Performance of a Reverse Osmosis System when Reclaiming High pH - High Temperature Wastewater

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Abstract

The performance of the RO membrane when reclaiming high fouling produced water at an elevated pH and temperature is distinctive from more common municipal wastewaters. This unique process offers an opportunity to better understand RO membrane salt passage and durability, as well as RO element and system design, at more extreme conditions. The purpose of this paper is to discuss the characteristics of the RO membrane in a system reclaiming high pH/high temperature produced water from the oil and gas extraction process. This characterization will be based on laboratory studies, pilot studies, and actual plant performance.

In addition to understanding salt passage when treating high pH water, a better understanding of membrane longevity is necessary considering the high pH and high temperature operation associated with this process. Operation at high pH can mitigate organic fouling of the RO and act as a kind of continuous cleaning. But exposure to high pH can also adversely affect the integrity of the membrane's polyester support. An analysis of flow, salt passage, and strength was performed to characterize the effects of long term exposure of the membrane to these extreme conditions.

Introduction

Produced water is that water which is brought to the surface as part of the oil and gas extraction process. The produced water contains a high level of dissolved salts 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 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 oil extracted.

The typical method for dealing with produced water is deep well injection. A portion of the produced water is reinjected into 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, the technologies have also improved to make treating produced water more economically attractive to the oil companies. Several treatment technologies, including membranes, are used to treat produced water for environmental and 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, silica and boron.

Produced water characteristics

The specific characteristics of produced water vary depending on the age and geology of the formation, but most produced waters contain contaminants that pose a challenge to the successful long term operation of the RO. These contaminants include suspended silt and clay, suspended oil droplets, dissolved organics such as acetic acid and acetone, dissolved gases such as hydrogen sulfide, heavy metals, and sparingly soluble salts. The temperature of the produced water can also pose a challenge to the RO system. The practice of steam injection can increase water temperatures to as high as 80 C while the RO membrane is limited to less than 40 C. **Table 1** below compares the produced water characteristics from two different sites in North America.

Table 1. Example of produced waters from two locations in North America.

	Site 1 (New Mexico)	Site 2 (California)
pH	7.0-7.5	7.5
Temperature (C)	80	185
Calcium	620	80
Magnesium	110	10
Sodium	5,088	2,300
Potassium	95	39.1
Strontium	15	1.0
Bicarbonate	561	670
Carbonate	0.6	-
Sulfate	2,150	133
Chloride	7,800	3,400
Silica	100	240
Boron	3.5	26
Total Dissolved Solids (TDS)	16,000	7,000
Total Suspended Solids (TSS)	55.0	10
Soluble Organics	30	80
Methyl Ethyl Ketone	1.0	-
Acetone	5.0	-
Oil and Grease	10-50	20 ~ 30

Pretreatment before RO

Extensive pretreatment is required for stable operation of the RO. The following technologies can be employed to reduce or eliminate oil and grease, hardness, metals, temperature, and suspended solids:

- **Free Oil.** Free Oil concentrations as high as 100 ppm can be reduced using induced gas floatation (IGF) , wallnut shell filters, or American Petroleum Institute (API) separators, to levels less than 1.0 ppm.

- **Hardness and heavy metals.** Softening and metal removal can be achieved through chemical softening and settling and ion exchange softening. Hardness levels will be reduced below 0.1 ppm as $CaCO_3$. Calcium levels will be as low as 0.08 ppm $CaCO_3$ and magnesium levels will be around 0.02 ppm $CaCO_3$.

- **Temperature.** Because steam injection is often used as part of the oil extraction process, it may be necessary to reduce temperatures using a heat exchanger. Temperatures as high as 80 C must be reduced below 40 C before sending to the RO.

- **Suspended solids.** Suspended solid concentration in the raw water to an RO system can exceed 50 ppm. With sufficient pretreatment in the form of multi media filters, the suspended solids concentration can be reduced below 0.5 ppm. The Silt Density Index is less than 4.0 for stable RO performance.

Effect of High pH Operation

The final step before the RO involves operating the RO at elevated pH condition. Feed water to the RO is increased in the pretreatment steps from a neutral pH to a pH of 10 to 11. Increasing the pH of the feed 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. Increasing pH can also influence the charge of an RO membrane and open the highly crosslinked molecules that form the polyamide structure. These changes in water chemistry and membrane characteristics can be used to the advantage of the designer of an RO system by improving rejection, increasing recovery and reducing fouling.

Boron

At a pH of 7, when boron is present in the form of boric acid, $B(OH)_3$, the RO membrane rejects only 50% to 93% of the boron, depending on membrane type. The ionization equilibrium of boric acid, a very weak acid, is represented as:

$$B(OH)_3\ (aq) + H_2O = H^+(aq) + B(OH)_4^-\ (aq) \qquad \text{Equation 1}$$

The lack of charge and small size of the boric acid molecule results in this poor rejection. But at higher pH, boron is present as the borate ion, $B(OH)_4^-$,which is well rejected due to its larger radius and negative charge. As **Figure 1** indicates, at a pH of 10, the RO membrane can reject as much as 99% of the boron. The removal of boron is especially important for reuse applications involving irrigation of citrus crops or involving certain industrial applications in the microelectronics industry.

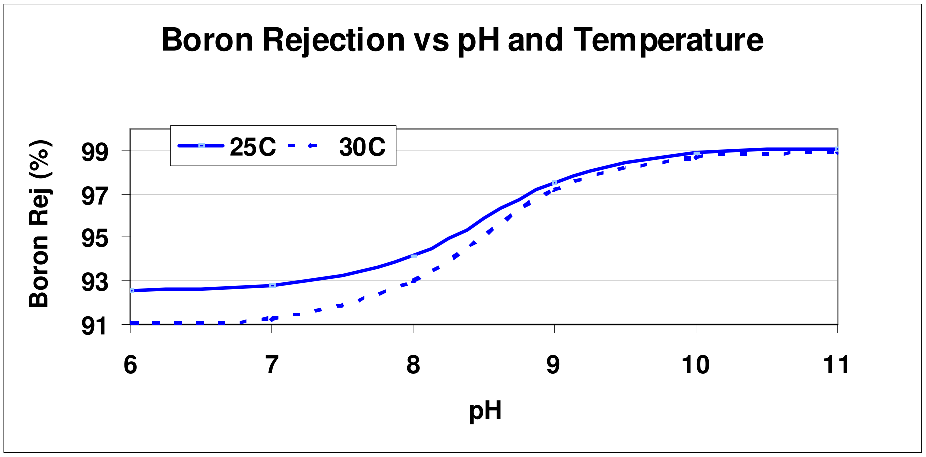

Figure 1. Estimated nominal boron rejection of the RO membrane at 24 C and 30 C as a function of feed pH.

Silica

The water chemistry of silica is a complex. Just as TOC reports the total concentration of organics as carbon without detailing the specific organic compounds, silica reports the total concentration of silicon (as silica) without detailing what silicon compounds are present. The "Total Silica" content of water is composed of "Reactive Silica" and "Unreactive Silica". Reactive silica, $Si(OH)_4$, is the form most desirable for stable RO operation. 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, only 10% of the reactive silica is ionized. As pH is increased to 10, as much as 50% of the reactive silica becomes ionized (Sheikholeslami et. all, 2002). This high degree of ionization at the higher pH has the combined benefit of preventing polymerization of the SiO_2, and therefore reducing the tendency to scale, while also increasing the rejection of the SiO_2 by the negatively charged membrane. (Bremere et all, 2000). **Figure 2** below shows this effect of increasing pH on the passage of silica through the membrane.

The test was done on a single RO element treating a concentrated city water of 2,000 mg/L. The element was run at a flux of 13 gfd and a recovery of 10%. The pH was increased using caustic soda. At the city water ambient pH of 8.1, the silica passage is 0.92%. This is twice the passage of a charged chloride ion at that pH. At the higher pH of 11, the passage of the more ionized silica drops to 0.4% - a passage value similar to that of the chloride ion.

The change in SiO2 rejection as a function of pH corresponds to the change in SiO2 solubility vs pH as shown in **Figure 3** below.

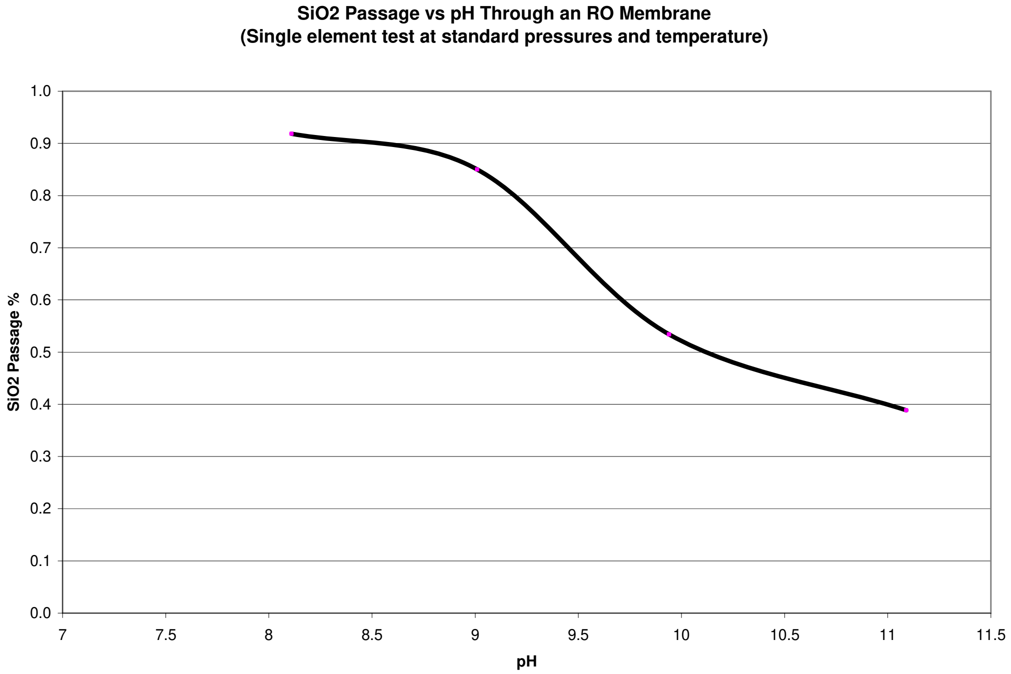

Figure 2. Effect of pH on silica rejection through a reverse osmosis membrane.

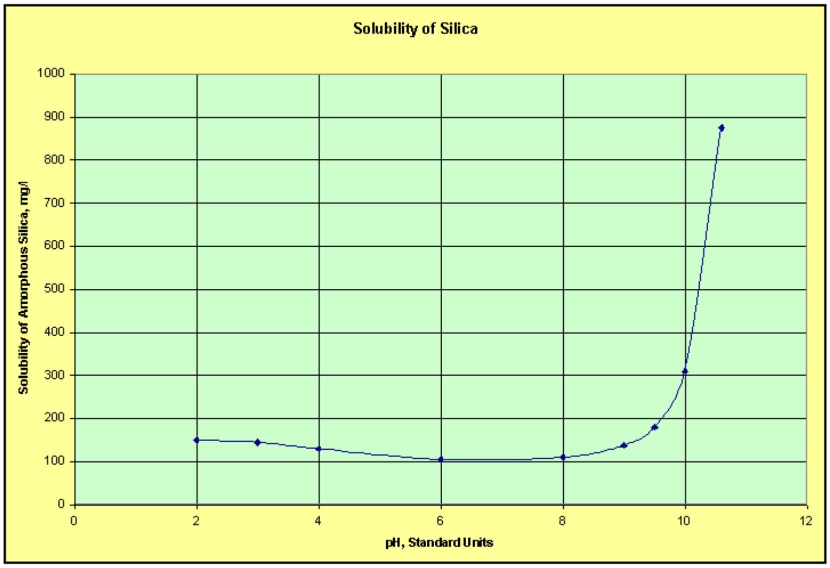

Figure 3. Effect of pH on silica solubility **(**Nagghappan, 2006**)**

Organics

Typical constituents found in the produced water include not only the dissolved salts such as sodium, calcium, silica, and chloride but also dissolved organic molecules such as natural occurring matter (NOM), and halogenated by-products. The most common soluble organics found in produced waters include low molecular weight carboxylic acids and volatile hydrocarbons (Bartels and Dyke, 1990). While the RO and NF membranes are designed to remove such dissolved species, certain organic contaminants in a produced water can be damaging to a composite membrane. There are a wide variety of chemicals which swell or dissolve polysulfone material used as a supporting layer. Chemicals in this class which can rapidly damage a membrane include all aprotic solvents such as dimethyl formamide (DMF), dimethyl acedimide (DMAc), n-methyl pyrrolidone (NMP), dimethyl sulfoxide (DMSO), etc. Likewise, polysulfone can be swollen or dissolved by many ketones, aldehydes, esters, and strong ethers. Aromatic hydrocarbons such as benzene, toluene, xylene, and phenol are also damaging to the polysulfone layer. There are also a wide variety of mixed chemicals which are damaging, such as diesel fuel and gasoline. If the membrane is exposed to high concentrations, >50 ppb levels, the membrane can lose its mechanical strength in a relatively short time. Exposure to this type of contaminant will not be seen initially. However, when the strength of the membrane reaches a critical minimum point, the salt passage can go up dramatically.

Like silica, organics tend to increase in solubility at high pH. This increase in solubility serves to limit organic fouling with running at high pH and act as a continual high pH cleaning on the membranes. The change in organic solubility as a function of pH is shown in **Figure 4** for a napthenic acid.

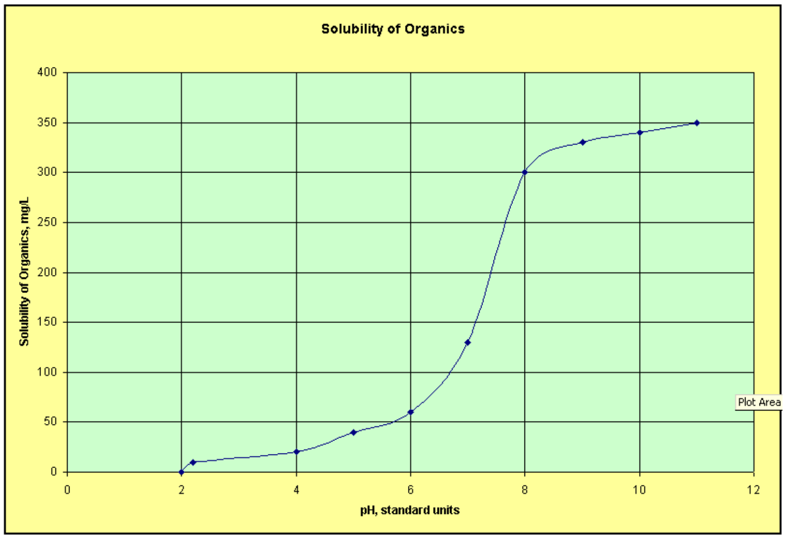

Figure 4. Change in organic solubility as a function of pH (Nagghappan, 2006)

Membrane Characteristics

Studies have been done to characterize the passage of salts through nano filtration membranes (Szabolcs et. al, 2002). The effect of passage through these membranes varies at different pH due to the corresponding variation in membrane charge. (**Figure 5**). Of the three membranes shown, membrane C is characteristic of a typical polyamide RO membrane used for treating the high pH produced waters.

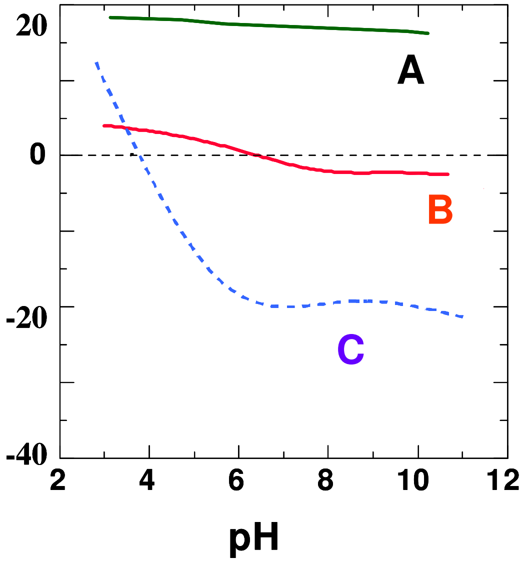

Figure 5. Variation in membrane charge with pH for three different membrane types.

At low pH the hydrogen ion attaches to the membrane's negative carboxyl groups and neutralizes the charge of the membrane. The absence of a negative charge at low pH reduces the membrane's ion rejection. At neutral and high pH, the absence of the hydrogen ion attached to the membrane's carboxyl groups, results in a negatively charged membrane. The presence of a negative charge improves the rejection at neutral pH.

At high pH, the membrane retains its negative charge. However, as pH increases and the hydroxyl ion concentration increases, the carboxyl groups on membranes surface are repelled or opened and the membrane "swells". This "swelling" effect increases the passage of certain ions. Hydroxyl ions (OH-), for example, pass through the membrane more readily than chloride ions (Cl-). This is evidenced by a negligible decrease in pH in the permeate of a produced water RO systems when running at high pH. At one site running at pH greater than 10.5, the pH in the permeate of the RO system actually increased to more than 11.

Along with the high passage of hydroxyl ions, an increase in the passage of sodium is also seen. The sodium acts as the counter ion to the hydroxyl ions in order to maintain charge neutrality in the permeate. Controlled studies were done on single elements running at 15 gfd flux. These studies used both membrane B and membrane C treating a 1000 ppm sodium chloride solution with caustic soda injected to increase pH. **Figure 6** shows the significant increase in sodium passage relative to chloride passage as pH is increased above pH=10. In the case of membrane C, the sodium passage was 7.5 times that of the chloride passage.

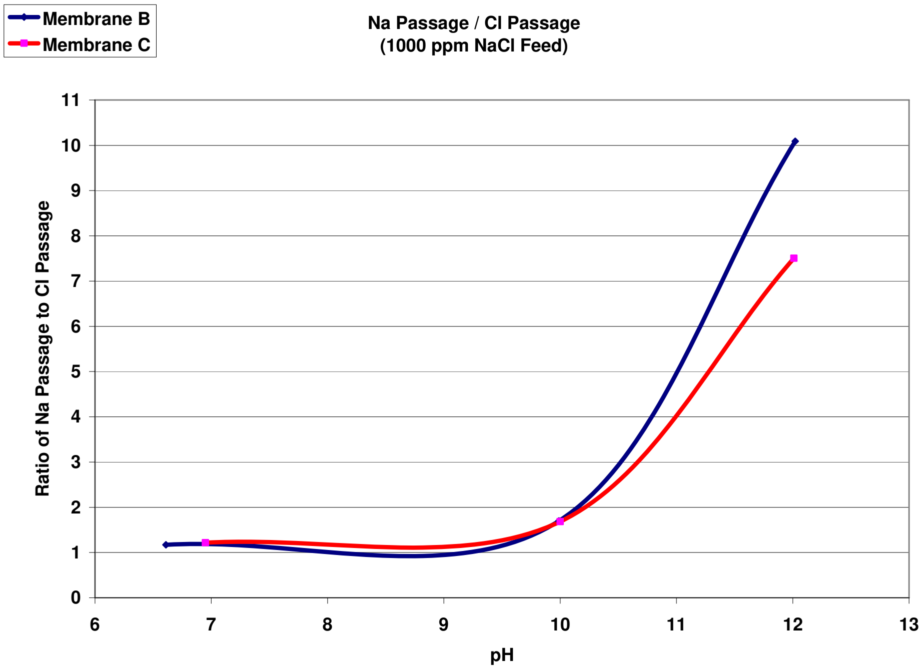

Figure 6. Ratio of sodium passage to chloride passage as a function of pH in two different membrane types. Test was done on single element at a flux of 15 gfd and at T = 25 C and a solution of 1000 ppm NaCl. Caustic soda was dosed to increase pH.

Membrane Life

The polyamide thin film composite membranes are suitable for purification of feed streams containing a wide variety of dissolved contaminants. A composite membrane, as shown in **Figure 7**, is a three layer structure that is comprised of a 0.2 micron crosslinked polyamide layer, a 50 micron porous polysulfone layer, and a 150 micron thick polyester fabric support layer. The characteristics of each layer results in certain feedwater limitations. For example, it is well known that the chemical structure of the top polyamide layer is incompatible with oxidants such as chlorine, ozone, bromine and peroxide. These chemicals cause a progressive "opening" of the polyamide which results in higher salt passage and higher water permeability.

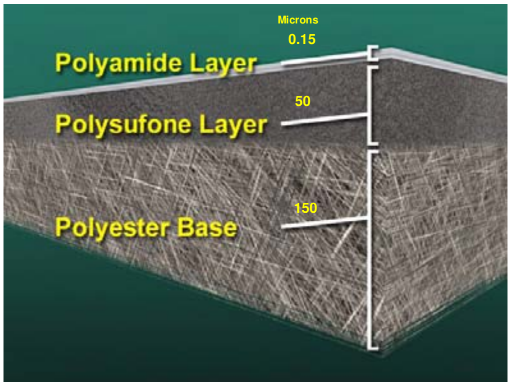

Figure 7. Composite polyamide membrane composed of three layers.

Other limitations on useful membrane life are related to the characteristics of the polyester support layer. Exposure to high pH and high temperature over an extended operating period, will lead to the hydrolysis of the polyester chains and a weakening of the fabric. The polyamide layer is actually more durable than the polyester when exposed to a combination of high pH and high temperature.

To demonstrate this effect in a controlled setting, samples of polyamide membrane from two different membrane manufactures were placed in three different solutions. Each of the three solutions was maintained at 35C and contained 1500 ppm NaCl in deionized water. The pH of each of the three solutions was maintained at pH=7, pH=10, and pH=13. After soaking for a designated period of one day and one month, samples of each membrane were extracted from each solution and tested for tensile strength. The results of the strength test for membrane 1 is shown in **Figure 8** and the results for membrane 2 is shown in **Figure 9.** The strength of each test is given relative to the maximum force (kg) before failure at a pH of 7. The reference failure strength for membrane 1 is 26 kg. The reference failure strength for membrane 2 is 18 kg. The polyester support maintained its original strength at pH=11 and 35 C for up to one month. A weakening of the membrane did not occur until one month of exposure at pH=13. After one month of exposure to pH 13 and temperature of 35, membrane 1 failed at 60% of the reference strength. Membrane 2 failed at 67% of the reference strength. This was true regardless of which membrane was tested since all membrane manufactures use a similar polyester support layer.

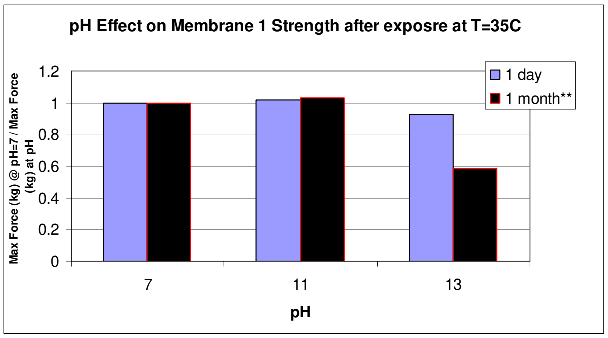

Figure 8. Effect of pH on Membrane 1 strength after exposure to different pH solutions at 35 C for a period of one day and one month. Results are presented relative to strength test at pH=7.

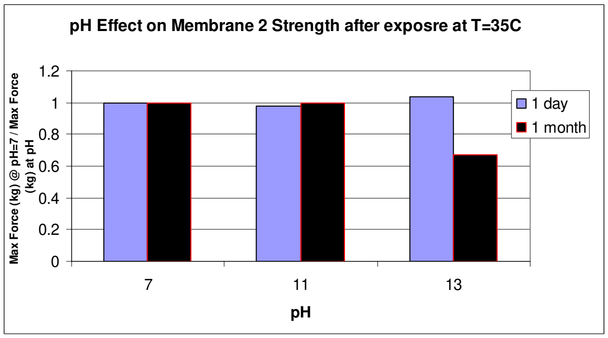

Figure 9. Effect of pH on Membrane 2 strength after exposure to different pH solutions at 35 C for a period of one day and one month. Results are presented relative to strength test at pH=7.

In addition to the strength tests, additional membrane samples were also cell tested to determine any change in rejection after exposure to high pH and high temperature. Cell testing was performed under standard test conditions of 32,000 ppm NaCl at temperature of 25C and pH= 7. The results of the cell test for membrane 1 are shown in **Figure 10** while the results of cell testing for membrane 2 are shown in **Figure 11**. Membrane 1 demonstrated a very stable and consistent rejection between day 1 and pH=7 and day 30 and pH=13. Membrane 2 rejection varied widely for each of the different solutions and exposure times. Due to these variations, no pattern could be established to suggest that the longer exposure and higher pH had any adverse effect on rejection of membrane 2.

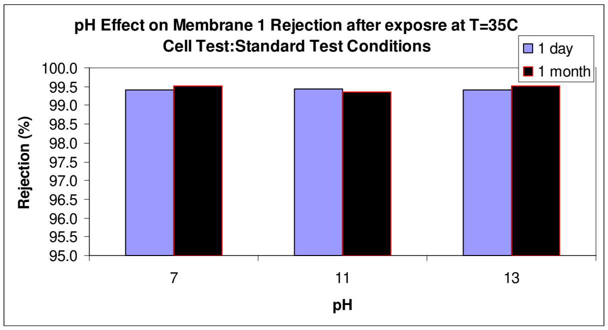

Figure 10. Effect of pH on Membrane 1 rejection after exposure to different pH solutions at 35 C for a period of one day and one month.

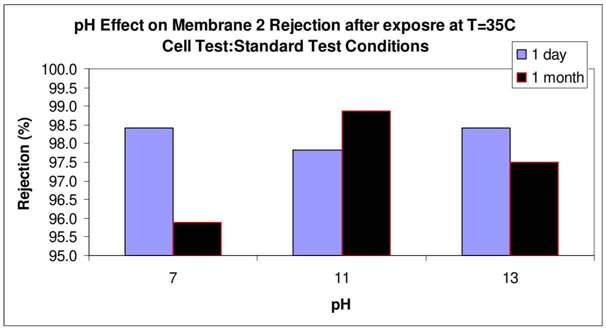

Figure 11. Effect of pH on Membrane 2 rejection after exposure to different pH solutions at 35 C for a period of one day and one month.

RO System Design

An RO system is designed to accommodate the challenging produced water feed while taking advantaged of the softened water and high pH conditions. Despite the extensive pretreatment, the average system flux is similar to a municipal wastewater RO at 10 gfd to 12 gfd. The more conservative flux will avoid particulate fouling, maintain stable performance, and reduce cleaning frequencies.

System recoveries can range from 75% to 90%. The ability to design for high recoveries is due to the removal of hardness, which reduces the potential for CaCO3 scaling, and the increase in pH, which reduces the potential for SiO2 scaling. Calcium carbonate scaling is measured by the Langlier Saturation Index (LSI). A combination of antiscalant and an LSI below 1.8 is necessary to control calcium carbonate scaling.

Assuming the pretreatment sufficiently reduces hardness to less than 0.1 ppm as CaCO3, then the other limiting factor for recovery may be the SiO2 concentration in the concentrate stream. Based on the SiO2 solubility curve in **Figure 3**, the SiO2 concentration in the concentrate should be kept below 720 ppm at pH of 11.2 in the concentrate. Because the SiO2 saturation decreases so rapidly with decreasing pH, it is essential that the produced water system be designed with real time monitoring safeguards and alarms on its caustic injection system. If the potential for CaCO3 scaling and SiO2 scaling is controlled, then the limit on recovery will depend primarily on osmotic pressure limitations. The maximum pressure for brackish elements is 600 psi and the maximum pressure for seawater elements is 1200 psi.

In order to maintain sufficient cross flow in the spiral RO elements, the RO design at high recovery may require a two or three stages with six to seven elements per vessel.

The number of stages selected depends on the target recovery. The lower recovery of 75% to 85% may require only two stages. A higher recovery design between 85% and 90% may require a three stage design. Regardless of the number of stages selected, the minimum concentrate flow from each stage should be no less than 12 gpm per vessel.

A comparison of two different RO system design and performance can be seen in **Table 2.** Both RO systems use similar pretreatments to reduce hardness, suspended solids and oil and grease. Both systems reclaim high pH, high temperature produced water.

Table 2. Two RO systems reclaiming high pH, high temperature water.

	Site A (USA)	Site B (Mexico)
Membrane	**CPA4**	**CPA4**
Brine Spacer (mil)	31	31
Flux (gfd)	10.8	10.8
Rec (%)	80.5	80.5
RO Feed		
pH (feed)	10.7	10.7
Temperature (C)	21	27
Sodium (mg/L)	3110	972
Chloride(mg/L)	2912	723
Silica(mg/L)	92	23
Boron(mg/L)	30	0.2
TOC(mg/L)	84	29
Total Dissolved Solids (mg/L)	7900	2500
Perm		
pH (perm)	11.2	9.9
Sodium (mg/L)	125	12.6
Chloride (mg/L)	102	12.4
Silica (mg/L)	0.53	1.4
Boron (mg/L)	6.6	ND
TOC (mg/L)	1.97	1.8
Use	Environmental	Industrial Reuse

RO Element Design

Even with extensive pretreatment, there is potential for fouling in the RO from suspended or colloidal material when treating produced water. To address this fouling potential, a spiral wound RO element with a thicker brine spacer can be selected. Typical brine spacer thickness is 26 mil or 28 mil. The design of a an RO element with a 31mil or 34 mil brine spacer will increase the height of the flow channel by as much as 30% - allowing particulates to more easily pass without becoming trapped in the spacer mesh. The use of thicker spacer also leads to more effective cleanings. A field study done using elements of varying thickness illustrates the advantages of the thicker brine spacer. The study was done on high fouling water with average SDI between 4 and 5. Three separate runs were completed. Each of the three runs lasted more than 250 days and used different spiral elements with brine spacer thicknesses of 28 mil, 31mil, and 34 mil. Performance parameters were monitored and a periodic clean in place (CIP) was initiated as necessary. **Figure 12** below shows the advantage of more stable differential pressures and fewer CIPs when using the thicker spacer. In the case of the 34 mil spacer, no cleanings were required during the 250 day test period.

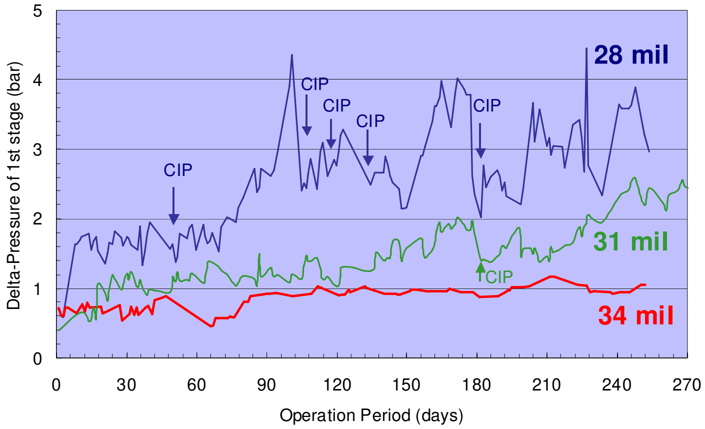

Figure 12. Performance of RO elements with different brine spacer thickness during operation on high fouling feed water with SDI between 4 and 5.

In the past, the increase in brine spacer thickness was accompanied by a decrease in membrane area. RO elements with a standard 8 inch diameter and a 26 mil spacer would contain approximately 400 square feet of membrane area. If a thicker, 34 mil spacer was used, the membrane area would be reduced to 365 sq ft. But the move by most membrane manufactures to automated manufacturing means that an element can be designed with 34 mil spacer while still maintaining 400 sq ft. This is achieved in part by the more accurate placement of glue lines on the membrane sheets.

Conclusion

The renewed interest in the reclamation of produced water at high pH affords an opportunity to understand the behavior of RO membranes operating at extreme conditions. This improved understanding can be applied to new, challenging reclamation applications that may benefit from RO operation at high pH. Based on laboratory testing and field performance, the increase in pH has been shown to benefit RO performance by:

- Improving boron rejection. Produced waters containing boron can be treated with an RO at pH greater than 10 and increase boron rejection from 93% to greater than 99%.

- Improving silica rejection. By increasing pH from neutral to pH 11, silica rejection has been shown to increase from 99.1% to 99.6% - a rejection similar to the chloride ion.

- Operating at higher recoveries. Operation at high pH allows the system to run at high recoveries without silica scaling. At pH of 11.4, RO systems in the field have run with silica levels as high as 720 ppm in the concentrate without scaling.

- Avoiding organic fouling. At high pH, organics become more soluble. Laboratory testing has shown organic solubility to increase by more than seven times at pH greater than 10. Systems with feed TOC greater than 80 ppm have been shown to perform stably with no sign of organic fouling.

Though there are many benefits to operating the RO at high pH, there are also challenges to be considered:

- Membrane life. In a 30 day laboratory test, high pH combined with high temperature has been shown to impact the strength of the membrane's polyester backing before impacting the integrity of the membrane's polyamide rejection layer. This weakening of the backing would eventually affect membrane performance. However, a system running for more than one year at a pH of 10.7 and a temperature of 35 C has shown very stable performance.

- Increase in ion passage. The increase in pH will increase the passage of some ions. Both in the field and in laboratory testing, the passage of the sodium ion increases by seven to ten times its passage at neutral pH.

Regardless of challenges associated with using an RO to reclaim water at high pH conditions, the need to reclaim more challenging waste streams is leading to an increasing number of these applications. As more water, including produced water, is reclaimed at high pH, an improved understanding of the membrane's behavior will allow for those challenges to be addressed.

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