

# **AIR BUBBLES ENHANCE MEMBRANE CLEANING: A FUTURE PERSPECTIVE**

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## **Abstract**

Air bubbles generated using a novel micro-bubble generator have displayed a dramatic enhancement in cleaning efficiency when used in conjunction with specially formulated cleaning chemicals. In order to establish the effect of this application on membrane performance, a series of experiments were conducted using both a flat sheet test rig and a small scale pilot plant. Experiments show that the size of the bubbles had a dramatic impact on the effects of cleaning. Air bubbles generated in combination with commodity chemicals are large and produce an inconsistent flow. However, in the presence of specially formulated cleaning chemicals, air bubbles become much smaller and refined (micro-bubbles), creating a pulsating-like action. This eases foulant removal and ultimately restores membrane performance to a greater magnitude. In addition to bubble size, the speed of the feed pump proves to be another important factor. An optimum flow speed and bubble size has been determined to achieve the best possible conditions for enhanced cleaning effects. Cleaning effectiveness was quantified by; flux increase, salt rejection increase, turbidity increase of the cleaning solution and by visual inspection of the membrane. Cleaning with air restores membrane performance to a greater extent than without air. Membranes from several major membrane manufacturers were used in this study to determine membrane compatibility with air. Membranes were then subsequently autopsied at Genesys labs in Madrid to establish the impacts of cleaning and whether the micro-bubbles had caused any damage to the membrane surface. A variety of analytical techniques were used including Scanning Electron Microscopy and Infra-Red Spectroscopy. Autopsy results are discussed in another paper. In this paper, the authors describe the equipment use, experimental methodology and results of cleaning with this novel approach.



## I. INTRODUCTION

Due to the rapidly growing world population, there is an increasing demand for desalinated water. Reverse Osmosis (RO) spiral wound membranes provide the finest form of water filtration, with an average salt rejection of 99%. However, membrane filtration is compromised by membrane fouling and scaling. All RO membranes are subject to fouling, where the type of foulant formed depends on the specific water chemistry and ability of pre-treatment filtration to remove suspended solids. Although regular cleaning procedures, often known as cleaning in place (CIP) can often remove the majority of a foulant, the membranes are not usually fully restored to their original condition. Membranes should be cleaned whenever the normalised permeate flow drops by 10%. Any improvements to the cleaning process will increase the operating efficiency of the plant, meaning that membranes will have to be cleaned less often which consequently saves on operational costs [1]. In order to improve membrane cleaning efficiency, research is required to develop new and innovative techniques. Using physically generated (non-pressurised) micro-bubbles to assist with the cleaning of RO membranes has been investigated by the authors.

The application of air to facilitate the cleaning of capillary membranes has been recognised as an effective and efficient method in removing foulants and scale deposits; thus improving the overall membrane performance [2]. There are very few reported studies of this application being applied to the cleaning of spiral wound RO membranes [3]. This paper demonstrates a novel approach into the removal of foulants and scale deposits from RO membranes using a combination of specially formulated cleaning chemicals and micro-bubbles. By comparison to conventional CIP cleaning, using cleaning chemicals alone, the cleaning success of this application can be determined.

A novel micro-bubble generator in combination with specially formulated cleaning chemicals is used to generate non-pressurised micro-bubbles, which would help agitate and facilitate the removal of deposits on the membrane surface as well as the membrane spacer material. Increasing the velocity of water creates a more turbulent cleaning system [4] and hence a good distribution of bubbles, therefore this concept can be easily implemented into most existing RO installations.

In order to investigate the effects of this concept on membrane performance, extensive tests were performed using a variety of micro-bubble generating devices along with a Flat Sheet Test Rig (FSTR). 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 [5]. Further experiments were conducted on an RO 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.

Results have shown that a combination of micro-bubbles, generated in situ with specially formulated cleaning chemicals enhances membrane performance, with an increase in both permeate flux and salt rejection. The cleaning effectiveness can be easily seen upon visual inspection of membrane coupons. Subsequent autopsy results reveal that air bubbles cause no damage to the membrane surface. It can be seen that when air bubbles are used in combination with commodity cleaning chemicals, membrane performance is not restored to the same magnitude as with specially formulated cleaning chemicals. It is evident that upon contact with these specialty chemicals, the size of the bubbles generated by the micro-bubble generating device is significantly reduced, which would create more turbulence within the cleaning solution and agitate the foulant on the membrane surface to ease its removal.

## II. METHODOLOGY

The FSTR and the pilot plant rig were set up to simulate real life RO conditions. A series of experiments were run on fouled and new membranes to show the effectiveness of the cleaning concept.

### 2.1 Flat Sheet Test Rig

A flat sheet test rig is a small frame mounted unit designed to enable trials of flat sheet RO membranes. It comprises of two mechanical; stainless steel plates that effectively ‘clamp’ a flat sheet membrane. It is a self-contained unit with its own instrumentation and control (Figure 1). The feed water to the test cell was pressurized to 15 bar, achieved using a high pressure pump. The cleaning procedure involved recirculating a cleaning solution around the flat sheet rig with the addition of bubbles produced using a novel micro-bubble generator. Bubbles produced were clearly visible in the CIP tank. Although the pressure was kept constant throughout most experiments, the flow velocity of the cleaning solution and bubble size were varied, in order to find the optimum cleaning conditions. A variety of fouled and new membrane coupons, obtained from various membrane manufacturers were tested, where permeate flux and salt rejection were recorded to evaluate the impact of bubbles on the membrane performance. Specially formulated cleaning chemicals were used, in conjunction with micro-bubbles, for cleaning procedures. For comparison, cleans were also performed using air bubbles and a selection of commodity cleaning chemicals, as well as some existing cleaning chemicals.



Figure 1: Flat sheet test rig

Membrane performance can be evaluated from permeate flux and salt rejection, which are dependent upon three factors:

1. **Feed water temperature** – An increase in temperature decreases the driving pressure required to produce permeate. Salt rejection decreases.
2. **Feed water concentration** – An increase in feed water concentration increases the driving pressure required to produce permeate. Salt rejection decreases.
3. **Feed water pressure** – An increase in driving pressure increases permeate flux as flow rate through membrane is proportional to differential pressure across membrane. Salt rejection is proportional to the concentration differential. So an increase in pressure will increase flux without changing the salt rejection, effectively giving a poorer quality permeate.

## 2.2 Pilot Plant

A pilot plant was designed for second stage testing of the air/chemical cleaning. It is a self-contained unit with its own integral instrumentation and control system (Figure 2). The ability to conduct tests on full 8-inch membranes gives a clearer indication of the effects of micro-bubbles and specialty cleaners. Pre-treatment is essential to remove contaminants that are likely to foul the RO membranes. Feed water is de-chlorinated using in-line carbon filters, which is then pressurised using a high pressure pump. The feed water then enters 10µm cartridge filters which reduce the quantity of any particulate matter from entering the RO membranes. These are generally replaced when the differential pressure increases by 1 bar. The plant consists of two 8-inch pressure vessels. One single element (40-inch) vessel and one three element (3 x 40-inch) vessel. The vessels are arranged in parallel with isolation valves. The plant includes an in-built CIP system to enable RO membrane cleaning/preservation. The micro-bubble generator can be easily installed into the feed pipework of the system in order to generate air bubbles during cleaning.

The pilot plant enables cleaning tests to be performed on many 8-inch membranes (both fouled and new) obtained from several membrane manufacturers. Likewise with the FSTR, cleans are performed using a combination of non-pressurised micro-bubbles and specialty cleaning chemicals. Selection of the optimum pressure, flow, and bubble size, gives a good distribution of air bubbles throughout the membranes during cleaning.

To assess membrane performance, there are important parameters which must be monitored:

1. Differential pressure
2. Permeate flux
3. Salt rejection
4. Conductivity
5. pH
6. Temperature



Figure 2: RO pilot plant

### 2.3 Micro-bubble Generating Device

Micro-bubble generating 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 existing chemical cleaners, in combination with a micro-bubble generating device, the bubbles generated are large and inconsistent. This regularly stopped the flow due to air locks in the feed line.

However, tests performed using specially formulated cleaning chemicals in combination with a micro-bubble generator produced much smaller and more refined bubbles (micro-bubbles). It is evident that upon contact with these cleaning chemicals, the size of the bubbles produced by the micro-bubble generator is significantly reduced. This creates a more turbulent cleaning solution, agitating the foulant on the membrane surface to ease its removal. 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.

### 2.4 Experimental Procedure

Experimental procedures involved extensive testing on both fouled and new membranes, with as many different types of foulant being tested. After initial testing on the FSTR, and subsequent pilot plant testing on full 8-inch membranes, the effectiveness of cleaning with a combination of air and formulated cleaning chemicals can be determined. Results are then compared to those obtained from traditional cleans, using these formulated chemicals alone, and also tests with air in conjunction with commodity chemicals. Autopsies enable thorough examination of the effects of air/chemical cleaning on foulant

removal, from both the membrane surface and membrane spacer material. Analytical techniques used to analyse the membrane surface included Scanning Electron Microscopy – Energy Dispersive X-ray Analysis (SEM-EDXA) and Infra-Red Spectroscopy (IR). Results show that micro-bubbles cause no damage to the membrane surface, and are discussed in another paper.

### III. FLAT SHEET TEST RIG RESULTS

Cleaning tests were conducted on membrane coupons with various foulants/scalants from different membrane manufacturers.

Cleaning tests were carried out following the set cleaning protocol:

1. The fouled membrane was characterised using a 2000ppm NaCl solution under standard test conditions
2. A 2-4 hour clean was performed using the desired cleaner product, after which the membrane was characterised again under standard test conditions.
3. An additional 2-4 hour clean was performed using the desired cleaner product, after which the membrane performance was characterised again using 2000ppm NaCl solution under standard test conditions.

Standard Test Conditions were:

- The flux rate was measured at standard operating conditions for each membrane type
- The recirculation rate was 1000 ml/min and normalized to 25°C
- The cleaning solution was recirculated at ~2 bar for 30 minutes followed by a soak for 30 minutes followed by recirculation for 30 minutes and so on for the full duration of clean
- Alkaline cleans were carried out at 30-35°C whereas acid cleans were carried out at 15-25°C

All cleaning tests were carried out both with and without air for comparison. The turbidity of the cleaning solution was measured before and after the clean as a measure of the quantity of foulant/scalant removed.

**Note:** Cleaners A and B are newly formulated powder cleaners with effervescent properties, containing a mixture of detergents, surfactant and chelating agents. Cleaner C is an existing liquid cleaning product, and Cleaner D is an existing powder alkaline cleaning product.

#### 3.1 Clay/Al-Silicates/Iron fouled membrane

The cleaning tests were carried out on a Clay/Iron fouled membrane. The membrane was a Koch 8040-XR-400 Brackish Water model with a standard permeate flux of 44.5 l/m<sup>2</sup>h and salt rejection of 99.75%.

**Table 1: Cleaning Programs for Clay/Iron fouled membrane**

Tests	Clay/Iron fouled membrane:
<b>1a</b>	Fouled membrane flux and salt rejection before clean
<b>1b</b>	Performance after clean with NaOH for 3 hours, pH 12 @ temperature 30-35 °C
<b>1c</b>	Performance after additional clean with Citric acid for 2 hours, pH 3-4 @ temperature 15-25 °C

<b>2a</b>	Fouled membrane flux and salt rejection before clean
<b>2b</b>	Performance after clean with NaOH + air for 3 hours, pH 12 @ temperature 30-35 °C
<b>2c</b>	Performance after additional clean with Citric acid + air for 2 hours, pH 3-4 @ temperature 15-25 °C
<b>3a</b>	Fouled membrane flux and salt rejection before clean
<b>3b</b>	Performance after clean with Cleaner A for 3 hours, pH 11.5 @ temperature 30-35 °C
<b>3c</b>	Performance after additional clean with Cleaner B for 2 hours, pH 2-3 @ temperature 15-25 °C
<b>4a</b>	Fouled membrane flux and salt rejection before clean
<b>4b</b>	Performance after clean with Cleaner A + air for 3 hours, pH 11.5 @ temperature 30-35 °C
<b>4c</b>	Performance after additional clean with Cleaner B + air for 2 hours, pH 2-3 @ temperature 15-25 °C

**Table 2: Results for Clay/Iron fouled membrane**

Test	2000 ppm NaCl Flux (l/m <sup>2</sup> h)	% Flux Change	% Salt Rejection	Change in Turbidity (NTU)
<b>Test 1: Clay/Fe fouled membrane (without air)</b>				
<b>1a)</b> Before Clean	25.3	-	95.2%	-
<b>1b)</b> After 3hr clean with 0.2% NaOH, pH 12	26.4	+4%	96.2%	4 → 19
<b>1c)</b> Follow on 2hr clean with 2% Citric acid, pH 3-4	25.6	+1%	96.2%	2 → 2
<b>Test 2: Clay/Fe fouled membrane + air</b>				
<b>2a)</b> Before Clean	26.9	-	97.9%	-
<b>2b)</b> After 3hr clean with 0.2% NaOH + Air, pH 12	31.6	+17%	98.2%	4 → 38
<b>2c)</b> Follow on 2hr clean with 2% Citric acid + Air, pH 3-4	26.5	-2%	98.5%	4 → 11
<b>Test 3: Clay/Fe fouled membrane (without air)</b>				
<b>3a)</b> Before Clean	29.2	-	97.0%	-
<b>3b)</b> After 3hr clean with 1% Cleaner A, pH 11.5	38.4	+32%	98.6%	1 → 112
<b>3c)</b> Follow on 2hr clean with 1% Cleaner B, pH 2-3	37.8	+29%	98.7%	5 → 15
<b>Test 4: Clay/Fe fouled membrane + air</b>				
<b>4a)</b> Before Clean	26.5	-	96.1%	-
<b>4b)</b> After 3hr clean with 1% Cleaner A + Air, pH 11.5	37.0	+40%	98.3%	4 → 110
<b>4c)</b> Follow on 2hr clean with 1% Cleaner B + Air, pH 2-3	40.2	+52%	98.7%	4 → 4

### 3.1.1 Membrane cleaning pictures for Clay/Iron fouled membrane

The cleaning pictures below show the extent of foulant removal from the membrane surface.

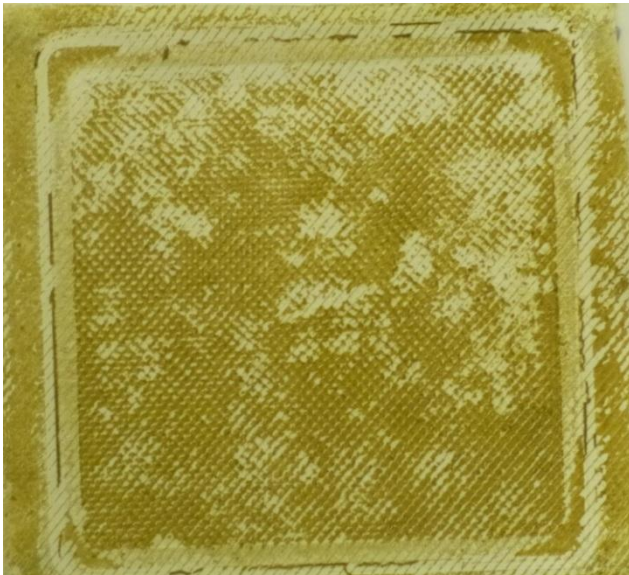


Figure 3: After 0.2% NaOH + air followed by 2% Citric + air

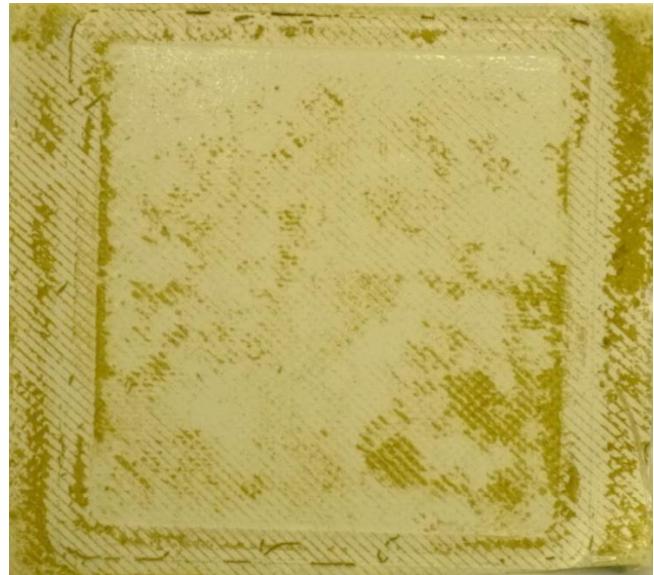
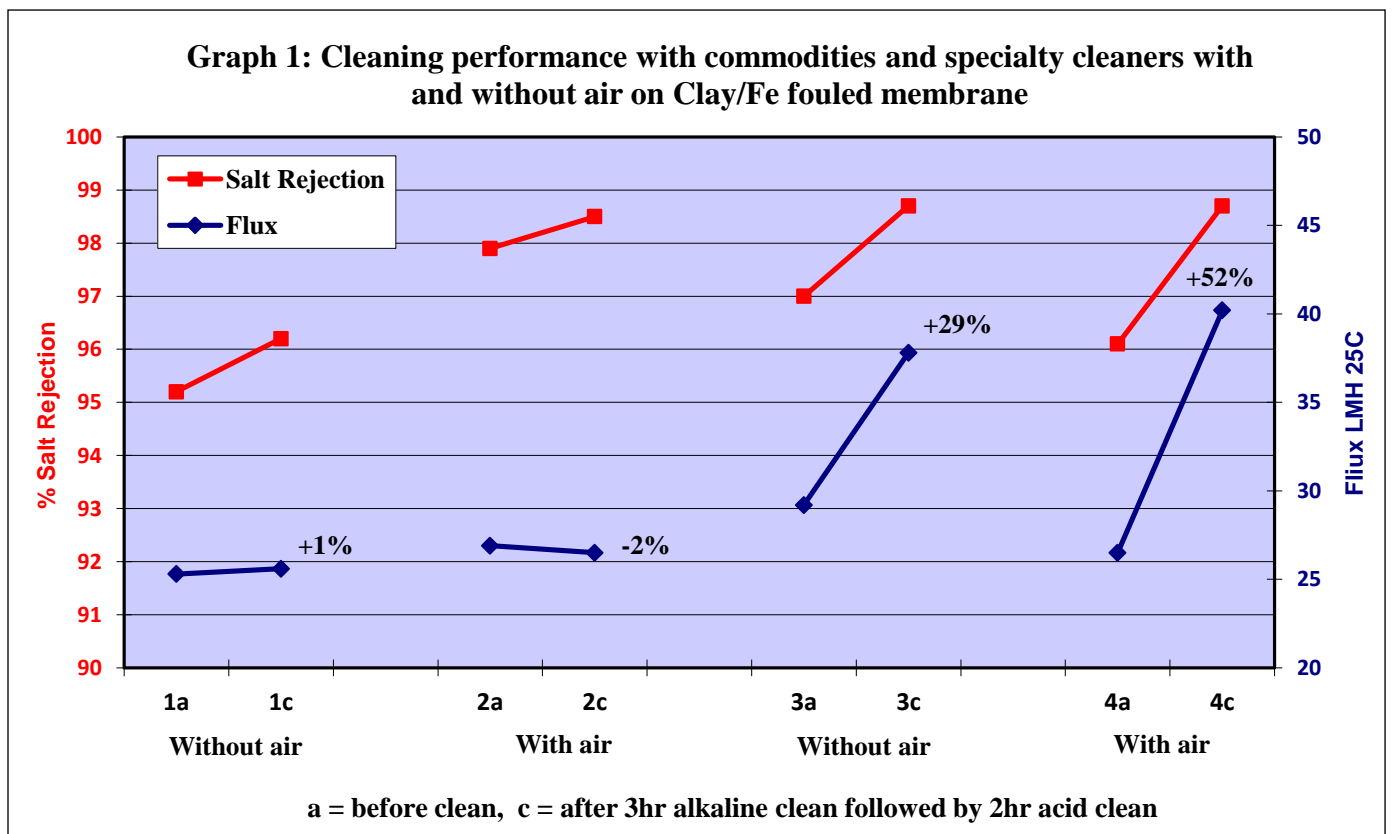


Figure 4: After 1% Cleaner A + air followed by 1% Cleaner B + air





### 3.2 Calcium Carbonate fouled membrane

The cleaning tests were carried out on a Calcium Carbonate fouled membrane. The membrane was a Dow Filmtec BW30XFR-400/34i model with a standard permeate flux of 45 l/m<sup>2</sup>h and salt rejection of 99%.

**Table 3: Cleaning Programs for Calcium Carbonate fouled membrane**

Tests	CaCO <sub>3</sub> fouled membrane:
<b>1a</b>	Fouled membrane flux and salt rejection before clean
<b>1b</b>	Performance after clean with Cleaner B for 2 hours, pH 2-3 @ temperature 15-25 °C
<b>1c</b>	Performance after additional clean with Cleaner B for 2 hours, pH 2-3 @ temperature 15-25 °C
<b>2a</b>	Fouled membrane flux and salt rejection before clean
<b>2b</b>	Performance after clean with Cleaner B + air for 2 hours, pH 2-3 @ temperature 15-25 °C
<b>2c</b>	Performance after additional clean with Cleaner B + air for 2 hours, pH 2-3 @ temperature 15-25 °C
<b>3a</b>	Fouled membrane flux and salt rejection before clean
<b>3b</b>	Performance after clean with Cleaner C for 2 hours, pH 3-4 @ temperature 15-25 °C
<b>3c</b>	Performance after additional clean with Cleaner C for 2 hours, pH 3-4 @ temperature 15-25 °C
<b>4a</b>	Fouled membrane flux and salt rejection before clean
<b>4b</b>	Performance after clean with Cleaner C + air for 2 hours, pH 3-4 @ temperature 15-25 °C
<b>4c</b>	Performance after additional clean with Cleaner C + air for 2 hours, pH 3-4 @ temperature 15-25 °C

**Table 4: Results for Calcium Carbonate fouled membrane**

Test	2000 ppm NaCl Flux (l/m <sup>2</sup> h)	% Flux Change	% Salt Rejection	Change in Turbidity (NTU)
<b>Test 1: CaCO<sub>3</sub> fouled membrane (without air)</b>				
<b>1a)</b> Before Clean	32.4	-	75.7%	-
<b>1b)</b> After 2hr clean with 1% Cleaner B, pH 2-3	49.4	+52%	90.0%	1 → 6
<b>1c)</b> Follow on 2hr clean with 1% Cleaner B, pH 2-3	51.9	+60%	90.0%	1 → 9
<b>Test 2: CaCO<sub>3</sub> fouled membrane + air</b>				
<b>2a)</b> Before Clean	33.3	-	82.8%	-
<b>2b)</b> After 2hr clean with 1% Cleaner B + Air, pH 2-3	47.3	+42%	90.0%	2 → 2

<b>2c)</b> Follow on 2hr clean with 1% Cleaner B + Air, pH 2-3	51.3	+54%	89.7%	1 → 2
<b>Test 3: CaCO<sub>3</sub> fouled membrane (without air)</b>				
<b>3a)</b> Before Clean	40.2	-	81.0%	-
<b>3b)</b> After 2hr clean with 3% Cleaner C, pH 3-4	46.2	+15%	90.8%	0 → 4
<b>3c)</b> Follow on 2hr clean with 3% Cleaner C, pH 3-4	44.8	+11%	90.5%	0 → 5
<b>Test 4: CaCO<sub>3</sub> fouled membrane + air</b>				
<b>4a)</b> Before Clean	37.6	-	86.0%	-
<b>4b)</b> After 2hr clean with 3% Cleaner C + Air, pH 3-4	42.9	+14%	87.7%	2 → 2
<b>4c)</b> Follow on 2hr clean with 3% Cleaner C + Air, pH 3-4	51.3	+37%	91.0%	2 → 5

**N.B:** Turbidity readings are undependable with acid cleaners because the foulant removed is readily soluble in the cleaning solution, so turbidity does not increase by much.

### 3.2.1 Membrane cleaning pictures for Calcium Carbonate fouled membrane

The cleaning pictures below show the extent of foulant removal from the membrane surface.

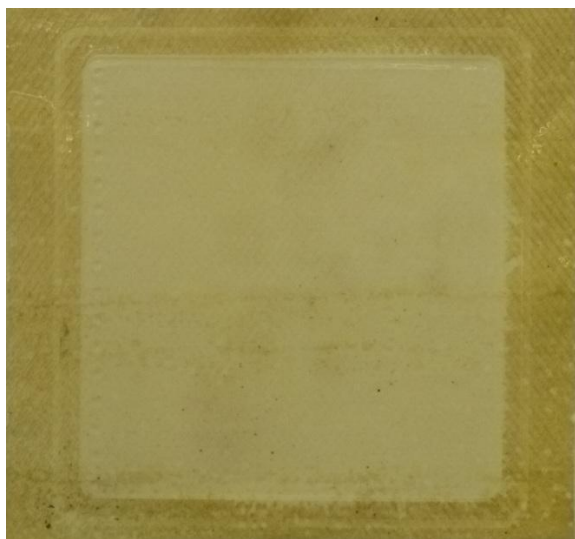


Figure 5: 1% Cleaner B + air followed by 1% Cleaner B + air

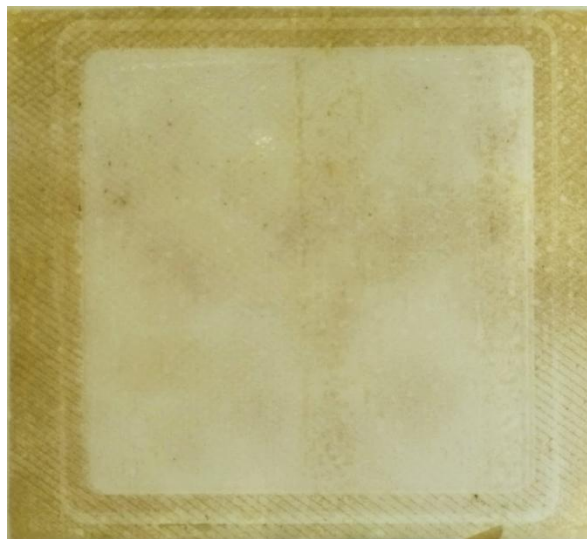
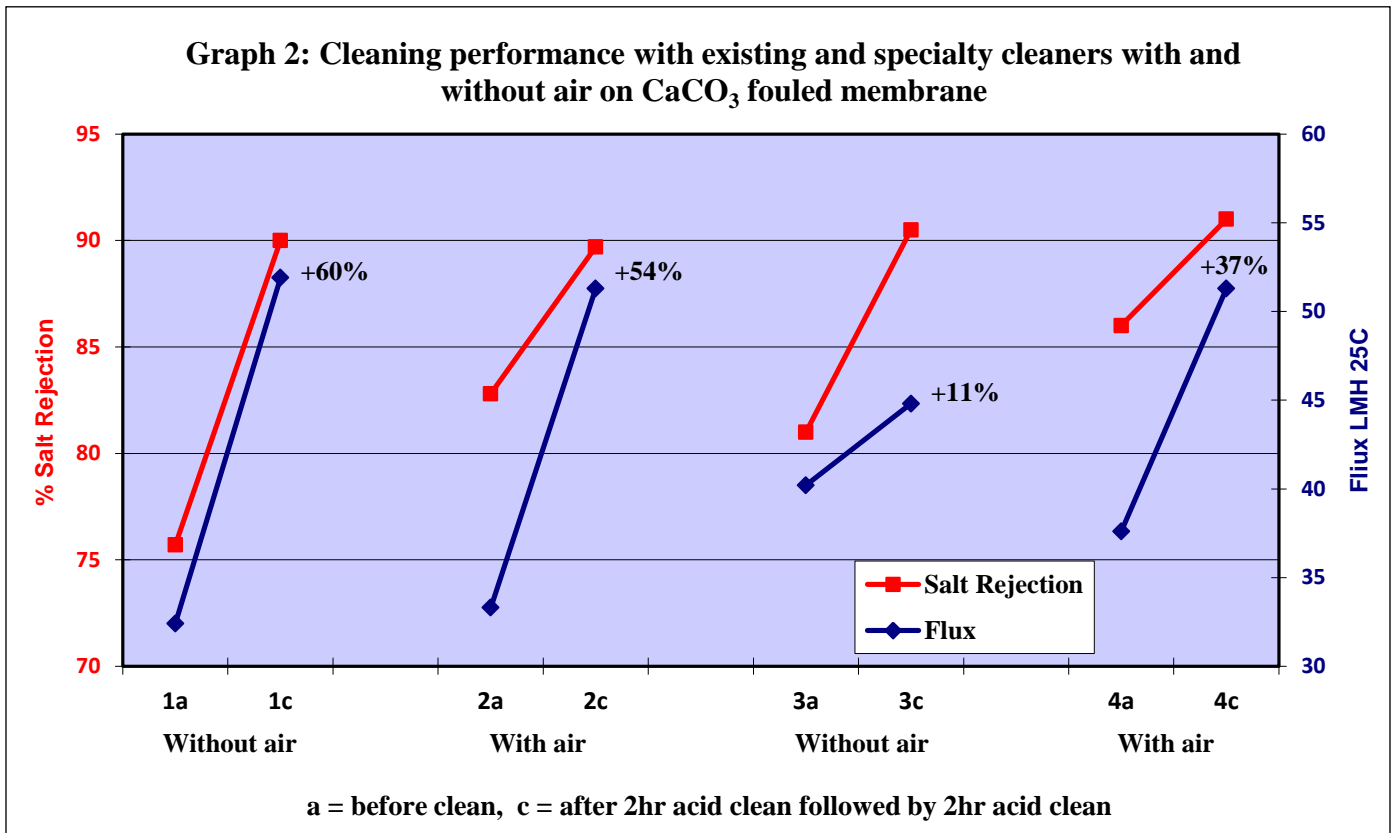


Figure 6: 3% Cleaner C + air followed by 3% Cleaner C + air



#### IV. MEMBRANE AUTOPSY RESULTS

After testing on the flat sheet rig, membrane samples were analysed at Genesys labs in Madrid. Autopsies enable thorough examination of the effects of air/chemical cleaning on foulant removal, from both the membrane surface and membrane spacer material.

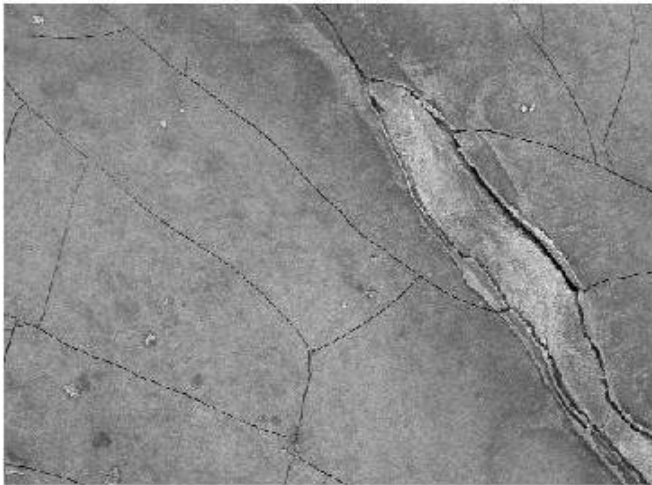
##### 4.1 Scanning Electron Microscopy – Energy Dispersive X-ray Analysis (SEM-EDXA)

SEM-EDXA was used to study the membrane surface and to verify the elemental composition of its foulant and deposits detected. For conventional imaging using SEM, the samples must be electrically conductive at the surface, and electrically grounded to prevent the accumulation of electrostatic charge at the surface. Membrane samples are therefore coated with an ultrathin coating of an electrically conducting material, in this case gold.

The main components of the membranes are carbon, oxygen, nitrogen (which are not detectable by this technique) and sulphur (polysulphone layer). In the absence of foulant, or when it is very thin, the electron beam used for analysis can reach the polysulphone layer and hence sulphur is detected. However, SEM cannot distinguish whether sulphur detected is from the membrane or the foulant; the obtained percentage gives information about the thickness of the foulant.

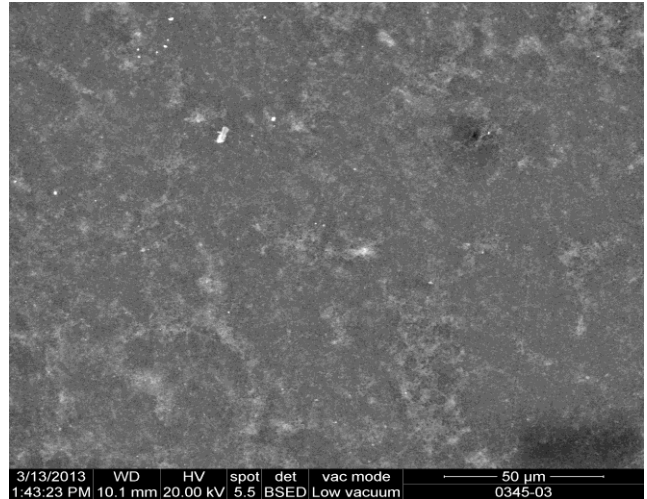
### 4.1.1 Clay/Fe fouled membrane

Micrographs obtained for the cleans performed with 1% Cleaner A followed by 1% Cleaner B (with and without air) appear undistinguishable, making it difficult to reach a good conclusion of the air performance. However, both show an improved performance as compared to the fouled membrane. It is therefore necessary to work with the percentage weight changes obtained from the general analysis.



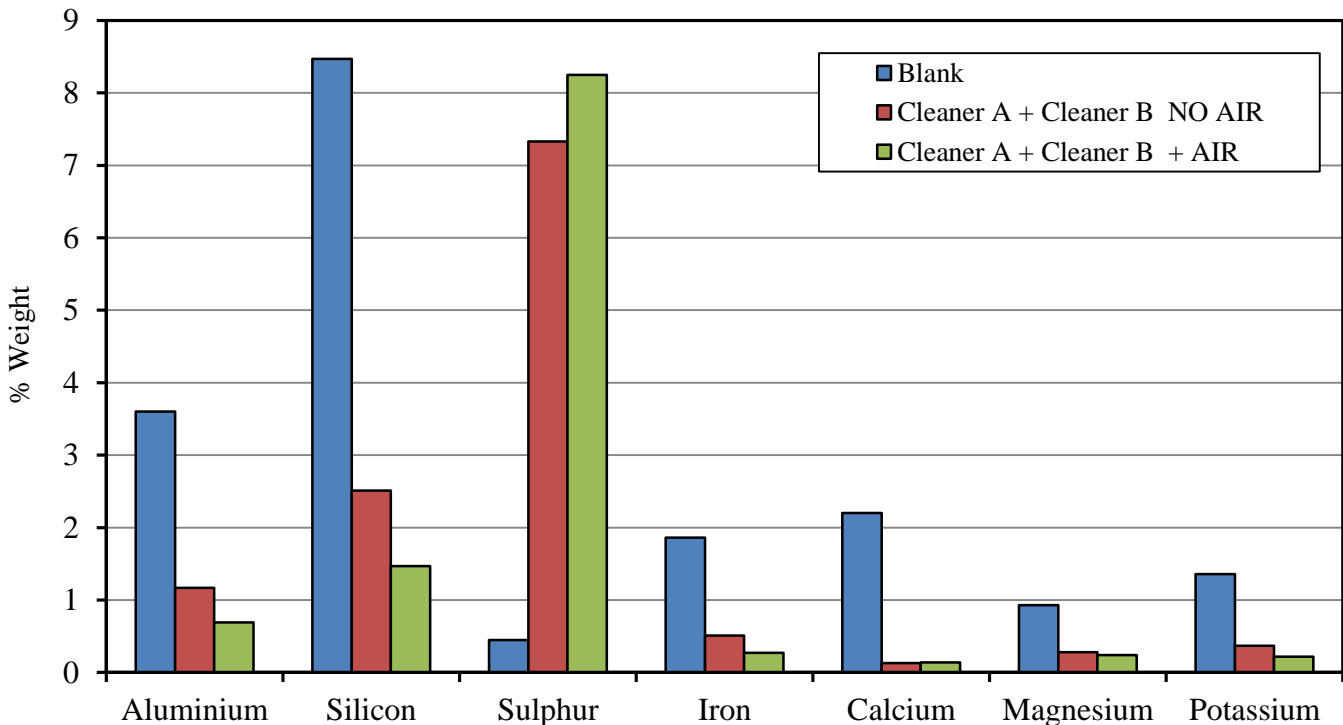
1mm Electron Image 1

Micrograph 1: Fouled Membrane

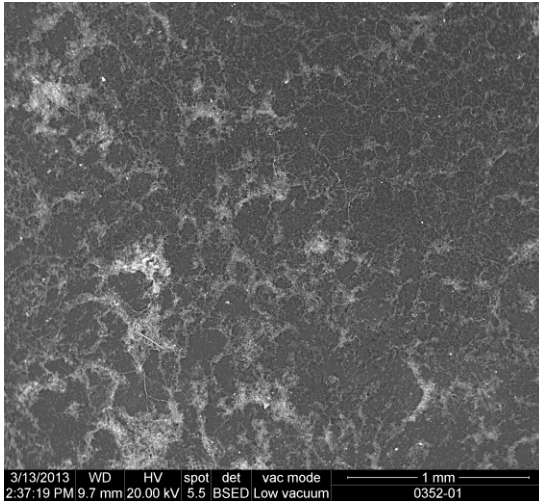


Micrograph 2: Membrane surface after 1% Cleaner A + air followed by 1% Cleaner B + air

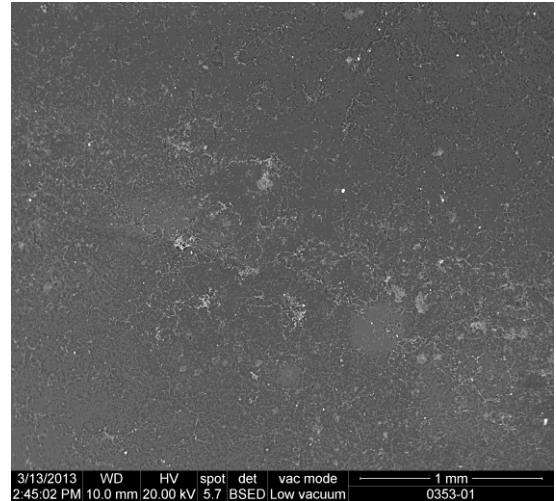
**Graph 3: Elemental composition of Clay/Fe fouled membrane surface after cleaning with specially formulated cleaners with and without air**



### 4.1.2 CaCO<sub>3</sub> fouled membrane



Micrograph 3: Membrane surface after 1% Cleaner B without air



Micrograph 4: Membrane surface after 1% Cleaner B with air

A 24% sulphur increase is observed after cleaning with air, whereas cleaning without air gives only a 1% sulphur increase. This is encouraging as it shows that more of the polysulphone layer is being detected, which means that there must be less foulant on the membrane surface.

## 4.2 Infra-Red Spectroscopy

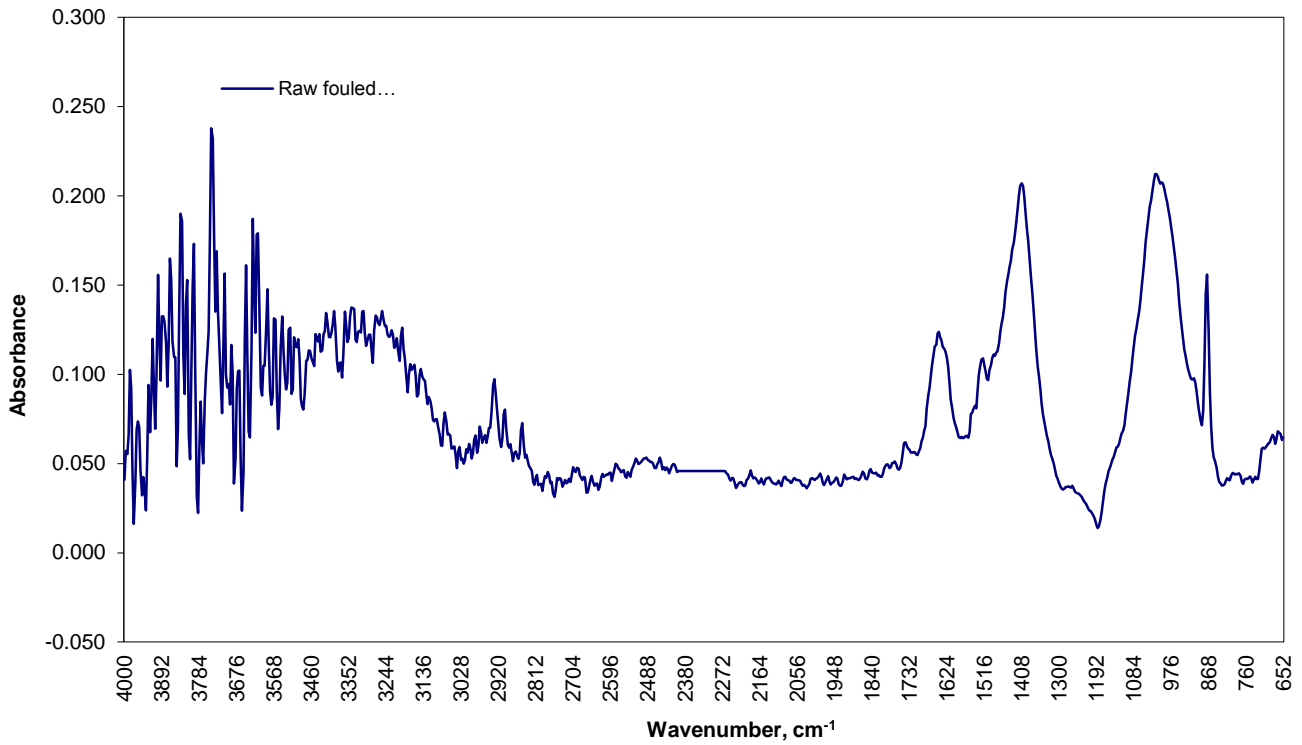
Infra-Red Spectroscopy (IR) can provide valuable information related to the chemical structure of membranes, or to characterize the fouling layer that may be present on the membrane surface.

In the mid-infrared, absorption of radiation is related to the fundamental vibrations of the chemical bonds. IR Spectroscopy provides information related to the presence or absence of specific functional group. Shifts on the frequency of absorption bands and changes in relative band intensities indicate changes in the chemical structure, or changes on the membrane surface. So if the sample spectrum looks like the blank, then deposits have been removed.

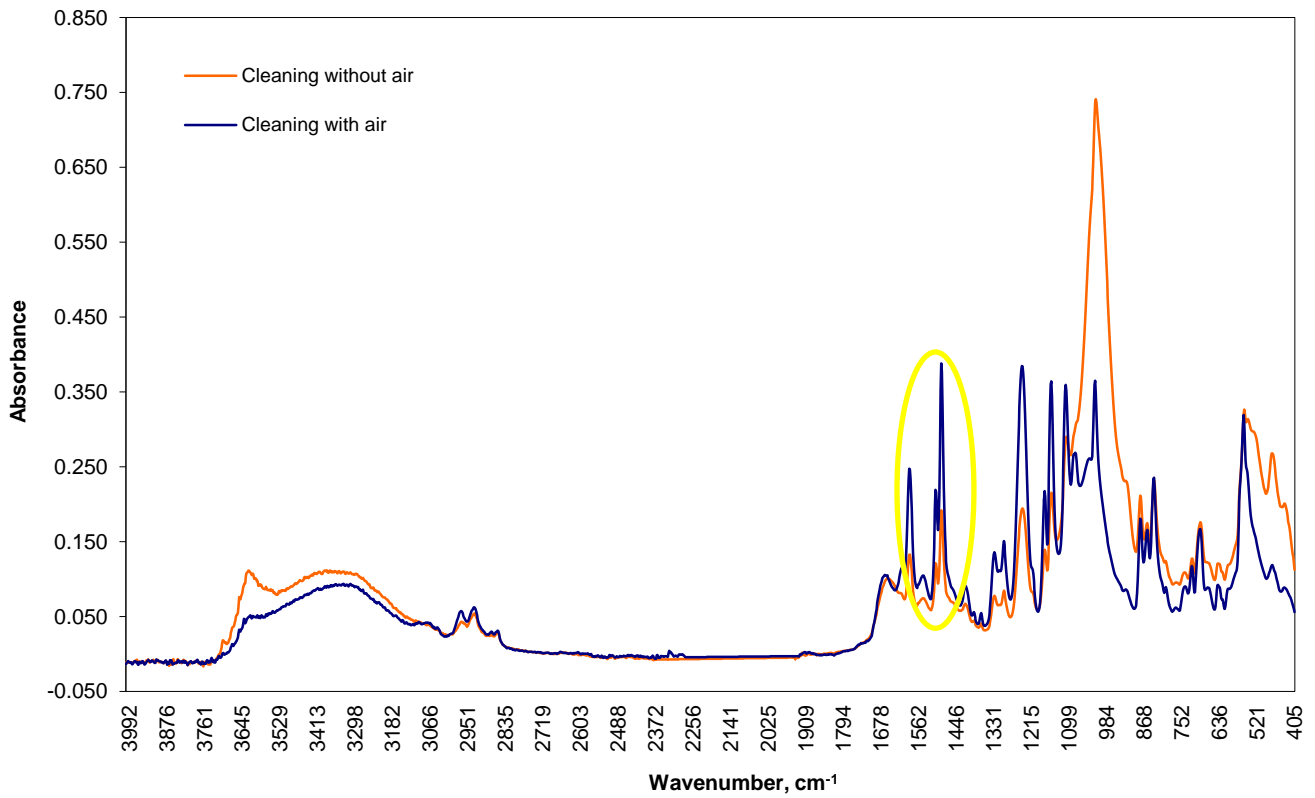
### 4.2.1 Clay/Fe fouled membrane

Spectrum 1 shows the absorbance peaks produced for the fouled ('raw') membrane.

Spectrum 2 shows the absorbance peaks produced for the membrane cleaned with 1% Cleaner A followed by 1% Cleaner B both with air (blue) and without air (red).



Spectrum 1: IR spectrum for 'raw' Clay/Iron fouled membrane



Spectrum 2: IR spectra for Clay/Iron fouled membrane after cleaning with Cleaner A followed by Cleaner B, with and without air

Commonly, the identification of polyamide damage concerns the following bands:

- Amide N-H bend:  $1540\text{ cm}^{-1}$
- C=C ring vibrations: near  $1610$  and  $1448\text{ cm}^{-1}$

From spectrum 2, these polyamide bands can be observed after cleaning both with air and without air and do not show any relevant changes (circled in yellow). This verifies that the polyamide layer has not suffered any structural changes during cleaning. These bands cannot be identified on the fouled membrane (spectrum 1) because there is a thick layer of foulant on the membrane surface so the polyamide absorption bands cannot be detected. Fouling bands ( $\sim 1010\text{cm}^{-1}$ ) intensity decreases more with air; this demonstrates that more foulant is removed with air.

The IR spectra for the  $\text{CaCO}_3$  membrane cleaned with air and without air show no relevant differences, and both appear characteristic to the blank. Like with the Clay/Iron fouled membrane, membrane bands are more distinguished and the intensity of fouling bands decreases after cleaning with air.

## V. PILOT PLANT RESULTS

Preliminary cleaning tests were conducted on full 8-inch membrane elements with various foulants from different membrane manufacturers.

Cleaning tests were carried out following the set cleaning protocol:

1. The fouled membrane was characterised using a 1500ppm NaCl solution under standard test conditions
2. A 4 hour clean was performed using the desired cleaner product, after which the membrane was characterised again under standard test conditions.
3. An additional 4 hour clean was performed using the desired cleaner product, after which the membrane performance was characterised again using 1500ppm NaCl solution under standard test conditions.

Standard Test Conditions were:

- The flux rate was measured at standard operating conditions for each membrane type
- The recirculation rate was  $\sim 11\text{ m}^3/\text{hr}$  and normalized to  $25^\circ\text{C}$
- The cleaning solution was recirculated at  $\sim 4$  bar for 30 minutes followed by a soak for 30 minutes followed by recirculation for 30 minutes and so on for the full duration of clean
- Recirculation rate without air was  $\sim 7\text{ m}^3/\text{hr}$ , and with air it was  $\sim 6.4\text{ m}^3/\text{hr}$
- Alkaline cleans were carried out at  $30\text{-}35^\circ\text{C}$

### 5.1 Clay/Organics/Biofilm fouled membrane

The cleaning tests were carried out on a membrane fouled with clays, organics and biofilm. The membrane was a Hydranautics ESPA2-LD Brackish Water model with a standard permeate flux of  $43\text{ lm}^2/\text{h}$  and salt rejection of 99.6%.

Cleaner D is an existing alkaline powder cleaning product containing a mix of detergents, surfactant and chelating agents. Preliminary tests on the pilot plant show improved cleaning performance when using air as shown by the example below. Additional test results will be presented in a separate paper when available.

**Table 5: Cleaning Programs for Clay/Organic/Biofouled membrane**

Tests	Clay/Organic/Biofouled membrane:
<b>1a</b>	Fouled membrane flux and salt rejection before clean
<b>1b</b>	Performance after clean with Cleaner D for 4 hours, pH 12 @ temperature 30-35 °C
<b>2a</b>	Fouled membrane flux and salt rejection before clean
<b>2b</b>	Performance after clean with Cleaner D + air for 4 hours, pH 12 @ temperature 30-35 °C

**Table 6: Results for Clay/Organic/Biofouled membrane**

Test	1500 ppm NaCl Flux (l/m <sup>2</sup> h)	% Flux Change	% Salt Rejection	ΔP (bar)	% Recovery
<b>Test 1: Fouled membrane (without air)</b>					
<b>1a</b> ) Before Clean	16.4	-	99.1%	2.3	3.9
<b>1b</b> ) After 4hr clean with 1% Cleaner D, pH 12	30.8	+88%	99.3%	0.2	13.1
<b>Test 2: Fouled membrane + air</b>					
<b>2a</b> ) Before Clean	16.4	-	99.3%	1.9	3.9
<b>2b</b> ) After 4hr clean with 1% Cleaner D + Air, pH 12	34.9	+113%	99.4%	0.5	7.5

## VI. CONCLUSION

### 6.1 Clay/Al-Silicates/Iron fouled membrane

With this particular membrane, fouling has not had significant impact on the salt rejection. Cleaning increases salt rejection from around 96% to 98%. Though cleaning has a much greater impact on permeate flux.

Graph 1 shows that the clean performed using commodity chemicals; NaOH followed by Citric gave only a small increase in flux (+1%), but a fairly significant increase in the turbidity of the cleaning solution (4 → 19 NTU). Cleaning with air gives a greater increase in flux and salt rejection compared to using commodity chemicals alone. A clean with NaOH gives a flux increase of 17% with air (test 2b table 2), compared to 4% without air (test 1b table 2). Although flux increases were a lot lower than with using the specially formulated cleaning products A and B. Cleaning pictures also show that less foulant was removed (Figure 3 compared to Figure 4).

A greater flux increase was seen after a clean with specially formulated Cleaner A followed by Cleaner B, (which are powder products). The flux increases by 29% (test 3c table 2) without air, and the turbidity of the cleaning solution increases dramatically from 1 → 112 NTU. However with air, the flux increases by 52% (test 4c table 2), almost twice as much (Graph 1). The greater increase in flux with air may indicate that some other (eg. Less coloured like organic) foulant was also removed as well as the coloured clay and iron foulants.



These results show that for this particular membrane/foulant, the specially formulated cleaning chemicals restore membrane performance to a greater extent than commodity chemicals. Visual inspection of the membrane coupons emphasizes the radical effects of cleaning (Figure 4 compared to Figure 3).

The micrographs produced using SEM show that the membrane surface appears very similar after cleaning with specialty cleaners both with and without air. However, micrograph 2 shows an improved appearance after cleaning compared to the fouled membrane (micrograph 1). The analytical data shows that the specially formulated cleaners in combination with air removes more aluminium silicates (clay) and iron deposits from the membrane surface compared to just using cleaning chemicals alone (Graph 3). In fact, there is a greater decrease in fouling components percentage with air than without air, indicating a better performance of cleaning procedure. The percentage of sulphur detected is greater after cleaning with air, which indicates that the electron beam used in the analysis has penetrated the polysulphone layer. This therefore indicates that the foulant thickness has been reduced.

It can be observed that the IR sample spectra for the clean with air (red line spectrum 2) shows all the characteristic absorption bands of a polyamide-polysulphone membrane, which are not observed on the fouled membrane (spectrum 1). Fouling bands (mainly at  $1010\text{cm}^{-1}$ ) decrease which verifies that there is not a relevant presence of foulant on the surface after cleaning with air. Absorption bands for the clean performed with air (blue line spectrum 2) are most characteristic of the bands for a blank membrane, as compared to those for the clean performed with no air (red line spectrum 2). Therefore more foulant is removed cleaning with air. The differences in results both with and without air are not drastic because the cleaners themselves work very well alone.

## 6.2 Calcium Carbonate fouled membrane

With this particular fouled membrane, both the flux and salt rejection are below the standard membrane manufacturer guidelines for operation ( $45\text{ lm}^2\text{h}$  and 99%). In all cases, cleaning profoundly increases the flux by 11-60%, but salt rejection is only restored to around 90%. This could mean that the membrane surface has been damaged, allowing more salts/ions to pass through the membrane.

Cleaner C is an existing acidic liquid cleaner. Two successive cleans with Cleaner C with no air gives a flux increase of 11% (test 3c table 4). Results show that cleaning with air gives a greater increase in flux and salt rejection compared to cleaning without air. Two successive cleans with Cleaner C plus air gave a flux increase of 37%, compared to 11% without air (Graph 2).

However, two cleans using the specially formulated Cleaner B, which is a powder product, gives a much superior flux increase of 60% (test 1c table 4), with a larger change in the turbidity of the cleaning solution ( $1 \rightarrow 9\text{ NTU}$ ). The clean performed using Cleaner B in combination with air restores membrane performance to roughly the same extent (54% flux increase with air compared to 60% flux increase without air). Although there is a slightly greater increase in flux without air, the turbidity does not increase by much more than with air because the foulant removed is readily soluble in the cleaning solution, so the solution does not become very turbid. However, visually the membrane coupon looks much cleaner with Cleaner B and air (Figure 5) than without air. Overall, Cleaner B gave a greater increase in both flux and turbidity both with and without air, compared to Cleaner C with and without air. This shows that the specially formulated Cleaner B has removed more foulant from the membrane surface than Cleaner C.

The SEM results show a heterogeneous covering of foulant on the membrane surface. Visual inspection reveals that more deposits have been removed from the membrane surface after cleaning with Cleaner B and air (micrograph 4), as compared to Cleaner B alone (micrograph 3). A 24% sulphur increase is observed after cleaning with air, whereas cleaning without air gives only a 1% sulphur increase. This is encouraging as it shows that more of the polysulphone layer is being detected, which means that there must be less foulant on the membrane surface.

The IR spectra for the CaCO<sub>3</sub> membrane cleaned with air and without air show no relevant differences, and both appear characteristic to the blank. Results show that air has a more profound effect when used in combination with alkaline cleaning products in the removal of composite fouling, as compared to using acidic cleaners to remove scales.

### 6.3 Clay/Organic/Biofouled membrane

With this particular membrane, salt rejection was very high even though the membrane appeared heavily fouled, but permeate flux was low. Cleaning increases salt rejection slightly, but has a much greater impact on permeate flux.

Cleaner D is an existing powder alkaline cleaner. A 4hr clean with Cleaner D with no air gives a flux increase of 88% (test 1b table 6), which itself is quite impressive. However, results show that the same clean performed with air gave a much greater increase in flux of 113% (test 2b, table 6).

### 6.4 Summary

- Cleaning using specially formulated cleaning chemicals in combination with micro-bubbles improves overall membrane performance
- Cleaning with specially formulated cleaning chemicals increases membrane performance to a greater magnitude than with existing cleaning chemicals
- Cleaning with micro-bubbles and specialty cleaners restores membrane performance to a greater extent than with air and commodity cleaning chemicals
- Cleaning with commodity chemicals and air improves membrane performance compared just commodity chemicals alone
- Overall membrane appearance is improved after cleaning
- Autopsy results show that membranes do not show any signs of damage after cleaning

## VII. REFERENCES

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