THE UNEXPECTED PERFORMANCE OF HIGHLY PERMEABLE SWRO MEMBRANES AT HIGH TEMPERATURES

Authors:
Rich Franks, Satish Chilekar, Craig R. Bartels, PhD

Presenter :
Rich Franks, Sr. Manger – Applications, Hydranautics, 401 Jones Road, Oceanside CA 92058 USA

Abstract

In recent years, the development of new seawater reverse osmosis elements has focused on maximizing membrane area and membrane permeability. Such developments led to a new generation of SWRO elements with significantly increased permeate flows and lower pressures. When tested at the same pressures and temperatures, today's membranes produce nearly twice as much permeate compared to SWRO membranes from ten years ago and compared to today's tighter, higher rejecting SWRO membranes. Utilizing the highly permeable membranes leads to lower energy consumption and lower operating cost for the SWRO plants.

Membrane permeability is further increased with increasing feed water temperature. As temperature increases, the membrane structure is affected and seawater viscosity decreases. This leads to a further reduction in energy consumption and operating cost.

While permeability of the membrane increases with increasing temperature, the seawater osmotic pressure is also increasing. At temperatures above 25 C, osmotic pressure is more sensitive to temperature changes than membrane permeability. This leads to the diminishing influence of permeability and the increasing influence of osmotic pressure on the system feed pressure. In some situations, the net effect leads to very little change in feed pressure as temperature increases above 25C.

This paper will review the theory behind the competing influences of membrane permeability and osmotic pressure on overall feed pressure. The paper will demonstrate how the evolution of the SWRO permeability has resulted in the increasing influence of osmotic pressure on the membrane performance. The theoretical results will be supported with actual membrane tests performed in the laboratory and on a pilot unit. The paper will identify the temperature ranges and the membrane permeabilities that have the least and greatest influence on the operating cost of an SWRO system.

I. Introduction

The evolution of the seawater reverse osmosis (SWRO) membrane has lead to improved rejection and increasing permeability. In the past 25 years, the permeability (specific flow) of SWRO membranes has more than doubled (**Figure 1**). And even today, there exists a wide range of SWRO membrane permeabilities.

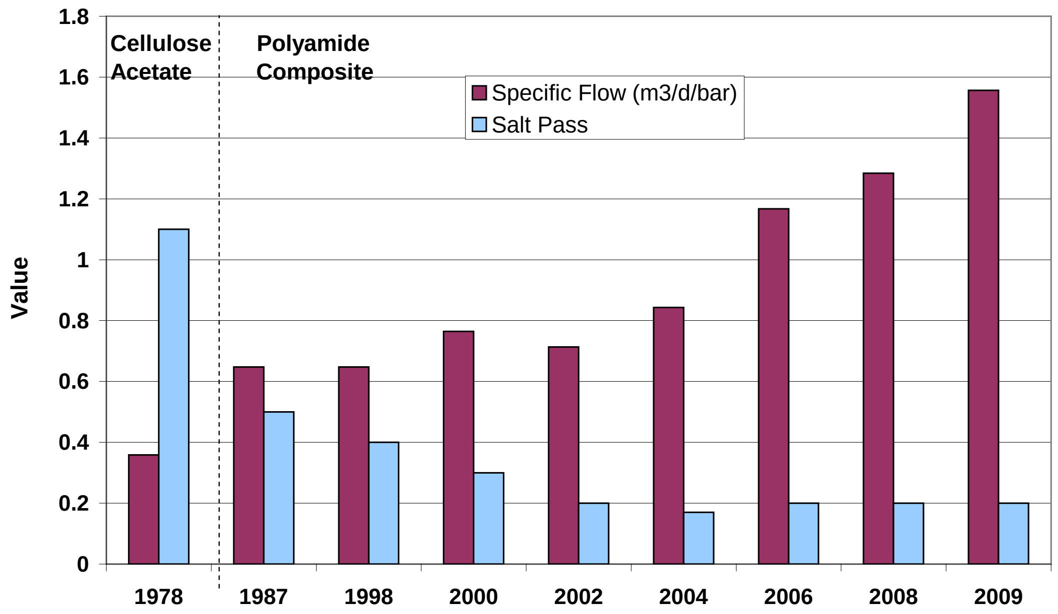

Figure 1. Historical improvements in SWRO membrane permeability (specific flow) and salt passage.

Using the a typical seawater element standard test condition of 800 psi and 10% recovery while treating a 32,000 mg/L sodium chloride feed at 25 C, **Table 1** compares the permeate flow from two commercially available, 400 square foot, SWRO membranes. At this standard test condition, one of the most highly permeable membranes available (SW-12000) gives a flow of 12,000 gpd while the lower permeability (but higher rejecting), SW-6500 produces a flow of 6,500 gpd.

Table 1. Performance of current SWRO membranes at manufacturer's standard test condition of 800 psi and 10% recovery, treating 32,000 mg/L sodium chloride at 25 C.

Membrane	Flow (gpd)	Flow (m3/d)	Permeability
SW-12000[1]	12,000	45.4	High
SW-6500[2]	6,500	24.6	Low

The higher permeability membranes offer lower feed pressures and, in turn, lower operating cost for the SWRO system. Comparing a 20,000 m3/d train using current high permeability membranes such

[1] SWC6, Hydranautics, Oceanside, CA.
[2] SWC4, Hydranautics, Oceanside, CA

as the SW-12000 with the same train using, tighter, higher rejecting membranes such as the SW-6500, the reduction in feed pressure of 8.7 bar would translate to an energy savings of 13%. Despite these savings, the lower permeability, high rejecting membranes are often selected for new plant designs in order to meet stringent permeate quality requirements, especially boron requirements.

In addition to the benefits of increasing membrane permeability, energy savings is increased further with increasing feed water temperatures. For this reason, SWRO plants are sometimes "co-located" with existing power plants which use seawater as part of their cooling process. After using the seawater for cooling, the power plant discharges the same water at a temperature that is 5 C to 10 C warmer than the ambient seawater. The higher temperature power plant discharge is used as feed to the SWRO. The operational savings associated with co-location are reported as a between 3 bar and 6.7 bar (40 psi and 100 psi) reduction in feed pressures and an associated energy savings 5% [1,2,3]. However, the actual magnitude of energy savings depends on several parameters, one of them being the permeability of membrane used. Though the higher permeability membranes will operate at lower pressures than the lower permeability membranes regardless of temperature, theoretical calculations and actual data will show that the relative benefit from increasing temperature will be less when using higher permeability membranes.

II. EFFECT OF TEMPERATURE ON SWRO FEED PRESSURE

The applied feed pressure of an RO system is the pressure required to overcome the resistance of two independent pressures. The feed pressure must overcome the net driving pressure (NDP) associated with the permeability of the membrane as well as the osmotic pressure associated with the differential in salt concentrations across the surface of the membrane. The NDP and the osmotic pressure are inversely influenced by feed water temperature. In other words, as temperature increase, the osmotic pressure increases while the required NDP of the membrane decreases. Despite the opposing effect of temperature on these two pressures the permeability of the SWRO membrane has always been high enough that the effect of NDP dominates over the effect of osmotic pressure – regardless of temperature. This leads to an SWRO system feed pressure that decreases with increasing temperature. However, as the NDP associated with the highly permeability of SWRO membranes decreases while the influence of temperature on osmotic pressure remains constant, there potentially comes a point where the trend is reversed and the SWRO feed pressure starts to increase with increasing temperature. The current generation of highly permeable SWRO membranes is approaching a point where, under certain conditions, the feed pressure may begin to increase with increasing temperature.

The need to accurately predict feed pressures at higher temperatures, and the energy cost associated with those feed pressures, requires a better understanding at what permeability and under what operating conditions will the decreasing trend in feed pressure associated with decreasing temperatures reveres and begin to increase. This better understanding can be had by first reviewing the effect of temperature on NDP and osmotic pressure independently.

1.1 Temperature vs Osmotic Pressure

Osmotic pressure is measured as the pressure required to prevent natural osmosis, which is the natural flow of water through semi-permeable membrane from a solution with lower osmotic pressure (low salinity) to one with higher osmotic pressure (high salinity). The osmotic pressure is influenced by both feed water temperature and salinity. Osmotic pressure in psi (π) can be calculated using the universal gas law:

$$\pi = C * R * T \qquad \textbf{(1)}$$

Where:
C = concentration in moles/l
R = Universal gas constant = 0.08206 l.atm/^{o}K.moles
T = Temperature in ^{o}K

The slope of **Equation 1** is $\pi/T = 14.7 * C * R$.

Alternatively, osmotic pressure can be calculated by a similar, but empirically based formula such as the one in **Equation 2**.

$$\text{Osmotic Pressure} = 1.1266 * 0.001 * T * C \qquad \textbf{(2)}$$

Where T is temperature in ^{o}K and C is the sum of molar concentration of all constituents in a solution.

In order to study the behavior of the above equation, it was calculated using a simple system of sodium chloride (NaCl). Concentrations covered a range of feed and brine salinities between 3.2% and 16% NaCl. The calculations were also done over a range of temperatures from 5 C to 45 C. The extreme concentration of 16% and very high temperature of 45 C, though beyond the normal operating conditions of a SWRO, were considered only to better analyze the behavior of osmotic pressure. The calculated osmotic pressures are given in **Table 2**. Difference in osmotic pressure values at 45 C and 5 C are reported as Δ in the second to last row and the overall slopes of the curves are reported in the last row. This table confirms that as the concentration increases the osmotic pressure correction for temperature also increases. This happens because of the increase in the slope of the equation. Therefore, at high concentrations the slope is expected to be higher in proportion to the increase in the value of C. In **Table 2**, slope varies in exact proportion to NaCl concentration.

Table 2. Osmotic pressure (psi) as a function of NaCl concentration (%) and temperature (^{o}C).

Molal sum (moles/L)	**1094**	**1823**	**2735**	**5470**
NaCl Concentration, %	**3.2**	**5.3**	**8**	**16**
5 ^{o}C	342.6	571.1	856.6	1713.2
10 ^{o}C	348.8	581.3	872	1744
15 ^{o}C	355	591.6	887.4	1774.8
20 ^{o}C	361.1	601.9	902.8	1805.6
25 ^{o}C	**367.3**	612.1	918.2	1836.4
30 ^{o}C	373.4	622.4	933.6	1867.2
35 ^{o}C	379.6	632.7	949	1898
40 ^{o}C	385.8	643	964.4	1928.9
45	391.9	653.2	979.8	1959.7
$\Delta = \pi_{45} - \pi_5$	**49.3**	**82.1**	**123.2**	**246.5**
psi/deg C	1.23	2.05	3.08	6.16

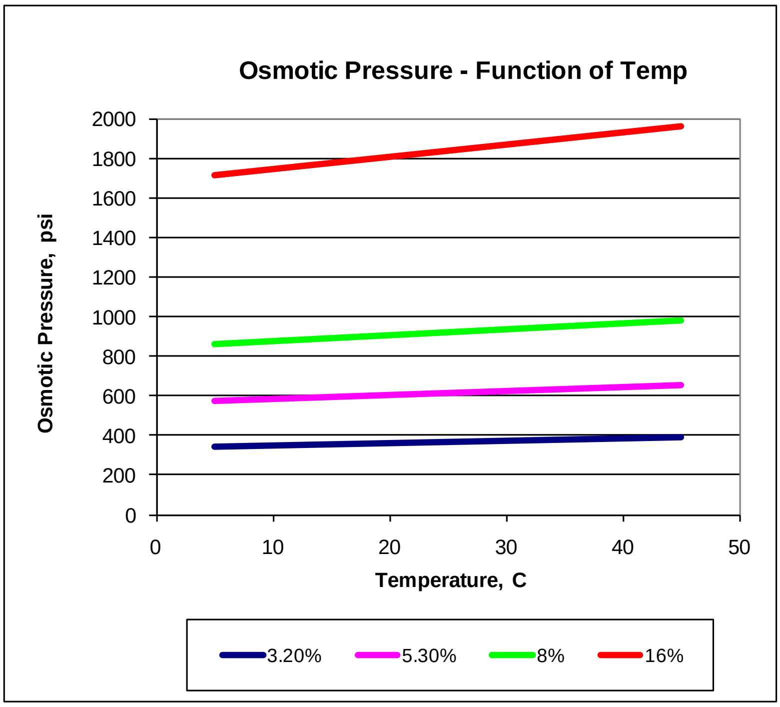

Figure 2. Change in osmotic pressure (psi) as a function of temperature (^{o}C) at various NaCl (%) concentrations.

Figure 2 confirms that the osmotic pressure varies as a linear function with the temperature when using the given correction equation. This is re-confirmed by comparing the slope of the part of the data with the overall data, which are equal. The slope of the 16 % NaCl concentration is the greatest.

1.2 Temperature vs Net Driving Pressure

Net Driving Pressure (NDP) is that portion of the feed pressure, beyond the osmotic pressure, required to induce a water flux through the membrane. The NDP is directly proportional to the water flux and inversely proportional to the permeability of the membrane. As membrane permeability increases, the NDP for a given flux decreases. The effect of temperature on NDP is also inversely proportional since temperature directly affects the membrane's permeability. As temperature increases, the membranes permeability increases so the required NDP decreases. This relationship is shown in the following NDP equation:

$$NDP = (J\ * TCF) / A \qquad \textbf{(3)}$$

Where:
J = water flux (gfd or lmh)
A = membrane permeability (gfd/psi or lmh/bar)
TCF = temperature correction factor (dimensionless)
NDP = Net driving pressure (psi or bar)

This change in membrane permeability with changing temperature is a function of the change in the viscosity of the water as well as a change in the characteristics of the membrane itself. As water temperature increases, the speed of the water molecules increases and the amount of time those water molecules remain in contact with each other decreases - which in turn decrease the water's viscosity. Though this change in viscosity is not recognizable in a liquid with a viscosity range as low as water, it is observable in more highly viscous fluids such as motor oil or honey. The relationship between membrane permeability and water viscosity is easily recognizable when comparing the change in water viscosity with the temperature correction factor (TCF) used to predict the membrane permeability as a function of temperature. The TCF is an empirically based, exponential function that is inversely proportional to temperature:

$$TCF = \text{Exp} [Ke * (1/(273 + Temp) - 1/298)] \quad \textbf{(4)}$$

Where:
T is the feed water temperature in Celsius.
Ke is an empirically derived constant for a given membrane chemistry.

The constant, Ke, in the TCF equation accounts for different types of membrane and their different responses to temperature. The Ke value for a typical polyamide RO membrane falls in the range of 2500 to 5500. To better understand this relationship between temperature, water viscosity, and the Ke constant, the TCF is plotted in **Figure 3** for various values of Ke in the temperature range of 5 C to 45 C. The measured water viscosity in that same temperature range is plotted as well in units of centipoise (cp).

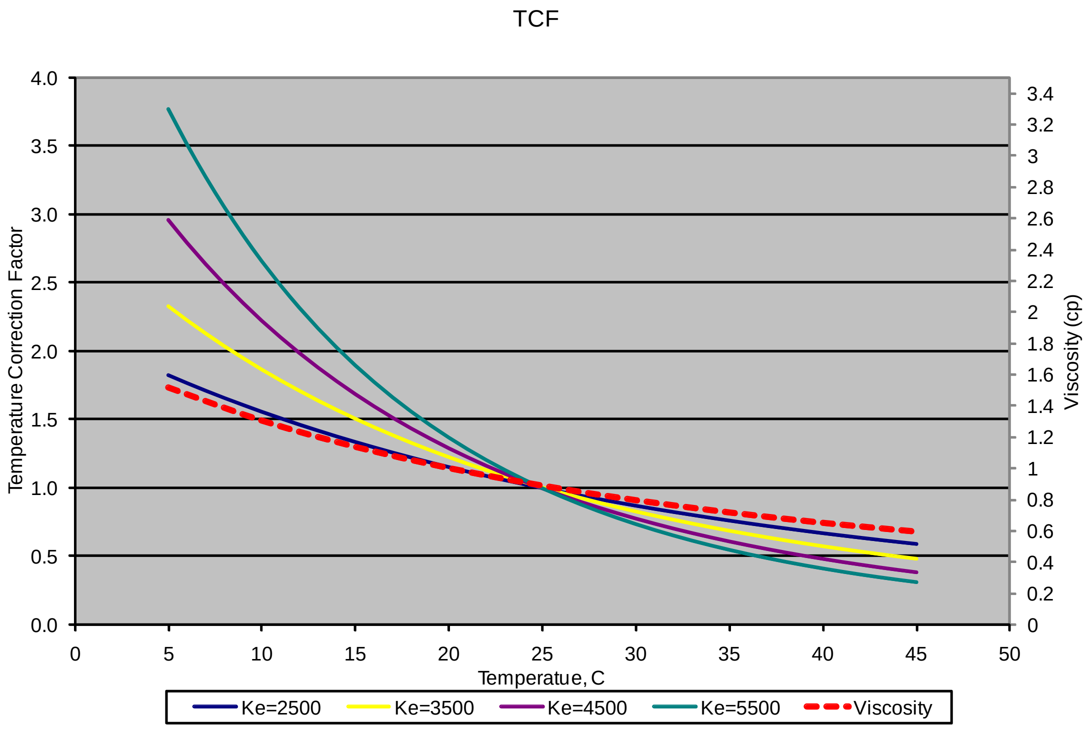

Figure 3. Variation in TCF with temperature for various values of the Ke constant (solid lines) and the viscosity of water (dashed line)

The following observations can be made based on the information presented in **Figure 3.**

- The TCF equation follows the same curve as that of water viscosity.
- A Ke of 2500 accounts only for the change in water viscosity. A Ke greater than 2500 accounts for the impact of temperature on the permeation characteristics of the membrane itself.
- Determining the Ke value associated with a specific membrane can only be done empirically.
- At temperatures less than 25 C, the TCF is > 1 which reduces the membrane permeability and increases the required NDP. At temperatures > 25 C, TCF is < 1 which decreases the required NDP. At 25 C temperature, TCF is = 1 for all Ke values.

- Slope of the curve (the correction factor per degree Celsius) reduces as the temperature increases.
- As the constant Ke increases, the overall temperature correction range increases. However this increase is more pronounced for temperatures < 25 C.
- At temperatures < 25 C, the higher the Ke, more non-linear is the correction factor.
- At temperature > 25 C, the TCF changes in almost linear manner for all Ke values.
- At temperatures > 25 C, the TCF value changes in a narrow range. Whatever the value of Ke, very little temperature correction is made at temperatures > 25 C.

This last point is important for understanding the diminishing influence of membrane permeability on feed pressure at higher temperatures. At these higher temperatures, the rate of change in membrane permeability decreases. As shown in the next section, the rate of change in permeability and the pressure benefit associated with increasing temperatures may become negligible when operating with today's highly permeable membranes.

1.3 Osmotic Pressure vs Net Driving Pressure

As demonstrated above, increasing temperature leads to increasing osmotic pressure and decreasing NDP. Though these two pressure work inversely, the net result has historically led to a reduction in feed pressure with increasing temperatures. However, with the increasing permeability of the membranes and associated lower NDP, SWRO systems are approaching a point where the increasing osmotic pressure has proportionally greater influence on the feed pressure than the membrane permeability.

This is illustrated in **Figure 4** which shows the calculated NDP, osmotic pressure (π), and resulting feed pressure of a simulated SWRO system operating at 8.0 gfd on a typical Mediterranean seawater at temperatures ranging from 5 C to 40 C. As the temperature increases, it is clear that the osmotic pressure (in blue) increases while the NDP (in red) decreases. When going from 5 C to 25 C, the NDP begins as 41% of the feed pressure and decrease 23%. In the same interval, osmotic pressure increases only 7%. The result is a 6.4 bar, or 10% drop in feed pressure. When the temperature climbs from 25 C to 40 C, the change in pressures is very different. The NDP decreases only 2 bar, or 12%, over this range while the osmotic pressure continues its linear 7% increase. The NDP at 40 C has been reduced to 27% of the feed pressure. The 2 bar reduction in NDP is equal to the increase in osmotic pressure so that there is no change in overall feed pressure between 25 C and 40 C. This constant pressure over such a change in temperature does not occur with lower permeability SWRO membranes because the NDP makes up a greater portion of the overall feed pressure and therefore changes in the NDP have a greater impact on overall feed pressure.

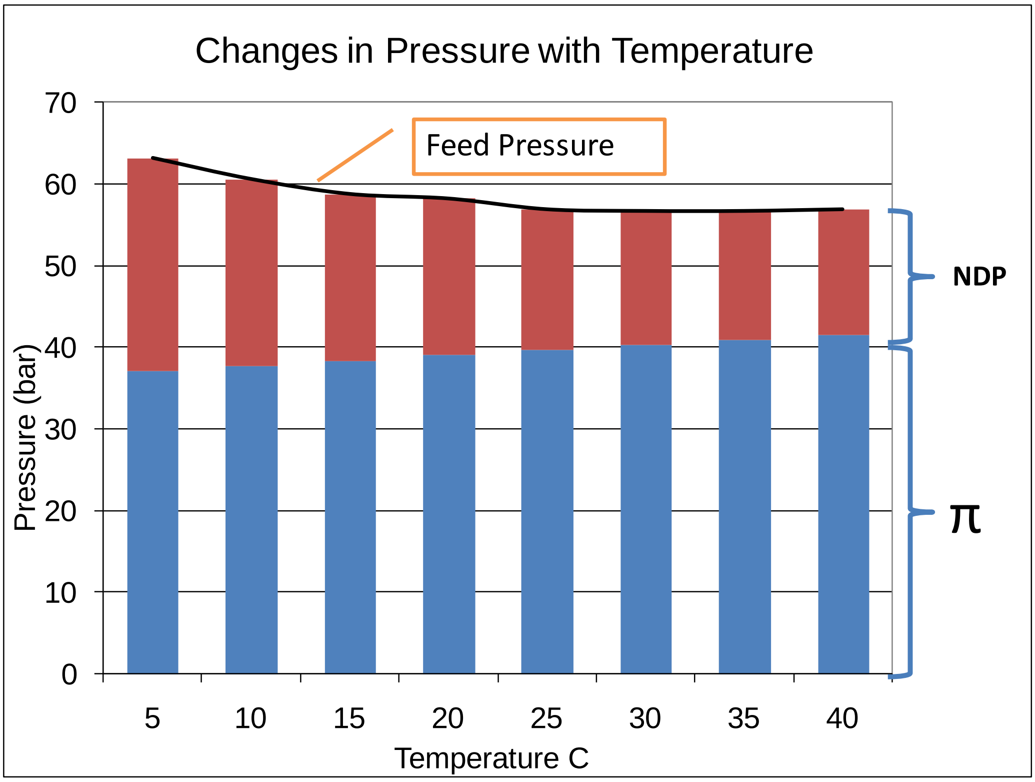

Figure 4. Calculated changes in feed pressure, osmotic pressure (π) and net driving pressure (NDP) for a simulated SWRO system running at 8 gfd and 45% recovery on a typical 38,000 mg/L feed.

The effect of increasing temperature on the feed pressure of a highly permeable SWRO membrane was observed on a single element test run in the laboratory. The element was run on a high salinity, 50,000 ppm NaCl feed to maximize osmotic pressure. The flux was kept low at 7.2 gfd in order to minimize the NDP. As **Figure 5** below shows, the feed pressure decreased only 0.34 bar (5 psi) when temperature decreased from 25 C to 30 C, and then realized almost no change in pressure between 30 C and 35 C as the effect of membrane permeability diminished and the effect of the osmotic pressure became more pronounced.

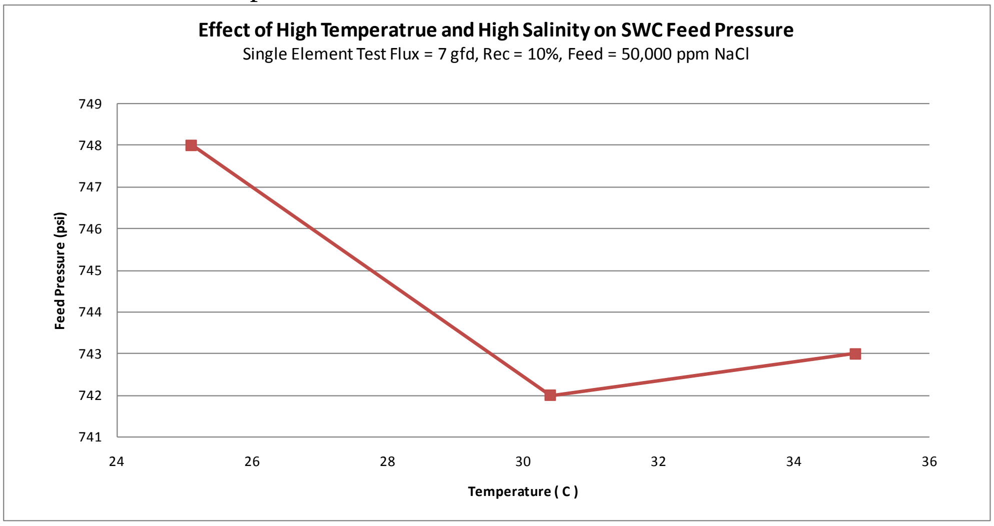

Figure 5. Effect of increasing temperature on the feed pressure of a single highly permeable SWRO membrane running at 7 gfd and 10% recovery on a 50,000 ppm NaCl feed.

The effect of increasing temperature on the feed pressure of a highly permeable SWRO membrane was also demonstrated on pilot unit treating 34,000 mg/L Pacific Ocean feed (**Figure 6**). The pilot contained a single vessel with six elements per vessel. The unit ran at 50% recovery and a flux of 6 gfd. The temperature was increased from 25 C to 39 C in a three hour period by re-circulating the permeate and the concentrate back to the feed tank and allowing the high pressure feed pump to heat the water. During this 19 C increase in temperature the feed pressure decreased by less than 1 bar from 52.9 bar (767 psi) to 52.0 bar (755 psi).

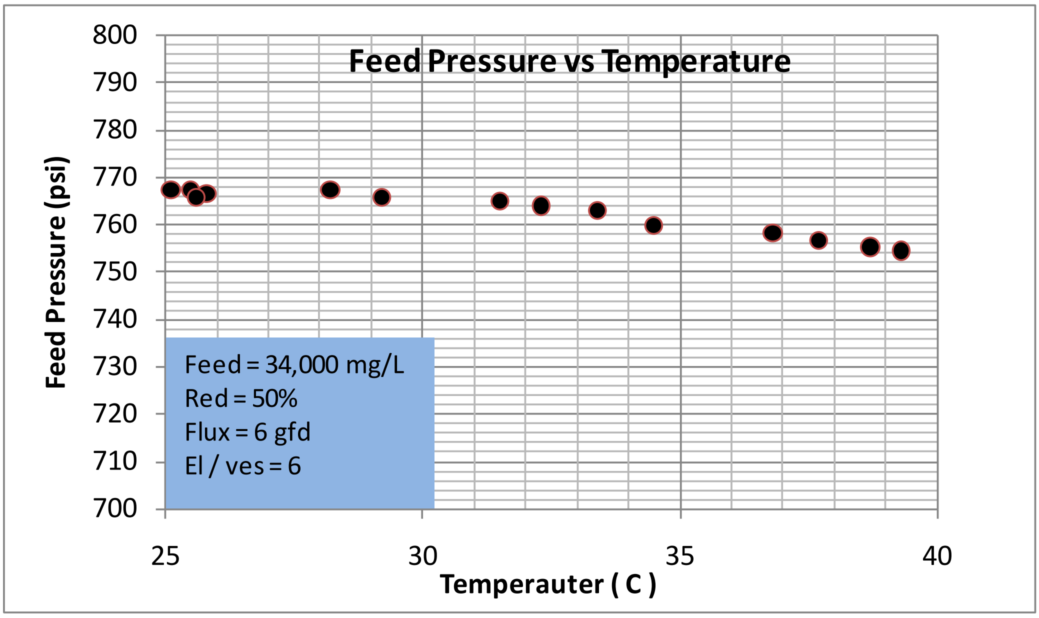

Figure 6. The effect of increasing temperature on feed pressure of an SWRO pilot treating Pacific Ocean feed.

II. EFFECT OF TEMPERATURE ON SWRO ENERGY CONSUMPTION

The general assumption associated with an SWRO system is that increasing temperature leads to lower energy consumption. But a more thorough understanding of the relationship between NDP, osmotic pressure, and temperature, suggests that the energy benefit associated with running an SWRO at elevated temperatures will be significant when using lower permeability membranes or when operating at temperatures less than 25 C. To illustrate the energy savings, the feed pressure was calculated on a typical SWRO system treating a Mediterranean feed of 38,700 ppm at a flux of 13.7 lmh and a recovery of 45%. If the system, using lower permeability membranes, were to increase its feed temperature from 15 C to 25 C, the feed pressure would decrease 6 bar (87 psi) from 71.3 bar to 65.3 bar and reduce energy by 6.3%. In contrast, if the same SWRO system operated at a temperature range from 25 C up to 35 C using higher permeability membranes, there would be no notable decrease in feed pressure and no reduction in energy consumption. To be clear, the lower permeability membranes still offer a significant energy savings at high temperatures relative to the lower permeability membranes. In the example design at 35 C, low permeability membranes would operate at 6.1 bar lower feed pressures and provide a 10% reduction in energy consumption.

III. CONCLUSION

It is assumed that an increase in feed water temperature leads to a reduction in SWRO feed pressure and a reduction in the associated energy consumption. However, since Net Driving Pressure and osmotic pressure are inversely affected by temperature and since the required Net Driving Pressure has been significantly reduced in the latest generation of high permeability seawater membranes, the assumption of deceasing feed pressure with increasing temperature will not always be valid.

The magnitude of energy savings associated with increasing temperature depends on the range of temperature change and the permeability of the membrane. A temperature reduction of 10 C may reduce energy consumption by as much 6.3% (using low permeability membranes at lower temperature). However, the same 10 C reduction in temperature may have no effect on energy consumption when using high permeability membranes at higher temperatures above 25 C.

The effect of increasing temperature on the latest high permeability membranes at higher temperatures has been demonstrated theoretically as well as in laboratory tests and in small scale pilot tests. High permeability membranes are operating at low pressures in full scale commercial seawater RO systems. Due to permeate quality limitations, most of these systems operate in the mid to low temperature range. As highly permeable membranes are installed and operated in commercial seawater RO systems operating at higher temperatures, the diminishing effect of increasing temperatures on their feed pressure and energy consumption should next be analyzed and verified in full scale plants.

IV. REFERENCES

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