EVALUATION OF ANTISCALANT FOR A NF MEMBRANE IN AN NF-SWRO SYSTEM[1]

Ahmed Al-Amoudi, Dr. A.M. Farooque, Ghazzai Al-Otaibi and N. Kither Mohammad

Research & Development Center,
Saline Water Conversion Corporation (SWCC),
P.O.Box 8328, Al-Jubail 31951, Saudi Arabia.
E-mail :rdc@swcc.gov.sa

SUMMARY

One of the main causes of reverse osmosis system failure is membrane fouling as the result of the presence of organic and inorganic materials in feed seawater. When the hardness ions concentration exceeds the solubility limits, the salts start to precipitate on the desalination device, causing scaling. Introduction of NF-SWRO system leads to the overcoming of this scaling problem. In earlier studies, to avoid scale formation on the NF membrane surfaces, the NF product recovery also was limited to about 65 to 70%. It is recognized that higher NF product water recovery leads to a higher overall reduction of water production and therefore in water cost. In order to increase the product recovery in seawater NF process and to prevent scale formation, the use of antiscalant was tried. To increase NF product recovery, three types of antiscalants, namely Permatreat 191, Permatreat 504 and Flocon 135 were evaluated at various concentrations and pH. The chemical and biological analyses were carried out on a routine basis as required for the seawater feed, permeate as well as the reject. The product of NF was passed to the SWRO unit to evaluate the total NF-SWRO recovery. The study demonstrated that only 70% NF product recovery was achieved using both antiscalant Permatreat 191 and Flocon 135, while 77% NF product recovery was achieved by using Permatreat 504. The percent rejection of hardness ions as well as TDS were almost similar by the use of any of the three antiscalants. However, in the three cases, the percent rejection of calcium and magnesium ions decreased with time, contrary to sulfate and bicarbonate rejections which remained steady during these three trials. Under the present operation conditions of NF and SWRO pilot units, the total recovery of NF-SWRO with antiscalant is about 38.5% compared to that of NF-SWRO without antiscalant at about 32.5%. These values, however, can be raised significantly under different operation and plant design conditions.

---

[1] Issued as Technical Report No. EVP 3807/20001 in June 2004.

1. INTRODUCTION

One of the principal causes of reverse osmosis system shutdown and premature membrane replacement is membrane fouling. Fouling, which is formed by the accumulation of deposits from feed water, impedes the flow of fluid through the membrane and increases the differential pressure across membranes (ΔP). Membrane fouling results from the presence of both organic and inorganic materials in the feed water [1,2]. The major problems in SWRO process are due to seawater itself, which is characterized by having high concentrations of (1) hardness forming ions of $SO_4^{=}$, HCO_3^{-}, Ca^{++} and Mg^{++}, (2) TDS, (3) turbidity and (4) microorganisms. During the seawater desalination process the extraction of fresh water from feed seawater concentrates those dissolved salts in the brine. If their concentration exceeds the solubility limits, the hardness scale forming ions and salts precipitate on the desalination devices leading to scale formation. On the other hand, the process of separation of product from feed also increases turbidity and bacteria in the brine within the desalination device, leading to membrane fouling, both (inorganic and biofouling). The pretreatment of seawater feed by the NF process proved not only effective in removal of turbidity and bacteria, thereby preventing fouling of the seawater desalination devices, but it also removes the hardness ions from the NF permeate, in some cases up to 98%, thereby preventing scale formation on seawater desalination plants. This NF pretreatment, also lowers the NF permeate TDS, thus allowing for higher fresh water recovery from NF permeate when used as feed to the conventional seawater desalination processes. Although, the NF pretreatment improves significantly the quality of feed to conventional seawater desalination plants. But, it has certain limitations such as NF permeate recovery. Depending on type and physical structure of NF membrane, the permeate recovery is normally ranges between 50-76% without scale formation on the NF membrane surfaces [3]. High NF permeate recovery could lead to scale formation on the NF membrane surfaces, as indeed was the case when permeate recovery was raised to higher recovery levels (about 70%) in trial tests conducted at RDC pilot plant utilizing Osmonic NF HC-8040 membranes.

There are various types of scale inhibitors (antiscalant) which are used to prevent scaling in desalination process and are referred to as follows based on their chemical composition: phosphate, phosphonate, carboxylate, acrylate and sulphonic acid and out of these scale inhibitors, only two types had been investigated in this study: phosphonate and carboxylate based[4]. Phosphonate based antiscalant used were: Permatreat 191, Permatreat 504 and carboxylate based antiscalant was used: Flocon 135. There are three different mechanisms, by which scale inhibitors prevent scale formation: distortion, dispersion and threshold mechanisms. The threshold mechanism works by maintaining the calcium and magnesium ions within the solution at concentration higher than their solubility unit without precipitation. Some of these threshold additives have a marked effect on the crystallization of the scaling compound, the crystal either stops growing or get distorted. The distorted crystals are less likely to adhere to each other and to precipitate forming large crystals. On the other hand, dispersant is adsorbed on surface of crystal and retards further growth. Dispersants prevent agglomeration of crystals and thus effect ultra-fine dispersion of solid particles [5&6].

Scale inhibition mechanisms have been studied in detail, and chemists have confirmed that the "threshold mechanism" is the prevention key of scale formation on membranes. There are many antiscalants available in the market. For example, a specific manufacturer, claims that phosphonate based Permatreat 191 antiscalant is a powerful threshold agent, which is capable of stabilizing supersaturated salt solution and is claimed to function as a scale inhibitor for a wide range of scaling compounds.

The Permatreat 191 was used in seawater as well as in brackish water desalination processes. In one case, brackish water reverses osmosis plant located at AI-Kharg dosed the Permatreat 191 in the feed water to achieve 80% recovery. On the other hand, a SWRO plant (located at Gibraltar) used Permatreat 191 in the feed water at a low recovery of 30% [7]. There is no reference available on operational data related to seawater process at high permeate recovery of >40%. But from the manufacturer's threshold calculation, it seems that this antiscalant can be used at high permeate recovery of more than 30%. There are few other antiscalants available in the market, which are claimed also to be effective at high permeate recovery.

It is well-known fact that higher water recovery leads to overall reduction of water production cost. In order to achieve more than the present 65% recovery in seawater NF process at Ummlujj NF-SWRO train requires the use of antiscalants. As it was described earlier, the operation without antiscalant at high recovery of about 78% leads to scaling of the

NF membranes. Our aim in this investigation is to achieve NF product recovery with use of selected antiscalant now available in the market.

2. RESEARCH OBJECTIVES

The main objectives of the study are summarized as follows:

1. To increase the recovery of NF pretreatment to more than 70% by dosing suitable antiscalant.
2. To increase the total NF-SWRO recovery with the ultimate objective of lowering the cost of potable water production.

3. EXPERIMENTAL WORK

All experiments were carried out on a pilot plant stage, utilizing 4"x 40" NF membrane elements in 3 vessels, each fitted with 6 elements of Osmonics DK4040 NF membrane, arranged in series. As shown in Figure 1, the first two elements were placed in the vessel # 6 and the second two elements were placed in vessel # 8 and the last two elements were in vessel # 9. The NF unit received pretreated seawater from a conventional coagulation filtration pretreatment unit. The pretreatment consists of simple coagulation by the addition of coagulant, ferric chloride (Fe^{+3} =0.6ppm) and dual media filtration followed by fine sand filtration. Three different antiscalants at various concentrations were independently tried in the pretreated seawater feed ahead of NF high-pressure pump. The evaluation of the effect of antiscalant on increasing NF permeate recovery from 65% to 70-77% was carried out at feed pressure of 600 psig and pH in the range of 5.5 to 8 where the feed flow was maintained at about 80-85 l/min. During the experiment, the temperature was mostly maintained at about 35 ^{o}C by mixing warm seawater from heat rejection section of MSF plant with seawater. (The overall water recovery of the NF-SWRO process can be enhanced by upgrading the SWRO operation, which is being investigated under a separate R&D study).

In this experiment, three antiscalants were used namely, Permatreat 191, Permatreat 504 and Flocon 135 and their concentrations were varied from 1.2 ppm up to 7.2 ppm (Table1) at different pH values of 5, 5.5, 6, 6.5, 7, 7.5 and 8. However, the duration of each trial was varied from one week to four weeks (according to its performance and chemical profile).

The SWRO unit is made of high pressure pump followed by six SWRO modules, each contains one spiral wound membrane element (size 2.5"), all arranged in series as shown in the Figure 2. The NF permeate was passed to the SWRO unit where it was separated under pressure of 55 bars into product and reject. However, NF-SWRO system was operated for only 800 hours due to the system failure.

Chemical analyses were conducted according to the latest standard analysis methods, which are already fully established at the RDC chemical laboratories. These analyses were performed on a routine basis and as required, for the seawater feed, permeate as well as the reject.

Bacteria were counted immediately after sampling, and this count was designated as 0-h count. Further counting was carried out after 24h (24 – h count) following the incubation of samples at a temperature of 30^{o}C on a thermostatically controlled incubator. The samples were first mixed well on a vortex mixer, and a pour plate count in marine agar was employed to reveal the colony forming units (CFU) [8].

Zero-hour counts were used as a base to calculate the generation time for 24h of incubation as per the following formula [9].

$$\text{Generation time (h)} = \Delta t K / (\ln N_t - \ln N_{t0})$$

Δt = 24h

K = 0.693

N_t = count at 24h

N_{t0} = count at 0h

The generation time reflects the speed of bacterial multiplication and was used to reveal whether the antiscalant is acting as nutrient for bacteria or not. Samples were taken from seawater feed without antiscalant, from nanofiltration feed with antiscalant and from the nanofiltration product, which is void of antiscalant.

4. RESULTS AND DISCUSSIONS

In desalination of seawater or brackish water, the two processes, the distillation and membrane technology processes, share a common problem of surface fouling by scaling. The main types of scales encountered in RO or NF processes are calcium carbonate ($CaCO_3$) and calcium sulfate ($CaSO_4$). The NF membrane was introduced to seawater desalination in 1997 at R&D Center to improve the quality of pretreated seawater feed. The recovery of NF obtained varied with type and performance of NF membrane. NF membranes suitable for NF-SWRO operation are safely operated at about 65% recovery without use of any scaling in the feed as can be drawn from the performance of NF membrane [3, 10, 11, 12 & 13]. To obtain NF recovery of more than 65% without any scale formation on NF membrane, trials of three different antiscalant were carried out in these experiments.

4.1 Trial with Permatreat 191

In the first trial, the antiscalant Permatreat 191 was used. Figure 3 shows the performance of NF membrane for a period of about 11000 h. To improve the NF recover, the antiscalant Permatreat 191 was introduced at various concentration (1.2, 1.4, 1.7, 3.05 & 4 ppm)) during the first 3000 hours. The total NF product recovery was increased from 65% to 70% at feed pressure of 21 bar and maintained constant at concentration of antiscalant of 1.3 ppm. Figure 4 shows the percent rejection of Ca^{++}, Mg^{++}, HCO_3^- and $SO_4^=$ at pH = 6 in the total product recovery which were 62%, 70%, 56% and 99.5%, respectively. It can be drawn from Figure 4 that the average TDS of the total product water was maintained at about 35000 ppm or less throughout the experiment. However, the TDS of the product water from last vessel (#9) was about 43000 ppm compared to 27000 ppm from the first vessel # 6 and 35000 ppm from the second vessel # 8. Figure 3 shows the total NF product water recovery which was later on further increased to 75% at feed pressure of 41.3 bar, while maintaining the antiscalant Permatreat 191 at about 4 ppm at pH of 6. This resulted in total NF product water recovery decreased as well as the total product flow. Figure 4 shows that the TDS of the total NF product was improved while the reject TDS of NF was increased which caused a slight decline in the total product water. Moreover, the increase in osmotic pressure which caused a drop on net driving pressure [14]. Also the total NF recovery declined with time to about 72% or less from 75%, even after the Permatreat 191 dosing concentration was increased.

4.2 Trial with Permatreat 504

The second trial was conducted using antiscalant, Permatreat 504. Figure 3 shows the NF performance when the antiscalant, Permatreat 504 was introduced at various concentrations (1.2, 1.4, 2.3, 3.8, 4.6, 5.5, 6 & 7.2 ppm) during the second trial period to improve the NF recovery during the period of 3000 to 9000 hours. The maximum total NF product recovery of 77% was achieved while 75% the total NF product recovery of 75 % was maintained most of the time. The total NF product recovery was maintained constant at 75% up to 77%, while concentration of Permatreat 504 was varied as well as the feed pH (5.5, 6, 6.5, 7, 7.5 & 8) that proved the ability of antiscalant Permatreat 504 in preventing scale formation on NF membrane. Moreover, the total product flow of the NF was maintained steady. However, it can be seen from Figure 4 that the rejection of hardness ions was slightly decreased. For example, the calcium percent rejection decreased from 72% to 54% and magnesium percent rejection also was reduced from a value of 90% to about 80% while the sulfate and bicarbonate percent rejection remained constant of 99.7% and 52% respectively compared to Permatreat 191 (Figure 4). It can be also drawn from Figure 4 that the average TDS of the total product water was maintained at about 33500 ppm or less. The TDS of the product water from last vessel (#9) was about 40000 ppm compared to 29000-30000 ppm from vessel # 6 and 34000 ppm from vessel # 8.

4.3 Trial with Flocon 135

Last trial was conducted using antiscalant Flocon 135. Figure 3 shows the performance of NF membrane during last 2000h where the antiscalant Flocon 135 was introduced at concentration of 4 ppm to improve the NF recovery as well as NF performance. The total NF recovery was maintained constant at 75 % in the earlier stage and later the NF recovery decreased gradually from 75% to 70% and was maintained steady at about 70%. Moreover, the product water flow was also decreased gradually and this reduction of NF recovery could have resulted from scale formation that could have precipitated on the membrane surface in the earlier stage of experiment. The percent rejection of Ca^{++}, Mg^{++}, $HCO3^{-}$ and $SO4^{--}$, during this trials, at pH of 6 in the total product which was 54%, 80%, 56% and 99.7%, respectively.

It can be drawn from Figure 4 that the average TDS of the total product water was maintained to about 35000 ppm or less and the rejection of these ions were steady during this trial.

However, the TDS of the product water from last vessel (#9) was about 40000 ppm compared to 31000 ppm from vessel # 6 and 34000 ppm from vessel # 8 similar to permatreat 504.

In view of the above trials, the performance in term of the NF total recovery using antiscalant Permatreat 504 was much more steady compared to the NF performance using antiscalant, Permatreat 191 as well as Flocon 135. The percent rejections of hardness ions and TDS were almost similar by using of any of the antiscalant during these trials, with the exception of the antiscalant Permatreat 191, where magnesium ions, calcium ions and TDS rejection were higher (Figure 4). Moreover, sulfate and bicarbonate ions percent rejection were almost steady while the magnesium and calcium ions percent rejections were gradually decreased with operation time, regardless of the feed pH for all the antiscalant. In addition to that the product TDS of vessel # 9 (the last vessel) was about 41000 ppm, which is considered to be high compared to the product TDS of vessel # 6 (29000 ppm) and vessel # 8 (33000 ppm) for all the antiscalants.

4.4 NF-SWRO Operation

Figure 5 shows the operation up to 800 hrs at applied pressure of 55 bar and feed temperature of about 25^{o}C, the conductivity of the NF product, which constituted the feed to the SWRO unit in the NF-SWRO hybrid system, was about 41000 μs/cm. The SWRO permeate flow and recovery ratio were maintained steady at 3.5 l/min and about 50% respectively. It can be concluded that the total recovery of NF-SWRO with antiscalant is about 37.5% while the total recovery of NF-SWRO without antiscalant is about 32.5%[10 &11]. Changing operation conditions and NF and SWRO unit design a induces changes in those values by raising of this total recovery ratio. This step is being investigated under a separate project.

4.5 Bacteriological Analysis

Bacterial generation times were found to be 2.69 ± 0.26h for seawater without antiscalant, 2.84 ± 0.23h for nanofiltration feed with antiscalant and 3.43 ± 0.17h for the nanofiltration reject. Data (N = 35 for each sample) were analyzed using One Way Analysis of variance and Tukey Test ($P < 0.001$). Means are preceded by the 95% confidence internal (Table 2).

From the biological studies it can be drown that samples with the antiscalant have the same or slower bacterial growth rates than the control sample without antiscalant. This implies that the antiscalant was not effecting bacterial growth, i.e., antiscalant can not be used as food for bacteria.

5. CONCLUSIONS

1. The study demonstrated that NF unit can be operated at over 65% recovery using any of the three different antiscalant of Permatreat191, Permatreat 504 and Flocon 135.

2. Only 70% NF recovery was achieved using antiscalant, Permatreat 191 or antiscalant Flocon 135.

3. Although a maximum of 77% NF recovery was achieved using antiscalant Permatreat 504 but a recovery of 75% was maintained.

4. The percent rejections of hardness ions as well as TDS by use of any of the three antiscalants were almost similar.

5. During these trials the percent rejection of sulfate and bicarbonate remained steady while that of calcium and magnesium ions decreased with time.

6. Under the present operation conditions of NF and SWRO pilot units, the total recovery of NF-SWRO with antiscalant is about 38.5% compared to that of NF-SWRO without antiscalant at about 32.5%. These values, however, can be raised significantly under different operation and plant design conditions.

7. All the antiscalants are not assimilated by bacteria.

6. RECOMMENDATION

The recovery of NF at Umm Lujj NF can be increased to more than 65% up to 77% or even higher without scaling by using antiscalant Permatreat 504.

Table 1. Types of Antiscalant used and their concentration

Name of antiscalant	Type	Dose rate (ppm)
Permatreat 191	Phosphonate	1.2-4
Permatreat 504	Phosphonate	1.2-7.2
Flocon 135	Carboxylent	~4

Table 2. Bacterial growth[1] rates in a seawater nanofiltration system with and without antiscalant (n = 35)

	Sample		
	Source Water	Nanofiltration feed	Nanofiltration reject
Growth rates (h)[2]	2.69 ± 0.26^a	2.84 ± 0.23^a	3.43 ± 0.17^b

[1]Growth rate (Generation time) in hours = Δ t k / (ln Nt - ln Nt_0)   (see text)

[2]Calculated for 24 h growth

[abc]Means that are followed by the same letter superscript are similar and means that are followed by different letter superscripts are different, Analysis of Variance and Tukey Test ($P< 0.001$).

± 95% confidence interval

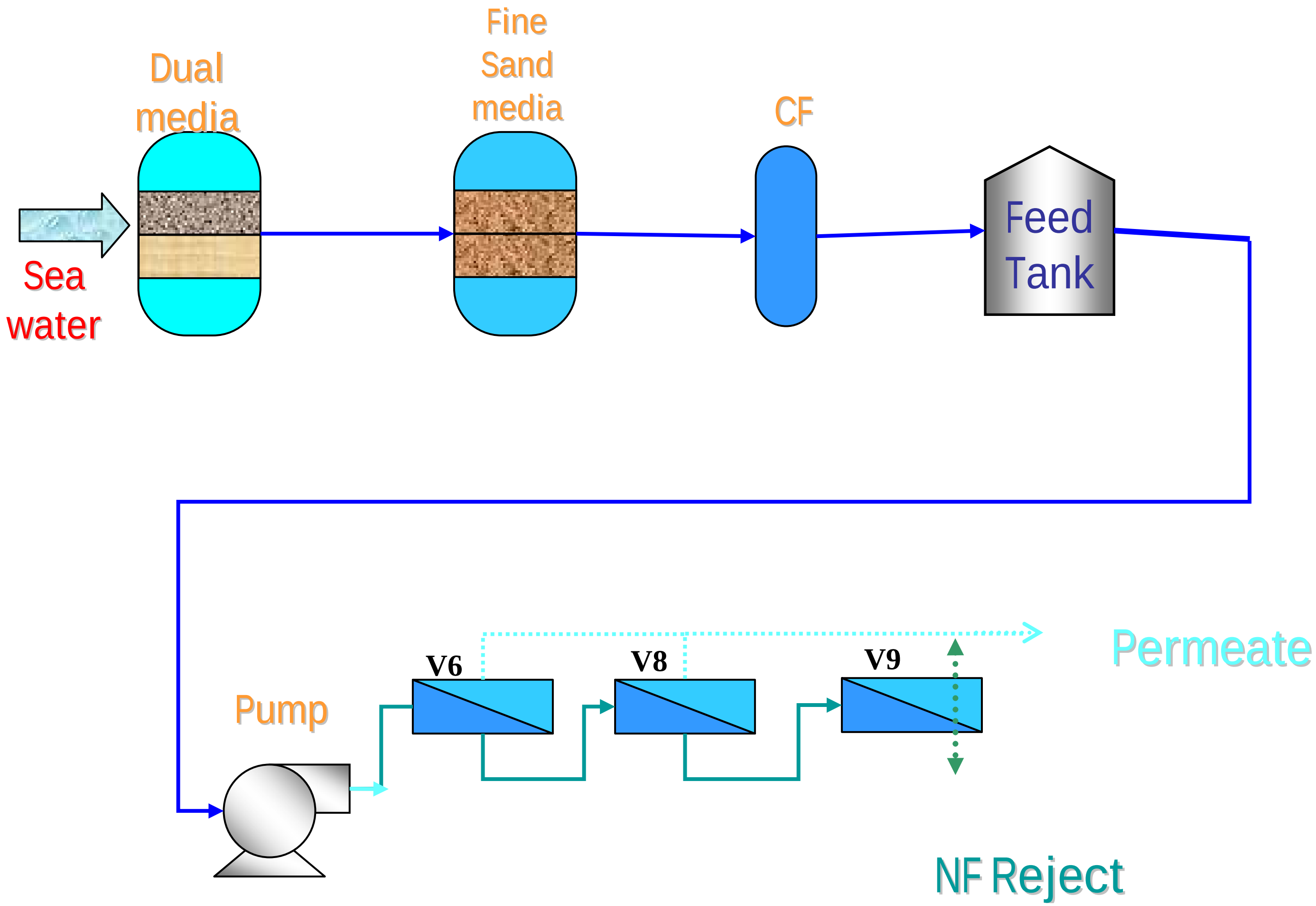

Figure 1. Schematic flow diagram of NF4" pilot plant

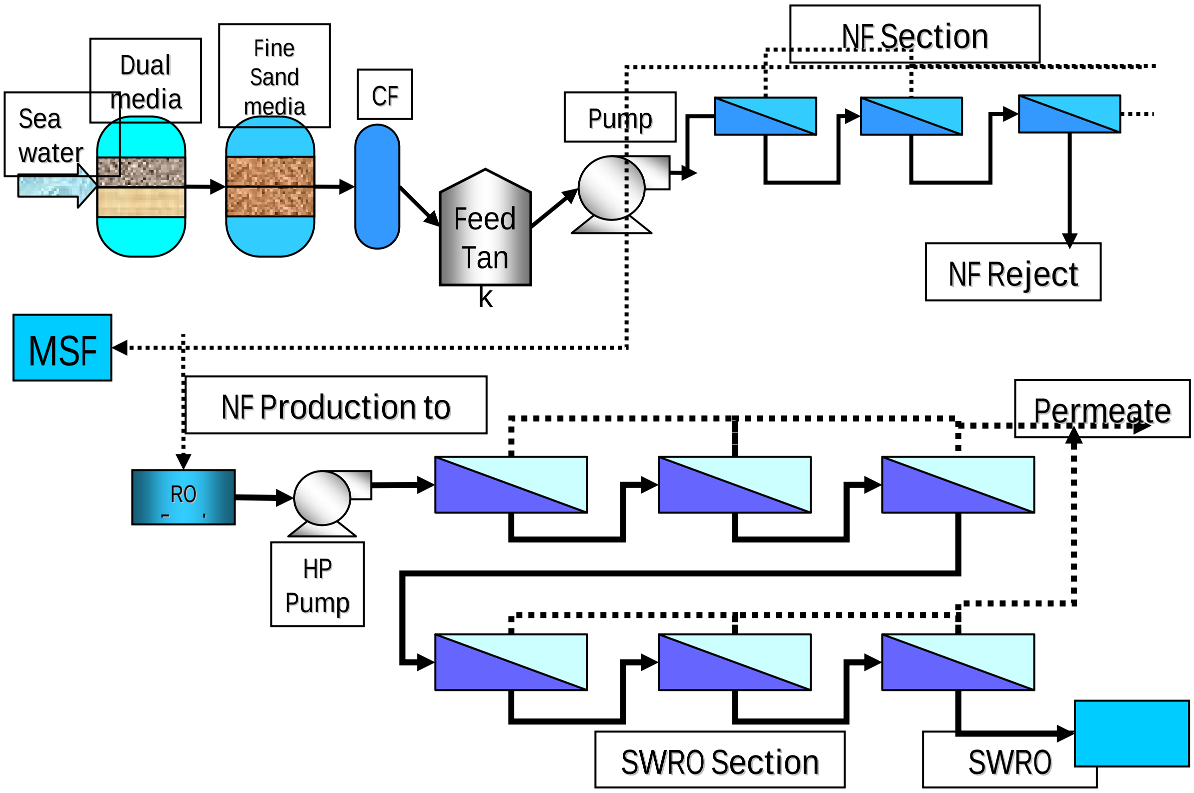

Figure 2. Schematic Flow Diagram of NF-SWRO Desalination Pilot Plant

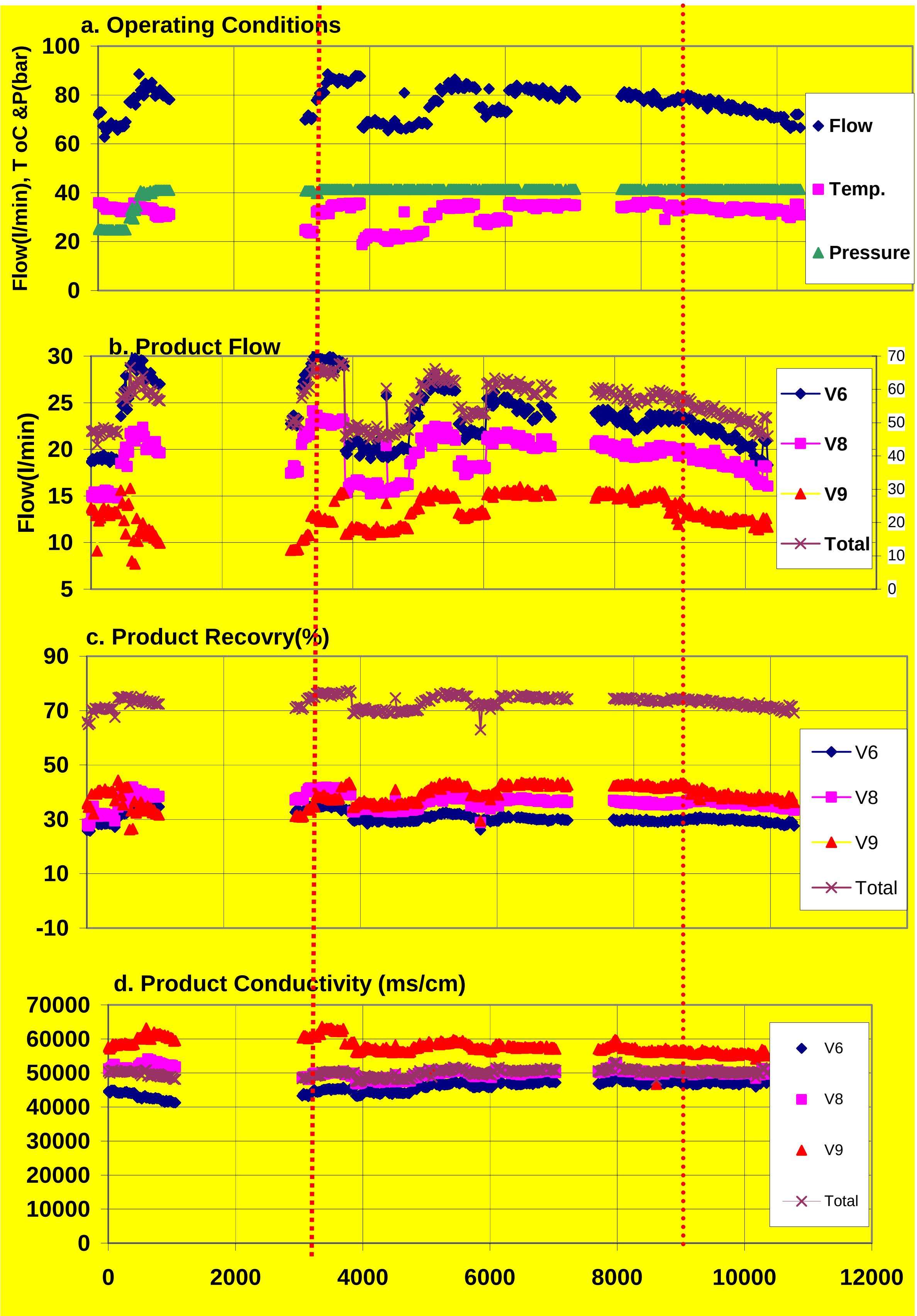

Figure 3. Performance evaluation of NF-4" Osmonic DK4040 at recovery more than or equal to75% using various antiscalant

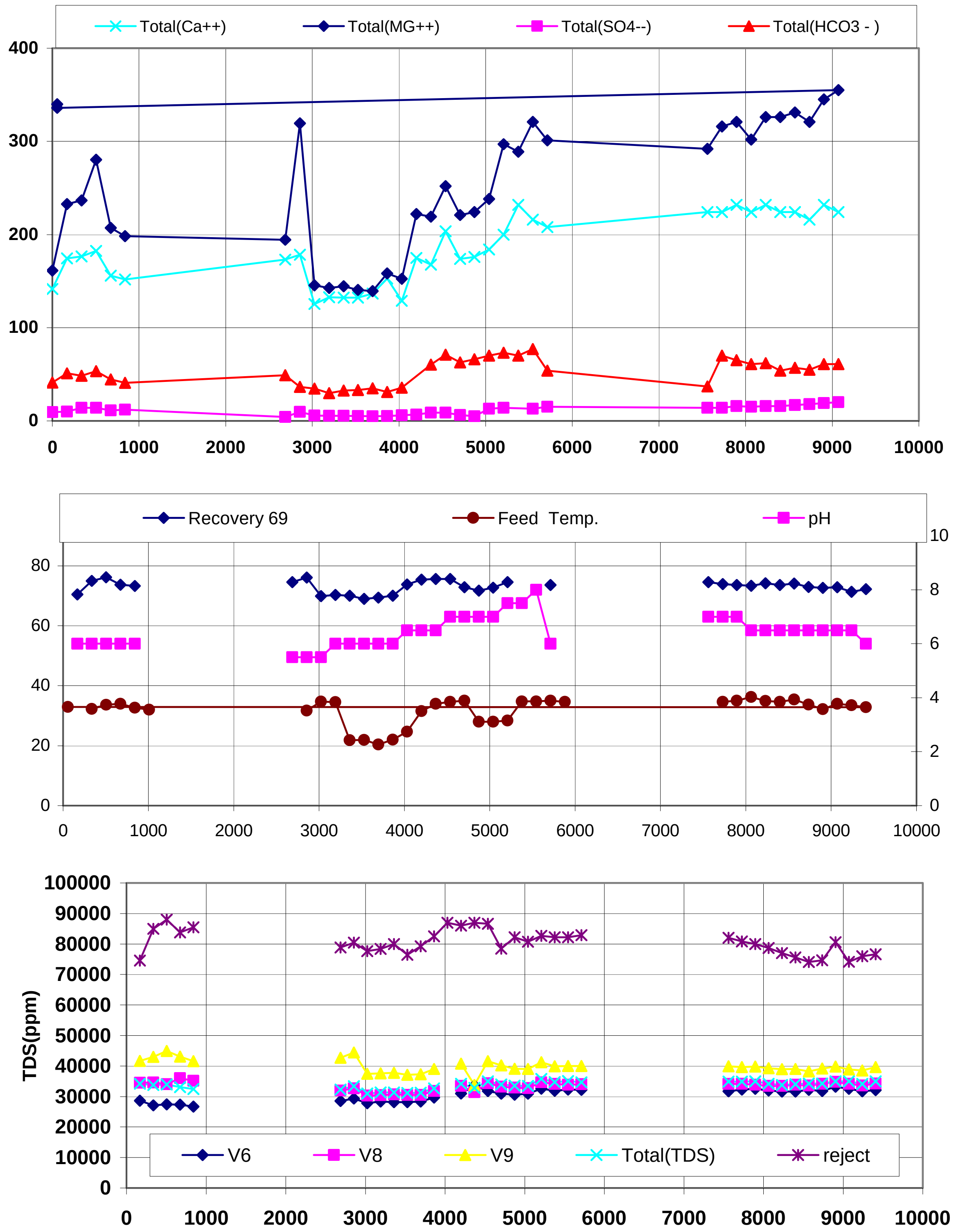

Figure 4. **Concentration of scale forming hardness ions and TDS in NF product from an NF-4" Osmonic DK4040 membranes at an NF product recovery of more than or equal to70%, using various different antiscalants**

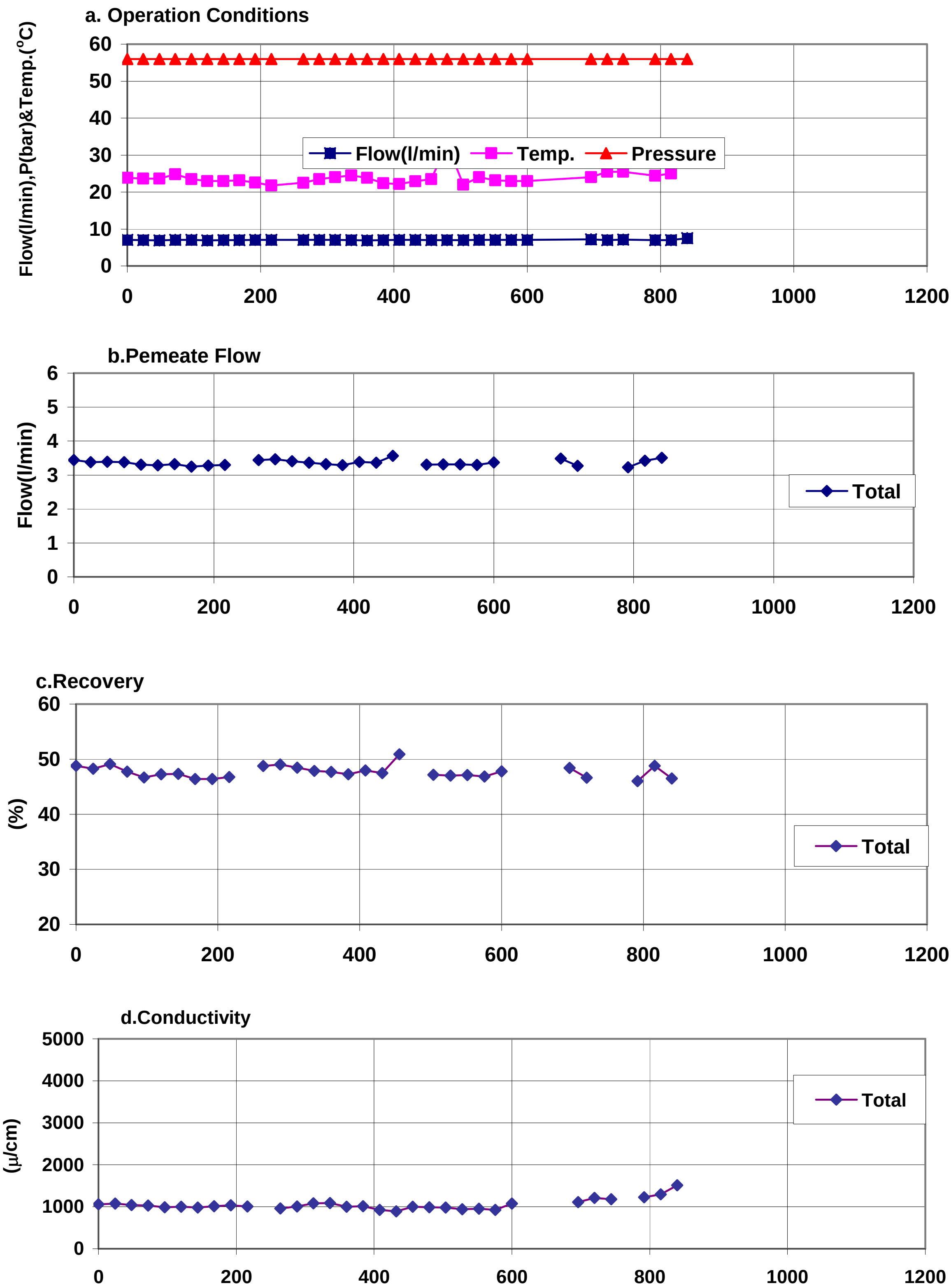

Fig. 5. Performance Of SWRO-2.5" Toray membranes fed by NF product

REFERENCES

1. Wiesner, M. R., (1992), J. AWWA, January 59.
2. Bergman, R. A., (1969), J.AWWA, November 30.
3. Hassan, A. M., AI-Sofi, M. AK., AI-Amoudi A. S., Jamaluddin A. T. M., Dalvi A.G.l., Kither N. M., Mustafa G. M. and AI-Tisan, (1997), A New Approach to Membrane and Thermal Seawater Desalination Processes Using Nanofiltration Membranes, A Paper presented at IDA, Madrid, Oct. 6-9 and D&" The International Desalination & Water Reuse Quarterly, P 54, May-June Issues, 1998.
4. Sorbie, K.S., Graham, G.M., Jordan, M.M., (2000), How scale inhibitors work and how this affects test methodology, A paper presented at 4th chemistry Conference & Exhibition, April 18, pp. 1-17.
5. Patel, S. and Finan, M. A., (1999), New antifoulant for deposit control in MSF and MED plants, UK, *Desalination*, **124**, 63-74.
6. Perner, Johannes, Kistenmacher Axel, Buechner Karl-Heinz,Huauck Klemens Urooj And Ahmed, B.E, (1997), Substituted polymaleic acid- experience with a new scale inhibitor in multi-stage flash distillation plants, paper presented at IDA, Madrid, Oct. 6.
7. Permacare Manual Hand Book.
8. Saeed, M.O., Jamaluddin, A.T.M., Al-Tisan, I.A., Lawrence, D.A., Al-Amri, M.M. and Chida, K., (2000), Biofouling in a seawater reverse osmosis plant on the Red Sea coast, Saudi Arabia, *Desalination* **128**, 177-190.
9. Brooks, G.F., Butel, J.S. and Ornston, L.N., (1991), Eds, Jawetz, Melnick and Adelberg's Medical Microbiology, 19th Ed., Appleton & Lange, East Norwack, CT, USA.
10. Hassan, A.M., Al-Sofi, M. AK., Al-Amoudi, A., Jamaluddin, A.T.M., Farooque, A.M., Al-Rowaili, A., Dalvi, A.G.I., Kither, N.M., Mustafa, G.M. and Al-Tisan, I. A., (1998), A New Approach to Membrane & thermal Seawater Desalination Processes Using Nanofiltration Membranes - Part 1, Desalination**, 118,** 35-51**.**
11. Hassan, A.M., Al-Sofi, M. AK., Al-Amoudi, A., Jamaluddin, A.T.M., Farooque, A.M., Al-Rowaili, A., Dalvi, A.G.I., Kither, N.M., Mustafa, G.M. and Al-Tisan, I. A., (1999), A New Approach to Membrane & thermal Seawater Desalination Processes Using Nanofiltration Membranes - Part 2, The 4th Gulf Water Conference, Bahrain, WSTA, **Vol. 2,** 577 - 594.
12. Hassan, A.M., Farooque, A.M., Jamaluddin, A.T.M., Al-Amoudi, A.S., Al-Sofi, M. AK., Al-Rubian,A.F., Al-Gurashi, M.M., Kither, N.M., Dalvi, A.G.I., and Al-Tisan, I. A., (1999), Optimization of NF Pretreatment of Feed to Seawater Desalination Plants, *Proceedings of IDA World Congress on Desalination Water Reuse, San Diego, USA,* 1999, **Vol. II ,** 15 –28.
13. Hassan, A.M., Farooque, A.M., Jamaluddin, A.T.M., Al-Amoudi, A.S., Al-Rubian, A.F., Al-Rowaili, A., Al-Sofi, M. AK., Kither, N.M., and Al-Tisan, I. A., (2000), A Demonstration Plant Based On The New NF-SWRO Process**,** *Proceedings of the Conference on Membranes in Drinking and Industrial Water Production, Paris, France*, **Vol. 1,** pp. 313 – 328.
14. Lee, S., Cho, J. and Elimelech, M, (2004), Influence of colloidal fouling and feed water recovery on salt rejection of RO and NF membranes, *Desalination*, **160,** pp.1-12.