CHEMICAL CLEANING EXPERIMENTS FOR PERFORMANCE RESTORATION OF NF MEMBRANES OPERATED ON SEAWATER FEED[1]

A. Mohammed Farooque, Ahamed S. Al-Amoudi and Ata M. Hassan

Saline Water Conversion Corporation
P.O.Box 8328, Al-Jubail -31951, Saudi Arabia
Tel: + 966-3-343 0012, Fax: + 966-3-343 1615
Email: rdc@swcc.gov.sa

ABSTRACT

The pioneering work of utilizing nanofiltration (NF) membranes for pretreatment of seawater feed to SWRO and MSF has gained attention of many in the desalination industries. During the performance evaluation study of NF membranes, one particular type of NF membrane experienced a decrease in their product flow along with increase in salt rejection and attempts to restore its performance by chemical cleaning was a failure, rather it produced an adverse affect on the membrane performance. As the attempts to restore the NF membrane performance failed, autopsy was conducted on 2 selected NF membranes out of 10 membranes after operation of about 1 year. Based on the autopsy results, chemical cleaning of the NF membranes was conducted to restore their performance. The cleaning was initially conducted on flat-sheet membranes cut from two NF membranes, which were autopsied. Since it was found that the major foulants were primary organic matter followed by iron, both low pH cleaning as well as high pH cleaning were tried utilizing standard chemicals such as citric acid, HCl, SBS, sodium lauryl sulfate, NaOH and high pH cleaning with Cl_2 as well as a combination of Cl_2 and hydrogen peroxide (H_2O_2). From the chemical cleaning experiments it was found that only cleaning at high pH resulted in NF performance improvement (increased product flow along with increase in product conductivity) indicating the major cause for the flux decline is primary organic matter deposited on the membrane surface. It was also noticed that an increase in product flux after chemical cleaning was always accompanied by a proportional increase in salt passage.

Chemical cleaning using combination of Cl_2 with H_2O_2 at high pH resulted in remarkable increase both in the product flux, up to about 600% and in salt passage, up

[1] Paper presented at IDA Conference March, 2002 at Manama, Bahrain.

to about 250% depending on the concentration of both Cl_2 as well as H_2O_2. The Cl_2/H_2O_2 cleaning method was further optimized by varying the concentration of Cl_2 as well as H_2O_2. After optimizing the cleaning method, the cleaning experiments were conducted on 4² ´ 40² membrane elements as well as on 8² ´ 40² commercial size membranes. This resulted in improved performance of membranes without damaging the membrane. However, it was found that the performance of this particular type of NF membrane continues to decline even after restoring its performance. It is reported that this type (in comparison to many other similar types) of NF membrane experienced rapid fouling when used to treat surface water, especially at high flux operation. The paper describes details of various chemical cleaning procedures utilized for restoring the NF membrane performance and the results obtained thereof.

1. INTRODUCTION

For the first time in the history of seawater desalination NF membranes were used as pretreatment to supply feed water to SWRO and also to MSF [1-4]. This break through approach not only increased product quantity but also reduced the scaling and fouling of both RO and MSF. Such an improvement was possible because of the ability of NF membranes to reduce TDS, mainly scale forming ions as well as microorganism and turbidity. The NF-SWRO process is at present successfully applied to a commercial SWRO plant and the details of the same can be found elsewhere [5].

Although NF membranes are used widely for treating surface waters, it was first time used as pretreatment for seawater desalination at SWCC. NF membranes in general closely resemble RO membranes in structure, however, they differ with RO in certain properties such as lower rejection of monovalent ions and high rejection of divalent or multivalent ions especially anions, as most of the NF membranes are negatively charged at the normal operation condition. Moreover, NF membranes are characterized by their high product flux compared to RO. Hence it is expected that as in the case of RO or UF membranes, performance of NF membranes can be deteriorated with time due to fouling. It has been reported that the NF membranes receiving feed from conventional pretreatment, which are used to treat surface water for softening purpose experienced decline in membrane performance due to fouling by humic acids and more frequent cleaning of the membranes are to be carried, especially at high flux operation

[6 - 8]. It is also reported that NF membranes are extremely susceptible to natural organic matter (NOM) fouling, especially in the presence of divalent cations [9]. To avoid NF fouling, extensive pretreatment such as microfiltration (MF) or ultrafiltration (UF) is to be applied to the feed of NF membranes, which will render the process highly expensive [10].

During the pioneering experiment of NF pretreatment, 10 NF membrane elements (4″× 40″) of particular brand was used to pretreat the feed water to SWRO and occasionally also to the MSF unit and details of which are available elsewhere [1-4]. During the long term operation of NF membranes, their performance started slowly declining with time and it should be noted that the NF membranes received seawater feed from a pretreatment unit, which consists of a dual media filter followed by fine sand media without dosing any coagulant. Also, no acid was dosed to the pretreated seawater and pH of the feed to NF remained same as that of seawater, i.e., about 8 except for a short period of 1 month. During this 1 month, NF was operated at pH of 6.5 to check the flux decline but without success, subsequently high pH operation was resumed. After operation of more than 190 days, when the permeate flow declined remarkably, chemical cleaning was carried out to restore the performance, but it produced reverse effect as it further reduced the flux instead of increasing it along with reducing the salt passage [4]. Further attempt by various cleaning methods did not improve the permeate flux. Finally 2 membranes out of the 10 NF membranes, viz., one lead element and another last element were removed and autopsied for finding out the reason for the flux decline. The details of the autopsy results can be obtained elsewhere [11]. It was concluded from the autopsy results that the foulant deposits found on the membrane surface might have partially contributed in reducing NF membrane performance, especially the lead element membrane performance. Also, it was found that primary organic matter was the major foulant followed by Fe. No membrane scaling occurred in spite of no antiscalant or acid was used during most of the operation. Moreover, operation of NF unit without disinfection did not cause any biofouling for the NF membrane [11]. Based on the results obtained from autopsy, membrane cleaning was conducted to restore membrane performance

This paper describes details of various chemical cleaning experiments conducted to restore the performance of NF membranes which were in operation with seawater feed for more than a year and whose product flux as well as salt passage has been declined with time.

2. EXPERIMENTAL

2.1 Flat-sheet membrane cleaning

All the membranes were cleaned in place in a flat-sheet membrane tester unit (RUW-5), where four cells are connected in series. Each cell can hold one flat-sheet membrane of 75 mm diameter. The NF membrane flat-sheets, which were cut in proper dimensions from previously autopsied NF membranes were placed in the cells and were flushed with RO permeate or MSF product water prior to each cleaning operation and also after each cleaning. Before and after each cleaning operation, performance (flux and salt rejection) of flat-sheet NF membranes were determined at feed pressure of 35kg/cm^2, feed flow of 6 l/min and at ambient temperature. Feed temperatures were in the range of 27 to 33^{o}C. The feed consists of pretreated seawater, which has been passed through dual media filter followed by a fine sand media filter and no chemicals were dosed during the performance test. For each cleaning experiment product flow as well as product conductivity of four flat-sheets were measured at a time and the average of the four are reported. Moreover, fresh flat-sheet membranes cut from NF membrane were used for each of the cleaning experiment.

The detailed procedure adopted for each cleaning method is as follows:

Sodium bisulfite (SBS):

About 25 liters of 1% of SBS in low TDS water was recirculated (after discarding initially about 3 liters of solution) at pH $\approx$ 4 and at feed pressure $\approx$ 2.0 kg/cm^2 for about 2 hours. The membranes were then kept under soaking condition for overnight and repeated recirculation next day for another 1 hour prior to discarding the cleaning solution to drain. The membranes were then flushed with RO permeate until a constant value of conductivity was obtained for the reject.

Sodium hydroxide (NaOH):

About 20 liters of low TDS water was recirculated through the membrane cell and NaOH solution was added slowly until the pH was adjusted to about 12. The NaOH solution was then recirculated through the membrane cells for about 2 hours and kept under soaking for overnight. The solution was then flushed out by operating the unit once through and also by flushing with RO permeate until the solution pH reached the normal value.

Citric acid:

The same cleaning procedure as in the case of SBS cleaning was used except that after overnight soaking the cleaning solution was recirculated for about 3 hours instead of 2 hours.

Hydrochloric acid (HCl):

Cleaning procedure used was similar to that used for NaOH cleaning. However, the pH here was adjusted to about 2.

Sodium Lauryl Sulfate (Sodium Dodecyl Sulfate, SDS):

0.5% of SDS in 15 liters of low TDS water was prepared and the procedure used was similar to that used for SBS cleaning. However, the pH of cleaning solution was 11.5.

Tap water:

Tap water as such from the service water line with pH ≈ 7 and residual chlorine of about 0.3 ppm was used to flush once through for about 45 minutes

High pH chlorine / hydrogen peroxide:

The procedure adopted here is based on a patented chemical cleaning method [12]. A known concentration of NaOCl was prepared and recirculated through the membrane cells for 20 minutes at pH > 10 after discarding initial few liters of solution. Immediately after 20 minutes, a known amount of hydrogen peroxide (H_2O_2) was added to the recirculating solution of Cl_2 at high pH to obtain a specific concentration of H_2O_2 and pH was maintained > 10 by adding sufficient amount of NaOH. The recirculation was continued for another 20 minutes and after that the system was operated in once through mode to discard all the cleaning solution. The membranes were then flushed once through with high pH low TDS water (adjusted by adding NaOH) to flush out any residual chemical remaining on the membrane surface and the pH of flushing solution was reduced progressively until the pH reached to about 7.

2.2 NF membrane element cleaning

After completing the experiments using flat-sheet membranes, two of NF membranes of size 4″ × 40″ were cleaned independently as single element using the unit which has been used for flat-sheet membrane cleaning. Another 6 membranes of same size were cleaned together in place in the NF unit, where it was being evaluated. Two commercial membranes of size 8″ × 40″ were also cleaned in their respective unit, where it was being operated. The performance of all these membranes were evaluated before and after the cleaning procedure.

3. RESULTS AND DISCUSSION

The cleaning experiments were conducted in order to regain the initial flux of the membrane, which was reduced remarkably after operating using pretreated seawater feed for more than a year. It was observed that the decline in flux is also associated with a favorable decline in salt passage. The present experiment is aimed at increasing the flux to a maximum with minimal increase in the salt passage. Selection of cleaning chemicals was based on results obtained from autopsy, which showed that the foulants mainly consists of primary organic matter followed by iron [11]. It is known that cleaning at lower pH favors the removal of iron whereas cleaning at high pH favors the removal of primary organic matter.

Average permeate flow and conductivity before and after cleaning as well as the percentage improvement in their respective values achieved as a result of cleaning using various cleaning chemicals are given in Table 1. It was found that chemicals used at lower pH such as SBS, citric acid as well as HCl did not improve the flux rather it declined along with reduction in the salt passage. Whereas cleaning at higher pH range using NaOH as well as SDS showed slight increase of flux. The increase of both the flux as well as salt passage was remarkable in the case of Cl_2 and more so with Cl_2/H_2O_2 at high pH. These results clearly indicate that the main foulant which has affected the membrane performance is primary organic matter, whereas iron foulant, which was found on the membrane surface, had least effect on the membrane performance. The decline in flux as well as salt passage after tap water cleaning can be explained on the basis of chlorine attack of the membrane. Here chlorine available in the tap water is highly active at the pH of 7, which could attack the top layer of the thin film composite membrane, namely polyamide based layer. It is known that during the early stages of chlorine attack of polyamide membrane, membrane gets tightened up due to cross linking before undergoing further membrane degradation [13]. Hence, it can be concluded that the tap water cleaning of the NF membrane shows up signs of the initial stages of chlorine attack, i.e., tightening up of the membrane.

As the preliminary experiments proved that high pH cleaning based on Cl_2 is effective in increasing the flux, further optimization of high pH cleaning based on Cl_2 was tried. The results of the same are shown in Table 2. Here the concentration of Cl_2 as well as H_2O_2 were varied without altering other parameters. The study, however, did not provide a conclusive result. In general, it can be seen from the table that larger improvement in flux has been observed the when the concentration of Cl_2 is more than 1000 ppm as well as H_2O_2 concentration is more than 0.5%. Highest increase in the flux (596%) as well as salt passage (256%) was observed in the case of Cl_2 of 5000 ppm and H_2O_2 of 1%. Concentration greater than this value did not increase the percentage improvement. The results also reveal that the higher the improvement in flux the higher will be the salt passage.

Based on the results obtained from flat-sheet membranes, the experiment with chlorine at pH were tried on actual NF membrane element of size $4'' \times 40''$, which has been in operation for more than one year and whose flux as well as salt passage have declined tremendously. One of the membrane was cleaned with Cl_2 (1100 ppm) alone at high pH without H_2O_2. It was found that product flow was increased by about 237% and salt passage by 56% immediately after cleaning (Fig.1), which declined with time. After operating about 160 hours at the same operation conditions, the flow as well as salt passage declined, which resulted in 148% increase in flow and 33% increase in salt passage compared to situation before cleaning.

Similarly another $4'' \times 40''$ membrane was cleaned with Cl_2 (1100 ppm) as well as H_2O_2 (1%) at high pH. In this case the result was better than cleaning with Cl_2 alone as the flux increased by 338% and salt passage by 60% percent (Fig. 2). Here also the both the flux as well salt passage decreased with time and after operating about 105 hours the increase compared to before cleaning situation is only 272% for flux and 44% for salt passage.

Remaining six elements of size 4″ × 40″ were cleaned together in place, which were operated in series. They were cleaned with Cl_2 (2000 ppm) and H_2O_2 (1%) at high pH and the results are shown in Figure 3. Here, the increase in flux was about 520% and salt passage about 59% immediately after cleaning which after about 290 hours operation became 350% and 47%, respectively.

Cleaning of commercial size (8″ × 40″) membranes (2 elements in series) with Cl_2 (800 ppm) and H_2O_2 (0.5%) increased flux by 780% and salt passage 98%, which declined to 642% and 79%, respectively after operation of about 105 hours operation (Fig. 4).

It was found from the present study that chemical cleaning procedure using Cl_2/H_2O_2 at high pH is highly effective in removing the foulants from the NF membrane surface without damaging the membrane polymer and restoring the membrane performance. However, the performance of NF membranes used in the present study continued to decline rapidly even after restoring their performance by chemical cleaning. This can be attributed to the nature of membrane. It has been reported [6] that this particular type of membranes is susceptible to poor performance with time. The increase in the salt passage has been found to be within the value which has been observed for the membrane during the initial operation period, thus ruling out the possiblity that the Cl_2 / H_2O_2 cleaning at high pH damaging the membrane.

4. CONCLUSION

The chemical cleaning of NF membranes proved that cleaning with Cl_2 / H_2O_2 at high pH was highly effective in removing the foulants (especially primary organic matter) from the membrane surface, which restored membrane performance. It was also found that higher the increase in membrane flux after cleaning, the higher was the salt passage. Moreover, the cleaning procedure using Cl_2 / H_2O_2 at high pH did not cause any damage to the membrane. This particular brand of NF membrane was found to be prone to fouling, which resulted in their poor performance with operation time.

5. REFERENCES

1. Hassan, A.M, M. Ak. Al-Sofi, A. Al-Amoudi, A.T.M. Jamaluddin, A.G.I. Dalvi, N.M.Kither, G..M. Mustafa and I. A. Al-Tisan, (1998), A New Approach to

Membrane & Thermal Seawater Desalination Processes Using Nanofiltration Membranes - Part 1, Desalination & Water Reuse, 8(1), 53-59.

2. Hassan, A.M., M. Ak. Al-Sofi, A. Al-Amoudi, A.T.M. Jamaluddin, A.G.I. Dalvi, N.M.Kither, G.M.Mustafa and I. A. Al-Tisan, (1998), A New Approach to Membrane & Thermal Seawater Desalination Processes Using Nanofiltration Membranes - Part 2, Desalination & Water Reuse, 8(2), 39-45.

3. Hassan, A.M., M. Ak. Al-Sofi, A. Al-Amoudi, A.T.M. Jamaluddin, A.M.Farooque, A.Rowaili, A.G.I. Dalvi, N.M.Kither, G.M.Mustafa and I. A. Al-Tisan, (1998), A New Approach to Membrane & Thermal Seawater Desalination Processes Using Nanofiltration Membranes - Part 1, Desalination, **118**, 35-51.

4. Hassan, A.M., M. Ak. Al-Sofi, A. Al-Amoudi, A.T.M. Jamaluddin, A.M.Farooque, A.Rowaili, A.G.I. Dalvi, N.M.Kither, G.M.Mustafa and I. A. Al-Tisan, (1999), A New Approach to Membrane & Thermal Seawater Desalination Processes Using Nanofiltration Membranes - Part 2, The Fourth Gulf Water Conference, Bahrain, WSTA.

5. Hassan, A.M., A.M.Farooque, A.T.M.Jamaluddin, A.S.Al-Amoudi, M. AK. Al-Sofi, A. Al-Rubaian, N.M.Kither, A.M.Al-Ajlan, A.A.Al-Azzaz, A.Abanmy, A.Al-Badawi, A.S.Al-Mohammadi, A.Al-Hajouri and M.B.Fallata, (2001), Conversion & Operation of the Commercial Umm Lujj SWRO Plant from Single SWRO Desalination Process to the New Dual NF-SWRO Desalination Process, to be presented at IDA World Congress on Desalination & Water Reuse, Bahrain, October.

6. Bertrand, S., I. Lemaitre and E. Wittman, (1997), Performance of a nanofiltration plant on hard and highly sulphated water during two years of operation, Desalination, 113, 277-281.

7. Speth, T.F., R.S.Summers, and A.M. Gusses, (1998), Nanofiltration Foulants from a Treated Surface Water, Environmental Science & Technology, 32, 3612-3617.

8. Chellam, Shankararaman, J.G. Jacangelo, T.P. Bonacquisti, and B.A. Schauer, (1997), Effect of pretreatment on surface water nanofiltration, Journal AWWA, (10), 77-89.
9. Hong, Seungkwan, Menachem Elimelech, (1997), Chemical and physical aspects of natural organic matter (NOM) fouling of nanofiltration membranes, Journal of Membrane Science, 132, 159-181.

10. Chellam, Shankararaman, Christophe A. Serra, and Mark R. Wiesner, (1998), Estimating costs for integrated membrane systems, Journal AWWA, 90 (11), 96-104.

11. Farooque, A.M., A. M. Hassan, and A.S. Al-Amoudi, (1999), Autopsy and Characterization of NF Membranes After Long Term Operation in an NF-SWRO

Pilot plant, Proceedings of IDA World Congress in Desalination and Water Reuse in San Diego, California, U.S.A., vol. II**,** 77-87.

12. Fremont, H.A., R.C.Agar, J.W. Bray, and G.W. Marquart, (1988), Membrane Cleaning Process, United States Patent, Patent no. 4,740,308, April 26.

13. Avlonitis, S., W.T.Hanbury and T.Hodgkiess, (1992), Chlorine Degradation of Aromatic Polyamides, Desalination **85**, 321-334.

Table 1 : Performance of NF flat-sheet membranes before and after cleaning with various chemicals

S. no.	Cleaning Method	Average Permeate Flow (ml/min)		Average Permeate Conductivity (μS/cm)		Percentage Increase (%)	
		Before Cleaning	After Cleaning	Before Cleaning	After Cleaning	Permeate Flow	Permeate Conductivity
1	SBS (1%) at pH = 4.0	1.65	1.58	14633	12543	-4	-13
2	NaOH at pH = 12.0	1.45	1.57	11180	11423	8	3
3	Citric acid (1% wt) at pH = 2.2	1.57	1.41	10980	9453	-10	-14
4	HCl at pH = 2.0	1.57	1.36	11470	10708	-13.1	-6.8
5	SDS (0.5%) at pH = 11.5	1.62	1.71	13040	12613	5	-3
6	Tap water for 45 minutes once through.	1.44	1.19	11963	10060	-17	-16
7	Cl_2 (300 ppm) at pH = 12.0	1.15	2.08	9848	15393	81	57
8	Cl_2 (5000 ppm) at pH = 12 followed by 2.5 % of H_2O_2 at pH = 10.0	1.44	7.26	10420	32775	406	215

Table 2 : Performance of NF flat-sheet membranes before and after cleaning during optimization of CL_2 / H_2O_2 chemical cleaning

S. no.	**Chemicals Concentration**		Average Permeate Flow (ml/min)		Average Permeate Conductivity (μS/cm)		Percentage Increase (%)	
	Cl_2 (ppm)	H_2O_2 (%)	Before Cleaning	After Cleaning	Before Cleaning	After Cleaning	Permeate Flow	Permeate Conductivity
1	300	0	1.15	2.08	9848	15393	81	57
2	500	0	1.45	2.53	11853	17860	74	51
3	500	1	1.75	2.58	11095	17250	48	55
4	1250	1	1.66	4.58	11515	25250	177	119
5	2000	0.6	1.54	7.92	11035	33475	415	203
6	2500	1	1.18	5.21	15028	33175	342	121
7	5000	1	1.50	10.40	10808	38525	596	256
8	5500	2.5	1.44	7.26	10420	32775	406	215

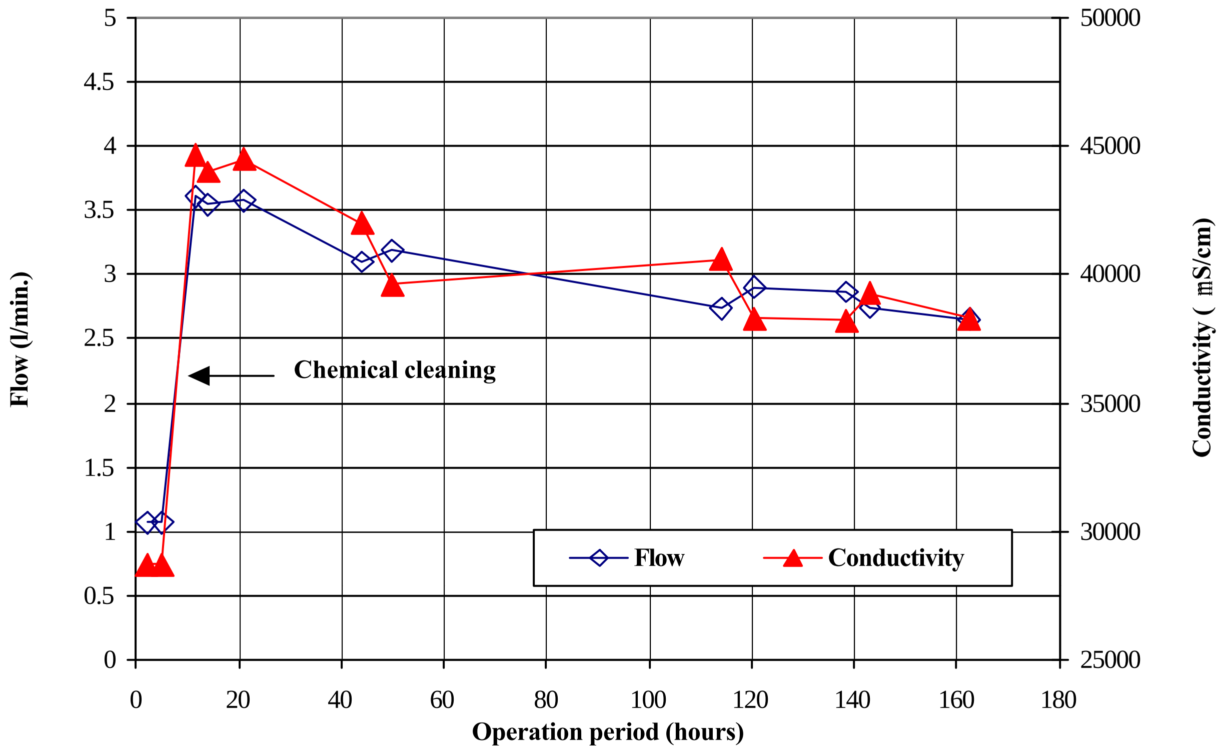

Fig. 1 : Product flow and conductivity of single NF 4 inch element cleaned with NaOCl (1100 ppm) at high pH

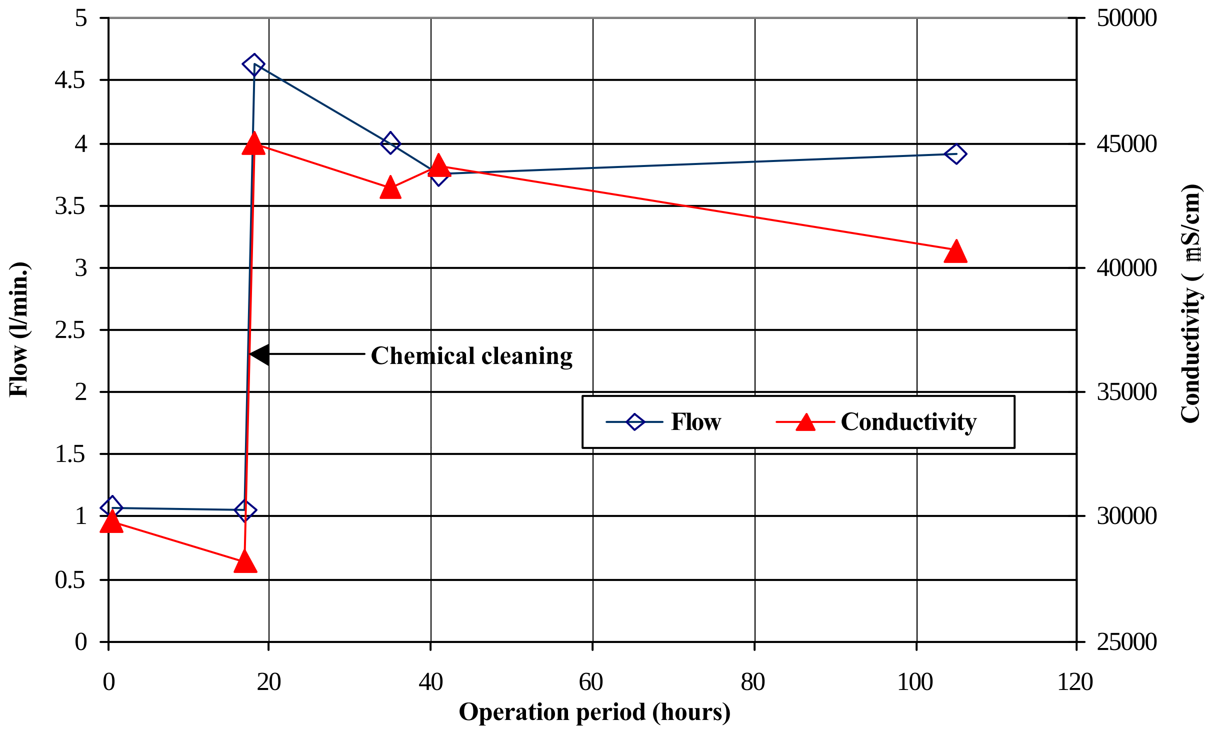

Fig. 2 : Product flow and conductivity of single NF 4 inch element cleaned with NaOCl (1100 ppm) and H_2O_2 (1%) at high pH

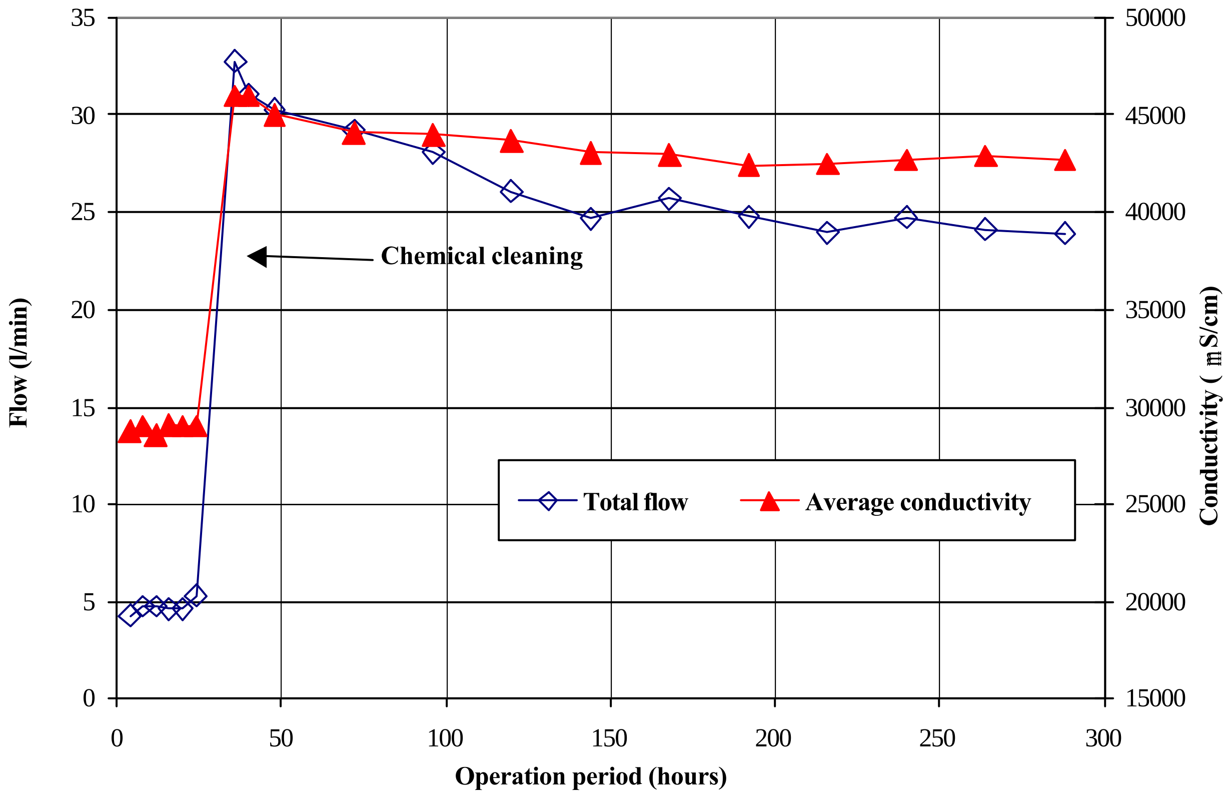

Fig. 3 : Product flow and conductivity of NF 4 inch (6 elements in series) cleaned with NaOCl (2000 ppm) and H_2O_2 (1%) at high pH

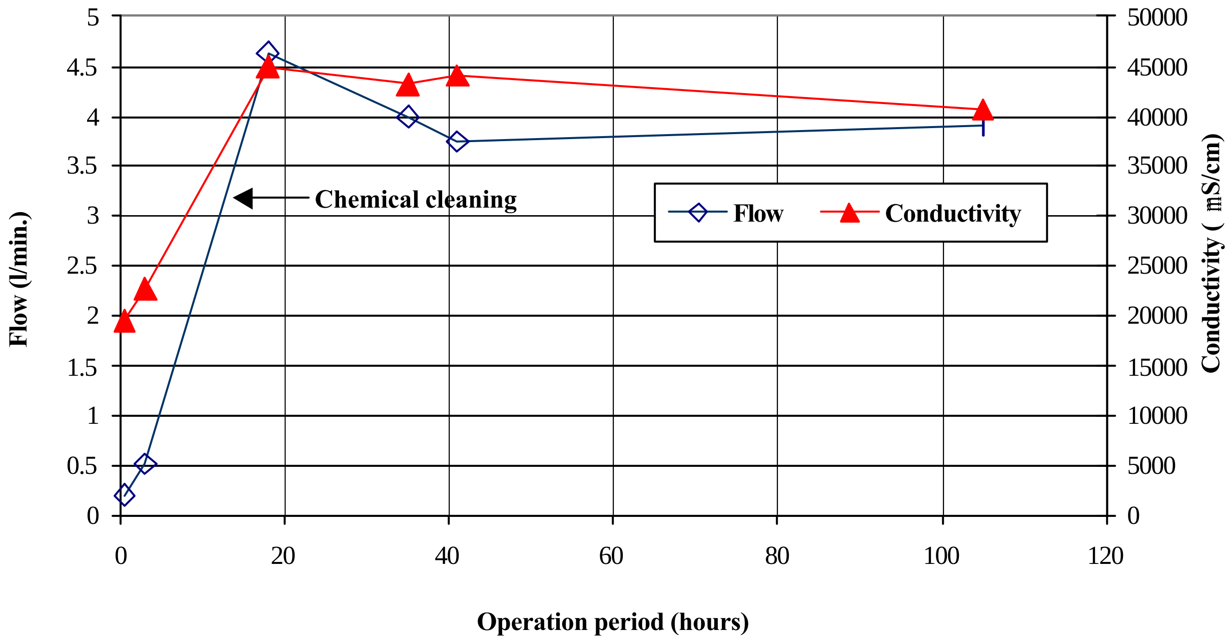

Fig. 4 : Product flow and conductivity of NF 8 inch (2 elements in series) cleaned with NaOCl (800 ppm) and H_2O_2 (0.5%) at high pH