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The effect of feed ionic strength on salt passage through reverse osmosis membranes

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Abstract

Several parameters are known to influence the passage of salts through a reverse osmosis membrane. These parameters include characteristics of both the membrane and the feed water. Of these parameters, the least understood is the effect feed water concentration has on salt passage. At high and very low feed salinities, salt passage can increase by a factor of two or more. As an increasing number of RO systems are designed to treat water at these salinity extremes, a better understanding of this salinity effect is necessary to accurately predict the permeate quality of these systems. This study seeks to demonstrate and characterize the salinity effect on different RO elements treating different feed waters. The magnitude of the salinity effect at any given feed salinity is shown to be influenced by membrane charge and feed water composition. The results of the study on individual elements are used to accurately predict the salt passage in an existing full scale RO system.

Keywords: RO membranes, Feed water, Salt passage

1. Introduction

It is well known in the membrane industry that salt passage through a reverse osmosis membrane is affected by both membrane and feed water characteristics. Specifically, membrane age, chemistry, thickness, pore size, and charge density as well as feed water temperature and composition all contribute in varying degrees to the passage of ions through the membrane. But less widely

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recognized is the role feed salinity has on salt passage. Though this feed salinity effect has appeared in experimental and theoretical studies, only in the past few years has it been acknowledged by the industry when projecting membrane performance. As demand for RO treated water increases, an increasing number of brackish systems are being designed to treat higher salinity waters at higher recoveries. For this reason, a practical understanding of the effect of feed salinity on salt passage is essential for predicting and optimizing the design and operation of these RO systems.

The experiments presented in the paper will investigate the effect feed salinity has on salt passage. Six membranes will be tested over a range of salinities on two different feed waters consisting of sodium chloride and concentrated city water. A consistent trend will be shown in which salt passage increases at very low and high feed salinities. The increase in salt passage can be as high as four times the salt passage at standard test conditions.

2. Theoretical Background

A typical RO membrane allows only a small percentage of the feed ions to pass. Given the concentration of salt in the permeate (Cp) and in the feed (Cf), the salt flux is given as:

$$\mathrm{Js} = \mathrm{B}\ (\mathrm{Cf} - \mathrm{Cp}) \tag{1}$$

where B, referred to as the salt permeability coefficient or simply the *B*-value, is a function of the membrane thickness and the membrane's diffusivity. Salt permeability is specific to different membrane types and is arrived at by analytical methods.

The passage of salt through a membrane is expressed as a percentage using the following equation

$$\mathrm{SP\%} = (\mathrm{Cp}/\mathrm{Cf}) \times 100 \tag{2}$$

In a single spiral wound element, the concentration on the feed side increases as the stream flows from the feed end to the brine end of the element and volume is reduced due to the removal of permeate. Salt passage through an element is measured using the average of the feed concentration and brine concentration (Cfb) so that Eq. 2 becomes:

$$\mathrm{SP\%} = (\mathrm{Cp}/\mathrm{Cfb}) \times 100 \tag{3}$$

Though the actual mechanism of membrane salt passage is not well understood, theories have been developed to predict the concentration of salt on the permeate side given the characteristics of the membrane and the feed water. Basic calculations for predicting salt passage treat the membrane as a black box and require little understanding of the transport mechanism within the membrane [1]. These theories consider the following parameters when predicting salt passage:

- Temperature. An increase in feed water temperature will lead to an increase in membrane salt passage. A temperature correction factor is used to compensate for this increase in salt passage when normalizing data of an RO system.
- Membrane type. Brackish membranes, for example, have higher passage rates than seawater membranes. Even among brackish membranes, salt passage varies with the specific membrane chemistry.
- Membrane age. Wearing of the membrane from continuous use and repeated cleanings will increase salt passage over time.
- Feed water composition. Certain ionic species in the feed water, such as monovalent ions, pass more readily than other ions such as the divalent ions.

Given the nature of the membrane and an understanding of the degree that the membrane allows different ions to pass, basic theories assume salt passage is unaffected by feed concentration.

A more in depth understanding seeks to explain the passage of salt through the membrane in terms of several interacting mechanisms including convection, diffusion, and charge repulsion. Specifically, the combined influence of membrane charge and feed ionic strength is known to play a significant role in rejecting salts. As shown in Fig. 1, when a typical feed solution containing both positively charged ions (cations) and negatively charge ions (anions) comes in contact with the negatively charged membrane, the concentration of the cations in the membrane is greater than their concentration in the bulk solution. At the same time, the concentration of the anions in the membrane becomes less than that of the bulk solution. This ion shift creates an electrical potential known as the Donnan potential at the boundary between the membrane and the solution. The Donnan potential attracts cations to the membrane while repelling anions away, thus increasing anion rejection. According to this theory, the overall salt rejection is heavily dependent on the rejection of anions. Therefore, a higher Donnan potential leads to an increase in overall salt rejection of the membrane [2,3]. It can also be inferred from this theory that a membrane with a strong negative charge will have better rejection than a membrane with a weak negative charge.

The benefit of the Donnan potential in the form of increased rejection is greatest at low to mid salinities (1000 mg/L $<$ TDS $<$ 3000 mg/L). At very low salinity (TDS $<$ 300) the concentration of anions and cations is so low that the Donnan potential is negligible. The Donnan potential is also affected at high feed salinity. Increasing the feed salinity beyond 3000 mg/L weakens the Donnan potential and leads to a decrease in membrane rejection. The theory behind this phenomenon suggests that along with increasing feed concentration, comes an increase in the cations at the membrane surface and thus a shielding of the Donnan potential (Fig. 2). As salinity continues to increase, the rejection advantage created by the Donnan potential is gradually diminished to a point where it is no longer effective and the increase in salt passage with feed salinity levels off [3].

Donnan potential is also known to be heavily influenced by the valance of ions present in the feed. Specifically, the Donnan potential is weakest in solutions with a higher concentration of divalent cations [4]. This is because the divalent cations at the membrane surface shield the repulsive force of the

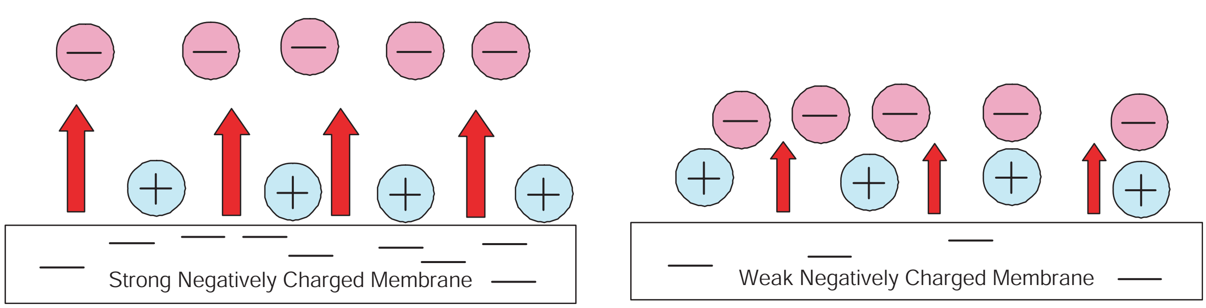

Fig. 1. Donnan potential created by the repulsion of anions and attraction of cations by a negatively charged membrane. The membrane with a strong negative charge will produce a greater repulsive force than a membrane with a weak negative charge.

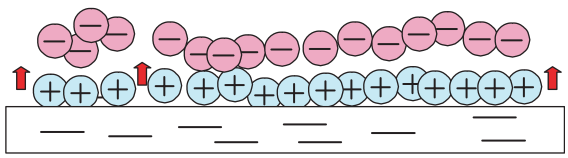

Fig. 2. An increase in feed salinity leads to an increase in cation concentration at the membrane surface which shields the repulsive force of the membrane's negative charge on the anions in the bulk solution.

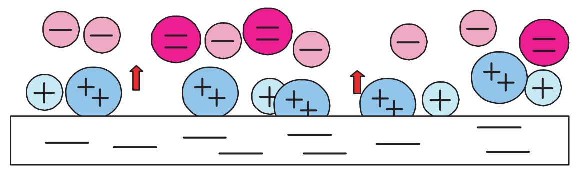

Fig. 3. The divalent cations at the membrane surface shield the repulsive force of the membrane's negative charge on the anions in the bulk solution.

membrane's negative charge on the anions (Fig. 3).

3. Laboratory studies

3.1. Single element test

Testing for this study was done on composite polyamide brackish RO elements of various permeabilities and rejections. Table 1 compares each of the elements used in this study at a single standard test condition.

Element testing was done on a closed loop RO system at 15 gfd, 13% rec, and 25°C. Elements were tested over a range of salinities on both a straight sodium chloride solution and concentrated city water. The single salt solution was created by mixing deionized water with sodium chloride. Concentrated city water was used to simulate a more realistic feed and investigate the effect of multivalent ions on the salinity effect. The concentrated city water feed was created by running municipal city water through an RO while returning concentrate to the feed tank and sending permeate to drain. This was done until the desired concentration was achieved (up to 5000 ppm) and then spiked with sodium chloride when a higher salinity was needed. After running an element for 30 min, measurements were taken for pH, temperature, and conductivity (feed, brine, permeate).

3.2. Cell test

Cell testing was also performed on several membrane samples. For each cell test, six different samples measuring approximately 5 square centimeters were taken from the same flat sheet of membrane and tested simultaneously. The cell test was run for one hour using a sodium chloride solution at salinities, fluxes and temperatures similar to those of the element tests. A final salt passage value was calculated for each test based on the

Table 1
Characteristics of brackish RO elements at standard test conditions of 25°C, 15 gfd, pH 7, Rec 13% and 1500 mg/L NaCl

Membrane Number	Membrane Manufacturer	Pressure (psi)	Rej (%)	Flow (GPD)	Negative Charge at pH 7
1	A	91	99.15	6439	Strong
2	A	121	99.72	6240	Strong
3	A	129	99.72	6240	Strong
4	A	160	99.68	6752	Weak
5	B	108	99.27	6942	Weak

average salt passage of the six cells. When any of the six cells showed greater than 30% deviation in permeate conductivity from the other five, it was discarded.

In the case of both the membrane cell test and the single element test, the measured feed and permeate concentrations were used in Eqs. 2 and 3 to determine the effect of changing feed salinity on salt passage and membrane salt permeability.

3.3. Results and discussion

The results of this study demonstrate the impact feed salinity has on salt passage. This salinity effect is presented in Fig. 4 for elements treating a sodium chloride solution and Fig. 5 for elements treating concentrated city water.

The salinity effect follows a general trend for all elements tested. At feed salinities less than 100 mg/L, salt passage is several times higher than the manufacturer's stated salt passage. But as feed salinity increases beyond very low concentrations, salt passage rapidly decreases. A minimum point is reached between feed salinities of 500 mg/L and 1000 mg/L after which the salt passage begins to gradually increase again.

What stands out in both the NaCl and city water case is how membrane 1 appears to be more influenced by the salinity effect than the other membranes tested. But this is due in part to the fact that membrane 1 has the highest salt passage of all the membranes at standard test conditions. A clearer picture of the relative impact of feed salinity on the different membranes can be had by comparing the normalized change in salt permeability (*B*-value).

Using Eq. 1, salt permeability was calculated at the various salinities and then normalized relative to the membrane's salt permeability at approximately 1500 ppm.

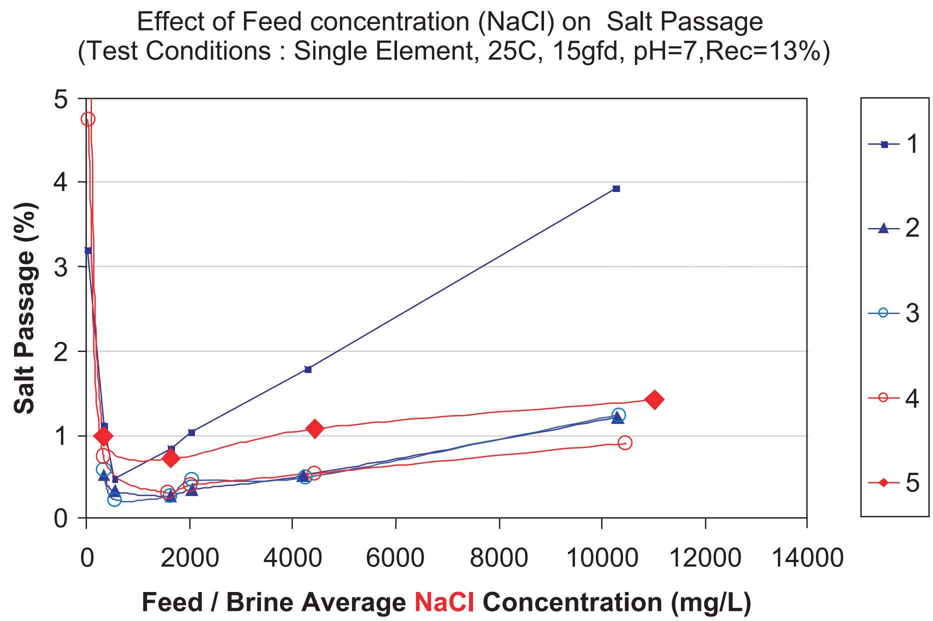

Fig. 4. Effect of Feed concentration (NaCl) on Salt Passage through elements 1–5 (Test Conditions: Single Element, 25C, 15 gfd, pH = 7, Rec = 13%)

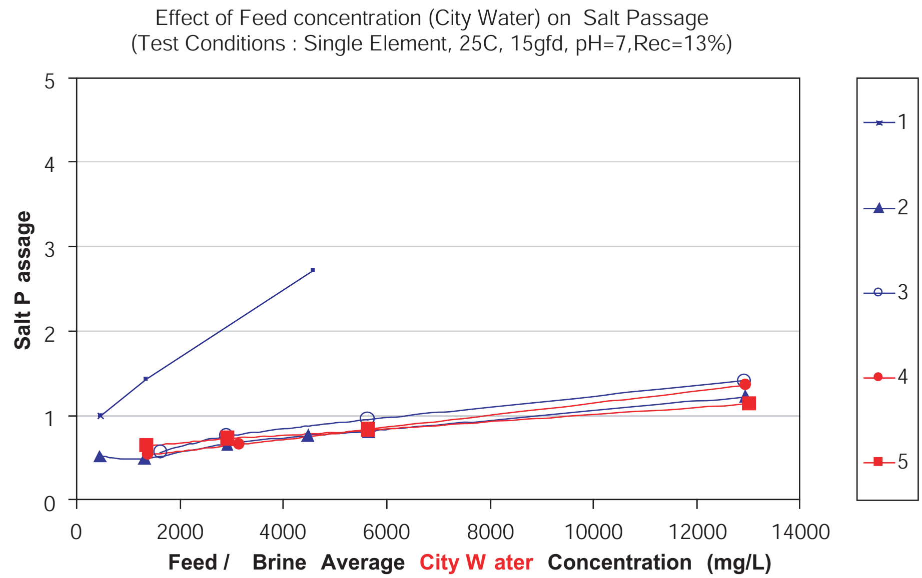

Fig. 5. Effect of Feed concentration (City Water) on Salt Passage through elements 1–5 (Test Conditions: Single Element, 25C, 15 gfd, pH = 7, Rec = 13%)

The 1500 ppm reference salinity was chosen due to the fact that most membrane manufactures test their brackish RO membranes at or near this concentration. Figs. 6–8 show the effect of feed salinity on relative salt permeability. When considering salt permeability the same general trend is observed for all elements that was observed when considering salt

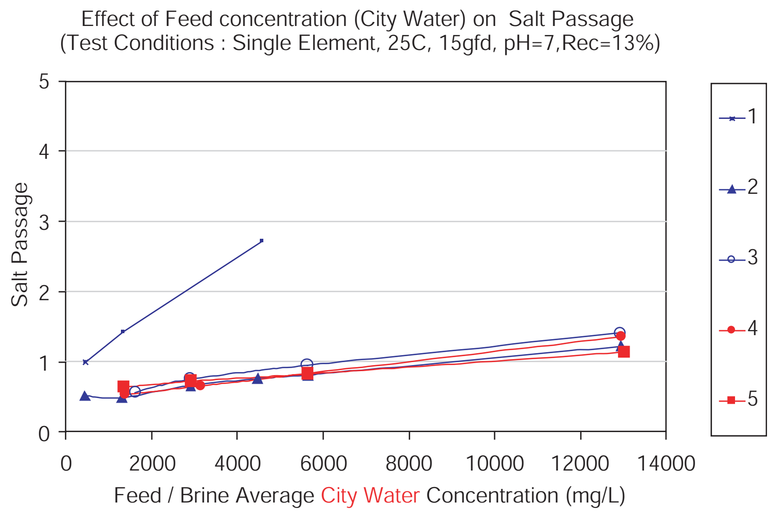

Fig. 6. Effect of feed concentration (NaCl) on relative salt permeability through elements 1–5 (Test Conditions: Single Element, 25C, 15 gfd, pH = 7, Rec = 13%)

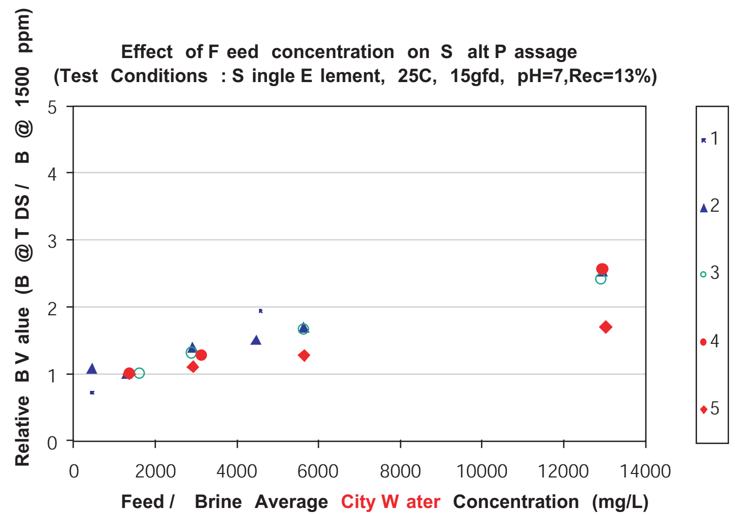

Fig. 7. Effect of feed concentration (City Water) on relative salt permeability through elements 1–5 (Test Conditions: Single Element, 25C, 15 gfd, pH = 7, Rec = 13%)

passage—a significant dip at very low feed salinities followed by a gradual increase as feed salinity increases. Using the relative salt permeability, the salinity effect at high and low feed salinities can be analyzed in more detail and the relationship of membrane charge and feed water type can be more clearly understood.

3.4. Salinity effect at high feed salinities

When considering the magnitude of the salinity effect at high feed salinities, a noticeable difference emerges between the different membranes treating the NaCl feed (Fig. 6). Specifically, membranes 1 through 3 are more impacted by the increasing salinity than

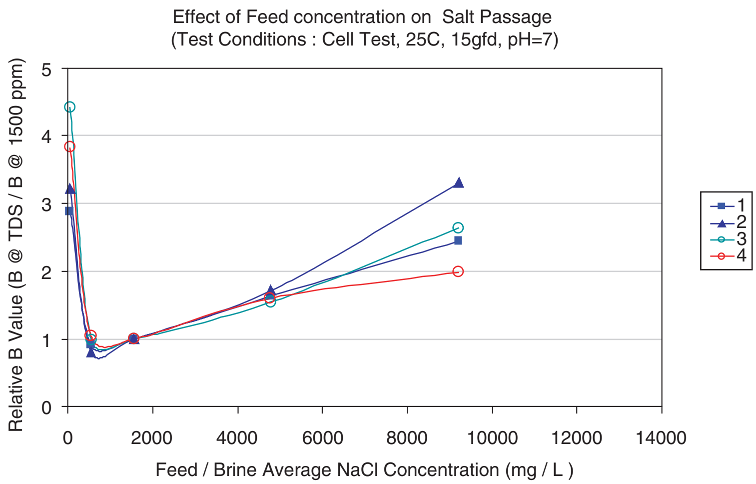

Fig. 8. Effect of Feed concentration on Salt Permeability through membranes 1–4 (Test Conditions: Cell Test, 25C, 15 gfd, pH = 7).

membranes 4 and 5. The salt permeability of membranes 1 through 3 increases more than four times whereas the increase in salt permeability of membrane 4 and 5 is nearly two to three times. A distinguishing characteristic of membranes 1 through 3 is their strong negative charge compared to the weaker negative charge of membranes 4 and 5. To understand the difference in the behavior of the membranes with different charges, recall that the increase in salt permeability at the high salinity is related to a weakening of the strong Donnan potential that exists in strong negatively charged membranes. A weakened Donnan potential leads to an increase in anion passage and therefore to a relative increase in salt permeability [2,3]. This would explain why the salt permeability of the membranes with the strong negative charge tends to be more influenced by the high feed salinity than the membranes with the weaker negative charge.

Membrane charge plays a less significant role when treating concentrated city water with multivalent ions. (Fig. 7). Compared to the NaCl feed, the relative increase in salt permeability is less for the strong negatively charged membranes when treating the concentrated city water. On the other hand, the weak negatively charged membranes show a similar increase in salt permeability regardless of feed type. For this reason, the difference in salinity effect between membranes of different charge all but disappears when treating the multivalent city water. In contrast to the NaCl solution, which contains only monovalent ions, the city water contains both divalent and monovalent ions. The presence of divalent anions is known to diminish the effect of the Donnan potential and allow for greater salt passage at lower salinities which explains why there is less of a relative increase at the higher salinities [4].

3.5. Salinity effect at very low salinity

A marked increase in salt permeability occurs at feed salinities less than 500 mg/L. But unlike the high salinity tests, the data does not reveal a correlation between membrane charge and salt permeability. For example, referring to a feed salinity of 320 mg/L in Fig. 8, membranes 1 and 2, with strong negative charges, increase less than membrane 4 with its weak negative charge. At such low feed salinities, the Donnan potential is weak and plays a less significant role in the passage of salts through the membrane. This increase in salt passage at low feed salinities is most probably caused by some other dominant salt passage mechanisms. Further research is needed to determine the exact mechanism governing this increase.

Additionally, the magnitude of the salt permeability increase is inconsistent at very low salinities. At a feed salinity of 10 mg/L, the increase for membrane 1 is 4 times, but the increase for membrane 2 is 30 times and could not be plotted on the *Y* axis of Fig. 6. Such dramatic increases do not appear at low salinities in the cell test (Fig. 8). The absence of these anomalies in the cell tests is puzzling. One cause for the very high salt passage in some element tests may simply be instrumentation error which is magnified when working with such low conductivities. But even if the tests which showed a very large increase in salt passage are discarded, it is still apparent that very low feed salinity can increase salt passage by at least three times.

3.6. Predicting performance of full scale systems

The salinity effect has appeared over the years in empirical studies presented in the literature [5–8]. Data from large scale RO systems currently in operation also reveals the salinity effect. This effect was originally noted by the authors in 1998 when brackish membranes at a newly installed RO system in North Carolina, treating a feed water of 8100 ppm., produced a permeate salinity almost twice the projected level. A number of the elements were returned to the manufacturer and retested at standard test conditions with acceptable results. Field and laboratory tests were conducted to determine the cause of the high salt passage. The test results, including those presented in this paper, led to the conclusion that the salt passage of a polyamide membrane is significantly affected by variations in feed salinity.

Another occurrence of the salinity effect was observed at a 1 MGD plant treating well water with a TDS of 2300 mg/L. Data was collected for both the first and second stages. The second stage, loaded with Membrane 2, treated concentrate coming from the first stage at a TDS of 5600 mg/L. Operating the second stage at 45% recovery led to a feed to brine average salinity of 8000 mg/L, well into a feed salinity range in which salt passage would increase. Based on the salinity effect on a single element (membrane 2), a factor of 1.75 was applied to the calculated salt passage. Fig. 9 compares the calculated salt passage with and without the salinity factor with actual startup data. Initially both calculated results fail to accurately predict the actual salt passage of the system. However, after 30 days, when the salt passage had stabilized, the calculated salt passage containing the salinity effect comes very close to the actual data.

The evidence for increasing salt passage at the salinity extremes along with the increasing number of RO systems designed to treat water in at these salinities has prompted the membrane industry to account for the salinity effect when predicting the performance of their membranes. Fig. 10 below compares the membranes' relative salt permeability with a commercially available RO projection program. The program accurately predicts the increase in salt permeability through a range of feed salinities from very low to very high.

4. Conclusions

Salt passage through a polyamide membrane is affected by feed salinity. The magnitude of this salinity effect at high feed salinities is related to membrane charge, membrane chemistry and feedwater composition. Specifically, the relative increase in salt passage at high salinities is most pronounced when treating a sodium chloride (i.e. monovalant) solution with a strong negatively charged membrane. This is because the Donnan potential, which is strongest under these

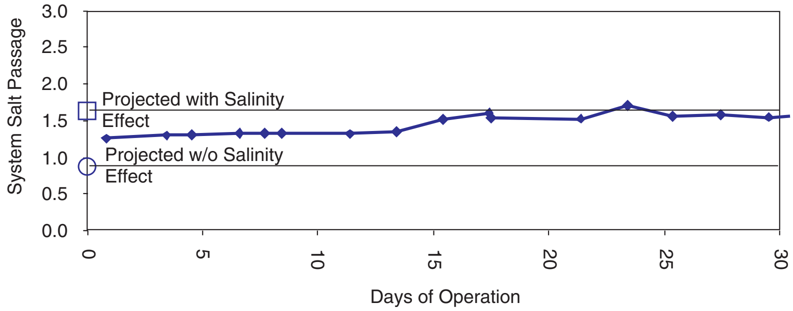

Fig. 9. Thirty days of normalized salt passage for a full scale RO system compared to projected salt passage with and without the 1.75 salinity factor.

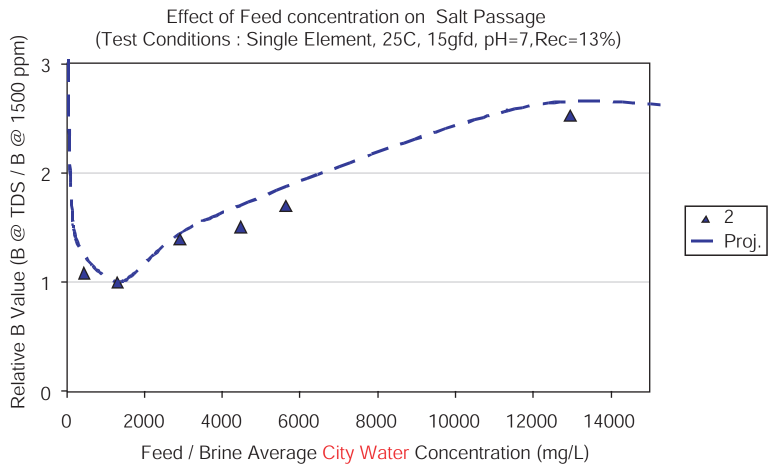

Fig. 10. Comparison of actual salt permeability through element 2 with projected salt permeability using a commercially available software program treating concentrated city water.

conditions at mid salinities, is depleted at the higher salinities—increasing salt passage by as much as four times. But the city water feed, with its mix of monovalant and divalent ions, is more representative of a typical RO system feed. When treating such a feed, the Donnan potential is weaker at mid salinities and therefore its depletion at the higher salinities has less of an impact on salt passage. For this reason, the presence of a strong negative charge on the membrane which is advantageous in the mid salinity range due to the presence of a strong Donnan potential, also posses a disadvantage at the higher salinities.

An increase in salt passage also occurs at very low feed salinities. The data showed no correlation between membrane charge, membrane chemistry and salt permeability increase at these very low feed concentrations. However, this increase in salt passage is an important consideration when designing high purity water systems.

Based on the findings in this study, it is clear that feed salinity effects salt passage through a reveres osmosis membrane. The extent of that effect is influenced by the feed composition and membrane charge and chemistry. When designing an RO system, the salinity effect at both high and low feed salinities must be considered in order to accurately predict permeate quality.

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