SAFE USE OF MICROBUBBLES FOR REMOVAL OF RO MEMBRANE FOULING

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Abstract

The authors have shown a dramatic improvement in cleaning efficiency when effervescent cleaning reagents are used in conjunction with bubbles created using a specially designed microbubble generator. One potential problem associated with this new technique is that the bubbles will cause damage to the delicate polyamide layer and other structures in the RO element. In order to establish if any damage occurred the authors ran a series of experiments with different manufacturer's membrane elements on a flat sheet test rig and pilot plant. Samples of membrane were then autopsied to establish if any damage had occurred. The authors describe the equipment use, experimental methodology and results of cleaning with this novel approach and results of autopsies which demonstrate that no damage was detected using this novel cleaning method.

I. INTRODUCTION

All RO membrane elements are subject to scaling and fouling and the vast majority are subjected to some attempt at cleaning. Formation of a fouling layer during continuous filtration can result in the formation of both reversible and irreversible foulant layers. The irreversible fouling is normally caused by strong attachment of particles, which is impossible to be removed by physical cleaning method [1]. The success of cleaning is very variable and is dictated by the type of foulant, chemistry used to remove the foulant and the method used. Any improvement to the cleaning process will increase the operating efficiency of the plant and decrease the frequency between cleans thus prolonging membrane life. The authors have been investigating the effect that generated bubbles and microbubbles have on cleaning reverse osmosis membranes. Compressed, injected air [2], [3], is used in cleaning and backwashing membrane bioreactors, microfiltration and ultrafiltration membranes but has not been applied to reverse osmosis (RO) membrane elements.

A direct result of the separation of water and particulate material by use of membranes is the accumulation and deposition of material on the membrane surface. These processes are known as fouling. Fouling is the result of concentration polarization of particulate material and dissolved solutes. Fouling is a complex process and occurs mostly due to colloidal and scale precipitation as well as microbial growth. Permeation through the membrane is achieved by pressure driven convective flow, thus any fouling of the membrane surface will compact with time and lead to membrane flux decline. In order to recover these flux losses, the foulant layer needs to be effectively removed by chemical cleaning.

Bubbles and microbubbles can be generated by effervescing reagents producing gasses and by physical introduction of a liquid air mix. The effectiveness of effervescent in cleaning reagents is well documented and used extensively in the food and beverage industry and dental hygiene. Similarly the use of bubbles and microbubbles is also well documented for cleaning in a variety of industries and for different foulants. The cleaning effect occurs “when bubbles expand and collapse close to boundaries, a shear flow is generated which is able to remove particles from the surface, thus locally cleaning it.” [4] This phenomenon has been tested by numerous researchers notably Agarwal etal. “investigated the potential of air micro bubbles for biofilm detachment from a nylon membrane surface in comparison to chemical cleaning by sodium hypochlorite (NaOCl). About 88% of fixed biomass detachment was observed after 1 h air microbubbling, while only 10% of biofilm detachment was achieved in the control experiment without microbubbles.”[5] This effectiveness at removing biofilm is of particular relevance for enhanced cleaning of RO membranes.

A series of experiments were initially ran on a membrane flat sheet test rig which demonstrated greatly enhanced cleaning when using effervescent chemicals and a microbubble generator device as compared with conventional cleaners. These results are presented in a separate paper. In order for this new cleaning method to be adopted the authors thought it was necessary to investigate the potential for membrane damage due to the use of bubbles in conjunction with cleaning reagents. This paper describes the equipment used and experimental methodology to test different manufacturer’s membranes with the new cleaning method. The membrane elements were then autopsied to look for any damage. The autopsy results are presented here and show that none of the manufacturer’s membranes showed any signs of physical damage or wear.

II. METHODOLOGY

In order to prove the concept and then simulate real life conditions two pieces of equipment were designed, and built to run a series of experiments.

2.1 Flat sheet test rig

The flat sheet membrane test rig was used to characterize and evaluate the performance of fouled and clean membrane samples. It consists of two stainless steel plates which accommodate fouled or clean membrane samples, plastic spacer material and the permeate carrier. There is also a viewing window on the feed/concentrate side that enables one to see the fouled membrane sample and cleaning progress. The feed water is circulated around the system through the test cell at a known flow rate and transmembrane pressure. The concentrate was returned to the feed tank with the permeate stream to maintain a constant feed water concentration. Permeate samples are taken to measure the flux rate and conductivity for salt rejection determinations.
The size of the membrane pieces used for testing on the flat sheet rig was ~0.023 m^2.
Each membrane sample was characterized according to the specific membrane manufacturers' conditions for that membrane.

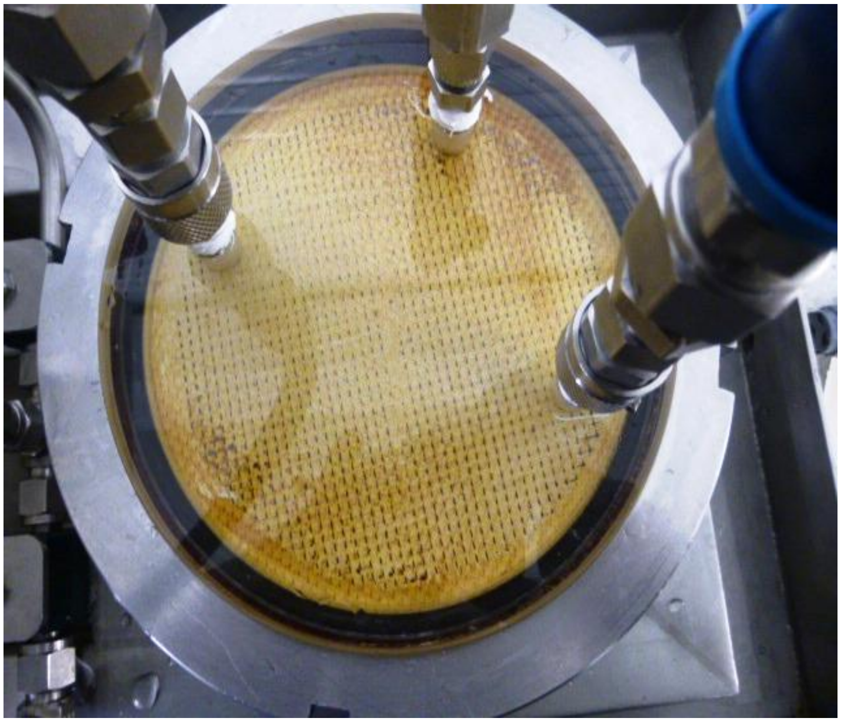


Figure 1: Flat sheet tests cell with viewing window

2.2 Pilot Plant

The 8" Membrane Test Rig was used for characterization and cleaning of fouled membranes. It can also be used to evaluate the performance of a fouled membrane before an autopsy was carried out. This can give additional information such as differential pressure, salt rejection and the flux rate which can be compared with design values. The rig comprises of carbon pre-filters, feed/CIP cleaning tanks, cartridge filters, low pressure pump for cleaning, high pressure pump for membrane characterization, 1 and 3 element pressure vessels and pressure and flow transmitters.

2.3 Microbubble generator

The use of air together with cleaning chemicals for the cleaning of fouled spiral wound RO/NF membranes was tested and evaluated.

The air bubbles were generated by two methods:

1) By use of a specially designed microbubble generator in the CIP line.
2) By use of proprietary powder cleaners. This was generated in situ by dissolution of the cleaning products causing some effervescence.

The use of air-liquid to introduce small microbubbles using a specially designed generator was initially investigated in the laboratory using the Flat Sheet Rig. It was noticed that using only water and air created large bubbles that quickly coalesced and had minimum impact on the membrane surface. A dramatic change in the number and size of the bubbles was seen when using specially formulated cleaning chemicals compared to commodity cleaners or water and air only (see Figures 8 and 9). In order to optimize cleaning the bubble size is very important [6]. The proprietary cleaners produced a large number of smaller bubbles. The formation of small bubbles increased the turbulence of the cleaning solution mixture leading to an improved cleaning effect.

The air generator at atmospheric pressure was opened to allow sufficient air to enter and mix with the cleaning solution creating small air bubbles that can be seen upon the return of the cleaning solution to the CIP tank.

In order to investigate the effects of this concept on membrane performance, extensive tests were performed using a variety of venturi-type devices along with a flat sheet test rig with a viewing window to observe the mechanism of air bubbles during cleaning action. To achieve optimal cleaning and foulant/scale removal, both the velocity of flow of the cleaning solution together with the air bubble size was investigated. Further experiments were conducted on a small scale pilot plant in order to test the compatibility of air with 8-inch spiral wound membranes obtained from several major membrane manufacturers. In this study both fouled and new membranes were used, which were then subsequently autopsied to examine the cleaning performance.

Microbubble generator devices were constructed using different sized tubing. By changing the size of the air inlet tubes, the bubble size can be controlled more accurately. Experiments have shown that when cleaning tests are performed using only air and water with the venturi device, the bubbles generated are large (Fig 2 and 9) and inconsistent; the bubble size was measured using an endoscope. If bubble size was too large, this regularly stopped the flow due to air locks in the feed line.

Figure 2: Air bubbles produced with only air/water

Figure 3: Air bubbles produced using proprietary cleaning chemicals

However, tests performed using proprietary cleaning chemicals in combination with a specially designed bubble generator produced much smaller and more refined bubbles (Fig. 3 and 8). It was evident that upon contact with proprietary cleaning chemicals, the size of the air bubbles was significantly reduced This created a more turbulent cleaning solution, agitating the foulant on the membrane surface for ease of removal.

In addition to modifying the size of the air inlet to vary bubble size, it has been observed that an increase in the feed flow also increases the quantity of bubbles produced. Increasing the pump speed does not necessarily give a proportional increase in the flow rate though when using the bubble generator device. This was because as the pump speed was increased, the air intake also increases and so the cleaning solution flow may even be reduced or stays the same after some value. Experiments on the flat sheet test rig show that the use of a ventrui with a number of small tubes, together with a feed flow of 2000-2500 ml/min was needed to generate a sufficiently turbulent cleaning solution to facilitate foulant removal (Fig. 4,5,6 and 7). It is important to note that a high enough feed velocity must be achieved to create a steady flow of bubbles across the membrane surface. The increased turbulence within the membrane element (boundary layer) with the air was achieved without the need of using any extra energy from the CIP pumps of the RO rigs.

Figure 4: Bubbles produced by Cleaner A at 1000 ml/min

Fig 5: Bubbles produced by Cleaner A at 2500 ml/min

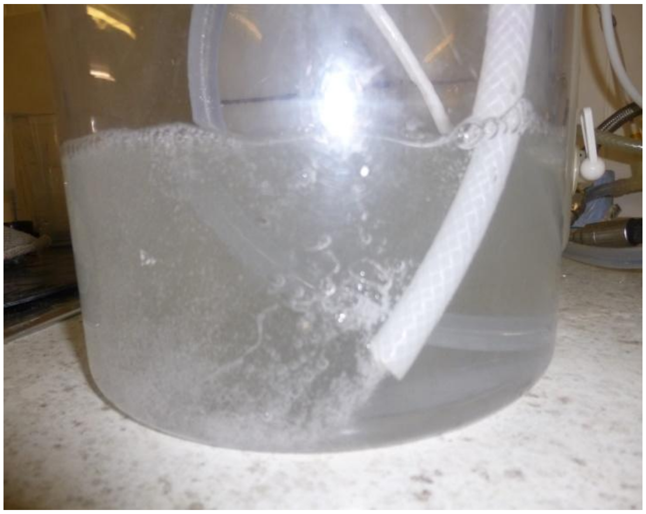


Figure 6: Bubbles produced with citric acid at 2500 ml/min

Figure 7: Bubbles produced with HCl at at 2500 ml/min

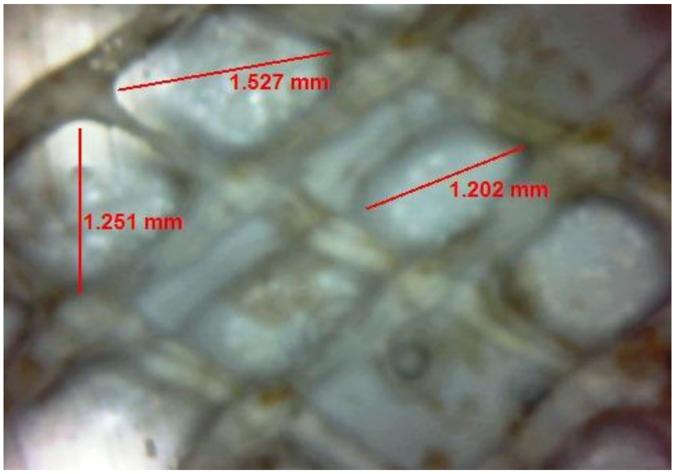


Figure 8: Bubbles produced with water + air only (>1mm in size)

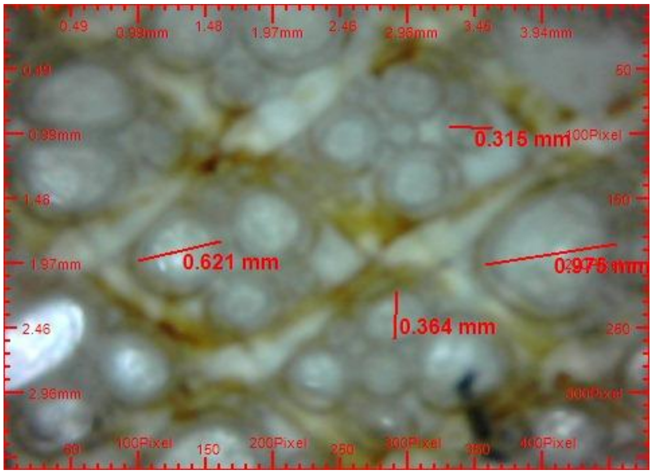


Figure 9: Bubbles produced with Cleaner A + air (vary from 0.3 to ~1mm)

2.4 Experiments

Tests were carried out on:

a) Virgin membranes from different membrane manufacturers for compatibility testing.
b) Different types of fouled membranes for cleaning performance efficacy.

2.5 Autopsy

Autopsies were carried out on virgin and cleaned membranes to establish effect of cleaning with air and effervescent chemicals. The autopsies were done in order to reveal membrane integrity and the amount of foulant removed by cleaning. The autopsy involved visual inspection of the elements, Scanning Electron Microscopy – Energy Dispersive X-ray Analysis (SEM-EDXA) and Infra-red to identify the elemental composition of the foulants and examine integrity of the membrane surface, Fujiwara and dye test for chemical, oxidation or physical damage of the membrane surface.

III. RESULTS

The results of cleaning are presented in another paper. This paper is focusing on the results of autopsies from membranes that have undergone the cleaning process.

3.1 <u>Flat Sheet Membrane Performance and Cleaning Studies</u>

Standard Test Conditions are:

The flux rate is measured at standard operating conditions for each membrane type. The recirculation rate was 1000 ml/min and normalised to 25 C.

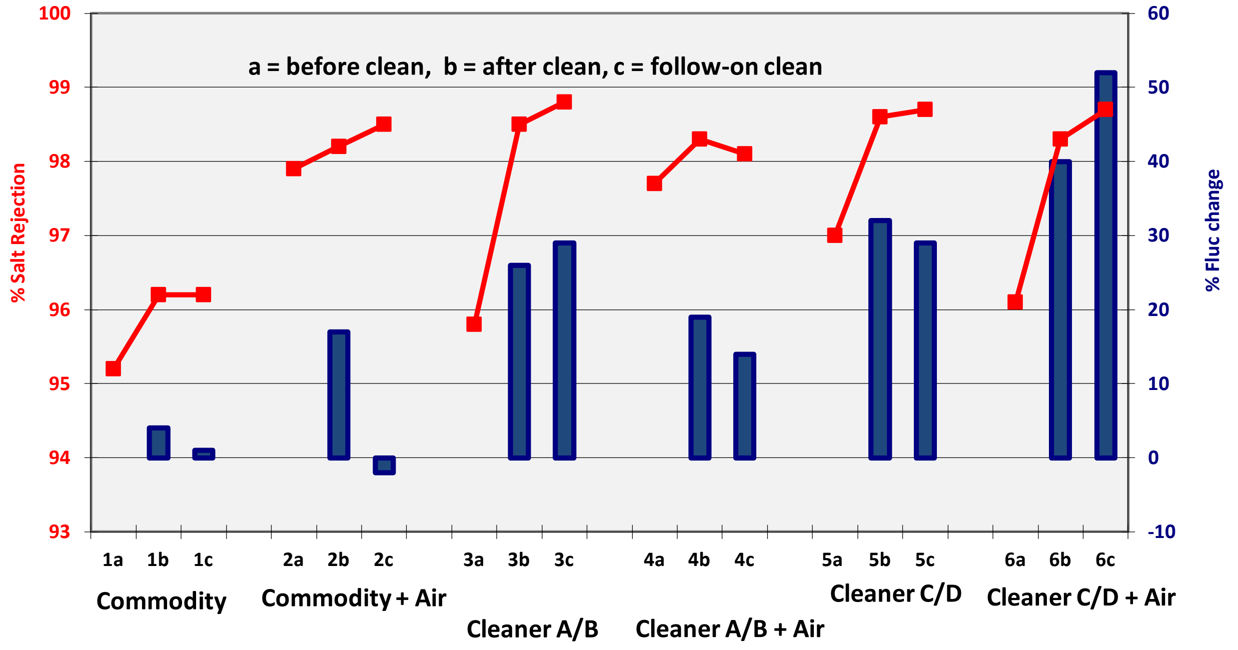
The cleaning solution was recirculated @ 40 psi for 30 mins followed by a soak for 30 mins followed by recirculation for desired cleaning time at 20 to 35 C.

The following cleans were carried out:

Table 2: Cleaning programs:

	Clay and Iron fouled TFC-HR membrane:
1a	Fouled membrane flux and salt rejection before clean
1b	Performance after 0.5% NaOH for 3 hours, pH 12 @ temperature 35 ºC
1c	Performance after 2% Citric for 2 hours, pH 2.5 @ temperature 20-25 ºC
2a	Fouled membrane flux and salt rejection before clean
2b	Performance after 0.5% NaOH + Air for 3 hours, pH 12 @ temp 35 ºC
2c	Performance after 2% Citric + Air for 2 hours, pH 2.5 @ temp 20-25 ºC
3a	Fouled membrane flux and salt rejection before clean
3b	Performance after 1% Cleaner A for 3 hours, pH 12 @ temperature 35 ºC
3c	Performance after 1% Cleaner B for 3 hours, pH 3.8 @ temp 20-25 ºC
4a	Fouled membrane flux and salt rejection before clean
4b	Performance after 1% Cleaner A + Air for 3 hours, pH 12 @ temp 35 ºC
4c	Performance after 1% Cleaner B + Air for 3 hours, pH 3.8 @ temp 25-30 ºC
5a	Fouled membrane flux and salt rejection before clean
5b	Performance after 1% Cleaner C for 3 hours, pH 12 @ temperature 35 ºC
5c	Performance after 1% Cleaner D for 3 hours, pH 2.7 @ temp 20-25 ºC
6a	Fouled membrane flux and salt rejection before clean
6b	Performance after 1% Cleaner C + Air for 3 hours, pH 12 @ temp 35 ºC
6c	Performance after 1% Cleaner D + Air for 3 hours, pH 2.7 @ temp 25-30 ºC

Figure 10: Cleaning Performance on Clay and Iron fouled Membrane



Results show that a combination of air bubbles, generated in situ with effervescent cleaning chemicals enhances membrane performance, with an increase in both permeate flux and salt rejection (see Figure 10 above, Cleaners C and D are effervescent based cleaners). The cleaning effectiveness was also revealed by visual inspection of membrane coupons before and after the cleaning tests. Closer examination of the cleaned membrane coupons together with the performance data and subsequent autopsy results, show that air bubbles did not cause any damage to the membrane surface. The Flat Sheet Test Cell with the viewing window also demonstrated that the bubbles were evenly distributed across the whole of the membrane area; thereby ensuring that the whole of the exposed fouled area was cleaned.

3.2 Compatibility Tests with Virgin Flat Sheet Membranes and Bubbles

Comptibility tests were carried out using the Flat Sheet Rig with:

i) Saehan CSM 4040BE – brackish water polyamide membrane
ii) Filmtec BW30LE – brackish water polyamide membrane
iii) Trisep X-20 – low fouling brackish water polyamide membrane
iv) Trisep ACM2 – brackish water polyamide membrane
v) Trisep SB50 – cellulose acetate membrane

Fig 11: Compatibility Performance with Virgin CSM Membrane

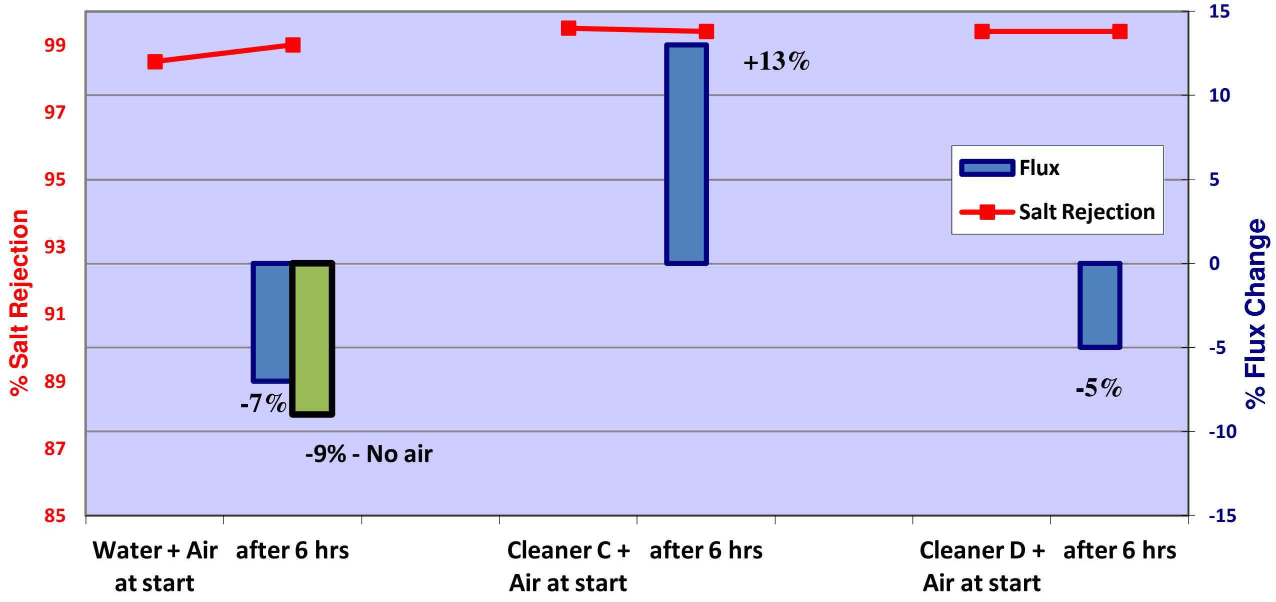


Fig 12: Compatability Performance with Virgin Filmtec BW30-LE400 membrane

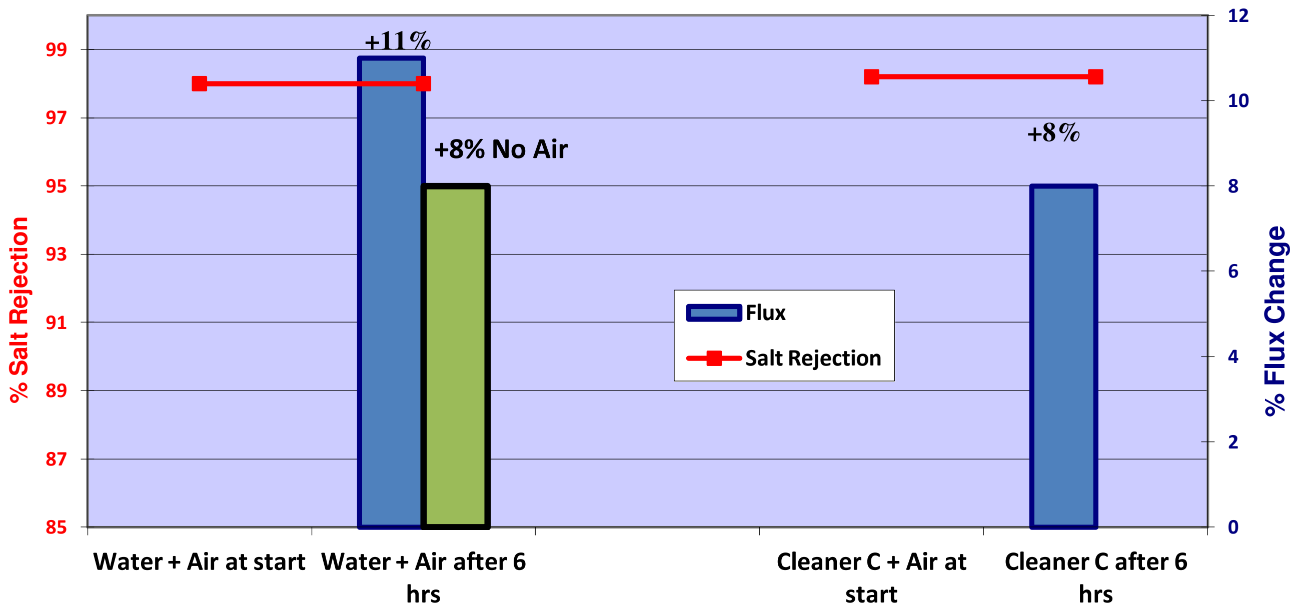


Fig 13: Compatibility Performance with Virgin Trisep X20 Membrane

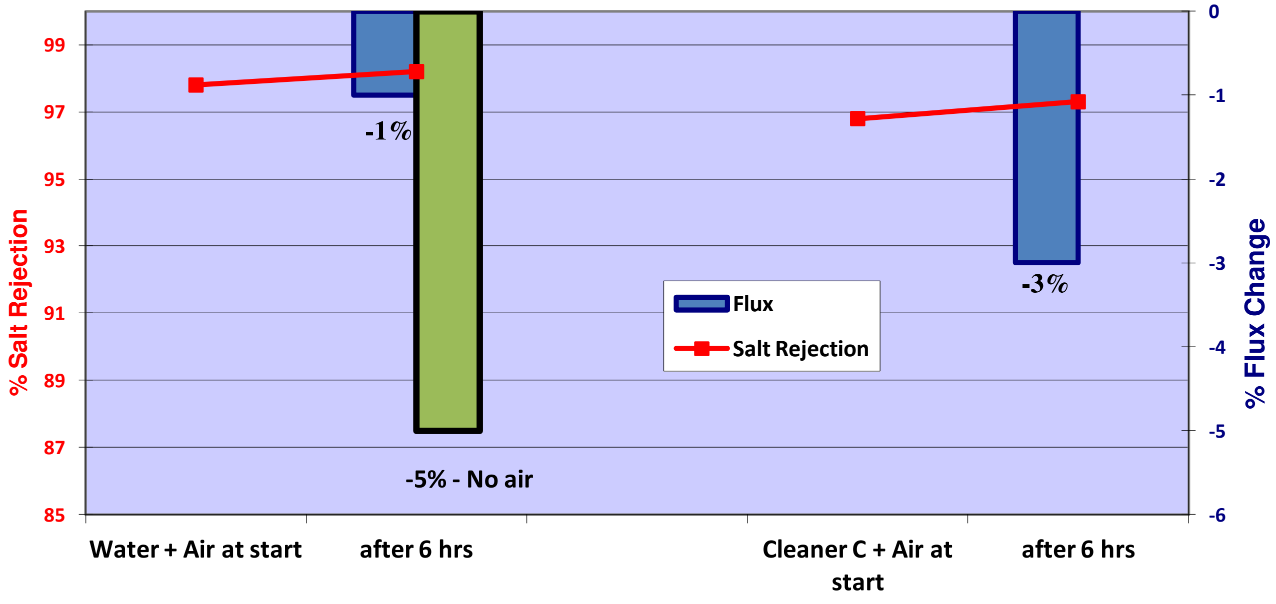
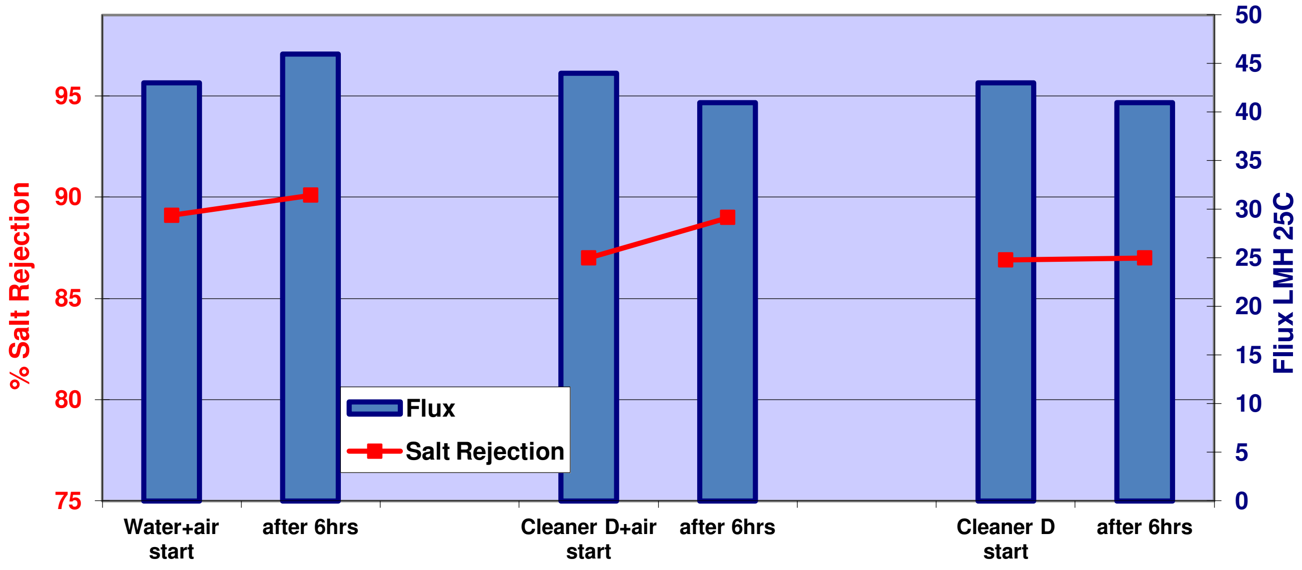


Fig14: Compatibility Performance with Virgin Trisep ACM2 Membrane

Fig 15: Compatability Performance with Virgin CA SB50 membrane



Figures 11 to 15 show that there was no significant flux or salt rejection loss after testing with virgin CSM 4040BE, Filmtec BW30LE, Trisep X20, ACM2 and CA SB50 membranes with air and cleaning chemicals. In fact, any flux loss was less than that obtained without air (ie, cleaning chemical or water alone). The minor flux losses reported here (<10%) can be attributed to membrane compaction and stabilization as these were virgin membrane samples.

3.3 Autopsy and Membrane Performance from Pilot Plant:

Results with Virgin Filmtec BW30-LE400 membrane and Virgin Koch TFC-HR membrane

3.3.1 Autopsy of Virgin Membranes after Cleaner + Air on Pilot Plant Rig

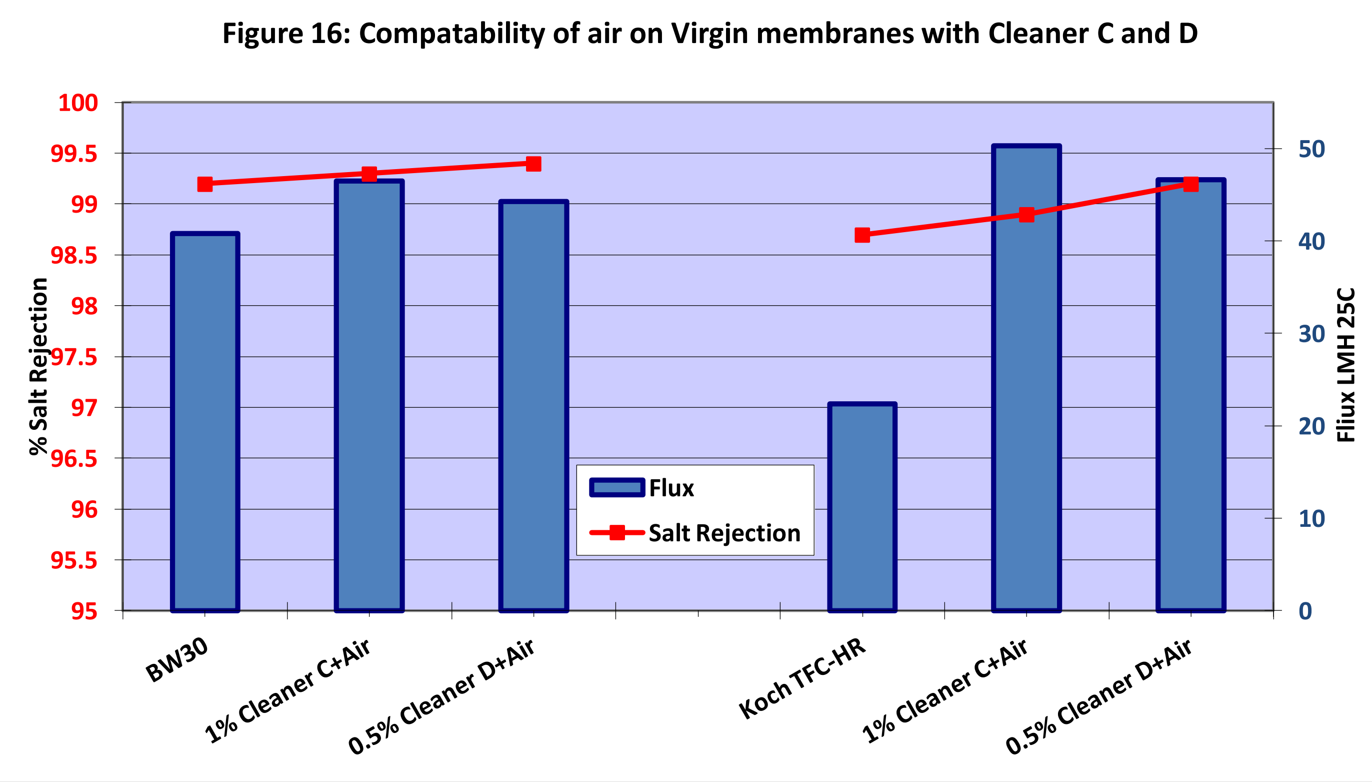
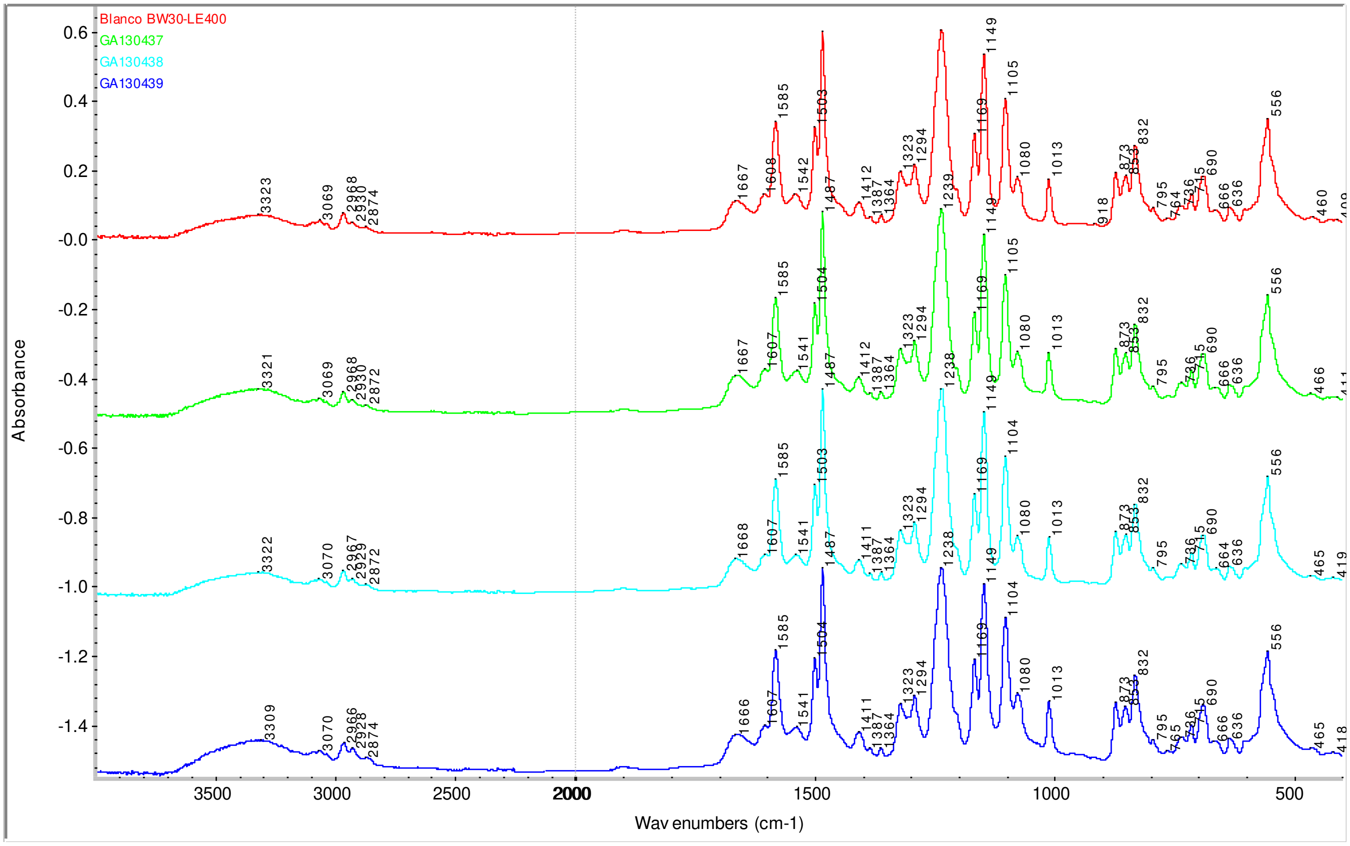


Fig 17: Filmtec BW30-LE Membrane autopsy

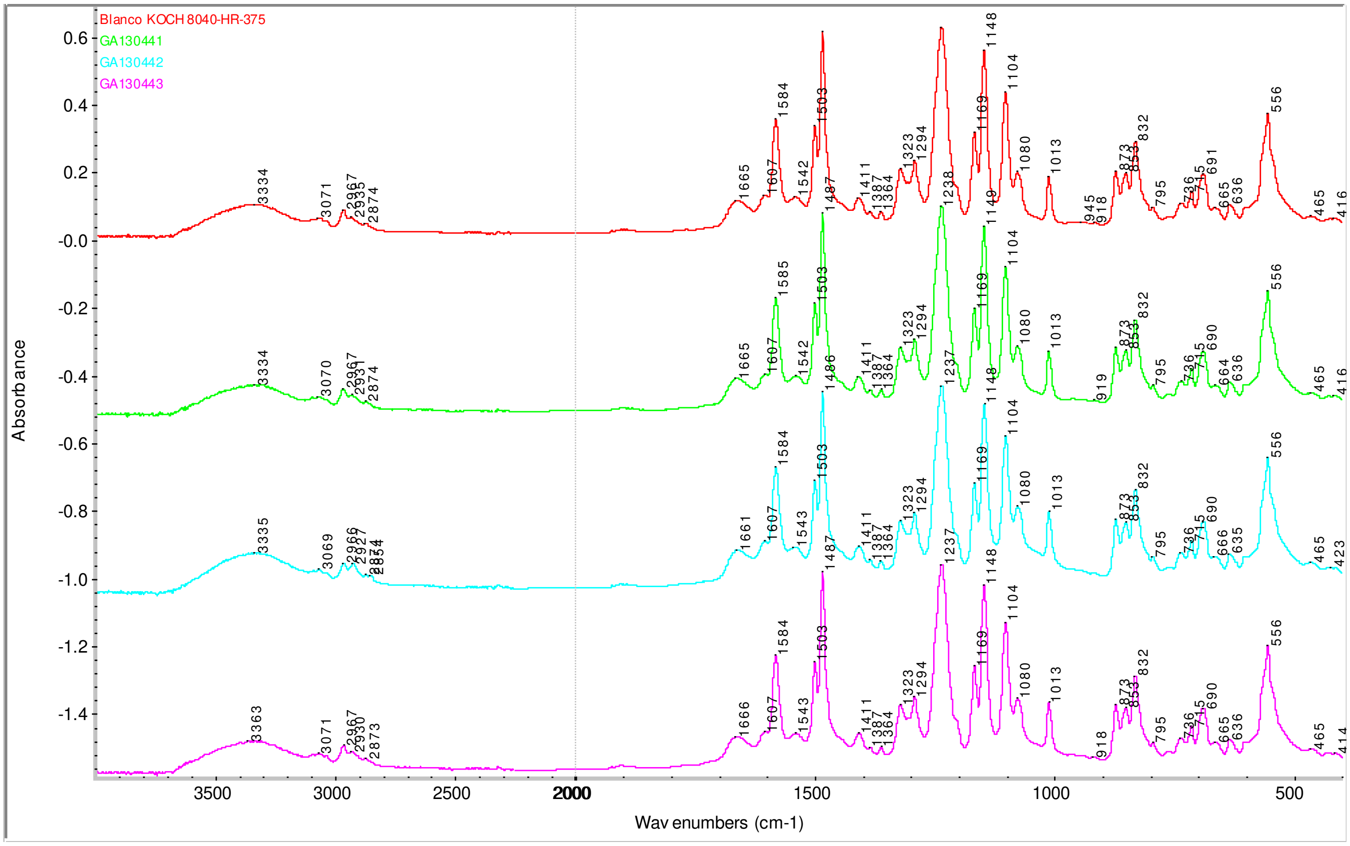
Fig 18: Filmtec BW30-LE Membrane surface x50 unrolled surface shows no surface damage.

3.3.2 Infrared and SEM Analayses of Autopsied Virgin Membranes from on Pilot Plant Tests



GA130436	Virgin Filmtec BW30-LE-400
GA130437	BW30-LE-400: Water + Air only - 4 hours
GA130438	BW30-LE-400: 1% Cleaner C + Air – 4 hour clean
GA130439	BW30-LE-400: 1% Cleaner D + Air – 4 hours

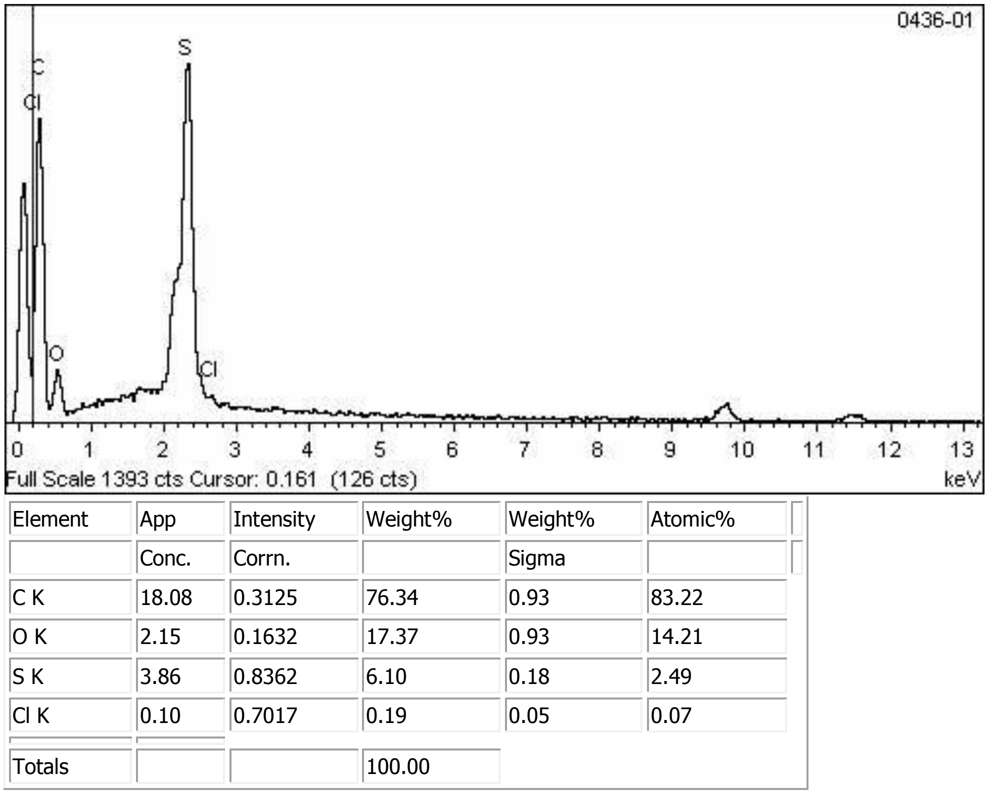
Fig 19: Infrared spectra of autopsied virgin BW30 membrane



GA130440	Virgin Koch 8040-HR-375
GA130441	Koch 8040-HR-375: Water + Air only 4 hours
GA130442	Koch 8040-HR-375: 1% Cleaner C + Air – 4 hour clean
GA130443	Koch 8040-HR-375: 1% Cleaner D + Air – 4 hours

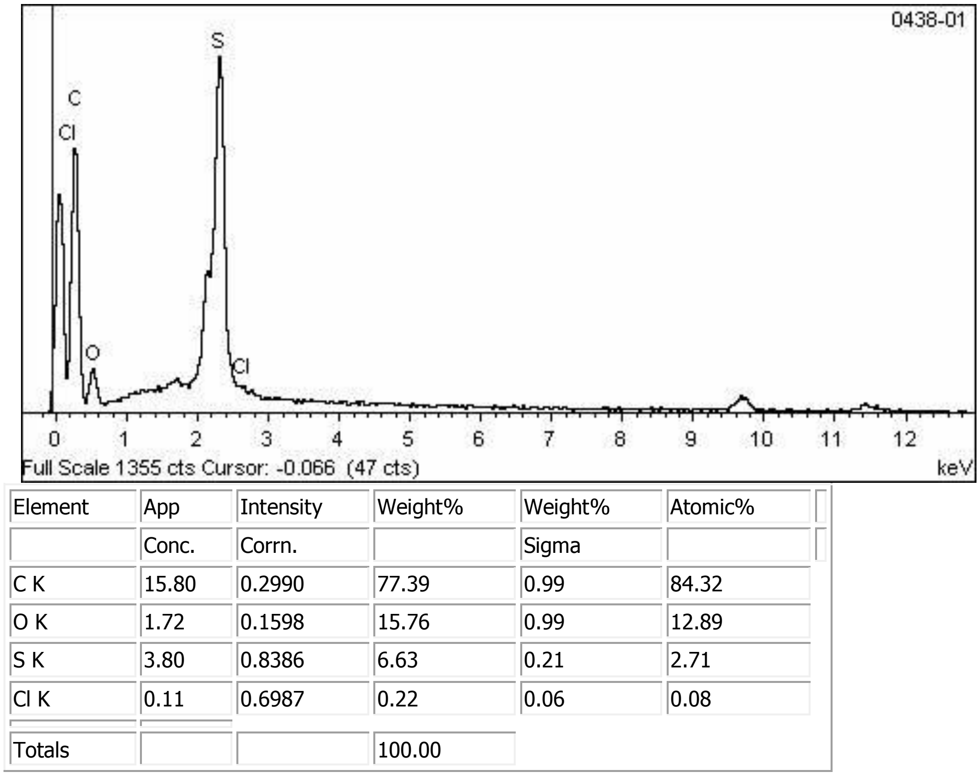
Fig 20: Infrared spectra of autopsied virgin Koch 8040HR membrane

Figures 19 and 20 show the infrared spectra of the membranes surfaces for virgin Filmtec BW30-LE and Koch 8040HR membranes respectively after various Pilot plant rig cleans. The spectra show that there were no fundamental changes in the relative peak positions (area of interest are the polyamide peaks around 1667 to 1542 cm^{-1}) between the air cleaned and virgin membranes, indicating that no damage to the polyamide layer was detected.



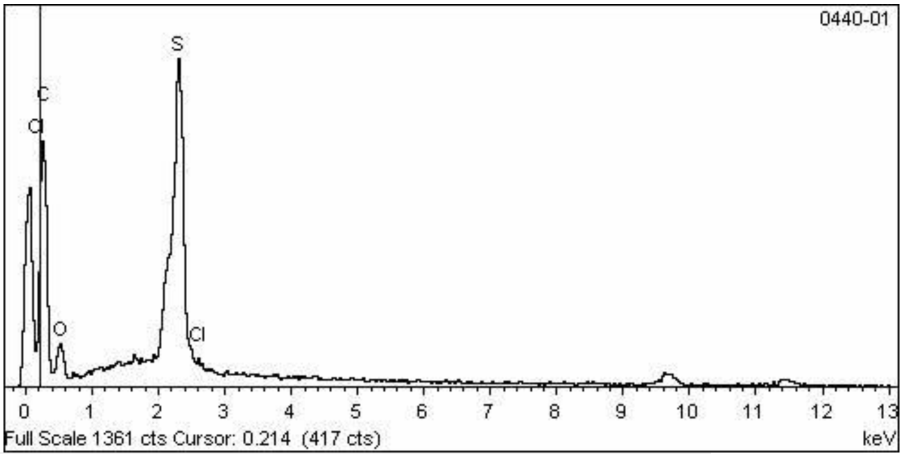
Element	App	Intensity	Weight%	Weight%	Atomic%
	Conc.	Corrn.		Sigma	
C K	18.08	0.3125	76.34	0.93	83.22
O K	2.15	0.1632	17.37	0.93	14.21
S K	3.86	0.8362	6.10	0.18	2.49
Cl K	0.10	0.7017	0.19	0.05	0.07
Totals			100.00		

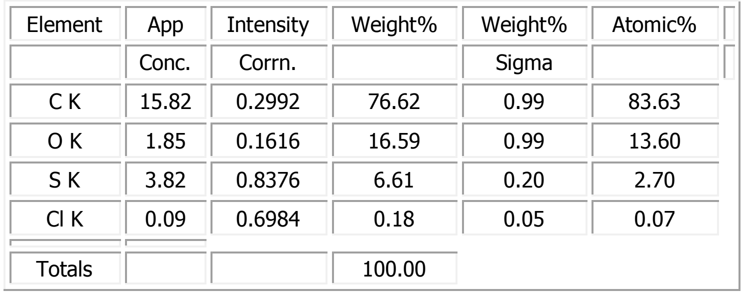
Figure 21: SEM Analysis of GA130436 membrane surface (BW30 LE-400)



Element	App	Intensity	Weight%	Weight%	Atomic%
	Conc.	Corrn.		Sigma	
C K	15.80	0.2990	77.39	0.99	84.32
O K	1.72	0.1598	15.76	0.99	12.89
S K	3.80	0.8386	6.63	0.21	2.71
Cl K	0.11	0.6987	0.22	0.06	0.08
Totals			100.00		

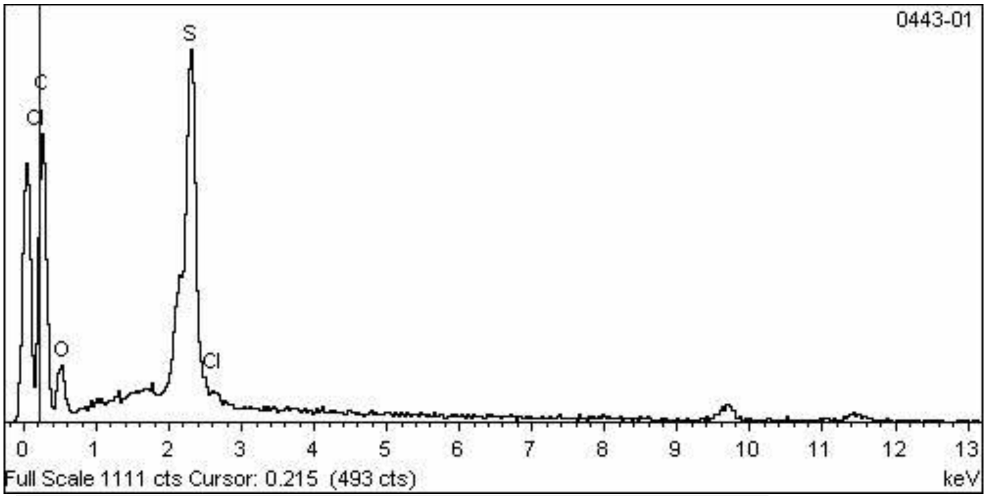
Figure 22: SEM Analysis of GA 130438 (BW30LE) membrane surface: 1% Cleaner C + Air

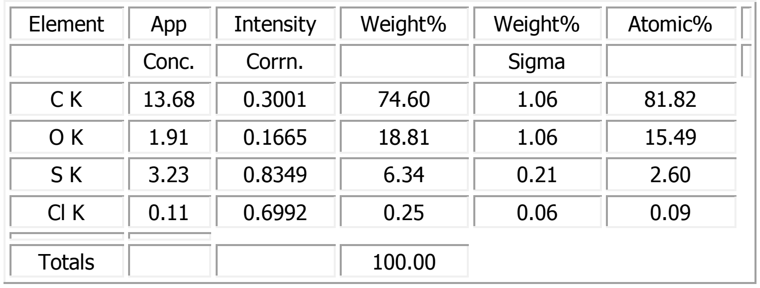




Element	App	Intensity	Weight%	Weight%	Atomic%
	Conc.	Corrn.		Sigma	
C K	15.82	0.2992	76.62	0.99	83.63
O K	1.85	0.1616	16.59	0.99	13.60
S K	3.82	0.8376	6.61	0.20	2.70
Cl K	0.09	0.6984	0.18	0.05	0.07
Totals			100.00		

Figure 23: SEM Analysis of GA 130440 membrane surface (Koch 8040-HR)





Element	App	Intensity	Weight%	Weight%	Atomic%
	Conc.	Corrn.		Sigma	
C K	13.68	0.3001	74.60	1.06	81.82
O K	1.91	0.1665	18.81	1.06	15.49
S K	3.23	0.8349	6.34	0.21	2.60
Cl K	0.11	0.6992	0.25	0.06	0.09
Totals			100.00		

Figure 24: SEM Analysis of GA 130443 membrane surface - 1% Cleaner C + Air

IV. CONCLUSIONS

- Membrane cleaning was improved after using effervescing cleaning compounds and air to remove foulants compared to using traditional cleaning method.
- A two-phase flow of air and chemical results in increased turbulence at the boundary layer without the need of any extra energy consumption of the CIP clean.
- Membrane performance data from Flat sheet and Pilot plant tests together autopsied infrared and SEM surface analyses show that cleaning with microbubbles resulted in no damage.
- Bubble size and shape was strongly dependent upon cleaning chemicals used. Bubble size dramatically changed when using specially formulated proprietary cleaners compared to commodity cleaners or using water and air only.
- Autopsies can identify fouling type and help design the best cleaning method to use.

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