RO Membrane Performance when Reclaiming Produced Water from the Oil Extraction Process

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Abstract

Produced water brought to the surface as part of the oil and gas extraction process is typically disposed of through deep well injection. Unfortunately, oil production may be limited by the deep well's capacity to receive the produced water. To remove this limitation, a combination of technologies is used to treat produced water for environmental, industrial, or agricultural reuse. Among these technologies is desalination by reverse osmosis. Specifically, reverse osmosis membranes are used as one of the final treatment steps after oil, grease, solids and hardness removal, and pH elevation. The RO step is designed to remove the remaining dissolved salts and organics, including sodium, chloride, silica, boron, benzene and xylene. The performance of the RO membrane when treating produced water at an elevated pH can be distinctive from performance on more common RO feeds at a neutral pH. This unusual condition requires a better understanding of the salt passage, flow, and membrane durability at high pH / high temperature conditions associated with the treatment of produced water. The purpose of this paper is to asses the performance of RO membranes treating high pH/high temperature produced water during its first year of operation. The assessment will be based on actual plant performance as well as the analysis of an element extracted from the plant.

At startup, overall performance of the RO system was as expected. Both silica and boron were rejected as well as or better than expected. However, the passage of sodium ion was higher than expected. The permeate pH also gave mixed results when compared to theoretical predictions. Instead of seeing a decrease in permeate pH relative to feed pH as is typical in RO systems operating at neutral pH, the permeate pH increased relative to the high feed pH.

In addition to better understanding the effect of the produced water on membrane permeability and salt passage, the membrane's durability was also analyzed. Exposure to high pH and high temperatures can adversely affect the integrity of the membrane and element construction. For this reason, an element was extracted from the RO system after six months of operation. The strength of the membrane's backing and the membrane glue lines were found to have weakened. However, the integrity of the elements was preserved and the polyamide separating layer of the membrane showed no sign of degradation and no significant increase in salt passage.

I. INTRODUCTION

Reverse Osmosis, a mature technology which has been used for decades to desalinate municipal and industrial waste streams, for potable purposes, is now applied to reclamation of difficult wastewaters within the petroleum industry. Specifically, the petroleum industry often uses the injection of steam into an oil formation to decrease the viscosity of the oil, which enhances the extraction of the oil. When the steam condenses as it cools, water is produced as a byproduct. The generic term “produced water” is used to describe the byproduct of the steam, oil and gas from this extraction process.

Produced water is a byproduct of the oil and gas extraction process. Produced water is created when steam is injected into the oil formation to increase the temperature and decrease the viscosity of the oil; thus enhancing the extraction of oil from the formation. The produced water contains a high level of dissolved salts, organic acids, and other organic and inorganic contaminants. The concentration of these contaminants can vary significantly due to natural variations in the geologic formations and due to the type of oil based product being produced. Not only does the poor quality make the disposal of produced water a challenge, but the large quantities make handling difficult as well. The volume of produced water can be as much as ten times the volume of the oil extracted.

One method for dealing with produced water is to return the water to the formation. A portion of the produced water is reinjected into the oil producing zones to improve oil recovery through water or steam flooding. Another portion of the produced water is disposed of through deep well injection. Deep well injection is limited by the capacity of the injection wells which in turn limits the oil field productivity and results in decreased revenue. As far back as the 1990s, processes for reclaiming and reusing the produced water were researched and piloted [(Bartels and Dyke, 1990, Tao et. all, 1993). These processes were shown to be effective, but were never widely used due to their high cost relative to the then low cost of oil. However, due to the increase in oil prices in recent years, with oil climbing above $150 a barrel in 2008, there has been a renewed interest in processes to reclaim and reuse the produced water and therefore increase oil production. Since the 1990s, process technologies have improved to make treating produced water even more economically attractive. Among the technologies that have seen significant improvements in recent years is desalination by reverse osmosis. This paper will demonstrate the use of reverse osmosis membranes to treat produced water at oil field in Central California. The RO system was used as the final steps after oil, grease, solids and hardness removal. Using polyamide membranes, the RO process was designed to operate at high pH for the removal of dissolved salts and organics such as sodium, silica, boron and TOC. The treated water was then reused for environmental augmentation purposes.

II. PRETREATMENT TO THE RO

Due to an incompatibility between the raw produced water and the RO element, the following technologies are employed before the RO system to reduce or eliminate the problematic oil and grease, hardness, metals, high temperature, and suspended solids. The extensive pretreatment ensures stable operation of the RO for at least eighteen months.

- Induced gas floatation (IGF) and walnut shell filters are used to reduce free oil concentrations from as high as 100 ppm to levels less than 1.0 ppm.

- Chemical softening/settling and ion exchange softening is used to soften the water. Hardness levels below 0.1 ppm as CaCO3 are achieved before the RO. Calcium levels are reduced to 0.08 ppm CaCO3 and magnesium levels are reduced to around 0.02 ppm CaCO3. A combination of anti-scalant and a Langlier Saturation Index (LSI) below 1.8 are necessary to avoid calcium carbonate scaling.

- Heat exchangers are used to reduce temperatures. The high temperature produced water reaches temperatures greater than 80 C and must be cooled below 40 C before reaching the RO.

- Multi media filters are used to reduce the suspended solids concentration from greater than 20 ppm to below 0.5 ppm. The Silt Density Index (SDI) is reduced to less than 4.0 for stable RO performance. After one year of operation the silt density index (SDI) of the feed to the RO was found to have averaged between 3 and 4. (**Figure 1**).

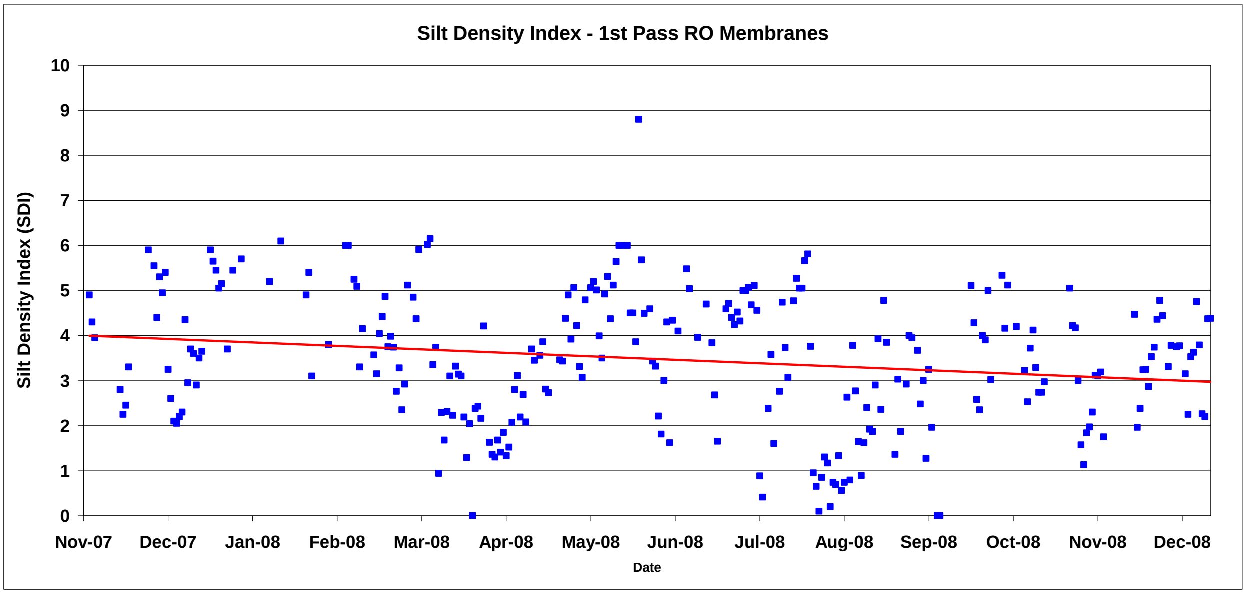


Figure 1. Silt Density Index (SDI) of the feed to the RO

In addition to the above pretreatment technologies, the pH of the produced water is elevated from 7.5 to above 10.7 before reaching the RO. Increasing the pH impacts both the water chemistry and characteristics of the RO membrane. Increasing pH can change the water chemistry by affecting charge, size or solubility of specific constituents in the feed such as boron, silica, and dissolved organics. Increasing pH can also influence the charge of an RO membrane and open the highly crosslinked molecules that form the polyamide structure. An analysis of the RO performance that follows demonstrates that these changes in water chemistry and membrane characteristics improved the rejection of some ions and allowed for higher recovery and more stable operation.

Salinity of the water coming to the RO started at 5700 ppm and climbed to 7000 ppm during the first year of operation. The produced water included boron levels as high as 26 ppm and silica concentrations of 160 ppm. Also present were problematic constituents such as oil and grease and specific hydrocarbons that are known to damage the RO membrane. Free oil, defined as oil droplets with diameter equal to or greater that 150 microns, were present in concentrations of 17 mg/L. Aromatic hydrocarbons such as benzene, toluene, xylene, which are potentially damaging to the polysulfone support layer of the membrane, were also present at lower concentrations of 6 to 28 ppb. **Table 1** gives a break down of the various constituents that are found in the produced water before pretreatment (raw) and the water going to the RO after pretreatment (feed). In the case where a change in the concentration of the constituent occurs in going from the raw produced water to the RO feed, the pretreatment technology that effected that change is also noted in **Table 1**.

Table 1. Changes in the characteristics of the raw produced water and the feed water to the RO. The pretreatment technology that affected the change is also noted in the left column.

	Raw	Feed	Note
pH	7.5	10.7	Caustic injection increases pH
Temperature (C)	80	35	Heat exchanger reduces temp
Calcium (ppm)	80	<0.1	Chemical and ion exchange softening reduces hardness
Magnesium (ppm)	10	<0.1	
Sodium (ppm)	2,300	2,300	No change
Potassium	39	39	No Change
Strontium	1.0	1.0	No Change
Bicarbonate (ppm)	696	119	Shift in carbonate distribution due to pH change
Carbonate (ppm)	2.2	604	
Sulfate (ppm)	133	133	No Change
Chloride (ppm)	3,400	3,400	No Change
Silica (ppm)	160	90	Some reduction of silica in clarification step
Boron (ppm)	26	26	No Change
Total Dissolved Solids (TDS)	5,500 - 7,500	5,500 - 7000	No Change
Total Suspended Solids (TSS)	20	<0.1	Multi-media filters remove TSS
TOC (ppm)	80	60	Organic material reduced by induced gas flotation and walnut shell filters
Benzene (ppb)	6.4	6.4	
Toluene (ppb)	11	11	
Xylene (ppb)	28	28	
Total Oil and Grease (ppm)	53	38	
Free Oil (ppm)	17	<1.0	

III. RO SYSTEM DESIGN

The produced water RO system under consideration was designed as a two pass system. Due to the high quality of the water feeding the second pass, this analysis will focus on the more challenging operation of the first pass only. The first pass of the RO system is designed to accommodate the challenging produced water feed while taking advantaged of the softened water and high pH conditions.

The first pass of the RO produces 688 gpm from a two stage array using a total number of RO elements to achieve an average system flux of 11 gfd. This flux is selected to reduce particulate fouling on the membrane surface, maintain stable performance, and limit the required number of cleanings. Due to the high salinity of the feed, the high recovery, and the relatively high permeability of the membrane, there existed a tendency for the first stage to flux much higher than the second stage. For this reason, the flux balance between the two stages was improved by applying 120 psi of back pressure to the first stage.

First pass recovery is 85%. As mentioned previously, the ability to design for higher recoveries is due to a combination of hardness and metals removal and elevated feed pH. With the potential for CaCO3 scaling and SiO2 scaling eliminated by the pretreatment, the recovery was then limited by osmotic pressure only.

The membrane selection was based on maximizing rejection of the very high salinity feed, including rejection of silica and boron. At the time the RO system was designed, the highest rejecting brackish membrane available had a sodium chloride rejection of 99.7% and a flow of 6500 gpd at standard test conditions of 225 psi and 1500 ppm NaCl feed. The element was manufactured with a thicker 31 mil brine spacer to increase the height of the flow channel by 25% relative to the thinner 26 mil brine spacer used in many standard brackish elements. The thicker brine spacer allowed particulates to more easily pass without becoming trapped in the spacer mesh. The use of thicker spacer was intended to reduce the differential pressure losses between the feed and brine end of the system. The thicker spacer would also potentially reduce the number of cleanings while increasing the effectiveness of each cleaning.

IV. RO SYSTEM PERFORMANCE

Upon startup in the fall of 2007, the feed temperature was 35 C and the feed conductivity was 12,500 us/cm. This resulted in a feed pressure of 407 psi; very close to the projected feed pressure of 400 psi. System salt passage at the high temperature and high pH was 3.4% (rejection of 96.6%). Permeate conductivity was 1,100 us/cm. The membrane's salt passage increased only 7% during the first twelve months of operation (**Figure 2**).

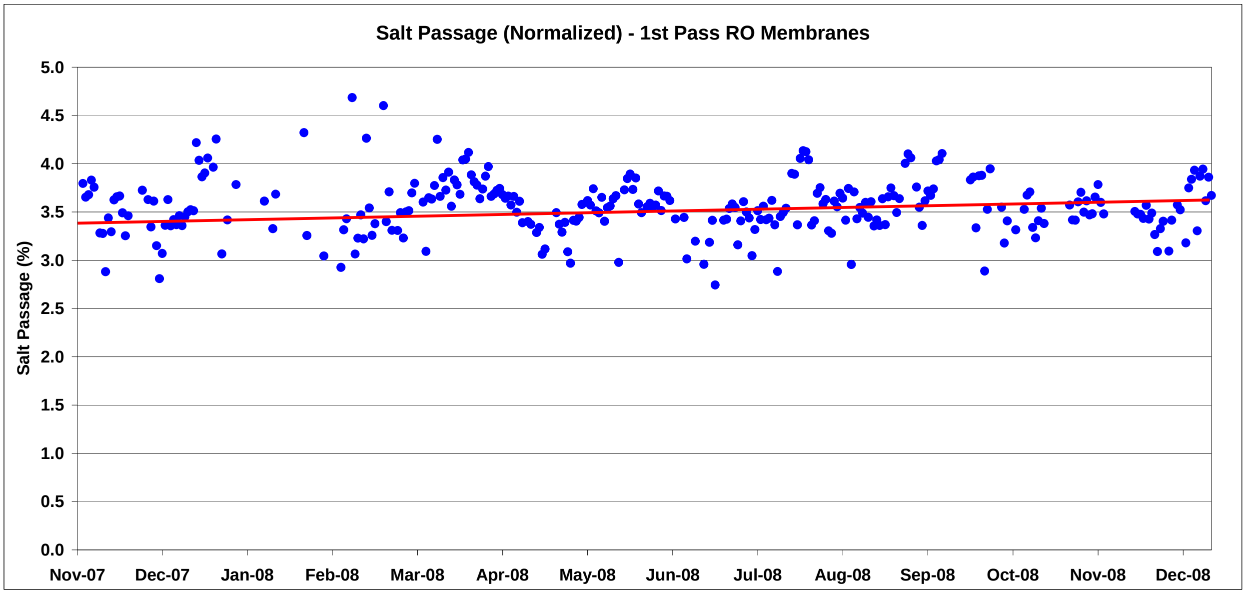


Figure 2. Normalized salt passage from the first pass of an RO treating produced water

The passage of most ions was as good as or lower than expected. Though the passage of most ions met expectations and overall permeate quality was good, the passage of the sodium ion through the membrane was higher than expected. An analysis of the feed, permeate and concentrate (**Table 2**) demonstrates some of the unique behavior of the membrane when treating produced water. As stated previously, the high feed pH of 10.75 allows for high recoveries despite the high concentration of SiO2. SiO2 concentration in the concentrate stream was 541 ppm.; more than twice the typical concentrations achieved when running at neutral pH. Similarly, the SiO2 rejection of 99.8% is far greater than the typical 99.0% rejection at neutral pH. This increase in silica solubility and silica rejection is due to the ionization of reactive silica at high pH. Reactive silica is monomeric and contains a single silicon atom. Also referred to as monsilicic acid, the reactive silica is only slightly ionized at neutral pH. At pH of 8.5, 10% of the reactive silica is ionized. As pH is increased to 10, as much as 50% of the reactive silica becomes ionized [3]. This high degree of ionization at the higher pH has the combined benefit of preventing polymerization of the SiO2, and therefore reducing the tendency to scale, while also increasing the rejection of the SiO2 by the negatively charged membrane. [4].The boron rejection of 96% was also good for a brackish membrane.

Table 2. Water analysis from the first pass of an RO treating produced water.

	Feed	Perm	Con	Rej %
pH (units)	10.75	11.5	10.3	
Na (mg/L)	2180	127	12800	98.3
Cl (mg/L)	2223	53.3	14890	99.4
SiO2 (mg/L)	92	0.528	**541**	99.8
Boron (mg/L)	22.3	2.68	118	96.2

Also notable was the increase in pH in the permeate relative to the feed. In a typical RO systems, treating neutral pH feed waters, the pH in the permeate decreases as much as one to two units relative to the feed. This is due to the fact that carbon dioxide (CO2), a gas, passes freely through the membrane while the bicarbonate (HCO3-) is rejected. Maintaining a constant carbon dioxide level while decreasing the bicarbonate level shifts the pH down. In the produced water RO, the opposite shift in pH occurred. The feed to the RO was high at 10.7. The permeate stream was higher at 11.5. This unlikely outcome may be caused by the increase in hydroxyl ion concentration at elevated pH. As pH increases and the hydroxyl ion concentration increases, the negatively charged carboxyl groups on the membrane surface are repelled or opened and the membrane “swells”. This “swelling” effect increases the passage of certain ions, including the hydroxyl ion. Hydroxyl ions (OH-) pass through the membrane more readily than chloride ions (Cl-). The high passage of the hydroxyl ions would require the high passage of a counter ion to maintain charge neutrality. This would explain the higher than expected passage of sodium. The sodium passage in this system is almost six times that of the chloride ion. Typically sodium passage is similar to that of the chloride [5].

V. SINGLE ELEMENT ANALYSIS

The feed of the produced water RO can pose a challenge to the long term performance of the RO membrane and the integrity of the element. The combination of high pH and high temperature can weaken the glue lines and the supporting layers of the membrane. Likewise, the presence of aromatic hydrocarbons can weaken the membrane support layer. To determine the effect of the produced water feed on the RO, a lead element was extracted from the RO system after six months of operation and subjected to a detailed analysis. The element was first tested at the standard test condition of 225 psi and 15% recovery on a 1500 ppm NaCl feed at 25 ^{o}C. The results can be viewed in **Table 3** below. The retest performance is compared to the original factory wet test performance. The retest indicates only a 16% flux loss in the element. Salt passage increased by only 5%. This change in element performance agrees with the increase of only 7% in the overall system salt passage. The differential pressure between the feed end and the concentrate end of the element increased substantially. This is to be expected considering the element was located in the lead position of the RO system.

Table 3 Standard Test Performance of RO Elements Before and After Six Months of Operation on a Produced Water Feed at pH of 10.7 and a Temperature of 35 C.

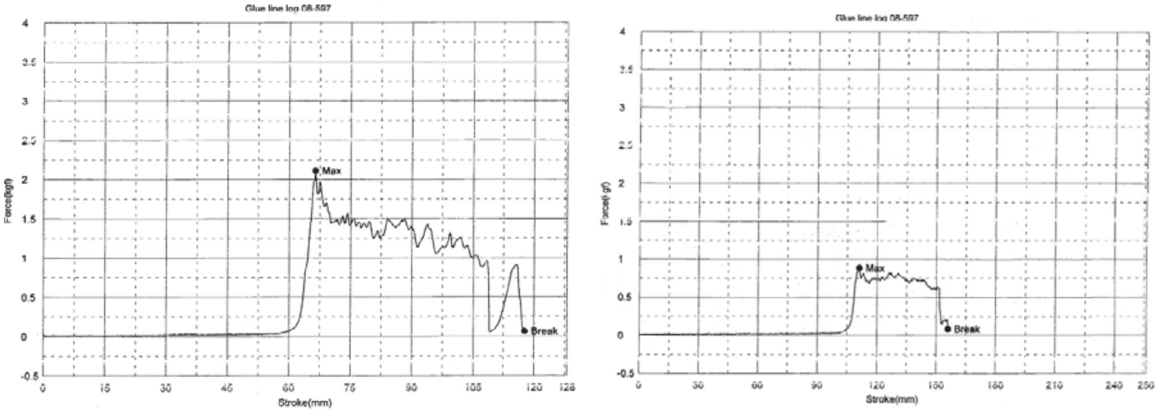
Original Factory Test			Retest after Six Months of Operation			% Change		
Rej (%)	**Flow (GPD)**	**Delta P (psi)**	**Rej (%)**	**Flow (GPD)**	**Delta P (psi)**	**Salt Passage**	**Flow**	**Delta P**
99.80	4,887	1.5	99.79	4,133	3.9	+5%	-16%	+160%

Additional testing was done on membrane samples extracted from the element to determine the effect of exposure to produced water on membrane backing strength and membrane glue strength. To determine membrane strength, four 25 mm by 130 mm strips were cut from different locations of the autopsied membrane sheet and tested in a tensiometer. The membrane exposed to the high pH, high temperature produced water feed for six months failed at a tension force that was 35% less than that of a new membrane. (**Table 4)**

Table 4 Tensile strength of new membrane and membrane operated on produced water feed for six months at pH = 10.7 and temperature = 35 C.

	Failure (kg) **Sample 1A**	**Failure (kg)** **Sample 1B**	**Failure (kg)** **Sample 3A**	**Failure (kg)** **Sample 3B**	**Failure (kg)** **Average**
New Membrane	18.5	18.6	12.5	11.6	**15.3**
After 6 months operation at pH = 10.7 and T = 35 C	10.1	10.2	10.5	8.8	**9.9**

The glue which seals the RO membrane leaves together to form the pocket where the permeate water is collected is an important component of an RO element. If glue lines are weakened, the integrity of the element can be compromised and feed can enter the permeate stream. The peel strength of the returned element's glue lines were tested using a tensiometer. The tesiometer was set for a pull rate of 10 inches per minute. **Figure 3** below shows the difference between a new membrane's peel strength (A) and the peel strength of a membrane exposed to produced water for six months (B). The maximum glue peel strength of 0.9 kg from the produced water element was less than half of the maximum peel strength of 2 kg from the new element.



(A) (B)

Figure 3. Glue peel strength of (A) new element and (B) element operated on produced water feed for six months at pH = 10.7 and temperature = 35 C.

VI. ACKNOWLEGEMENT

The authors would like to acknowledge A. Anit, J. Rockoff and R. Guial for their help in analyzing the returned membrane and carrying out the experimental work.

VII. CONCLUSION

Reverse osmosis membranes have been used as one of the final steps for the treatment of produced water from the oil and gas extraction process. The RO system demonstrated over one year of stable performance due to the effectiveness of the pretreatment process and the durability of the RO membrane. The operation of the first RO system has demonstrated:

- Most ions, including boron, silica, and chloride are rejected as well as or better than expected at the extreme conditions found in this application. However, the combination of high pH, high temperature, and high feed salinity led to a sodium passage that was six times higher than expected.

- The retest of a lead element extracted from the RO system after six months of operation confirmed the stable permeability and salt passage of the membrane operating on the challenging produced water feed.

- The RO was successfully run at a high pH of 10.7 and high recovery of 85% with little fouling. Based on the SiO2 solubility curve [6], the SiO2 concentration in the concentrate stream was kept below 600 ppm at pH of 11.2. Organics were kept in solution as well.

- The feed pH of 10.7, temperature of 35 C, and the presence of hydrocarbons in the feed, caused the strength of the membrane's backing and the membrane glue lines to weaken. However, the integrity of the elements was preserved and the polyamide separating layer of the membrane showed no sign of degradation and no significant increase in salt passage.

VII. REFERENCES

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