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Autopsy of NF membranes after 5 years of operation at the Ummlujj SWRO plant

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ABSTRACT

Application of nanofiltration (NF) membrane pretreatment to conventional seawater desalination processes at the Ummlujj SWRO plant generated much interest in the use of NF membranes in seawater desalination industries (thermal and SWRO). The present study was carried out to evaluate the condition of NF membrane elements after 5 years of continuous operation at the Ummlujj NF-SWRO plant. A total of 6 NF membranes removed from Ummlujj during annual replacements were subjected to performance evaluation. Out of the six elements, two NF elements from a single pressure vessel were subjected to autopsy and analyses based on their poor performance and also due to the fact both membranes (positioned 5th and 6th within the pressure vessel) were in continuous operation for 5 years. Autopsy included visual inspection, chemical and biological analyses of foulants as well as scanning electron microscopy and energy dispersive x-ray studies. The appearance and foulant contents on both membrane surfaces were the same and there was a remarkable reduction in their flux along with a significant increase in salt passage. Foulant deposits mainly consisted of organic matters that were easily scraped off from the membrane's surface but left stubborn stains difficult to clean, even with strong chemical cleaning agents. Thus, it was concluded that with long operation period, these foulants were strongly adsorbed onto the membrane surface and became irreversible in nature. The existence of organic foulants suggests the urgent need and application of a coagulation–filtration pretreatment process using a coagulant such as $FeCl_3$. This could be easily done by replacing the existing antiscalant SHMP, which is not necessary, as the current pH of the pretreated seawater feed of about 6.2 is sufficient to prevent scale formation on SWRO and NF membranes.

Keywords: Nanofiltration; Seawater; Fouling; Autopsy

1. Introduction

The desalination industry has expressed keen interest in the long-term performance of the first commercial NF–SWRO plant commissioned in September 2000. NF application to the SWRO plant increased water production and the product water recovery ratio while reducing the product energy consumption and water production cost [1]. The plant began operation with 27 pressure vessels (PVs) each containing 6 NF elements, totaling 162. A rapid increase in feed pressure and subsequent increase in chemical cleaning frequency (every 3 months) necessitated further investigation after 1 year of operation. The investigation involved autopsy of lead and end elements from a single vessel and results indicated that organic fouling in the lead element due to higher flux (44.4 $L/m^2/h$) was responsible for the performance decline [2]. Based on the recommendation from this study, the number of PVs were raised to 36 (216 NF elements) during February 2002 and then to 45 (270 NF elements) in October

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2004 to reduce the flux to an average value of 26.7 l/m^2/h and consequently to reduce fouling in lead elements. Such changes resulted in steady operation of the plant.

The operation of plant for the 2 years with 45 PVs resulted in a steady performance of the NF unit leading to lower chemical cleaning frequencies (from every 3 months to 6 months), a typical indication of lower fouling rate. As the foulants are mainly deposited on the lead elements, only these (lead) elements were replaced during the regular annual membrane replacements and while end elements (which were less fouled) remained in PVs during the entire 5 years of operation. However, at the end of 5 years of operation, the last two end elements that were in continuous operation for more than 5 years were removed and new elements were replaced as lead elements in each vessel. Out of the 90 NF elements removed, a total of six elements were subjected to autopsy and analyses.

During the 5 years of operation, these membranes were exposed to a total of 11 chemical cleanings, initially by using a mixture of ethylenediamine tetraacetic acid (EDTA), trisodium phosphate and sodium tripolyphosphate at high pH of 11 followed by low pH cleaning using citric acid. However, the last two chemical cleanings were carried out using only sodium dodecyl sulfate (SDS) at a high pH of 11. The present study provides valuable information on conditions of NF membranes operating on seawater feed for 5 continuous years which have not been studied before.

2. Experimental method

2.1. Membrane details

Details of all six NF elements which were removed from three different pressure vessels, identified as A, B and C, are given in Table 1. Each membrane was subjected to a performance test using pretreated seawater in an existing NF unit at the SWDRI pilot plant. The test unit consists of a medium high pressure pump that operates at a feed pressure of 25 bar, ambient feed temperature of about 26°C and a feed flow rate of 8 m^3/h. Two membranes were evaluated at a time in two different pressure vessels arranged in parallel and each vessel was fitted with a single NF element. The NF unit received pretreated water of SDI <3 from pretreatment unit employing a coagulation–filtration process using a dual media filter followed by a fine sand filter where ferric chloride was dosed at a concentration of 0.6 ppm as Fe^{3+}. In addition to coagulant ferric chloride, sulfuric acid was dosed to the pretreated seawater feed to maintain pH of 6.0 throughout the evaluation. Flow, conductivity and pH measurements were carried out for each individual pressure vessel after a half-hour following stabilization of operating conditions. Also, feed and permeate samples collected were subjected to detailed chemical analyses. The performance results obtained were then normalized using standard ASTM procedure [3]. The results were normalized to feed pressure of 25 bar, feed temperature of 25°C, and a recovery of 12%. The osmotic pressures of feed and permeates were calculated from respective conductivity values using an equation which was developed in house and described elsewhere [4].

2.2. Autopsy and visual inspection

Out of six NF membranes, only two were subjected to autopsy and analyses based on their individual performance as well as position within pressure vessels. The 5th (serial no. 7613781) and 6th (serial no. 7612404) NF elements from a single pressure vessel were cut open and visually inspected.

2.3. Chemical analysis

Chemical analyses which mainly involved quantitative identification of inorganic constituents were carried out for the foulant scraped off from surface of both membranes after thorough drying of the samples. Inorganic elemental analyses were carried out using Hitachi Model 306 Super Scan ICP emission analysis system and analyses of phosphate, sulfate and soluble silica were carried out using a Hach DR/4000U spectrophotometer. Loss of ignition at 600°C was used as a rough estimate of total organic content of the foulant deposit.

2.4. Bacterial/biochemical analysis

Two bacterial colonies were isolated from both membrane samples following a procedure described elsewhere [5]. Additionally, foulant samples extracted from membranes were lyophilized and assayed for proteins and carbohydrates (sugars) using the Lowry and phenol methods, respectively [6].

2.5. SEM and EDX

Samples were collected from different parts of both the membranes and dried thoroughly before analyzing deposits on membrane surfaces using a scanning electron microscope (SEM), Jeol JSM 6480LV and an energy dispersive x-ray (EDX) spectrometer, Oxford Inca Energy 250.

3. Results and discussion

Prior to performing the evaluation, all membranes were inspected and weighed; the wet weight was in the range of 17.8–18.8 kg (see Table 1) compared to new

Table 1
Performance of six brine side NF membranes removed from the Ummlujj plant and their permeate chemical analyses

Membrane Sl. No.	Feed seawater	7613781	7612404	7605615	7606864	7614144	7613958
Vessel		A	A	B	B	C	C
Position no. in the vessel		5	6	5	6	5	6
Weight (kg)		18.8	18.8	18.6	18.3	18.4	17.8
Product Flow (m^3/h)		0.672	0.696	0.714	0.756	0.852	0.834
Normalized product Flow (m^3/h)		0.49	0.51	0.52	0.54	0.64	0.60
Recovery (%)		8.43	8.78	8.98	9.5	10.62	10.44
Product conductivity (µS/cm)		54,600	54,500	54,200	54,200	52,900	54,700
ΔP (bar)		1.4	1.4	0.7	0.3	1	0.7
Permeate chemical analyses results:							
Ca (ppm)	492	366	366	361	361	321	370
Mg (ppm)	1,513	908	933	820	881	688	954
Total hardness as $CaCO_3$ (ppm)	7,457	4,654	4,754	4,279	4,529	3,553	4,854
SO_4 (ppm)	3,324	138	138	130	146	65	170
Chloride (ppm)	23,476	21,715	21,422	21,275	21,275	20,982	21,715
TDS (ppm)	44,280	35,900	36,600	35,400	35,600	34,920	36,600
Remarks		Autopsied	Autopsied	—	—	—	—

membranes of wet weight of about 15–16 kg indicating that about 3 kg of foulant deposits were present on the membrane surfaces of all six membranes.

3.1. Performance evaluation

Performance evaluation at standard conditions revealed that membranes have normalized product flow and product conductivity in the ranges of 0.49–0.64 m^3/h and 52,900–54,700 µS/cm, respectively (Table 1). This is in comparison to the normalized product flow of 0.81 m^3/h and 1.22 m^3/h and product conductivity of 48,300 µS/cm and 44,000 µS/cm of lead element and end element, respectively, after 1 year of operation [2]. It is to be noted that the value obtained for the end element closely matches with new membrane data of 1.26 m^3/h (normalized product flow) and 43,500 µS/cm (product conductivity). These results of flow and conductivity indicate a large decline of over 50% in the performance of all six evaluated membranes. The product TDS, which was determined gravimetrically at a temperature of 105°C, was about 36,000 ppm compared to the initial value of about 28,000 ppm. Even the hardness ion rejection had become very poor, ranging from 35–52% as compared to the 81% and 96% rejection of lead and end elements, respectively, after 1 year of operation. Moreover, there was a decline in sulfate rejection which ranged from 95–98% as compared to the initial 99.9% after 1 year of operation. All these results indicate that 5 years operation had a tremendous impact not only on flow but also on rejection of both TDS and hardness ions of the end elements, which should be the least affected and the area where most organic fouling is more unlikely to occur [7].

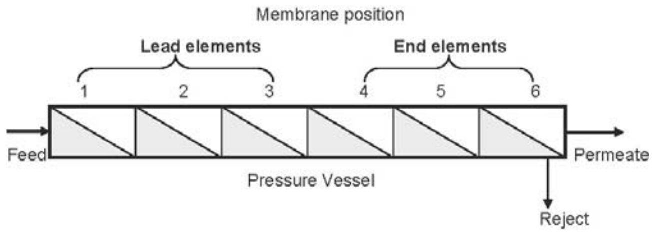

Fig. 1. Arrangement of NF membranes in the pressure vessel.

3.2. Visual inspection

Out of the six elements, two NF elements from a single vessel were subjected to autopsy and analyses based on their poor performance and also due to the fact both membranes were positioned 5th and 6th within the pressure vessel during plant operation (Fig. 1) for 5 years. Henceforth the two membranes are referred as no. 5 and no. 6 based on their position in the pressure vessel. Fig. 2 and 3 show different stages of autopsy. It was observed that appearance of both membranes was very similar and both had thick reddish brown deposits uniformly on the entire membrane surface. However, no signs of channeling were observed and no foulants were found to have adhered to the feed spacers. Moreover, the fouling did not increase the differential pressure (ΔP) as was evident from

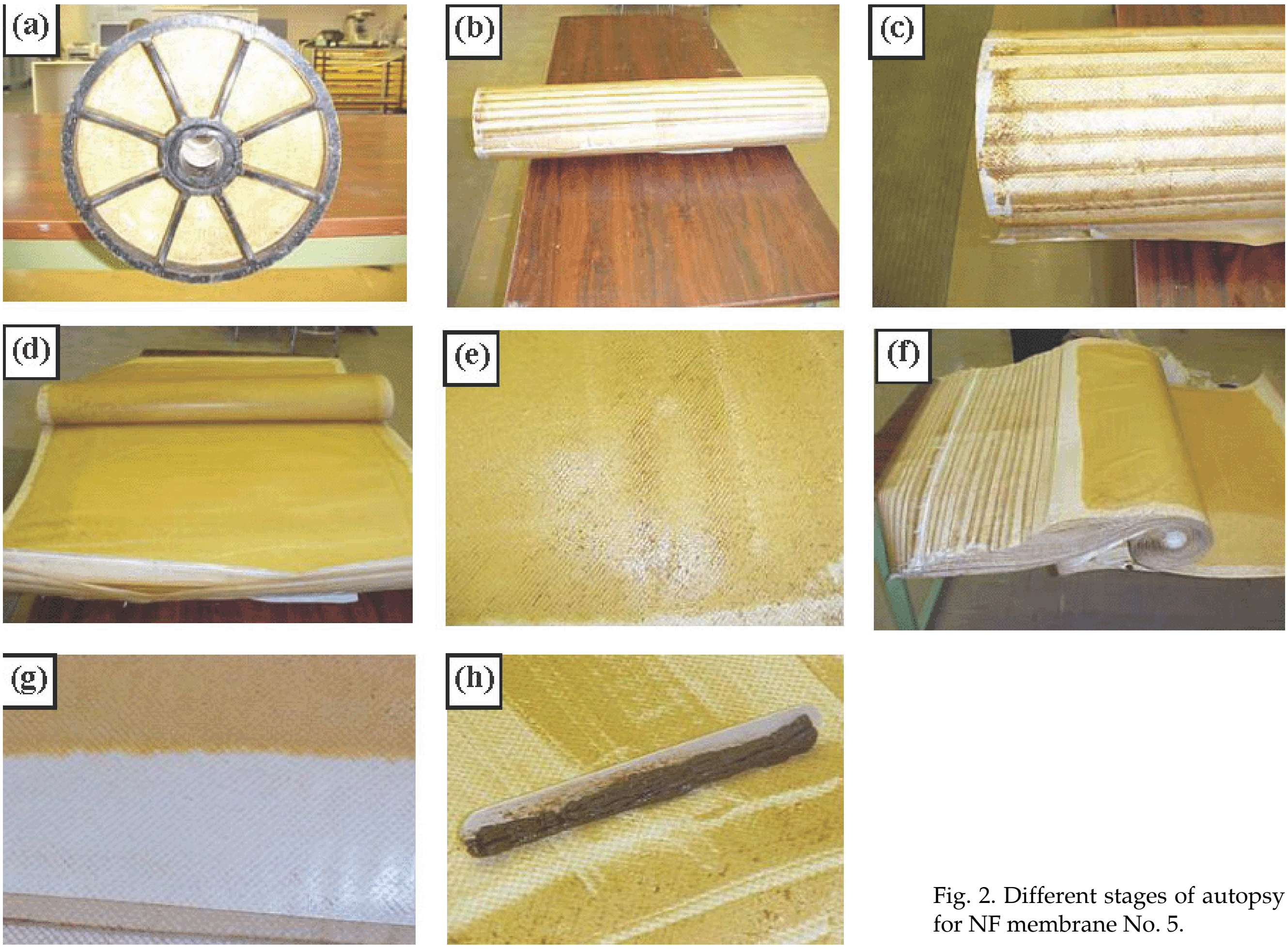

Fig. 2. Different stages of autopsy for NF membrane No. 5.

the long-term operation of the NF unit. The foulant deposits could be easily scraped off and were collected from both membranes for chemical and biochemical analyses. Also pieces of membranes were cut from different locations to determine deposition of foulant per unit area of membrane which is an indication of fouling intensity. There was a clear indication of difference in color due to foulant deposition on the membrane permeation area from the glue lines of membrane as can be seen in Figs. 2g, 3g and 3h.

3.3. Chemical analysis

The chemical analysis results of foulant scraped off from the surface of membranes are given in Table 2. Results for both the membranes are almost similar as can be seen from the table. The amount of dried foulant per unit area is about 0.7 mg/cm^2 which is higher than what was found on the lead element of 0.52 mg/cm^2 and the 0.15 mg/cm^2 found on the cleaner end element after 1 year of operation [2]. The foulant mainly consist of primary organic matter as measured by loss of ignition at 600°C,

Table 2
Foulant deposit analyses results of NF membranes No. 5 and 6

S. no.	Parameter	No. 5		No. 6	
		%	μg/cm^2	%	μg/cm^2
	Foulant (dry)	—	700	—	710
1	Iron	6.2	43.3	5.3	37.8
2	Chromium	0.2	1.7	0.1	0.8
3	Nickel	0.1	0.8	0.1	0.8
4	Aluminum	0.4	2.5	0.3	2.4
5	Calcium	1.7	11.7	1.7	12.1
6	Magnesium	1.0	6.7	0.8	5.6
7	Copper	0.1	0.8	0.1	0.8
8	Phosphate	3.3	23.3	3.5	25.0
9	Sulfate	4.0	28.3	4.5	32.2
10	Silica (Soluble)	0.2	1.7	0.3	2.4
11	Primary organic matter	73.2	512.5	73.8	524.0
11.1	Protein	3.31	23.2	3.50	24.9
11.2	Carbohydrates	6.63	46.4	6.66	47.3
12	Others	9.5	66.7	9.3	66.0

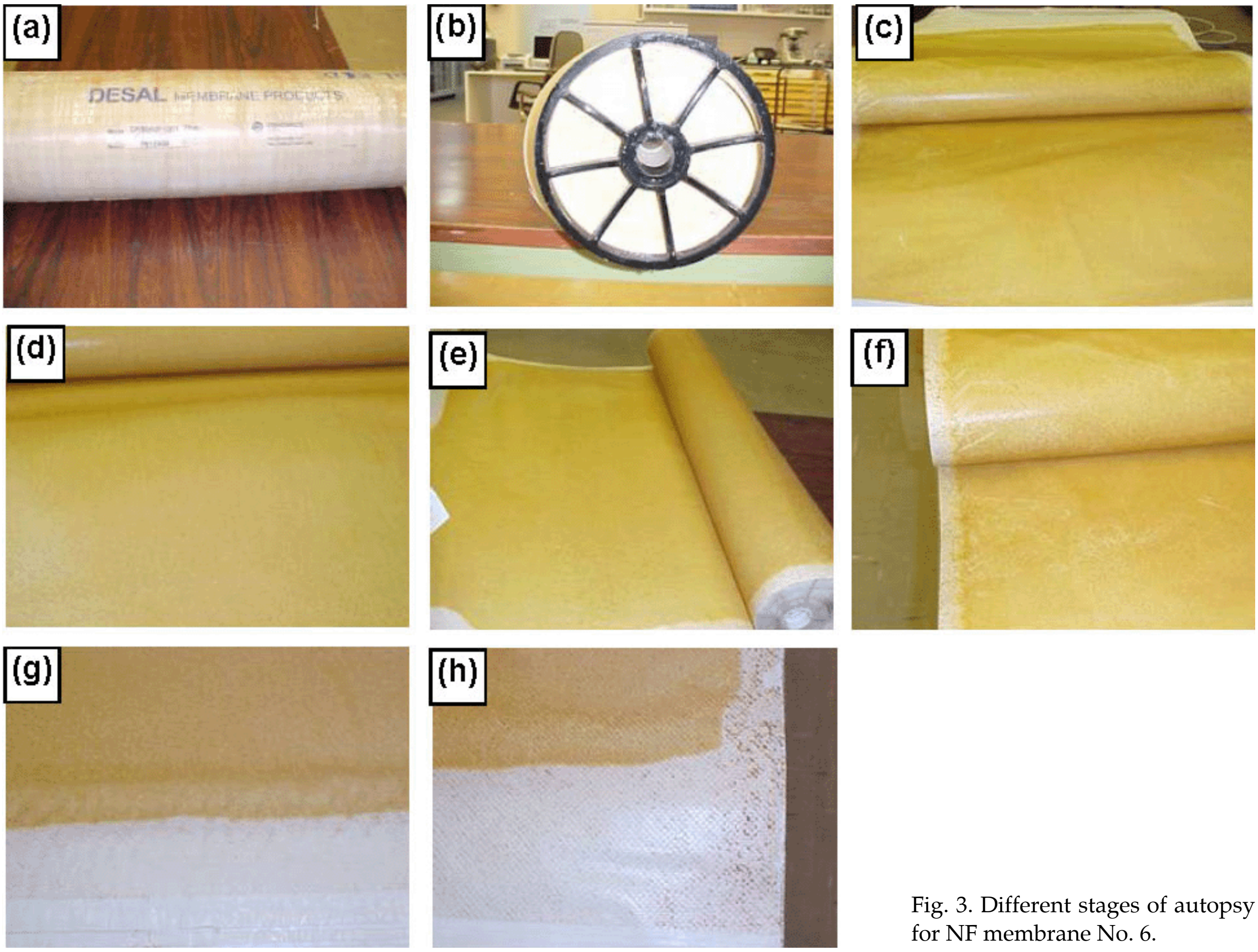

Fig. 3. Different stages of autopsy for NF membrane No. 6.

which is about 73% of the total foulant and is far higher than the previously found value for the lead element of 30% after 1 year of operation. This indicates a slow accumulation of organic matter on the membrane surface.

The amount of protein together with carbohydrates forms about 10% of total foulant and the remaining organic matter (about 63%) could be humic substances as it tends to form the predominant component of dissolved organic carbon [8]. This is in contrast to a recent finding by Her et al. [9] where it was shown that proteins and polysaccharides constitute the major fouling components rather than the humic substances. The main reason for this difference is that Her et al. used a hydrophilic NF membrane which has relatively high repulsive interactions with hydrophobic humic substances in addition to charge repulsion due to negative charges of both membranes as well as humic substances. However, in the present study, a hydrophobic membrane was used, which tends to exhibit favorable interaction with hydrophobic humic substances. The interaction is further enhanced by the neutralization of humic substances due to the presence of a relatively high concentration of divalent calcium in the seawater. Moreover, it was also shown that humic substances precipitate at lower pH and tend to foul membranes [10,11]. This organic matter can be removed by a coagulation–filtration process [12] which may be incorporated in the Ummlujj plant, the only SWCC SWRO plant operating without a coagulation–filtration pretreatment system. Coagulants such as $FeCl_3$ could be dosed in the pretreatment system [12] and probably the dosing system which is presently used for antiscalant sodium hexametaphosphate (SHMP) can be used. SHMP dosing can be stopped due to fact that the feed pH at Ummlujj is about 6.2, which is sufficient to suppress scale formation on the membrane at the present recovery of the SWRO unit of less than 30% and NF unit of less than 70%. Moreover, the phosphorous–oxygen (P–O) bond of SHMP tends to hydrolyze to form orthophosphate, which can further react with the calcium ion to form relatively insoluble calcium phosphate scale [13].

Among the inorganic constituents, iron was the major component, which forms about 6% of the total foulant found along with chromium and nickel. This indicates deposition of corrosion products from stainless steel piping as there are no other sources of iron exists in the pretreatment in the form of coagulant unlike the rest of SWCC SWRO plants. Presence of very low quantities of aluminum and silica is due to silt deposition which is a common foulant. Further, the presence of about 3% of phosphate indicates that some portion of antiscalant SHMP remains on the membrane surface among foulant deposits and most likely as calcium phosphate scale which is typical of RO plant where SHMP is used as antiscalant. The presence of about 4% sulfate indicate possible formation calcium sulfate (gypsum) scale, which might have occurred due to the hydrolysis of SHMP to an ineffective scale inhibitor orthophosphate.

Although foulants could be easily removed from the membrane surface, it was observed that even after chemical cleaning, with strong cleaning agent (hydrogen peroxide/sodium hypochlorite mixture), some portion of foulant remained adsorbed on the membrane surface as can be seen (Fig. 4) by the distinct color difference between the virgin membrane and cleaned membrane. These stains indicate irreversible nature of these foulants [7] resulting from long period of accumulation, which is also evident from failure of NF membranes in restoring salt rejection after chemical cleaning.

3.4. Bacterial/biochemical analysis

Two bacterial colonies were isolated. Morphologically, both were mobile gram negative bipolar rods. Biochemical analyses revealed that 73% of the dried foulant was comprised of organic matters of which about 6% was carbohydrate and 3% protein. The shining texture after dehydration indicates lipid presence. The foulant may also contain organic acids including humic substances.

3.5. SEM and EDX

SEM and EDX were utilized to identify the foulants adhering to the membrane surface. Analyses were in conformity with visual inspection results which showed the membranes covered with thick deposits (Figs. 5–7). However, no features of presence of any sort of biological species such as diatoms were observed on the samples analyzed. The corresponding EDX spectrum is also in conformity with chemical analysis result where elements observed in the chemical analyses were also identified in the EDX spectrum of both membranes. The EDX spectrum of one of the prominent particle on the membrane surface (Fig. 7) revealed strong peaks of phosphorous, aluminum and sodium in addition to carbon and oxygen indicating probably this could be from SHMP dosed in the system as antiscalant along with alumina from silt.

The SEM micrograph of NF membrane after cleaning with strong chemical cleaning agent is shown in Fig. 8

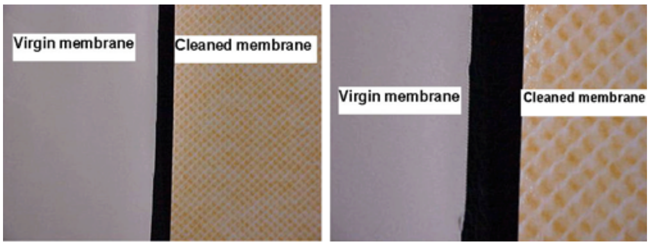

Fig. 4. Photographs showing distinct difference between virgin and cleaned NF membranes at different magnifications.

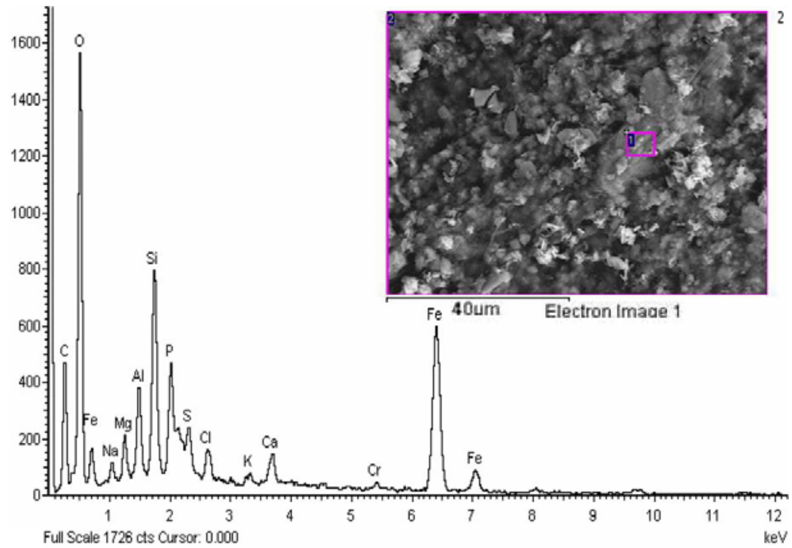

Fig. 5. SEM and EDX spectrum of NF membrane No. 5.

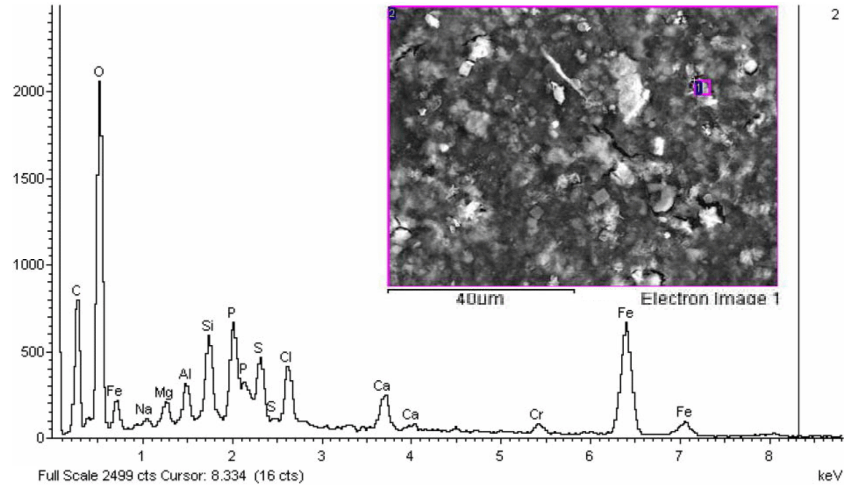

Fig. 6. SEM and EDX spectrum of NF membrane No. 6.

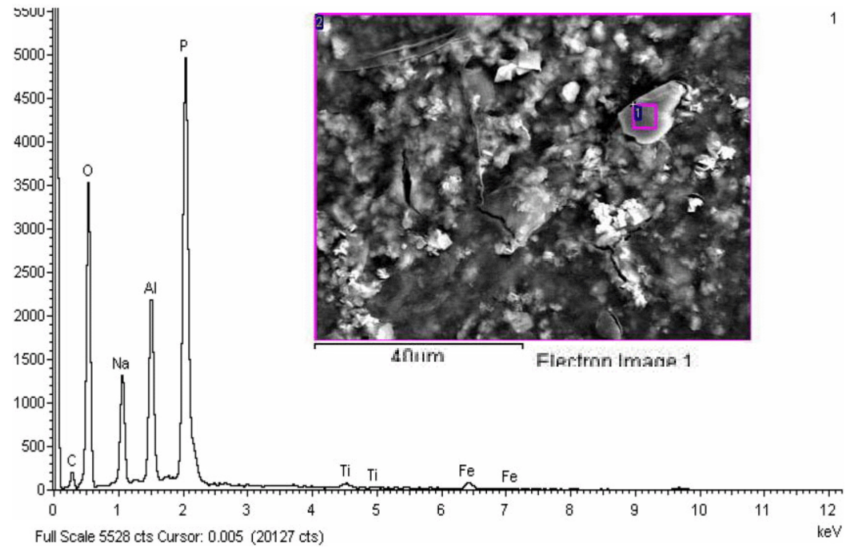

Fig. 7. SEM and EDX spectrum of a particle observed on NF membrane No. 5.

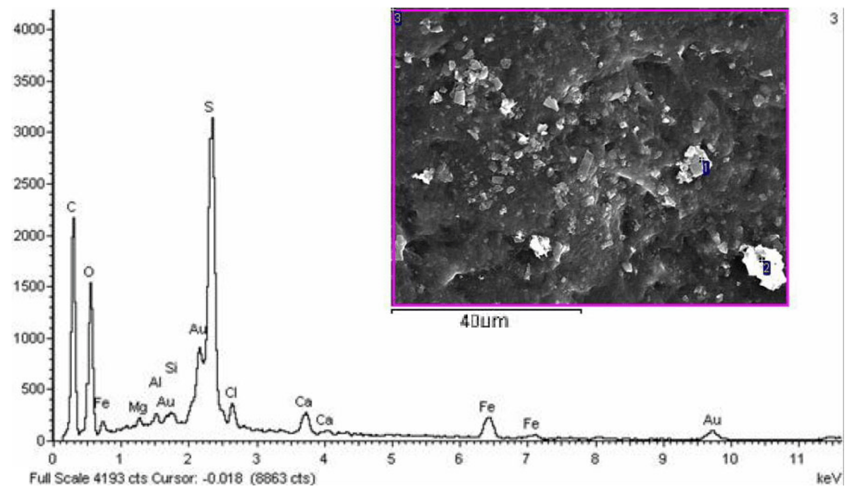

Fig. 8. SEM and EDX spectrum of a NF membrane cleaned with strong chemicals.

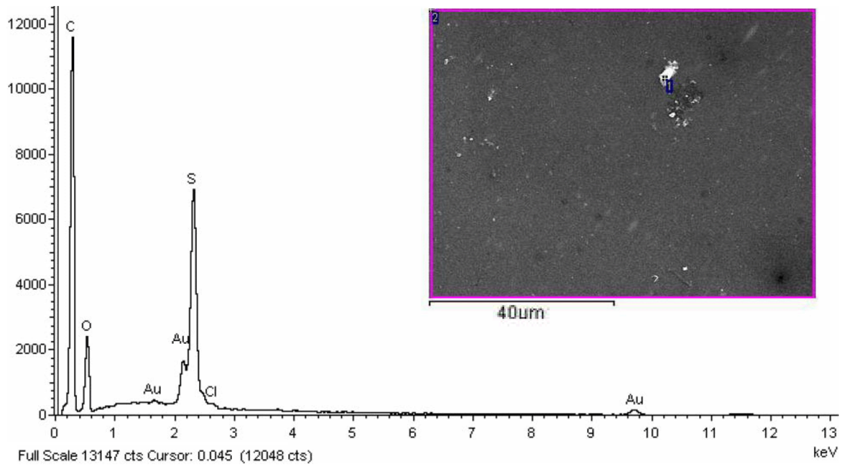

Fig. 9. SEM and EDX spectrum of a virgin NF membrane.

where the presence of foulant is clearly visible with existence of some inorganic components such as Fe, Si, Ca and Mg which are indicated by the corresponding EDX spectrum. This confirms the irreversible nature of foulants, which have shown strong adsorption onto the membrane surface, which is also evident from reduced salt rejection of membrane even after repeated chemical cleaning. This is in contrast to the new unused NF membrane of which SEM micrograph and EDX spectrum are shown in Fig. 9 where a clean image of the membrane surface with no deposits is clearly visible. The EDX peaks due to C, O, and S are due to the chemical composition of the NF membrane.

4. Conclusions

Performance evaluation and an autopsy study indicate a heavy deposit of foulants mainly consisting of organic matter on the membrane surface, even though the membranes are situated in the end side of the pressure vessel where occurrence of organic fouling is most unlikely to happen. This indicates that foulants, slowly accumulated over 5 years on the end elements, resulted in loss of salt rejection as well as flux, necessitating the use of a coagulant to remove the organic matter from seawater feed. The fouling resulted in substantial reduction in permeate flow as well as salt rejection of NF membranes. The use of SHMP as an antiscalant also adds to the fouling in the form of phosphate deposits. Moreover, the SWRO plant is suffering from corrosion of stainless piping as evidenced from the presence of iron among the foulant deposits along with nickel and chromium.

5. Recommendations

The presence of organic foulants on end elements suggests that a coagulation–filtration process needs to be introduced in the pretreatment design. This could be accomplished by discontinuing antiscalant SHMP and utilizing its dosing system for a coagulant such as $FeCl_3$.

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