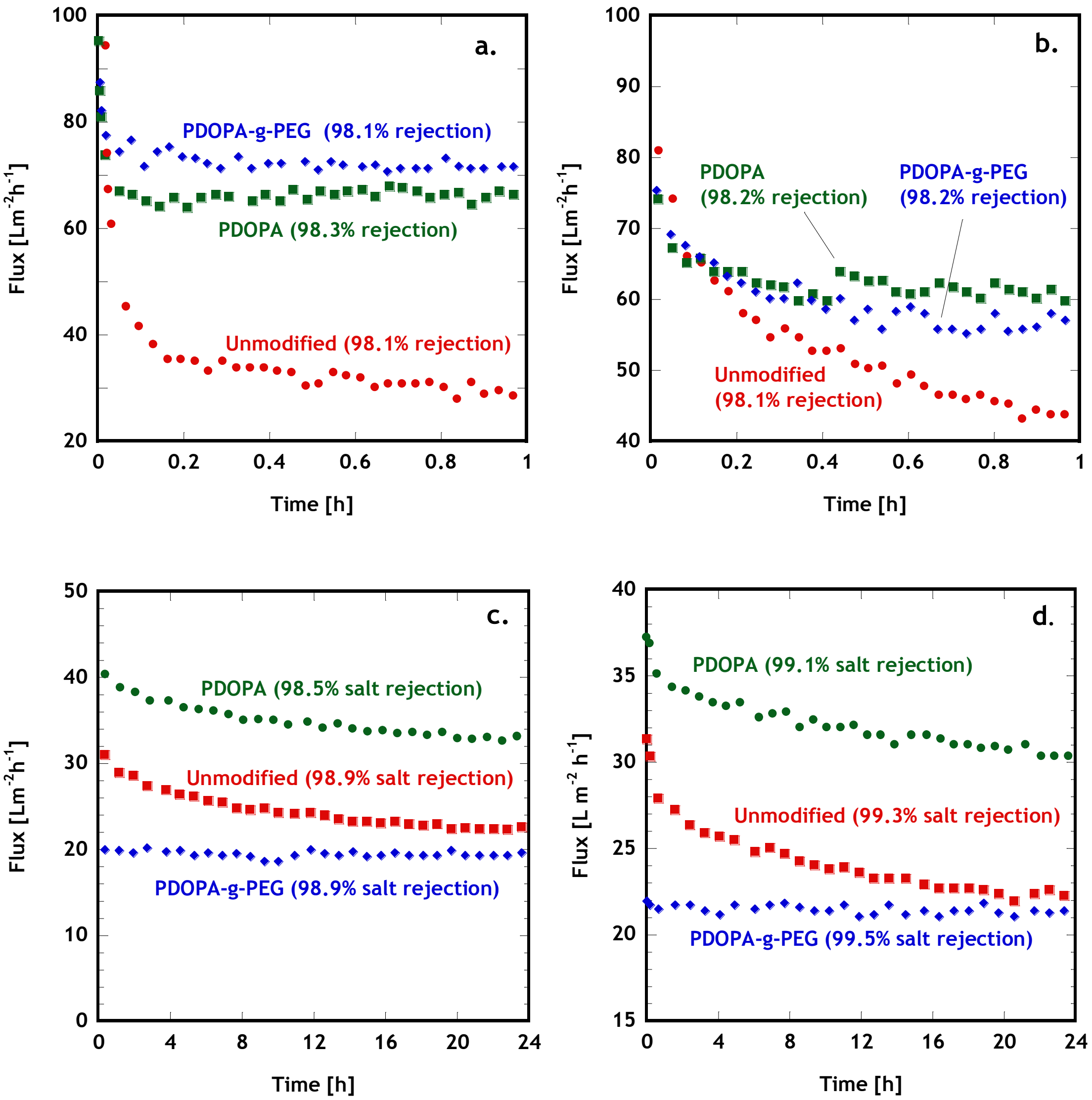

Figure 7. Effect of filtration time on membrane flux using unmodified, PDOPA-modified, and PDOPA-g-PEG-modified: a. PS-20 UF, b. PES UF, c. NF-90, and d. XLE RO membranes to filter oil/water emulsion. Rejection values (organic rejection for UF membrane, salt rejection for NF and RO membranes) were measured at the end of the filtration.

In the oil/water emulsion fouling experiments, the permeate flux of the membranes decreased over the duration of the experiments. In all cases, the PDOPA-modified membranes showed significant improvement in steady-state flux over that of the unmodified membranes.

Grafting PEG onto the PDOPA coating slightly enhanced the permeate flux of the PS-20 and PES UF membranes from that of the PDOPA-modified versions. On the other hand, the RO and

NF membranes produced lower permeate flux after they had been grafted with PEG. PEG coating adds an additional layer with mass transfer resistance. For membranes with pores, such as UF membranes, the added mass transfer resistance is small compared to the increase in hydrophilicity which enhances the permeate flux. However, the membranes with very small or no pores such as NF or RO membranes suffer from large additional mass transfer resistance introduced by the PEG grafting.

Effect of Surface Modification Conditions

In the previous section, PDOPA was shown to be an effective coating to improve membrane fouling resistance. This experimental set studied the effect of PDOPA modification conditions on the fouling behavior of the modified membranes. DOPA concentration, pH of Tris-HCl buffer, and PDOPA deposition time were the parameters used in this study.

The standard protocol of PDOPA membrane coating used a DOPA concentration of 2 mg/mL, Tris-HCl buffer solution of pH 8.8, and deposition time of 60 minutes. In this study, further modification conditions were investigated as listed in Table 3.

The experiments were conducted with polyamide RO membrane (XLE RO) from Dow Filmtec. The membrane pretreatment method and oil/water emulsion fouling crossflow tests were conducted using the same protocol as described in the earlier section.

Table 3. Summary of PDOPA polymerization conditions for membrane modification.

Dopamine concentration (mg/mL)	0, 0.1, 0.5, 2, 4, 8
Tris-HCl buffer pH	5, 8.8, 11
Deposition time (min)	30, 60, 120

*Underline indicates conditions used in previous section

Dopamine concentration study

XLE RO membranes were modified at five different concentrations of dopamine in Tris-HCl buffer solution at pH 8.8 and with deposition time of 60 minutes. The dopamine concentration was varied from 0 (control), 0.1, 0.5, 2, 4, to 8 mg/mL.

Corresponding to the previous results, all PDOPA-modified membranes showed higher permeate flux than that of the unmodified membrane. As shown in Figure 8a, the membranes modified with different DOPA concentrations showed little variation in the permeate flux during oil/water emulsion filtration. In Figure 8b, the increase in DOPA concentration reduced the pure water flux of the membranes.

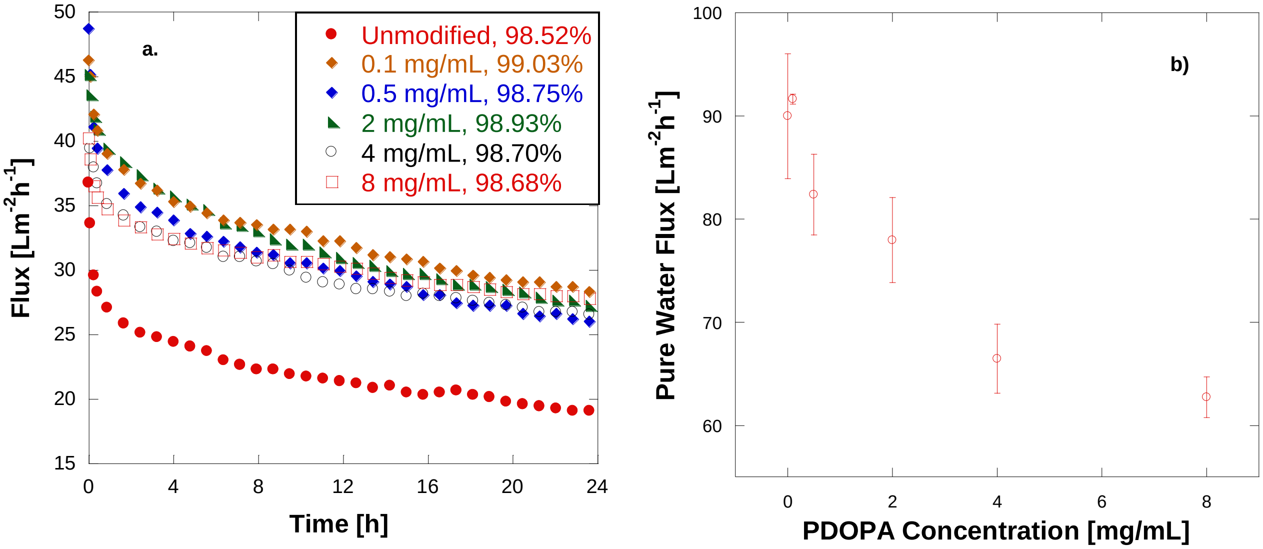

Figure 8. a. Effect of filtration time on membrane flux using unmodified and PDOPA-modified membranes at different DOPA concentration during oil/water emulsion filtration. The salt rejection is reported in the legend. b. Pure water flux versus DOPA concentration used during modification.

Higher DOPA concentrations used in modification results in thicker PDOPA layers on the membrane surface. This layer creates additional mass transfer resistance which reduces the pure water flux. However, during oil/water emulsion filtration, this behavior was not observed.

Tris-HCl buffer pH study

XLE RO membranes were modified at two different pH values (8.8 and 11) of Tris-HCl buffer using dopamine concentration of 2 mg/mL and with deposition time of 60 minutes. As shown in Figure 9, preliminary study of Tris-HCl buffer at pH 5 showed no observable polymerization reaction of polydopamine. At this pH, there was no visible coating layer formed on the membrane surface. Therefore, the buffer solution at pH 5 was not considered in this study.

Figure 9. DOPA in Tris-HCl buffer solution at pH 8.8 and 5.The dark brown color at pH 8.8 indicates that the polymerization of dopamine occurs, while there is no visible polymerization at pH 5.

As shown in Figure 10, PDOPA-modified membranes showed improved permeate flux relative to an unmodified sample. Little difference in flux was observed during oil/water emulsion filtration between the membranes modified at pH 8.8 and 11.

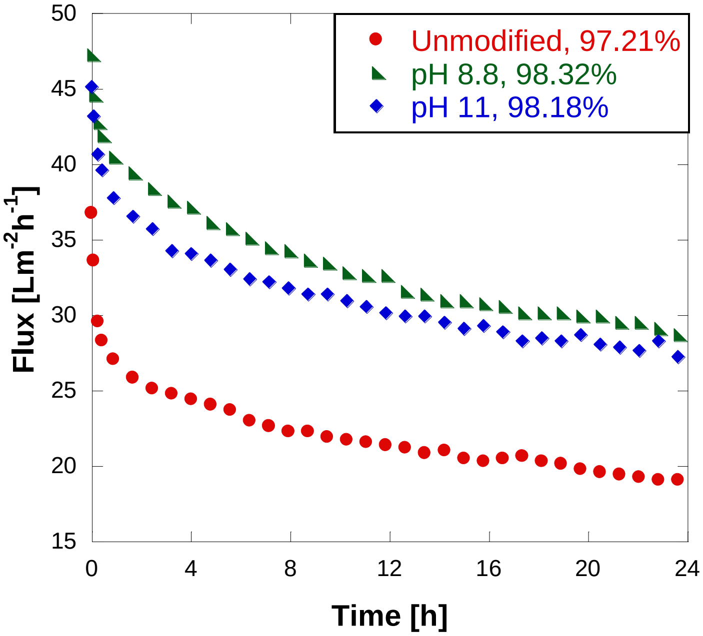

Figure 10. Effect of filtration time on membrane flux using unmodified and PDOPA-modified membranes at different pH during oil/water emulsion filtration. The salt rejection is reported in the legend.

Deposition time study

XLE RO membranes were modified at three different deposition times by using 2 mg/mL dopamine solution in Tris-HCl buffer solution at pH 8.8. The deposition time was varied from 0, 30, 60 (control), to 120 minutes.

The results in Figure 11 show that the membrane modified with 30 minutes deposition time had slightly lower permeate flux than that of 60 and 120 minutes. The different deposition time of 60 and 120 minutes did not have a significant effect on the permeate flux throughout the oil/water emulsion fouling experiments.

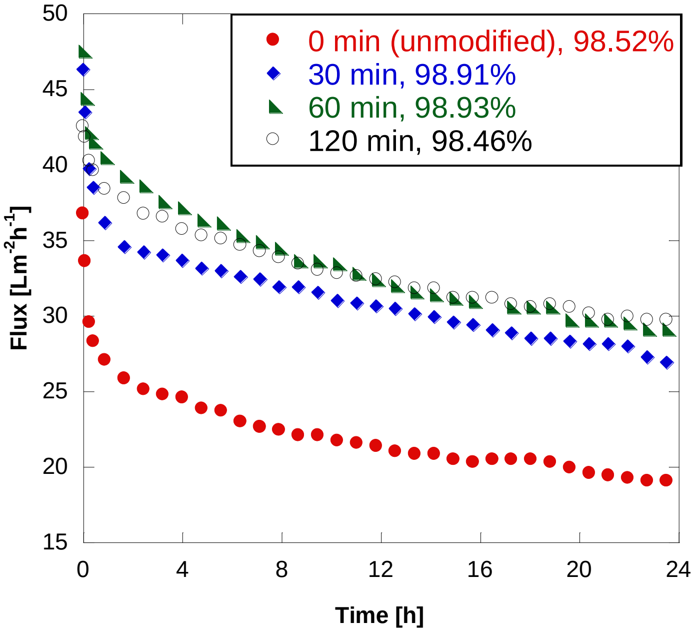

Figure 11. Effect of filtration time on membrane flux using unmodified and PDOPA-modified membranes at different deposition time during oil/water emulsion filtration. The salt rejection is reported in the legend.

Energy Savings

One benchmark of improved membrane performance is reduced energy use. Most of the energy consumed in a membrane process is the power required for the feed pumps. Feed flow rate and transmembrane pressure are used to estimate the power per unit permeate volume using Equations (1), (2) and (3) [9]

$$\dot{P}_{\text{output}} = Q_F \left(p_F - p_{ATM} \right) = Q_F \Delta p \tag{1}$$

$$\dot{P}_{\text{input}} = \frac{\dot{P}_{\text{output}}}{\eta} = \frac{Q_F \Delta p}{\eta} \tag{2}$$

$$\frac{\dot{P}_{\text{input}}}{Q_P} = \frac{Q_F}{\eta Q_P} \Delta p = \frac{E}{\eta V_P} \tag{3}$$

where $\dot{P}_{\text{input}}$ = Pump power input required to operate the membrane system

$\dot{P}_{\text{output}}$ = Pump power output ; η = Pump efficiency

Q_F = Feed flow rate ; Q_P = Permeate flow rate

p_F = Feed pressure ; p_{ATM} = Atmospheric pressure

Δp = Pressure drop across membrane ($\approx$ total pump dynamic head)

E = Energy required for membrane operation

V_P = Permeate volume

To compare the performance of polydopamine-treated membranes (case 2) with unmodified membranes (case 1), we calculated the ratio of energy used per unit volume of permeate of both membranes by using Equation (4). We assumed that the pump efficiency and feed flow rates in both cases were the same.

$$\frac{\left(\frac{\dot{P}_{\text{input}}}{Q_P}\right)_1}{\left(\frac{\dot{P}_{\text{output}}}{Q_P}\right)_2} = \frac{\frac{Q_{F1}}{\eta Q_{P1}}\Delta p}{\frac{Q_{F2}}{\eta Q_{P2}}\Delta p} = \frac{Q_{P2}}{Q_{P1}} \tag{4}$$

Figure 12 shows the flux ratio of PDOPA modified to unmodified membranes during oil/water emulsion filtration. All membranes were modified by using 2 mg/mL of dopamine, 60 minutes of deposition time, and Tris-HCl buffer solution pH at 8.8.

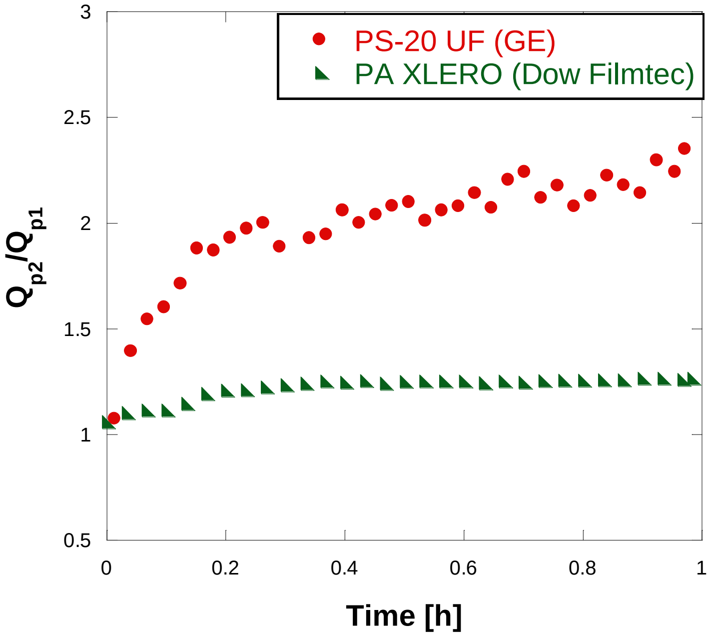

Figure 12. Flux ratio of PDOPA modified to unmodified membranes during oil/water filtration. RO membranes were tested at transmembrane pressure difference = 10.2 atm, crossflow rate = 3.8 L/min. UF membranes were tested at transmembrane pressure difference = 2.1 atm, crossflow rate = 0.8 L/min. 1500 ppm soybean oil/DC193 (non-ionic surfactant)/water emulsion was used as fouling solution.

Table 4. Comparison of flux ratio of PDOPA-modified to unmodified membranes after 1 hour oil/water filtration

	PS-20 UF membrane (GE)	**PA XLERO membrane (Dow FilmTec)**
Q_{p2}/Q_{p1} after 1 hour of filtration	2.35	1.26

The comparison of the final flux ratios after 1 hour clearly shows the energy advantages of PDOPA-modified membranes. At the same transmembrane pressure, the modified membranes produced much greater amounts of permeate than that of the unmodified membranes. The modified PA XLERO permeate volume increased by a factor of 1.26, and the modified PS-20 UF membrane permeate volume increased by a factor of 2.35 during oil/water filtration. This increase in permeate flux can translate directly into energy savings at an industrial level.

Table 5. Typical capital and operating cost breakdown for membrane plants[10]

Capital Costs	%
Pumps	30
Membrane Modules	20
Module Housings	10
Pipes, Valves, Frame	20
Controls/Other	20
Total	100
Operating Cost	%
Membrane Replacement	30-50
Cleaning Costs	10-30
Energy	20-30
Labor	15
Total	100

Table 5 shows a typical breakdown of a membrane plant capital and operating costs. By applying the anti-fouling PDOPA modification, many of these costs can be significantly reduced. The enhanced permeate flux that the PDOPA modified membranes provide in oil/water emulsion filtration provides two distinct benefits. The membrane modules and housings used in the plant can be smaller in size while maintaining high water purification capability. Additionally, in operation, the energy devoted to operating the membranes (mostly in providing power to the pumps) can be reduced. The improved anti-fouling properties of the PDOPA membranes also provide additional benefits in operating costs. With the decrease in fouling, cleaning cycles in operation can be run less frequently while keeping a higher permeate flux. Higher fouling resistance leads to longer membrane lifetime and results in less periodic need for membrane replacement. Overall, the factors influenced by PDOPA modification account for about 30% of the capital and 40-80% of the operating costs, which could be significantly reduced. We estimate that with this cost reduction in both capital and operating costs, produced water treatment with PDOPA-surface modified UF and RO membranes will be economically feasible for the oil/gas industry in the near future.

Chapter 4: Conclusion

Polydopamine (PDOPA) was found to be an effective anti-fouling surface coating for UF, NF, and RO membranes. The 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. To study the effect of PDOPA polymerization, three conditions were investigated during modification: dopamine concentration, Tris-HCl buffer pH, and polydopamine deposition time. The experimental results showed that the different conditions of dopamine concentration and deposition time did not yield significant variations in the permeate flux during oil/water emulsion filtration for XLE RO membrane.

Energy savings were estimated for the PDOPA-modified UF and RO membranes in oil/water emulsion filtration by comparing power required per permeate volume. With the same amount of energy provided by the pump, the modified RO membrane produced 1.27 times more permeate volume than the unmodified RO membrane after 1 hour oil/water emulsion filtration. The modified UF membrane permeate volume increased by a factor of 2.35 after 1 hour of oil/water emulsion filtration. For industrial membrane applications, PDOPA modification is estimated to provide savings for 30% of the capital and 40-80% of the operating costs.

Based upon the first year of study, PDOPA modification has been proven to be a simple and effective approach to improve anti-fouling properties of UF, NF, and RO membranes. The evaluation of PDOPA-coated membrane modules in the field is recommended for Barnett Shale flowback water reclamation.

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