Replaceable Skin Layer Membrane Technology for Produced Water Treatment: Five Case Studies

DAVID BROMLEY M.ENG., P.E.
DBE Hytec Ltd
Vancouver, BC

Technical Reviewer
SOBHAN IRANMANESH M.SC
DBE Hytec Ltd
Edmonton, AB

KEYWORDS: RSL, Produced Water, DAF, UF Membranes, Colloid, Colloidal, Hydrocarbons

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ABSTRACT

Produced water is the dichotomy of the oil and gas industry. Is it a waste or a resource? Water has become a serious operational impairment. Reuse for hydrofracking and enhanced oil recovery (EOR) is essential.

RSL Membranes™ are now being used to satisfy new specifications at a lower cost and energy consumption compared to previous best available technology.

At the 2013 IWC, David Bromley and Dr. Kavithaa Loganathan. Ph.D. - Canadian Natural Resources Ltd. introduced RSL Membranes™ as a novel third generation membrane technology. A one-year comparison with Veolia's ceramic UF membranes was provided. This paper reviews 5 case studies since the 2013 introduction.

INTRODUCTION

Conventional low-pressure membranes (i.e. microfiltration- MF and ultrafiltration-UF) are entrenched as the key process in most water treatment systems.

The common problem with conventional membranes is the fouling of the skin layer. To facilitate and reduce fouling, frequent backwash pulses are required. When the skin layer does become fouled, aggressive chemical cleaning is necessary. Unfortunately, the skin layer never recovers to its original condition and eventually deterioration requires the entire membrane to be replaced. However, one of the benefits of conventional membranes is consistent and high quality permeate water quality.

Before the development of conventional skin layer, low pressure microfiltration (MF) and ultra filtration (UF) membranes, dynamic membranes had a limited use. Dynamic membranes rely on the placement of a powder precoat and/or the placement of solids inherent with the liquid being filtered, on a porous substrate. This placement of solids on the porous substrate causes a bridging to create a small pore size for filtration. The more the bridging of solids, the smaller the pore size. As a result, the permeate (filtered liquid) from dynamic membranes improves in quality over the length of the filtration run. Dynamic membranes have also been introduced as a potential replacement to conventional membranes.

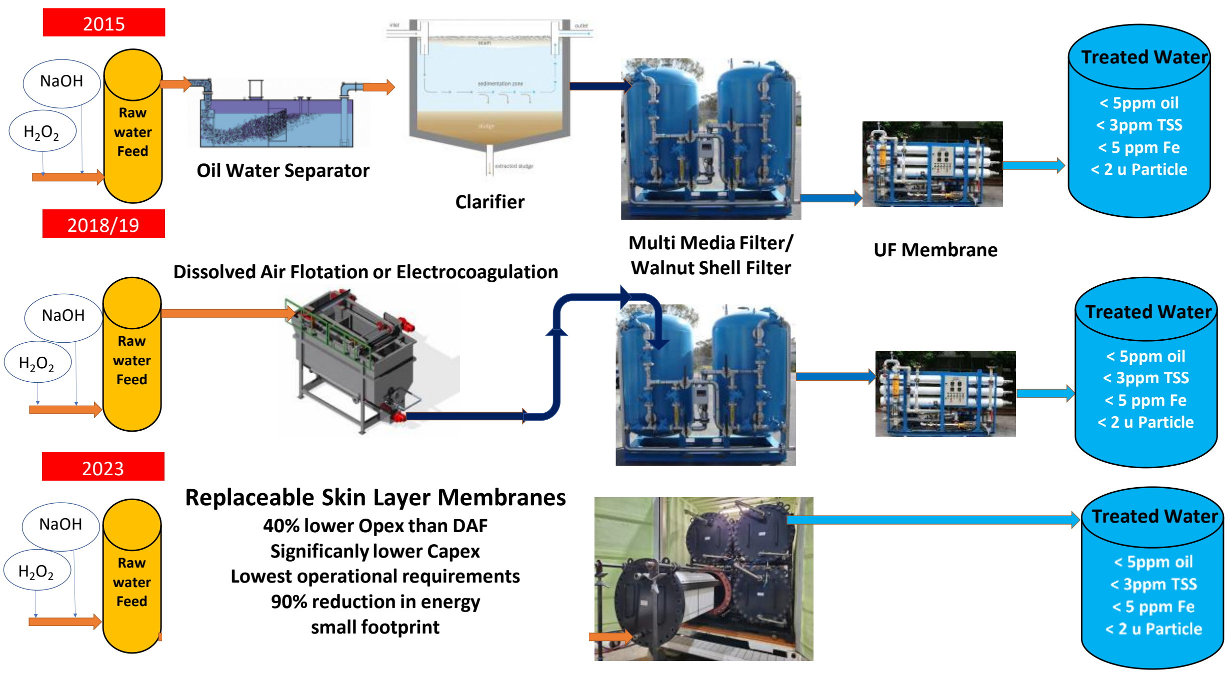
A new option, called Replaceable Skin Layer membranes (RSL Membranes™) has been developed to eliminate the operational issues of conventional membranes and dynamic membranes.

The replaceable skin layer membranes are now considered the best available technology (BAT) for the treatment of produced water from oil and gas operations.

In the production of oil and gas, three products are produced: oil, gas and water. In the Permian Basin of Texas and New Mexico, the volume of produced water is 4 to 8 times the amount of oil produced. Managing this volume of water is a serious issue for the industry. Approximately 10 years ago, the introduction of hydrofracturing (fracking) technology revolutionized the oil and gas production industry. Fracking, at the time, required a fresh water source. The industry made agreements with landowners and state governments to use their fresh water. There was a public outcry. The industry then developed technology (Alkhowaildi et al, Tomomewo et al) that facilitated the use of produced water from oil and gas operations instead of fresh water. However, there were two quality issues that needed to be addressed. Firstly, the amount of iron in the produced water caused a problem with the chemistry (polyacrylamides) required for the high TDS (>150000 ppm) water used for fracking. In an analysis undertaken by John Walsh, (Walsh et al, Sharma et al) it was found that the majority of the iron was in colloidal particles in the 1-3 micron size. A secondary concern was the colloidal solids in the water. In unconventional geological formations (known as tight formations) the pore size of the shale is sub 1 micron. As a result, to facilitate formation penetration of the fracking operation, removal of sub-micron colloidal solids in the water used for fracking is important.

To satisfy these treatment requirements of removing sub micron colloids the obvious treatment process, at the time required the use of conventional membranes (MF or UF). In 2015, major producers such as Conoco Philips and Occidental pursued the treatment of produced water using conventional low-pressure membranes. A variety of pretreatment methods were applied but the conventional membranes continued to prematurely fail.
Figure 1 shows the history of treating produced water to reach a higher quality and satisfy recycled produced water specifications for hydraulic fracking waters.

Figure 1 The Transition of treating Produced water for Recycle in the Oil and Gas Industry



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A similar failure in the use of conventional low-pressure membranes occurred with the Chinese oil and gas industry. In their efforts to undertake enhanced oil recovery (EOR -sometimes called water flooding) in unconventional geological formations, they realized they needed a high-quality water (Jin et al). North American operators in the Bakken unconventional (tight shale formations) also pursued the same high quality treated produced water. The Chinese developed a standard known as 5-1-1 (< 5 mg/l oil, <1 mg/l of TSS and <1 micron particle). This standard is essential for reusing the water in enhanced oil recovery operations where produced water is used to penetrate and pressurize the formation to drive oil and gas to existing wells located in the formation. The operators attempted treatment methods similar to figure 1 and the conventional membranes failed.

Today with the pursuit of using the produced water as a new source of irrigation and potable water, more specific treatment is required. The produced water contains residual oil, colloidal inorganic solids, salts (predominantly sodium chloride), organics, bacteria, some rare earth minerals such as lithium and vanadium and naturally occurring radioactive materials (NORMS). The latter is only a significant issue for high TDS waters and is not an issue in the permeate after thermal or membrane processes that remove the TDS. However, the concentrate stream from these processes would be a concern regarding radioactivity and would have to be handled similar to wastes from nuclear power facilities.

As reported by Mike Hightower (Hightower), and as shown in Figure 2, the only new water source available to depleted potable water regions in the US is produced water from oil and gas operations.

Figure 2: Location of Produced Water Basins Throughout North America

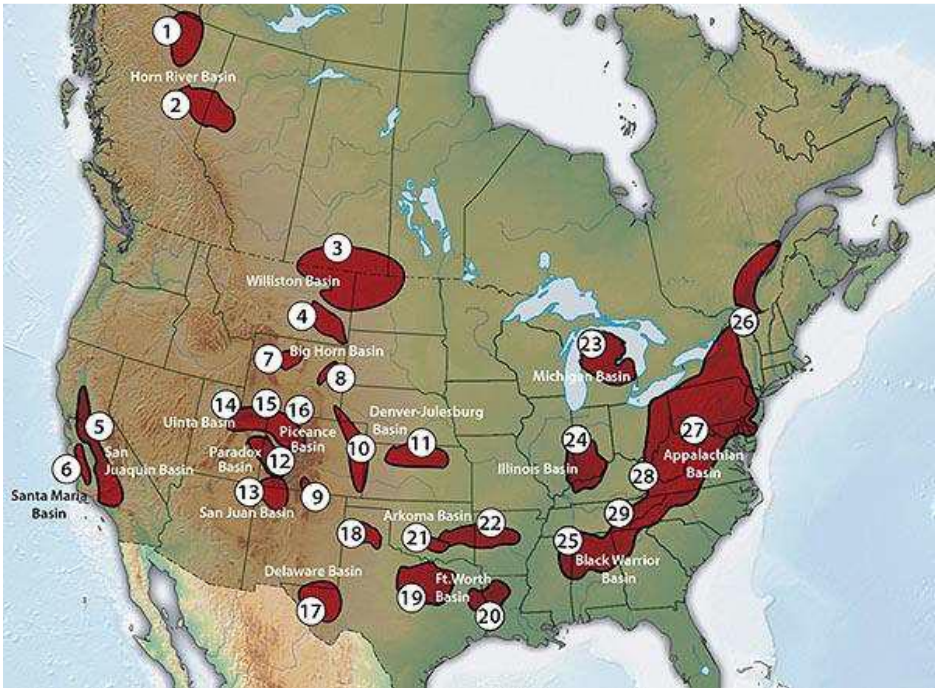
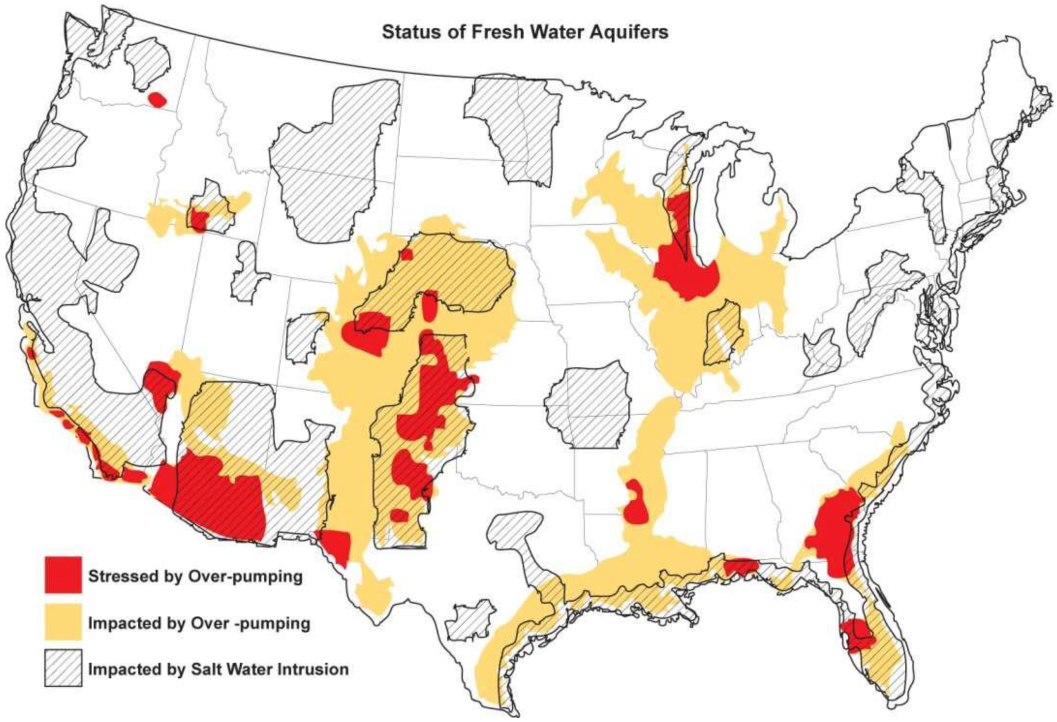


Figure 3: Status of Fresh Water Aquifers



As a result, because of the local proximity of hydrocarbon and saltwater aquifers to local freshwater aquifers, treatment of produced water has become the world's largest new source of water. Multi billion dollars of funding are being directed to desalination processes to deal with high levels of total dissolved solids >150000 mg/l. Technologies such as

1. High Pressure RO Membranes
2. Mechanical vapor recompression (MVR)
3. Evaporation- Multi-Stage Flash (MSF) and Multi Effect Distillation (MED)
4. Membrane distillation

are being pursued to satisfy irrigation and potable water demand. For these technologies to desalinate water, there is a need to pretreat the water before these technologies can be applied. Replaceable skin layer membranes are an excellent option to provide a pretreatment that minimizes fouling of the desalination technology, specifically pretreatment to remove colloidal solids and hydrocarbon-based oil simultaneously.

This paper will review the science behind replaceable skin layer membranes and five case studies where the replaceable skin layer membranes were used to treat produced water.

THE SCIENCE BEHIND REPLACEABLE SKIN LAYER MEMBRANES

Replaceable skin layer membranes rely on the use of an ionic charged powder to be placed on the surface of a membrane substrate where the powder simulates a well-known scientific theory called the DLVO theory (named after Boris Derjaguin, Lev Landau, Evert Verwey and Theodoor Overbeek). The DLVO theory teaches the impact of ionic environment on the strength of the electric double layer (EDL) around colloidal solids. Colloids in suspension (suspended solids) remain in suspension because of a strong EDL around the colloidal solid. Replaceable skin layer membranes use a strong ionic powder layer that causes a strong EDL on the surface of the membrane. This strong membrane EDL prevents the caking of solids on the surface of the membrane. However, there is a buildup of solids within microns of the powder surface on the membrane tube. As this solid layer builds, the pressure drop across the membrane (TMP) is close to zero and constant. In addition, this low TMP occurs at a flux rate of 300 to 800 litres per m^2 per hour (i.e.,10 times conventional membranes). The distance between the surface of the powder and the solids mat layer is called the colloidal gap however as the solid concentration builds inside the housing, the separated solids leak into the ionic powder causing the EDL to collapse and pressure across the membranes rises rapidly. See figure 8. The two stages of TMP development with first a low and constant TMP and then followed by a rapid increase in TMP defines replaceable skin layer membranes as a Generation 3 membrane.

Figure 4: Solids Mat Build-up

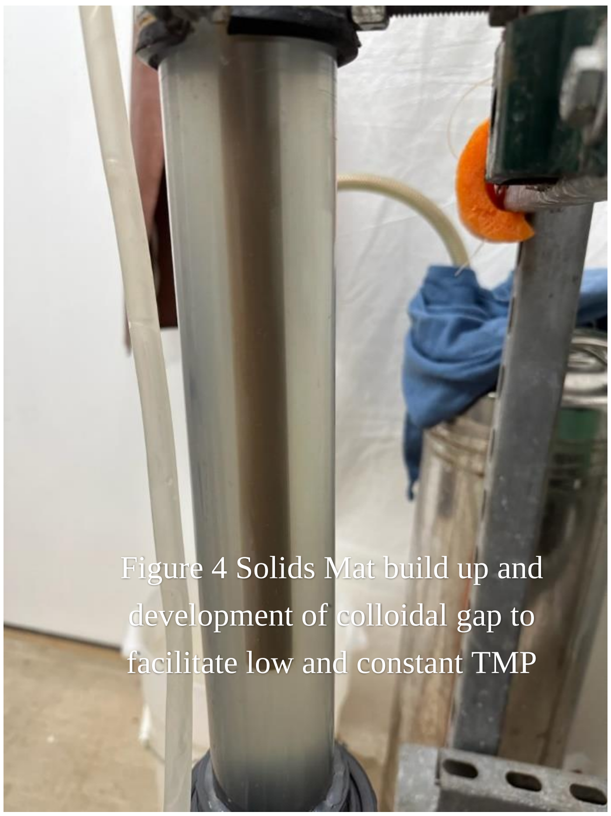
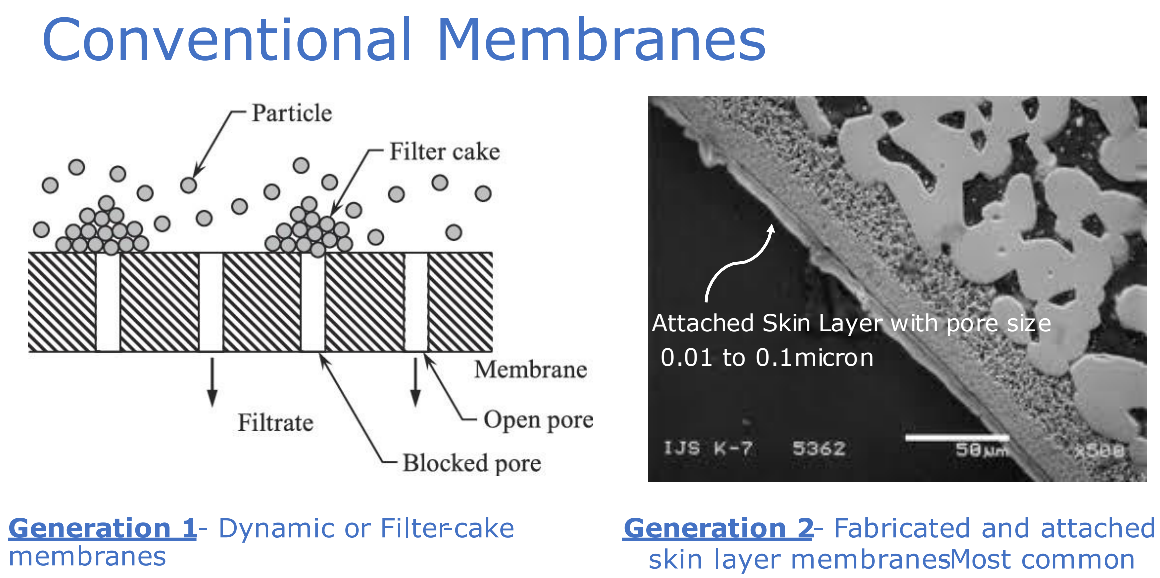


Figure 4 Solids Mat build up and development of colloidal gap to facilitate low and constant TMP

A comparison between Generation 1 and Generation 2 Membranes with replaceable skin layer membranes is helpful. Generation 1 Membranes are commonly referred to as dynamic membranes (see Figure 5). They rely on the placement of a powder precoat (filter cake) and/or the placement of solids inherent with the liquid being filtered, on a porous substrate. This placement of solids on the porous substrate causes a bridging to create a small pore size for filtration. The more the bridging of solids, the smaller the pore size. As a result, the permeate (filtered liquid) from dynamic membranes improves in quality over the length of the filtration run. A typical dynamic membrane will use a precoat material such as diatomaceous earth (DE).

Figure 5: Conventional Generation 1 and 2 Membranes



Subsequent to Generation 1, Dynamic Membranes, there was the development of conventional low-pressure membranes commonly referred to as Microfiltration (MF) Membranes and Ultrafiltration (UF) Membranes (see Figure 5). Conventional low-pressure membranes dominate the market today and are entrenched as the key process in most water treatment systems. Conventional membranes consist of a fixed skin layer that has a pore size which provides the barrier for solids larger than the pore size to pass through. The skin layer is affixed to a porous substrate material in a tube or sheet format. There are also small tube formats (2 mm diameter) that are constructed only of the skin layer itself. (i.e., there is no substrate).

The common problem with conventional membranes is the fouling of the skin layer. To facilitate and reduce fouling, frequent backwash pulses are needed. When the skin layer does become fouled, aggressive chemical cleaning is necessary. Unfortunately, the skin layer never recovers to its original condition and eventually deterioration requires the entire membrane to be replaced. However, one of the benefits of conventional membranes over dynamic membranes is the consistent and high quality permeate water quality.

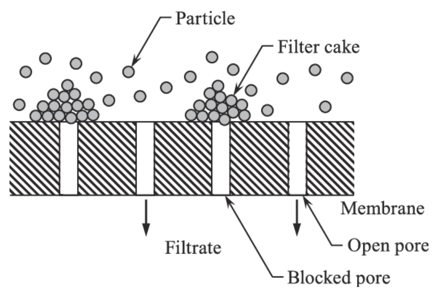
Both Generation 1 and 2 membranes rely on the separation of solids and colloids via a barrier. The smaller the pore size of the barrier, the smaller the solid or colloid that can be removed. Whereas replaceable skin layer membranes operate with pore sizes 10000 times greater than conventional low-pressure membranes yet achieve similar solid /colloid separation. Replaceable skin layer membranes rely on the colloidal solid being repelled away from the surface of the membrane and if the colloidal solid does penetrate the surface powder layer, the EDL around the colloid collapses, the colloid becomes destabilized and attaches to the powder. The powder eventually becomes fouled and must be backwashed/removed. A new powder is applied, and the filtration cycle repeats itself. The operation of replaceable skin layer membranes consists of three consistent and easy steps.

1. Apply the ionic powder to the surface of the membrane tube (15 minutes)
2. Filter the water at a flux rate between 300 to 800 lmh until the TMP reaches 70 kpa (10 psi) (3 to 20 hrs)
3. Backwash (air and water) and refill the housing with permeate, ready for Step 1

A comparison of the TMP and Turbidity (NTU) versus Time for each of the three generation of membranes is a helpful graphic for comparison of operating conditions and performance. Figure 6 ,7 and 8 show the typical TMP and Turbidity versus time for dynamic membranes (Generation 1), conventional MF and UF membranes (Generation 2) and replaceable skin layer membranes (Generation 3), respectively.

Figure 6 Generation 1- Dynamic (Filter Cake Membranes) TMP and Turbidity vs Time (Typical)

Note: The "X" plot where turbidity improves through the filtation cycle but as the filter cake builds on the surface of the membrane the TMP increases.



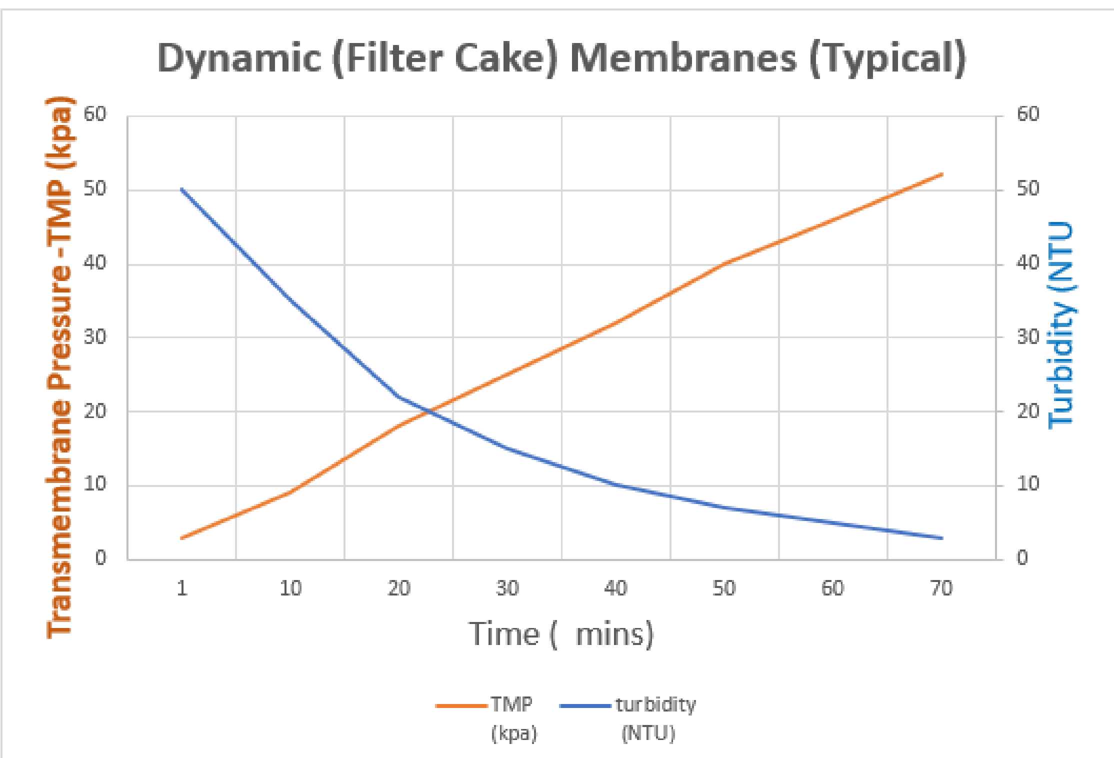
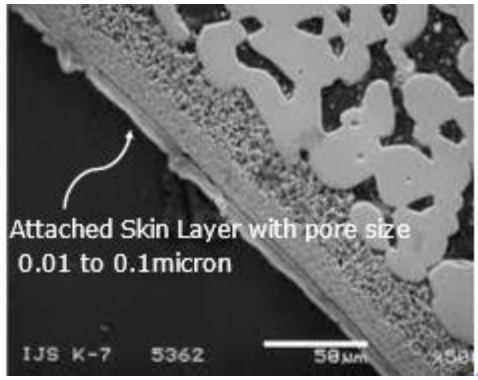


Figure 7 Generation 2- Conventional Microfiltration and Ultrafiltration (MF or UF Membranes) TMP and Turbidity vs Time (Typical)



Note: 1.TMP rises on a linear basis. In this case, after approximately 16 minutes, a backwash (BW) occurs. When the backwash occurs the TMP drops but never drops to the original new membrane TMP level. The linear increase in TMP is evidence of a thin filter cake building on the surface of the membrane skin layer.

2. Eventually a chemical enhanced backwash (CEB) is performed. The CEB provides a better recovery of the TMP than the BW pulse.

3. Once the TMP reaches 200 to 300 kpa, a clean in place (CIP) with acid and caustic washes occurs to cause the TMP to be significantly reduced but never to the level of a new membrane.

4. Turbidity remains consistent and of high quality throughout the filtration cycle

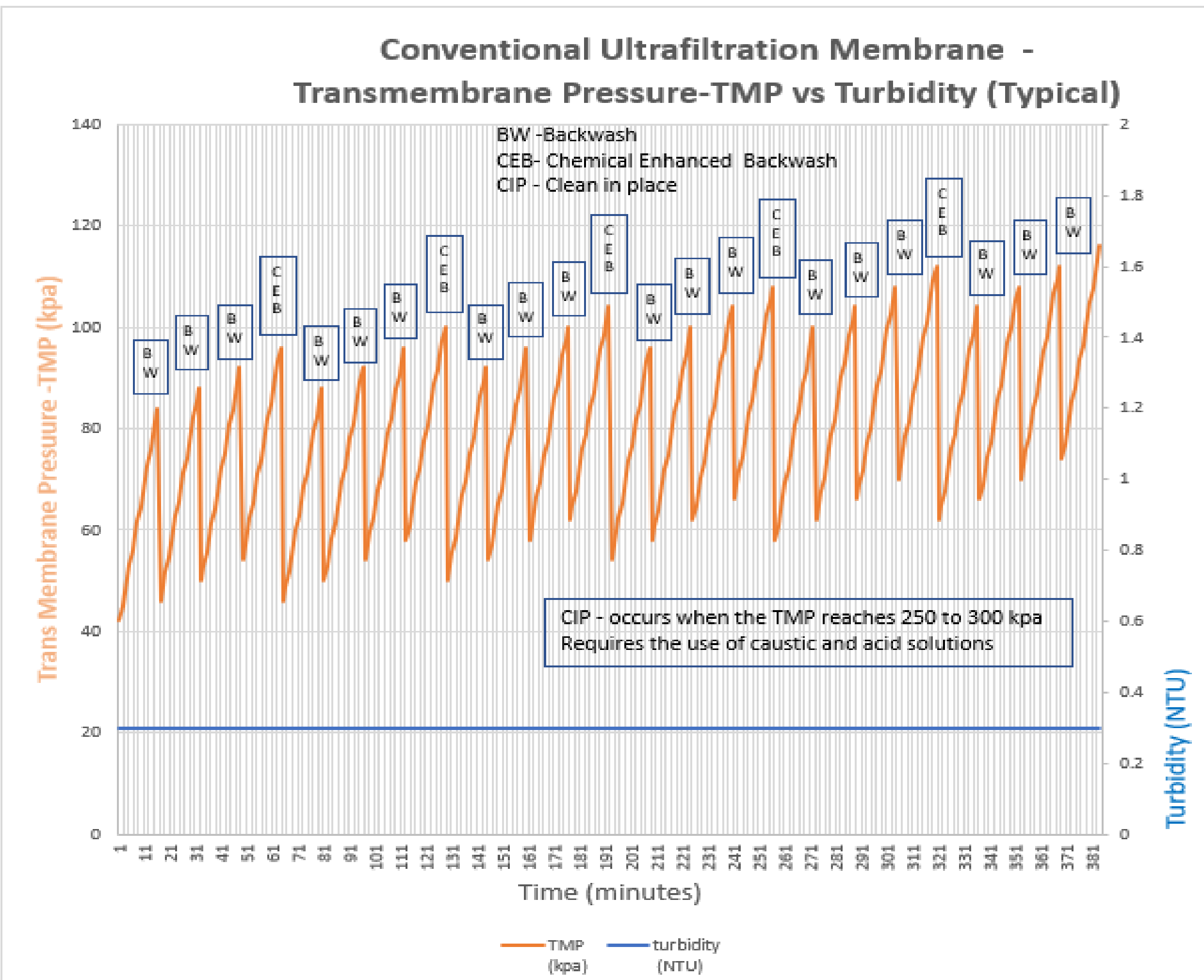
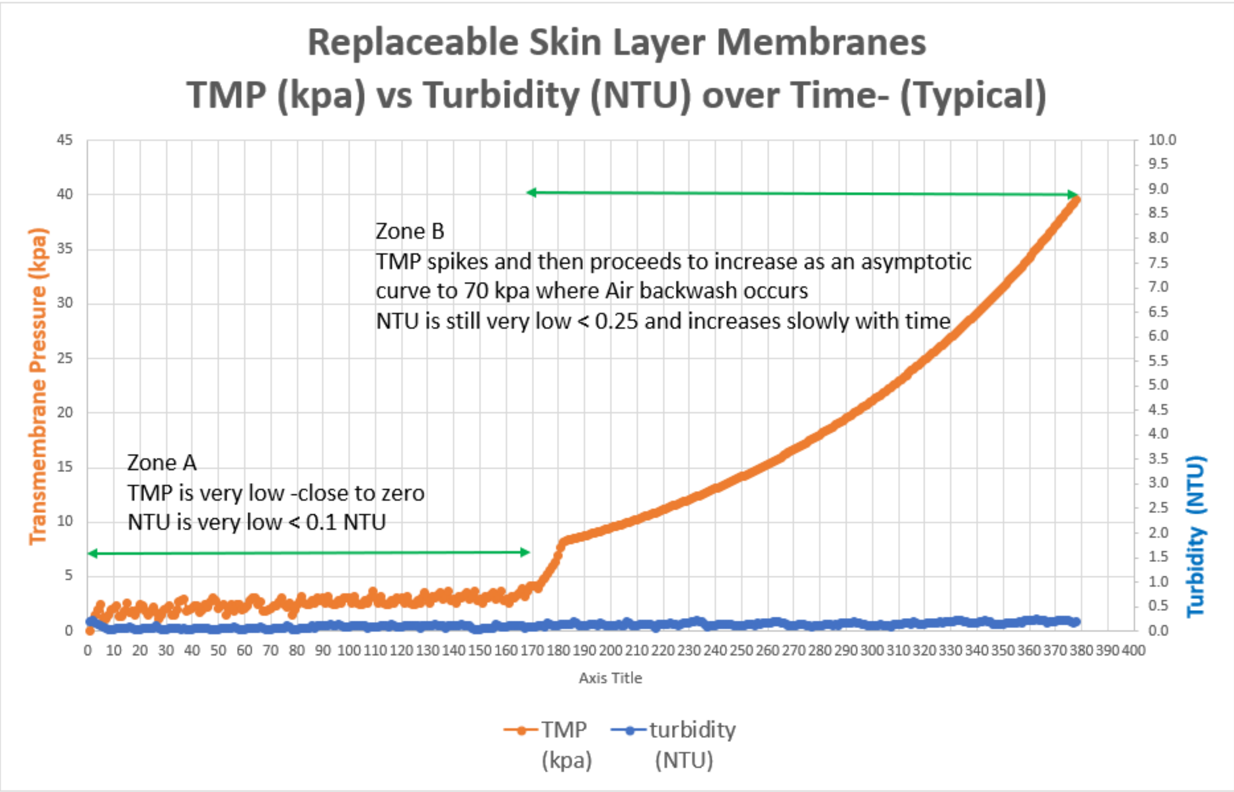


Figure 8 Generation 3-Replaceable Skin Layer Membranes- TMP and Turbidity vs Time (Typical)

Note1: Zone A where the TMP is very low and close to zero and Zone B where the TMP increases asymptotically.
2: B/W occurs after many hours and at a low TMP of 70 kpa. B/W typically restores membrane to original TMP



FIVE CASE STUDIES USING REPLACEABLE SKIN LAYER MEMBRANES

Figure 9 The New 100 m^3/ hour RSL Membrane™ treatment module

1. FT MCMURRAY, ALBERTA-HORIZON MINE - CANADIAN NATURAL RESOURCES LTD.(CNRL): The first long term assessment of replaceable skin layer membranes occurred at CNRL's Horizon mine site in Ft McMurray Alberta. The one-year assessment was controlled by a third party (Epcor Utilities) where the third party operated the technologies seven days a week and 24 hours per day. The third-party operator collected all the data and independently assessed the technology. This case study was reported at the IWC conference in 2013 (Bromley et al). In addition, a peer review paper authored by the CNRL project manager Dr. Kavithaa Loganathan. Ph.D, was published in the Journal of Environmental Management in April 2015 (Loganathan et al)
   CNRL needed pretreatment technology for an RO system they were considering for their recycled produced water used in their bitumen recovery process. The source of the water was their process tailings pond. They initially assessed twelve technologies. From that assessment, two technologies were selected for the year-long assessment: replaceable skin layer membranes and Veolia's ceramic membranes with a silica carbide skin layer. The replaceable skin layer technology was part of a hybrid system called "nanoflotation" which actually had a surfactant-based flotation system prior to the replaceable skin layer

membranes. In a similar fashion, the alternate technology (ceramic membranes) were preceded by a lamella clarifier. Because UF membranes had specific specifications as to the water they could treat, there was the need for pretreatment. The same requirements were believed necessary for the replaceable skin layer membranes hence the use of a flotation technology prior to the replaceable skin layer membranes. The replaceable skin layer membranes not only performed consistently, they also outperformed the ceramic membrane with a 10 fold improvement in flux rates. In addition, the replaceable skin layer membranes displayed a high level of robustness. In fact, there was no need for pretreatment with the flotation technology. On the other hand, the ceramic membranes were limited in operation up to TSS levels of <100 mg/l. Figure 10 shows the testing site. The white trailers were for ceramic membrane technology and the blue trailer (to the left of the white trailers) was the replaceable skin layer technology. The difference in footprint is significant. Table 1 provides a summary of the treatment results.

Figure 10 Testing Site at Canadian Natural Resources for the comparison of the replaceable skin layer membranes versus the ceramic membranes with the silica carbide skin layer.

Table 1 Water Quality Data for Replaceable Skin Layer Membranes treating Tailings Pond Water (EPCOR Study)

Average RCW and Treated Water Quality with % Reductions (Maxxam)

Parameter	Units	Average RCW	Average Membrane Tank	% Reduction by Flotation	Average NF Effluent	% Reduction by Filtration	Overall % Reduction
pH (on-site lab)	SU	8.27	8.08	2.4%	8.07	0.1%	2.5%
Turbidity	NTU	115	12	89.2%	0.2	98.3%	99.82%
Electrical Conductivity	µS/cm	2983	2817	5.6%	2850	NA	4.5%
Total Dissolved Solids	mg/L	1750	1600	8.6%	1650	NA	5.7%
Hardness (as CaCO3)	mg/L	48	52	NA	53	NA	NA
Bicarbonate	mg/L	853	780	8.6%	790	NA	7.4%
Total Alkalinity (as CaCO3)	mg/L	700	638	8.8%	647	NA	7.6%
Silica	mg/L	4.94	4.32	12.6%	4.58	NA	7.3%
Ammonia	mg/L	1.38	1.33	3.6%	1.37	NA	1.2%
Chloride	mg/L	473	443	6.3%	452	NA	4.6%
Sulphide	mg/L	0.0057	0.0022	62.2%	0.0026	NA	55.2%
Total Organic Carbon (C)	mg/L	36	31	13.8%	30	5.9%	18.8%
Dissolved Organic Carbon (C)	mg/L	34	30	11.8%	28	6.7%	17.6%
Oil & Grease	mg/L	30	24	19.8%	24	NA	17.5%
Naphthenic Acids	mg/L	63	55	12.7%	56	NA	11.1%
F1 Hydrocarbons (C6-C10)	µg/L	50	50	NA	50	NA	NA
Dissolved Aluminum	mg/L	0.37	0.43	NA	0.12	71.4%	66.8%
Dissolved Barium	mg/L	0.26	0.18	33.5%	0.17	1.9%	34.8%
Dissolved Boron	mg/L	2.30	2.10	8.7%	2.22	NA	3.6%
Dissolved Calcium	mg/L	10.3	11.8	NA	11.8	NA	NA
Dissolved Iron	mg/L	0.30	0.26	15.0%	0.26	NA	15.0%
Dissolved Magnesium	mg/L	5.30	5.33	NA	5.67	NA	NA
Dissolved Manganese	mg/L	0.032	0.021	35.1%	0.020	4.0%	37.7%
Dissolved Mercury	µg/L	0.001	0.001	8.0%	0.001	25.0%	31.0%
Dissolved Phosphorus	mg/L	0.50	0.45	9.7%	0.43	5.9%	15.0%
Dissolved Potassium	mg/L	10.2	9.2	9.3%	9.9	NA	2.5%
Dissolved Silicon	mg/L	3.00	1.93	35.6%	2.07	NA	31.1%
Dissolved Sodium	mg/L	640	593	7.3%	637	NA	0.5%
Dissolved Strontium	mg/L	0.30	0.28	7.8%	0.29	NA	3.3%
Dissolved Sulfur	mg/L	30.5	28.8	5.5%	30.2	NA	1.1%

2. DAJING CHINA -PETRO CHINA. In 2019, after two years of laboratory tests and small field applications to evaluate the replaceable skin layer membrane technology, Petro China purchased a 25 m3/hr (4000 bbl/day) produced water treatment unit. The system operated for one year until operations were closed due to Covid. The treatment system is now been refurbished and will be placed back into operation in the fall of 2023.

Isle Utilities, a third-party global water technology assessor, assessed the replaceable skin layer technology and the results of operation at the Dajing Oil field. The Isle Utility assessment was undertaken as per a contract via a group of major offshore oil production E & P companies. Their interest in the replaceable skin layer technology was the small footprint. Isle Utilities was responsible for an assessment that compared many technologies that could be used to treat produced water from offshore oil and gas production platforms. The conclusion of their assessment identified replaceable skin layer technology with its small footprint, as the lead technology to be considered for the treatment of produced water generated on offshore environments. The recommendation was based on the excellent performance data obtained from the operation of the replaceable skin layer technology in the Dajing oil field.

Figure 11: Dajing China: Operators taking samples on 25 m3/hr Replaceable Skin Layer Membrane.

Figure 12: Feed water and Permeate from 25 m3/hr replaceable skin layer membrane– Petro China-Dajing Production Zone

Petro China used their own laboratory and third-party testing facilities to develop a comprehensive data set for 90 consecutive days of operating 24 hours per day. There were two membrane housings. Data was obtained from each housing to create a duplicate set of turbidity, total suspended solids (TSS), oil and particle size. See Figures 13,14,15,16,17 and 18.

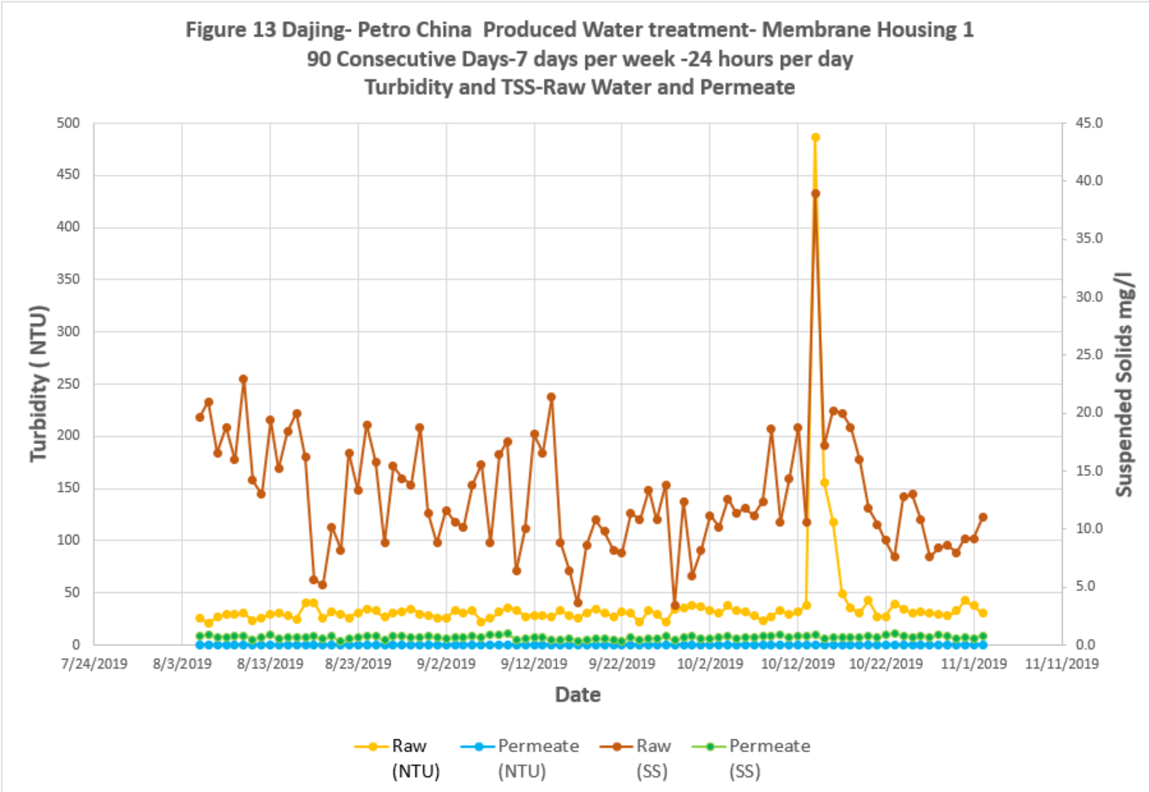


Figure 13 Dajing- Petro China Produced Water treatment- Membrane Housing 1
90 Consecutive Days-7 days per week -24 hours per day
Turbidity and TSS-Raw Water and Permeate
Turbidity (NTU)
Suspended Solids mg/l
Date
500
450
400
350
300
250
200
150
100
50
0
45.0
40.0
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
7/24/2019
8/3/2019
8/13/2019
8/23/2019
9/2/2019
9/12/2019
9/22/2019
10/2/2019
10/12/2019
10/22/2019
11/1/2019
11/11/2019
Raw (NTU)
Permeate (NTU)
Raw (SS)
Permeate (SS)

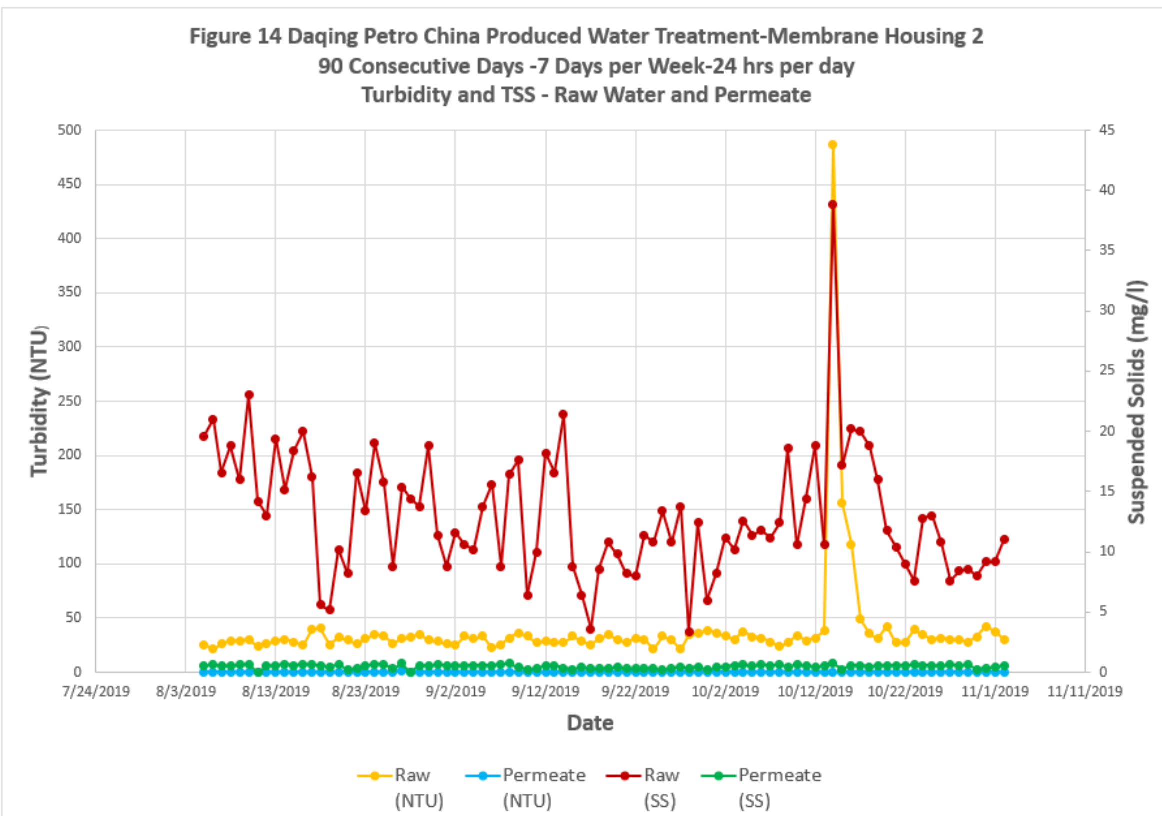
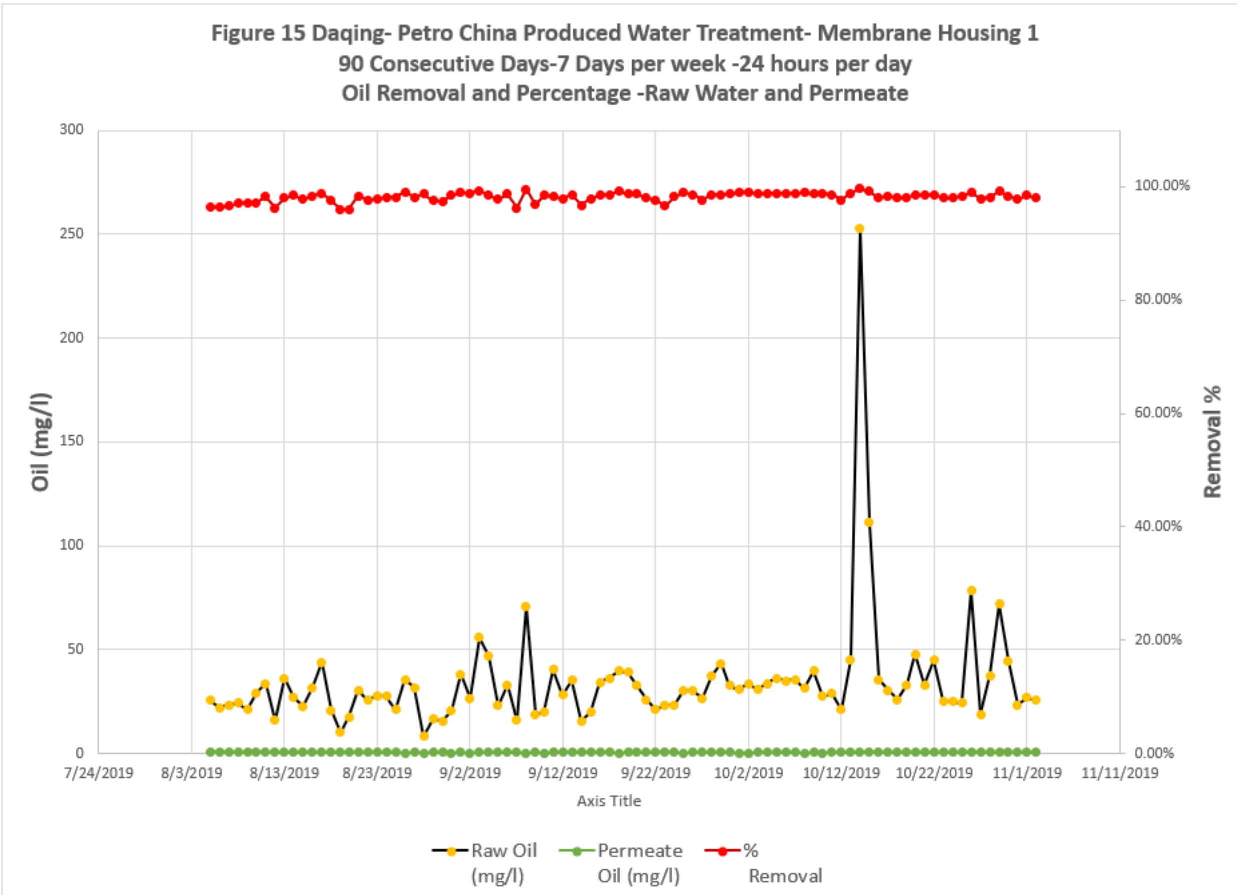
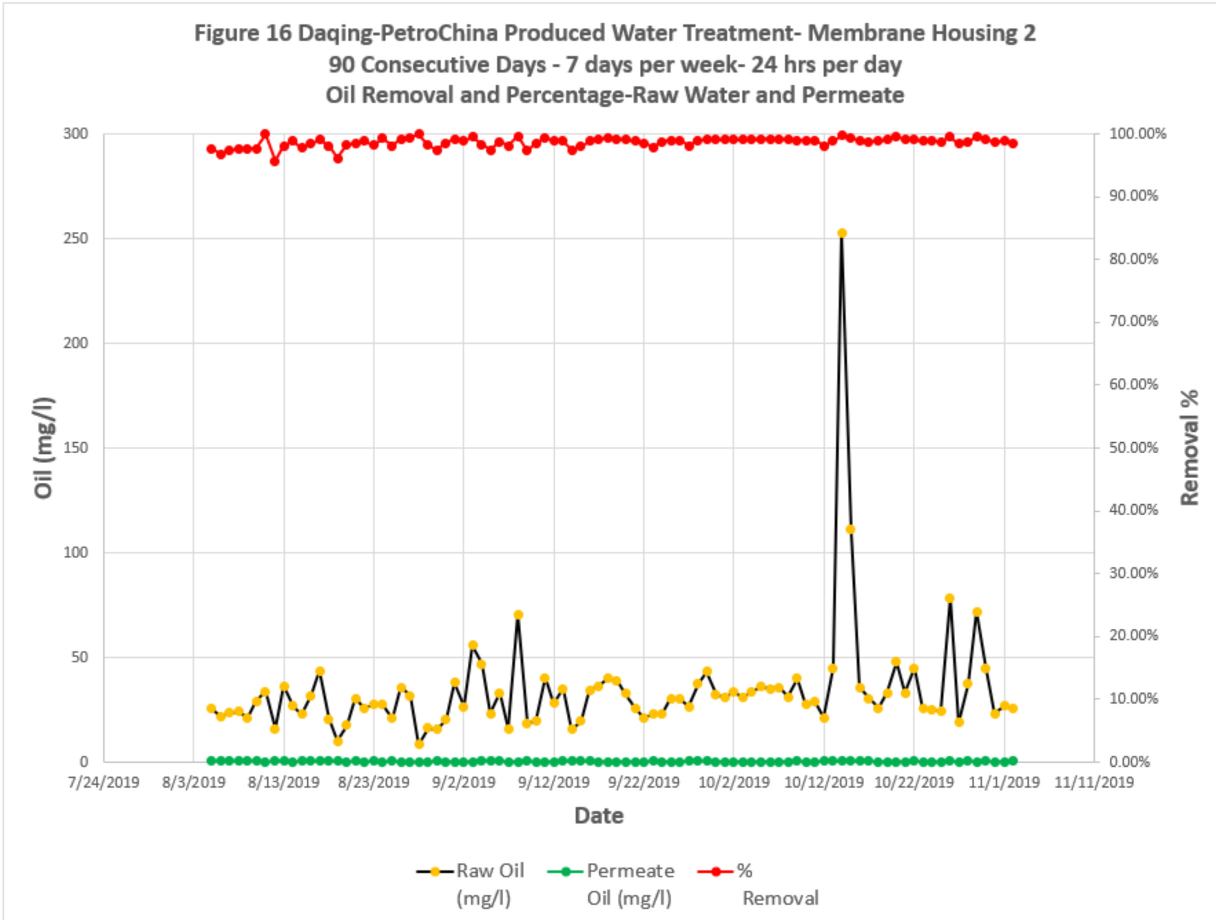


Figure 14 Daqing Petro China Produced Water Treatment-Membrane Housing 2
90 Consecutive Days -7 Days per Week-24 hrs per day
Turbidity and TSS - Raw Water and Permeate
Turbidity (NTU)
Suspended Solids (mg/l)
Date
500
450
400
350
300
250
200
150
100
50
0
45
40
35
30
25
20
15
10
5
0
7/24/2019
8/3/2019
8/13/2019
8/23/2019
9/2/2019
9/12/2019
9/22/2019
10/2/2019
10/12/2019
10/22/2019
11/1/2019
11/11/2019
Raw (NTU)
Permeate (NTU)
Raw (SS)
Permeate (SS)

For both turbidity and suspended solids, the raw water had some wide variations and specifically a spike in the October 14th time frame. Nevertheless, the replaceable skin layer membranes produced a consistent and high quality permeate for both membrane housings throughout the 90 consecutive days of data. The average raw and treated produced water had 38.5 NTU and 0.22 NTU respectively, and 13 mg/l and 0.67 mg/l of TSS respectively. For comparison, the averages for Membrane Housing 2 were the same for the raw water but for the permeate, the turbidity was 0.21 NTU and 0.5 mg/l for the TSS respectively.





With regards to oil, the spike in oil concentration in the raw water appeared at the same time as the spike in turbidity and TSS. As with turbidity and TSS, the replaceable skin layer membranes provided a consistent and high-quality water throughout the spike time frame and throughout the 90 days of analysis. Almost 100 % of the residual oil in the raw water was removed by the replaceable skin layer membranes. The average oil contents in the raw water and permeate for Membrane 1 were 34.2 mg/l and 0.5 mg/l respectively. For Membrane 2, the average the oil concentration in the permeate was 0.22 mg/l.

Figures 17 and 18 provide a plot of the D_{50} particle size. The particle size in the raw water was very small at an average D_{50} of 2 microns. The membrane tubes had a pore size of 3 to 5 microns. The average D_{50} in the permeate for housing 1 and 2 was 0.68 and 0.58 microns respectively.

Figure 17 Daqing-Petro China Produced WaterTreatment-Membrane Housing 1
90 Consecutive days-7 days/week 24 hourd per day
Particle size- Raw Water and Permeate

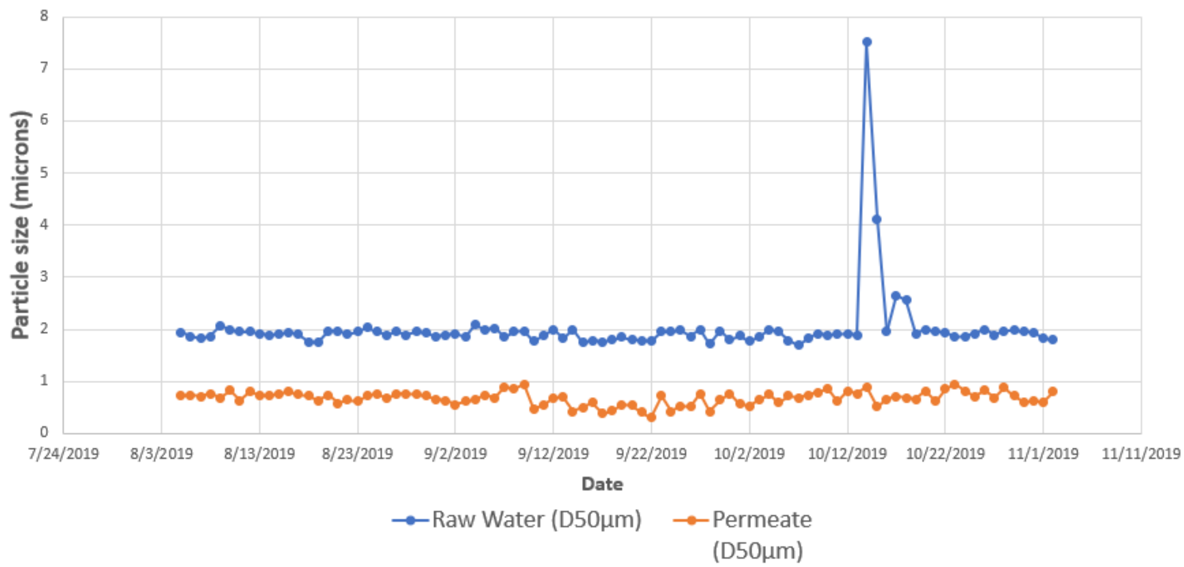
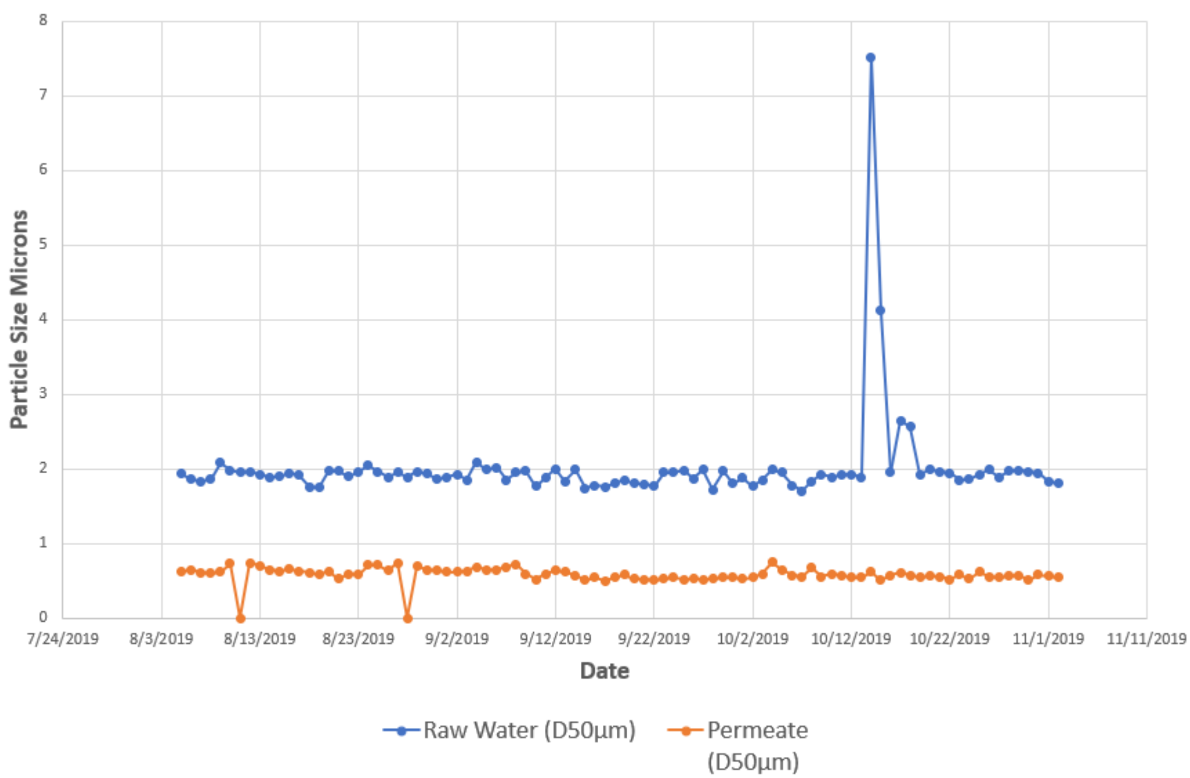


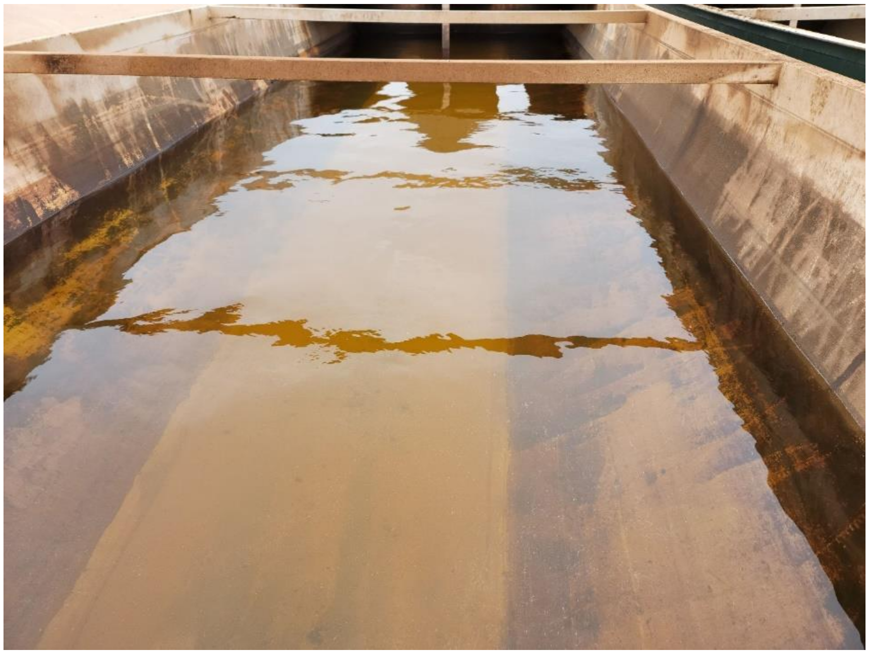
Figure 18 Daqing- Petro China Produced Water Treatmetn-Membrane Housing 2
90 Consecutive Days- 7 days/week-24 hrs/day
Particcle Size Raw Water and Permeate



3. MIDLAND TEXAS NOVEMBER 2021-FEBRUARY 2022: This case study was the result of a 9 million dollar financing where the financing consortium wanted to see physical real time proof that the replaceable skin layer technology could perform as stated. A 10 m3/hr (800 bbl/day) replaceable skin layer membrane system was operated for a four-month period and was reviewed by the financing consortium. The operating data confirmed the following.
    - Replaceable skin layer membranes provide the benefit of one process unit being capable of separating colloidal solids and oil simultaneously. In fact, the operator of the E & P facility, where the replaceable skin layer membrane treatment pilot was operating, declared that there was no oil in the produced water that would be the feed water to the pilot. The reason he made this declaration is because prior to the pilot unit, the produced water had already gone through three conventional oil water separation processes. As shown below,(see Figure 19) there was residual oil in the water being treated by the replaceable skin layer membranes and that oil was separated by the membranes. A frack tank was used to collect the mixture of water, and separated solids and oil vacated from the replaceable skin layer membrane housing during backwash. There is a distinct layer of oil on the surface of the frack tank. In fact, the frack tank has three distinct layers; the top oil layer, the bottom settled solids from the back wash and a relatively clean layer of water sandwiched in the middle. The middle layer of water was always conveyed back to the raw water tank feeding the replaceable skin layer membranes. The separated oil was skimmed and sent to the production tanks. The remaining small volume of solids/sludge waste on the bottom of the frack tank was sent to a solids handling facility.
    - The treated permeate water from the replaceable skin layer membranes was crystal clear with an NTU was <1
    - The cost to operate the replaceable skin layer membrane is significantly less than the closest competing technology, commonly known as DAF (dissolved air flotation technology). DAF which is widely used by the US Petroleum industry and global off shore oil and gas production platforms. More detail is provide in the 5th Case study below

Figure 19: Frack tank containing Backwash (Water, Oil and Solids) resulting from Produced Water Treatment using Replaceable skin layer membranes

Figure 20: Frack tank storing Permeate from the treatment of Produced water by Replaceable skin layer membranes.

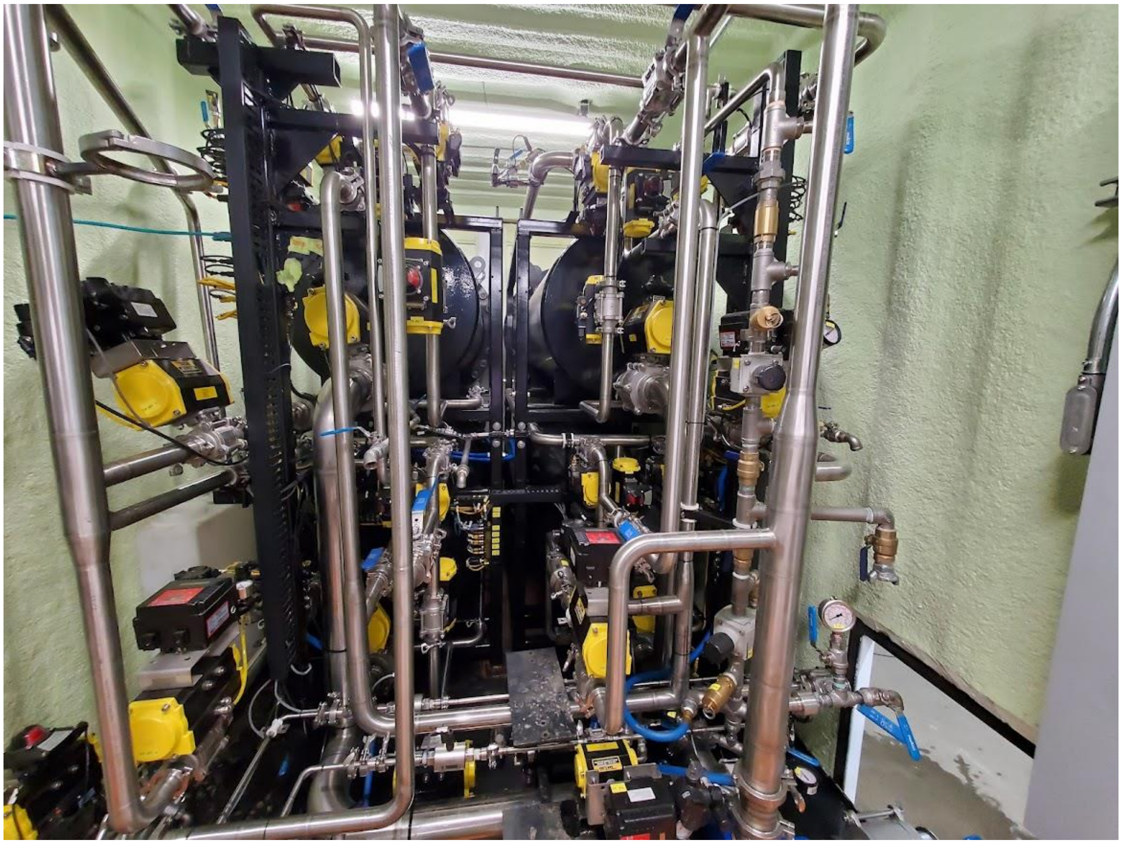


4. OPERATION AT A SALT WATER DISPOSAL (SWD) FACILITY- BARSTOW TEXAS- NEW 100 M3/HR (15000 BBL/DAY AUGUST -OCTOBER, 2022 This case study was generated as a result of the operator of an SWD wanting to apply the replaceable skin layer membranes to improve the capacity of their SWD by removing residual oil. The intent was to increase flow into the SWD but not increase the conventional oil water separation tankage known as a gun barrel. This field application was useful as the technology developer had just built its first 100 m3/hr (15000 bbl/day) produced water treatment system and needed a location to commission the process unit. The process unit treated water from two locations at the SWD facility.
    - The bottom of the gun barrel which is considered as tank bottom waters. Tank bottoms are one of the worst waters to treat.
    - The inlet to the gun barrel at the location where a layer (commonly referred to as a pad layer of emulsified oil) occurs and causes significant operational issues with the SWD.

The results of those two test locations are displayed in the table below. Unfortunately, the second location at the inlet of the gun barrel did not result in the treatment of a pad layer. Just prior to the replaceable skin layer membrane being connected to this location, the operator had cleaned the tanks and the pad layer did not develop during the time period that the replaceable skin layer membranes were treating water from this location. Nevertheless, this location did allow for the treatment of water directly from the pipeline which transports the produced water to this SWD facility.

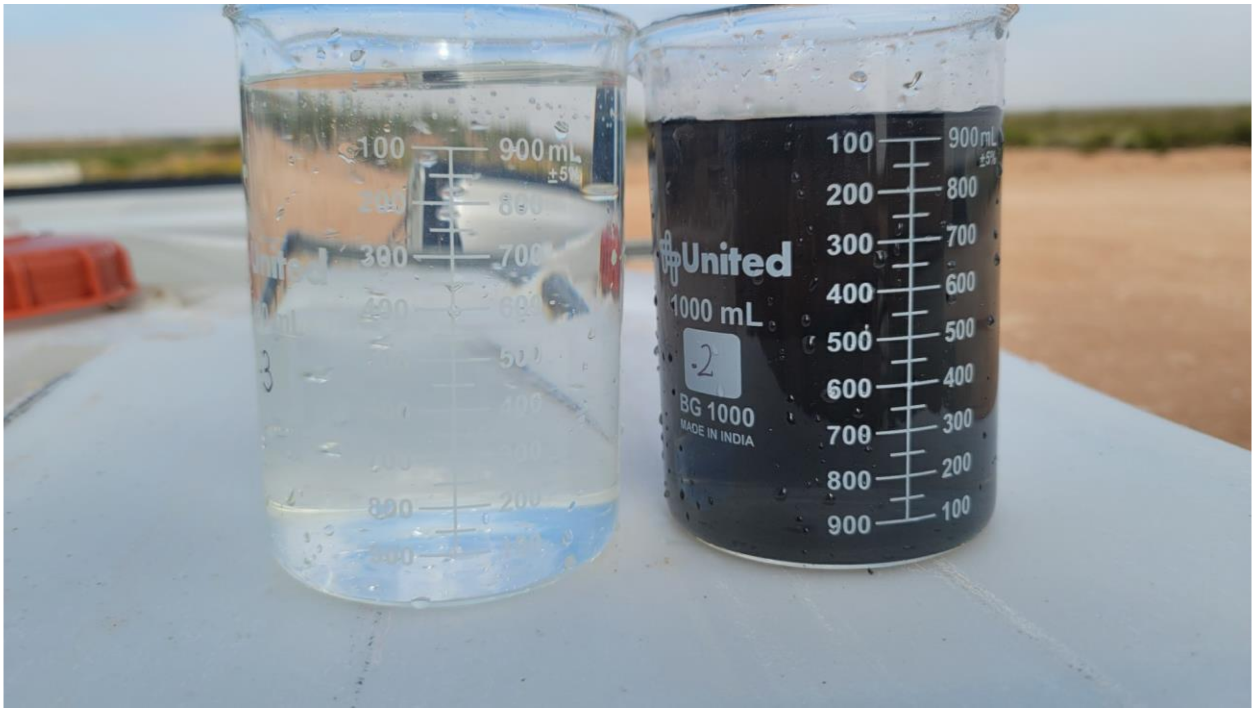
Figure 21 Setting up Replaceable skin layer membranes Sea Container unit at SWD Facility – Barstow TX

Figure 22 Inside Container there are two operating Skids with 4 housings.



By opening the double wide doors at the ends of the trailer unit, the membranes within the housings are accessible. The flange cover on the membrane housing can be removed exposing the membrane tube bundle which slides out of the housing via a slide out tray.

Figure 23 Treated Permeate water resulting from the treatment of the water from the bottom of the Gun Barrel



The following table provides a more detailed analysis of the treatment capability of the replaceable skin layer membranes.
The data confirms the ability of the technology to provide a high level of

- colloidal solid removal resulting in low turbidity water.
- residual oil removal
- Iron removal

In addition, the operation of the replaceable skin layer membrane at the inlet location of the gun barrel confirmed the replaceable skin layer membrane can treat water directly from a produced water pipeline thereby avoiding the use of a SWD for recycling purposes. This is a significant benefit in that a replaceable skin layer membrane module can be set up easily at any riser location along a produced water pipeline to provide water for fracking or EOR applications in proximity to the pipeline.

Table 2 Water Quality Data for Replaceable skin layer membranes treating Produced Water in West Texas at a Saltwater Disposal Facility

Water Quality Analysis of Waters from a Salt Water Disposal Facility- Barstow, Texas

Date	October 14-22					October 27-22		
	Raw water pipeline	% Reduction based on treated water	Bottom of Gun Barrel	% Reduction based on treated water	Treated water	Raw water from Pad layer region of Gun Barrel	Treated water	% Reduction based on treated water
Turbidity	73	100.00%	120	100.00%	<0.2	27	<0.2	100.00%
TSS (ppm)	94	100.00%	162	100.00%	<1	26	<1	100.00%
Oil (ppm)	10	100.00%	7	100.00%	<2.5	10	<2.5	100.00%
pH	6.51		6.47		6.78	6.54	6.52	
ORP	-95		-130		132	-42	95	
H2S	0		0		0	0	0	
CO2	246	-22.36%	285	-5.61%	301	198.00	282	-42.42%
Al (ppm)	0.15	0.00%	0.15	0.00%	0.15	0.15	0.15	0.00%
Arsenic (ppm)	0.15	0.00%	0.15	0.00%	0.15	0.15	0.15	0.00%
Barium (ppm)	33.669	-16.26%	30.663	-27.65%	39.142	37.00	36.2	2.16%
Boron (ppm)	46.443	9.26%	46.952	10.25%	42.141	45.00	39.3	12.67%
Calcium (ppm)	12204	-14.20%	16308	14.54%	13937	10422	8853	15.05%
Chloride (ppm)	127091	21.20%	128992	22.36%	100143	110790	101003	8.83%
Iron (ppm)	12.42	99.88%	2.168	99.31%	0.015	9.80	0.015	99.85%
Lithium (ppm)	23	8.70%	23	8.70%	21	17.40	17	2.30%
Manganese (ppm)	5	-20.00%	7.9	24.05%	6	5.50	5.8	-5.45%
Magnesium (ppm)	3102	15.22%	3415	22.99%	2630	1948.00	1879	3.54%
Potassium (ppm)	1295	12.28%	1365	16.78%	1136	894.00	732	18.12%
Sodium (ppm)	60630	30.20%	56740	25.42%	42317	50314.00	40657	19.19%
Strontium (ppm)	1657	4.59%	2017	21.62%	1581	1072.00	1581	-47.48%
Sulfate(ppm)	315	-23.81%	332	-17.47%	390	224.00	245	-9.38%

5. <u>OPERATION IN SOUTH TEXAS TO TREAT PRODUCED WATER AT AN E & P SITE: DECEMBER -2022 TO PRESENT-2023:</u> The replaceable skin layer membranes were moved from the Barstow SWD site to a E & P operating site where there was a need to operate on a 24 hour-7 day a week basis and treat water as generated at varying flow rates and quality. The membranes have been onsite for almost 11 months. The Operator paid for the treatment of the water at commercial rates. In addition, adjacent to this site was another site where the E & P operator was using flotation (DAF) technology, a technology considered as the competition to replaceable skin layer membranes.

Figure 24: Easy Mobility for the replaceable skin layer membrane Treatment Unit 100 m^3 / hr being moved from Barstow, Texas to a southern Texas E & P Operator Site.

Figure 25 The Replaceable skin layer membranes after two months of operation with the slide out tray for easy maintenance.

In this operation, the E & P operator was concerned with iron in the treated water. As a result, hydrogen peroxide H_2O_2 was used to oxidize the iron to a precipitated solid before the water was treated by the replaceable skin layer membranes.

Below are the results of

- the water as a raw water,
- the water pretreated with H_2O_2 and
- the final permeate (treated water) after the replaceable skin layer membranes.

The results confirmed the production of high-quality water, residual oil removal as well as iron removal. All these parameters were superior to the DAF technology output at the adjacent site. However, in this case study, a very significant new benefit of the replaceable skin layer membranes was demonstrated. When compared to the DAF technology, replaceable skin layer membranes have a 90% reduction in sludge production volumes. Managing sludge is very expensive. Furthermore, the DAF process required pretreatment with three weir tanks. Not only did the weir tanks increase the equipment footprint, but they also exasperated the sludge volumes. The replaceable skin layer membrane technology's ability to significantly reduce sludge volumes provides a further and significant cost advantage. In addition, DAFs rely on chemistry for the treatment process and as a result, temperature has a significant impact on the treatment performance. Temperature has little impact on the replaceable skin layer membrane performance.

Figure 26: Duplicate samples of Raw water without H_2O_2, Raw water with H_2O_2, and RSL Membrane treated water(permeate).

Table 3 Water Quality Data for Replaceable skin layer membranes treating Produced Water in South Texas

Produced Water Analysis- Treated by RSL Membranes South Texas					
Date	February 13-23- average of two separate samples (Feb 11 and 12)				
	Raw Produced Water before Hydroxide addition	% Reduction based on treated water	Raw Produced Water after Hydroxide addition	% Reduction based on treated water	Permeate (treated) from RSL Membranes
Turbidity	135	98.52%	190-390	99.31%	<2
TSS (ppm)	94	94.68%	110-290	97.50%	<5
Oil (ppm)	56	95.54%	93	97.31%	<2.5
pH	6.9		7		6.78
ORP	-95		180-310		200-375
H2S					
CO2					
Al (ppm)	<5	0.00%	<5	0.00%	<5
Arsenic (ppm)	<1	0.00%	<1	0.00%	<1
Barium (ppm)	13.7	1.46%	14	6.25%	13.5
Boron (ppm)	113	1.77%	116	4.31%	111
Calcium (ppm)	6570	10.35%	6500	9.38%	5890
Chloride (ppm)					
Cobalt (ppm)	<1	0.00%	<1	0.00%	<1
Chromium (ppm)	<1	0.00%	<1	0.00%	<1
Copper (ppm)	<1	0.00%	<1	0.00%	<1
Iron (ppm)	7	71.43%	10.5	80.95%	<2
Lead (ppm)	<1	0.00%	<1	0.00%	<1
Lithium (ppm)	94.4	10.70%	92.3	8.67%	84.3
Magnesium (ppm)	565	2.65%	606	9.24%	550
Manganese (ppm)	4.09	19.32%	3.75	12.00%	3.3
Nickel	<1	0.00%	<1	0.00%	<1
Phosphorus	4.28	69.63%	3	54.70%	1.3
Potassium (ppm)	1160	12.07%	1160	12.07%	1020
Sodium (ppm)	26400	5.68%	27400	9.12%	24900
Strontium (ppm)	622	6.27%	617	5.51%	583
Sulfate (ppm)					
Zinc (ppm)	12.4	89.11%	11	87.73%	1.35

Finally, this case study provided the benefit of comparing the cost to treat the same produced water with dissolved air flotation technology and replaceable skin layer membranes. Both technologies are accepted technologies by the oil and gas industry. Table 4 differentiates the opex cost and the five-year depreciation cost.

Table 4 Cost Comparison between DAF and Replaceable skin layer membranes

OPEX and 5 Year Depreciation Cost Comparison for Produced Water Treatment DAF vs Replaceable skin layer membranes					
		Fixed Site - $ USD /m3		Mobile-$USD/m3	
		DAF	RSL	DAF	RSL
Labor		$0.322	$0.049	$0.322	$0.194
Subsistance		$0.032	$0.016	$0.032	$0.016
Maintenance		$0.014	$0.061	$0.014	$0.061
Powder		$0.000	$0.232	$0.000	$0.232
Coagulants		$0.166	$0.000	$0.166	$0.000
Peroxide		$0.202	$0.202	$0.202	$0.202
Polymer		$0.358	$0.000	$0.358	$0.000
Fuel		$0.000	$0.000	$0.246	$0.246
Air Compressor		$0.000	$0.000	$0.015	$0.015
Generator		$0.000	$0.000	$0.013	$0.013
Electricity		$0.028	$0.010	$0.000	$0.000
Sludge disposal		$3.150	$0.315	$3.150	$0.315
Sub Total		$4.271	$0.884	$4.517	$1.293
Contingency	10%	$0.427	$0.088	$0.452	$0.129
Depreciation		$0.110	$0.372	$0.110	$0.372
Total Cost		**$4.808**	**$1.344**	**$5.079**	**$1.794**

There is no comparison between a DAF and replaceable skin layer membranes when considering permeate water quality. Typical water quality for DAF and replaceable skin layer membranes is shown in Table 5.

Table 5 Typical Permeate (treated water) Quality

Quality Parameters		DAF	RSL
Turbidity	(NTU)	10-25	<1.0 NTU
TSS	(mg/l)	15-25	<2 ppm
Oil	(mg/l)	25-50	< 3ppm

Nevertheless, the end user may find the water quality of a DAF acceptable. Therefore, cost is important. The key cost differences are circled in Table 4 and are as follows.

1. Labor is significantly lower on replaceable skin layer membranes because of the simplicity of operation and maintenance.
2. Maintenance is a higher cost due to the higher capex of the replaceable skin layer membranes compared to DAF technology.
3. Replaceable skin layer membranes utilize approximately 1/3 the electricity compared to DAF technology. Replaceable skin layer membranes provide an excellent opportunity for an end user of the technology to achieve net zero standards.
4. One of the very significant cost savings that was observed in case study 5 was the reduced costs to manage sludge (the reject volume) for replaceable skin layer membranes.
5. Depreciation is much higher for replaceable skin layer membranes because the capital cost is approximately 3.5 times higher than DAF technology.

CONCLUSIONS

The replaceable skin layer membranes are a third-generation membrane technology distinct from dynamic (filter cake) type membranes (Generation1) and conventional low-pressure microfiltration or ultrafiltration membranes (Generation 2). The oil and gas industry and their need to treat and reuse water that is produced from oil and gas operations, has provided a valuable opportunity to display the significant benefits of replaceable skin layer membranes. These benefits include.

1. High flux rates that are 10 times conventional MF and UF membranes
2. Very low energy requirements
3. Simplicity in operation and maintenance
4. High recovery rates and low rejection volumes
5. Simultaneous removal of oil, suspended solids and colloidal solids less than 1 micron
6. Small footprint, and
7. Low opex cost

Table 6 (https://en.wikipedia.org/wiki/Ultrafiltration) provides a summary of the specifications for replaceable skin layer membranes based on the experience of the five case studies presented.

Table 6 Process Requirement for Ultrafiltration Membranes

Process Characteristics - Manufacturers Recommendations				
Operating Parameters	**UF Hollow Fibre**	**UF Spiral-wound**	**UF Ceramic Tubular**	**RSL Membranes™**
Energy Requirements Kwh/M3	**0.8 + pretreatment energy (0.3-0.4)**	**0.8 + pretreatment energy (0.3-0.4)**	**1 to 5 + pretreatment energy (0.3-0.4)**	**0.1**
pH	2–13	2–11	3–7	2-13
Flux (Litres/m2/hr)	25-50	25-50	35-100	275-800
Feed Pressure (psi)	9–15	<30–120	60–100	0-10
Backwash Pressure (psi)	9–15	20–40	10–30	air 25-35
Temperature (°C)	5–30	5–45	5–400	2-400
Total Dissolved Solids (mg/L)	<1000	<600	<500	<250000
Total Suspended Solids (mg/L)	<50 max 100	<50 max 100	<300	<1000 max 2000
Turbidity (NTU)	<50 max 100	<1	<10	<1000
Iron (mg/L)	<5	<5	<5	<150 but no limit has been defined
TOC	<10	<10	<10	unknown- not identified as a problem parameter
Oils and Greases (mg/L)	<0.1	<0.1	<0.1	<1000 max 2000
Solvents, phenols (mg/L)	<0.1	<0.1	<0.1	unknown- not identified as a problem parameter

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