CLEANING BIOFOULED MEMBRANES EARLY IMPROVES PLANT OPERATION. COMPARISON OF AUTOPSY AND CLEANING RESULTS ON A SMALL BWRO AND LARGE SWRO.

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Abstract

It is a fact that all new reverse osmosis membranes start to foul as soon as they start operation. The only variable is the rate at which they foul. Most RO plants operate at a differential pressure (ΔP) of 1.5 - 3 bar. Cleaning usually occurs when the ΔP is 10-15% above the design specification. This paper explores the benefits of early identification of foulants through autopsy allowing predictive maintenance cleaning of the plant to be conducted at the first signs of fouling. This prevents a build up of difficult to remove deposits which reduce membrane performance and life expectancy.

Autopsies were conducted on a 1,200 GPM (6,650m³/day) brackish water reverse osmosis plant (BWRO) and a 22,000 GPM (120,000m³/day) sea water reverse osmosis plant (SWRO). Foulants identified included biofilm, clay and iron. Different cleaning solutions were then tested on samples of the actual membranes to determine the best cleaning protocol.

The authors present the results of autopsies, laboratory cleaning tests and full plant cleaning results with a number of different cleaning agents. A strongly alkaline cleaner with a high ionic strength appeared to be particularly effective at removing biofilm and clay. The authors theorise that during the soaking process the high ionic strength of the cleaning solution on the feed side of the membrane encourages natural osmosis of permeate water through the membrane to the feed side thus causing some physical disruption to the biofilm and clay fouling layer. This allows the detergent, surfactant and chelating molecules in the cleaner to break up the fouling layer allowing a more effective clean. Once biofilm is removed then an acid clean proved much more effective at removing iron deposits.

Comparisons are drawn between the results of cleaning early on the SWRO plant and late on the BWRO plant. It is much easier to remove deposits before they have formed a substantial cake layer resulting in more effective and less frequent cleaning which prolongs membrane life.

Introduction

Membrane manufacturers typically recommend that cleaning should be conducted when there is a significant drop in performance. The standard advice has not been changed in over 30 years. The DOW Filmtec Technical Manual states on Page 122 that: “Elements should be cleaned when one or more of the below mentioned parameters are applicable:

• The normalized permeate flow drops 10%

• The normalized salt passage increases 5 - 10%

• The normalized pressure drop (feed pressure minus concentrate pressure) increases 10 -15%

If you wait too long, cleaning may not restore the membrane element performance successfully. In addition, the time between cleanings becomes shorter as the membrane elements will foul or scale more rapidly." This is the same message offered in Hydranautics Technical bulletin of 1992: "If permeate flow drops, product water quality decreases, or applied pressure must be increased to maintain normal productivity more than 10 to 15 percent, then the elements need to be cleaned." Analysis of the results of 500 membrane autopsies by Pena et al has shown that 60% of the main foulants are biological and particulate/colloidal fouling. [2] Clay and biofilm tend to build up in layers and become compressed into the membrane surface if left to accumulate. This paper explores the benefits of cleaning early when membrane foulants are easier to remove.

Cleaning Early

It is a fact that all new reverse osmosis membranes start to foul as soon as they start operation. The only variable is the rate at which they foul. Most RO plants operate at a differential pressure (ΔP) of 1.5 - 3 bar. Cleaning usually occurs when the ΔP is 10-15% above the design specification. This is based on recommendations by membrane manufacturers. Figure 1 below measures fouling with time. The perception threshold line indicates the time at which the operator 'perceives' a change to system operation, whether this be a change in flux, pressure, or salt passage. In reality as soon as water passes along the membrane (initial time = T_0), the membrane starts fouling. It is important to appreciate this fact; the membrane is fouling from system start up, but nothing is observed until the fouling line crosses the perception line, at which point the observer can see there is some change in the operation. The membrane acts like a huge sponge with a myriad of active surfaces, so a significant amount of surface fouling can take place before any operational change is observed.[1]

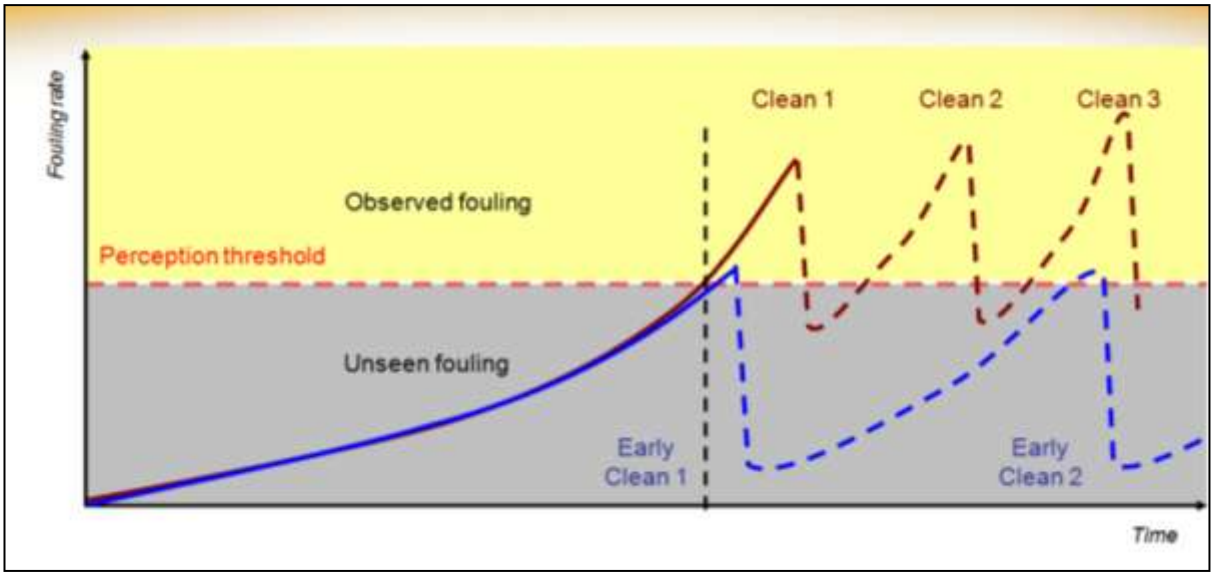

Figure 1. Membrane fouling rate

Laboratory studies from numerous autopsies have confirmed that the sooner the membrane is cleaned after fouling the easier it is to clean. If the foulant is not cleaned it becomes more difficult to remove until finally the membrane cannot be cleaned at all. Clean 1 will theoretically take place when perceived performance has dropped by 10-15%. The reality is that by the time cleaning chemicals are sourced and a shutdown period is arranged the performance may have got significantly worse. The clean may result in conditions returning to an acceptable level below the fouling perception threshold. The clean after a delay will not however be as effective as it could have been if performed earlier before more deposits added to the cake layer and became compressed. Because the clean did not remove the majority of deposits the underlying fouling rate is higher and the perception threshold of performance loss will be seen quicker and clean 2 conducted after a shorter period than may otherwise have been possible had the first clean happened earlier.

The whole process can be planned by conducting autopsies on a membrane element from the front and back of the plant. Foulants are most likely to appear at the front and scalants in the last position element. Convincing some operators to remove and autopsy almost new elements may be a struggle so smaller 2 or 4 inch sacrificial elements could easily be installed and used. The autopsy will identify typical foulants. Once the foulants are known cleaning protocols can be tested in the laboratory and appropriate cleaning agents can be stored on site ready for cleaning as soon as there is a notable change in operating parameters. Any delay in cleaning will mean the foulant will be become thicker and more compressed into the membrane surface and be much more difficult to clean. Early maintenance cleaning of the plant prevents a build-up of difficult to remove deposits which reduce membrane performance and life expectancy. Less time will be required to conduct the cleaning and a more effective “deeper” clean can be achieved. This means the subsequent fouling rate is lower, closer to the rate of the new membrane when installed. The lower fouling rate reduces the frequency between subsequent cleans increasing operational efficiency and further enhancing membrane lifespan.

Membrane Autopsy

In most cases, membranes are sent for autopsy because they have failed or are underperforming significantly. That is salt passage, flow, flux and pressure differentials are outside of the design specifications. The first stage of membrane autopsy is to record the element model, serial number, position in the plant along with the chemical treatment regimes being applied. External examinations and photographs are taken to record the physical condition. A vacuum test is conducted to assess physical membrane damage. Samples can be taken from the feed inlet and outlet. The outer casing is removed and membrane leaves unrolled in readiness for an internal examination of the membrane sheets, glue lines, vexar and permeate carrier. Representative deposit samples are taken from the membrane surface and photographs are taken. Membrane samples are cut and prepared for characterisation and cleaning tests in a specially designed flat sheet test rig. [Fig 2] Flow rate and salt rejection are determined and compared to design specifications.

Figure 2. Flat sheet Test Rig

Physical damage to the membrane samples is conducted using the methylene blue dye test and oxidation by halogens is tested using the Fujiwara method. The validity of the Fujiwara test has been questioned in some quarters so additional tests using attenuated total reflectance infrared spectroscopy (ATR/FTIR) are carried out. This can provide valuable information related to the chemical structure of membrane and deposits. In the mid-infrared, absorption of radiation is related to fundamental vibrations of the chemical bonds. Internal reflection spectrometry provides information related to the presence of specific functional groups which can determine the presence of halogens. Deposits are identified using elemental determination with the SEM-EDXA system. This is based on analysis of X-rays produced via electron beam excitation of a sample area. This technique allows analysis of a sample in selective areas. The limited depth of analysis (typically a few microns), and the possibility to select the area of interest under the electron beam, allows for local analysis to reveal differences in composition. The identification and measurement of individual peak intensities in the X-ray spectrum can be done with a computerized multichannel analyzer. In addition X- Ray diffraction is carried out to identify crystalline solids by measuring the characteristic spaces between layers of atoms or molecules in a crystal. Each crystalline solid has its unique characteristic X-ray powder pattern which may be used as a "fingerprint" for its identification. X-ray photoelectron spectroscopy analysis (XPS) or electron spectroscopy for chemical analysis (ESCA) is a quantitative spectroscopic technique that measures the empirical formula, chemical state and electronic state of the elements that exist within a material. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that escape from the top 1 to 10 nm of the material being analyzed. When the nature of the deposits on the membrane surface is understood then several membrane samples are cleaned with a variety of cleaning solutions at different pH and temperature to assess the best method for cleaning the plant. A full cleaning protocol can then be recommended. The autopsy is written up as a complete report and forwarded to the customer.

BWRO Plant Autopsy

The Ursus brewery in Buzau owned by SAB Miller is one of the biggest in Romania. The 1,200 GPM (6,500 m^3/day) brackish water reverse osmosis plant is supplied via four boreholes and was commissioned in 2002. The plant operated satisfactorily for three years and then increased iron levels in the well water resulted in an increasing fouling rate. The RO plant membranes were being cleaned every month with caustic and acid membrane cleaning chemicals. Results gave only a slight decrease in differential pressure and increase in flow rate and permeate production. The membranes had to be replaced on a two year cycle. In June 2008 the plant was surveyed and a last element second stage membrane taken for autopsy. On the 26th June the autopsy report on a Dow Filmtec BW 30LE-440 was issued. The membrane weighed 22.1 kg compared with a new element weight of 15kg. The autopsy revealed a very heavy red-brown gelatinous deposit which appeared on the feed inlet (Fig 3) and throughout the feed spacer and membrane surface. Samples of deposit were taken from the membrane surface (Fig 4) and analysed using Scanning Electron Microscopy – Energy Dispersive X-ray Analysis (SEM-EDXA) techniques to determine elemental composition. The deposit consisted of iron combined with alumina-silicate (clay) and a heavy biofilm. Bacteria and oxidation tests were also conducted revealing the presence of aerobic bacteria. The membrane did not show signs of oxidation damage but flow was significantly reduced. Cleaning tests were conducted on membrane samples and a powdered high alkaline high ionic strength cleaner containing detergent, chelant and surfactants followed by a mild acid cleaner gave the best results.

Figure 3. Deposit on feed inlet

Figure 4. Deposit on membrane surface

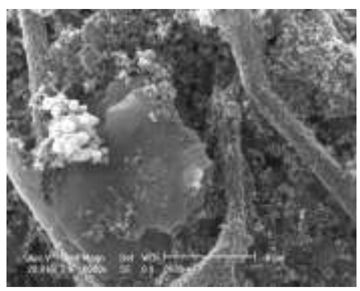

Figure 5. SEM of bacteria and clay

BWRO Cleaning Results

In September 2008 the RO plant membranes were cleaned. A 2% solution of alkaline cleaner (pH 11.8) was made up in the CIP tank and warmed up to 38°C and circulated through the membranes. After 10 minutes the cleaning solution turned brown and cloudy and was discharged and a fresh solution made up. Following circulation for 30 minutes the solution was left to soak for 30 minutes and then flushed with permeate water. A large amount of deposits was removed so the cleaning step was repeated a third time. Samples of each cleaning solution and rinse water in Figure 6 demonstrate the progressive removal of biofilm and clay. A mild acid cleaner containing surfactants was then circulated through the membranes. The cleaning solution turned a red brown colour and fresh cleaning solution had to be made up three times circulated and flushed out. Figure 7. The cleaning process was repeated three times over the next four months until the membrane performance was restored. Subsequent cleaning cycles are now on a 6 month basis and membranes have not been replaced for four years. Historically this plant suffered gross biofilm, clay and iron fouling which had been allowed to build up over a long period; due to poor understanding of the foulants and subsequent inefficient cleaning practice. Failure to fully remove the deposits during CIP resulted in increased fouling potential causing significant operating issues. Conventional cleaners were unsuccessful at removing deposits. The use of a high ionic strength cleaner with extended periods of soaking managed to remove sufficient biofilm and clay so that the acid stage of the cleaning could then take iron deposits into solution and flush them out. This cleaning reaction may be due to permeate water flowing through the membrane by direct osmosis during the soaking period. This would help dislodge deposits from the feed side of the membrane allowing the cleaning chemicals to break up any layered deposits. [3]

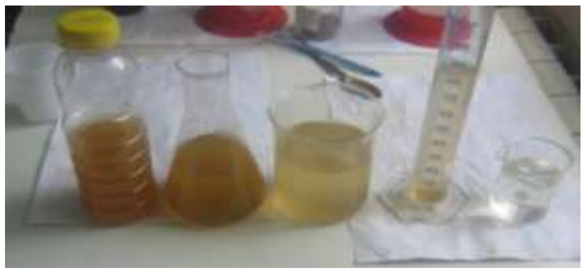

Figure 6. Cleaning solution from alkaline clean

Figure 7. Acid cleaning solution samples

SWRO Plant Autopsy

A very large 22,000GPM (120,000m³/day) sea water RO plant in the Middle East was commissioned in October 2009. A programme of predictive maintenance was a key feature of the operation of this plant. In March 2010 a Hydranautics SWC5 RO lead membrane element from the first stage of the plant was sent for autopsy. There was no indication of any fouling present from operational data but it was felt that an autopsy would identify typical foulants that would ultimately accumulate on the membrane surfaces. A very thin gelatinous deposit was found covering the membrane surface Figure 8. Analysis of the deposit revealed it consisted of 76.9% organic material in the form of protein derivatives relating to bacteria and biofilm formation. An aerobic bacteria count showed a significant number of 7,300 colony forming units per cm². Elemental analysis of the deposit also showed the presence of iron and aluminium-silicate in the form of clay. The membrane samples were charachetrised using simulated sea water with pH 7.2, Conductivity 49,000 µS/cm, and temperature of 25°C. Cleaning tests were conducted on membrane samples measuring improvement in flow rate and salt passage of a variety of cleaning chemistries. It was found that the use of a highly alkaline powder detergent and chelant (cleaner A) showed superior cleaning efficacy when compared with a more traditional programme of biocide (cleaner B) and traditional liquid alkaline cleaner (cleaner C). The use of a warm caustic solution circulated for 2 hours showed a minor improvement in flow rate of only 2.8%. The synergisitic effects of multiple chemistries and cleaning mechanisms in one clening compound are well recognised. [5]

Figure 8: Gelatinous biofilm

Table 1: Summary of flat sheet test rig cleaning results

	Sample	Sodium Hydroxide	Cleaner A	Cleaner B & C
Aerobic count	7,300 CFU/cm²	ND	ND	ND
Flow Rate	35.7 l/m²h	+2.8%	+39.7%	+15.3%
Salt Rejection	99.6%	99.6%	99.7%	99.6%
pH	NA	11.8	11.8	C – 11.8
Temp	NA	38.7°C	38.6°C	C- 38.7°C

SWRO Cleaning Results

After the first autopsy was conducted in March 2010 it was decided that cleaners A, B and C would be available on site to conduct cleaning as soon as there was an early sign of fouling. Differential pressure (DP) was monitored daily and a significant increase of 0.2 bar was observed in rack 21 over a two week period in January 2011. The increase in DP was seen after a leak on the shock chlorination system was fixed. While the pipework was leaking fouling rates were low. It is possible that the resumption of shock chlorination actually created additional nutrients for a proliferation in bacteria activity and subsequent biofilm growth leading to increased fouling rate. Based on the autopsy and cleaning test results it was decided to initially clean rack 21on 20th January 2011 with the traditional cleaning chemicals B & C namely a biocide followed by an alkaline clean. As can be seen from the graph of DP in Figure 9 there was an immediate reduction of 0.14 bar after the clean although the fouling rate remained the same. By 1st March the DP had risen by 0.2 bar. The increase was deemed to be due to microbiological fouling so a biocide clean was conducted. This did not achieve a reduction of DP but did seem to halt fouling for 3 weeks at which point the underlying fouling rate resumed. Three weeks later the DP had risen to 1.46 bar and at this point a biocide flush was followed by a full clean using

Cleaner A the powdered high alkaline, high ionic strength detergent, surfactant and chelant cleaner. The cleaning agent was repeatedly circulated and soaked for 30 minute intervals and flushing conducted with permeate. A much improved cleaning result was achieved with a pressure drop of 0.3 bar as compared with 0.2 bar when using the conventional liquid cleaner. Figure 10 shows pressure drops during a subsequent clean on 2nd July using just cleaner A which shows enhanced results with reduction in DP of 0.54 bar. Significantly a deeper clean seems to have resulted with DP reduced to 1 bar similar to that found during the first three months of plant operation. It must be recognised that this plant was being cleaned as soon as a rise of 0.2 bar DP was observed. Under normal circumstances operators would not start to react until a pressure drop of over 1 bar. Brusilovsky et al comment on the Larnaca SWRO "where the delta P in an 8 element vessel after 4 years operation is 1.1 to 1.2 bar." By reacting early with a predictive cleaning protocol this large SWRO plant has been able to operate within specification despite a challenging sea water source prone to red tide algal blooms.

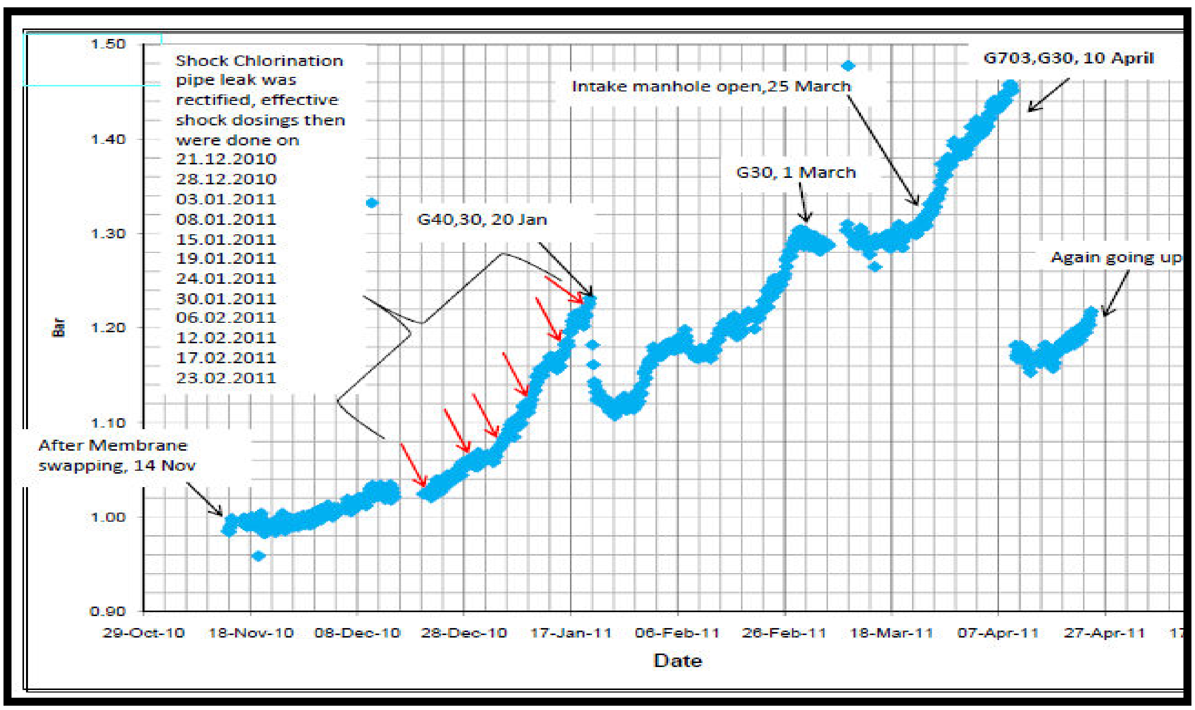

Figure 9. Differential pressure following cleaning Nov 2010 – May 2011

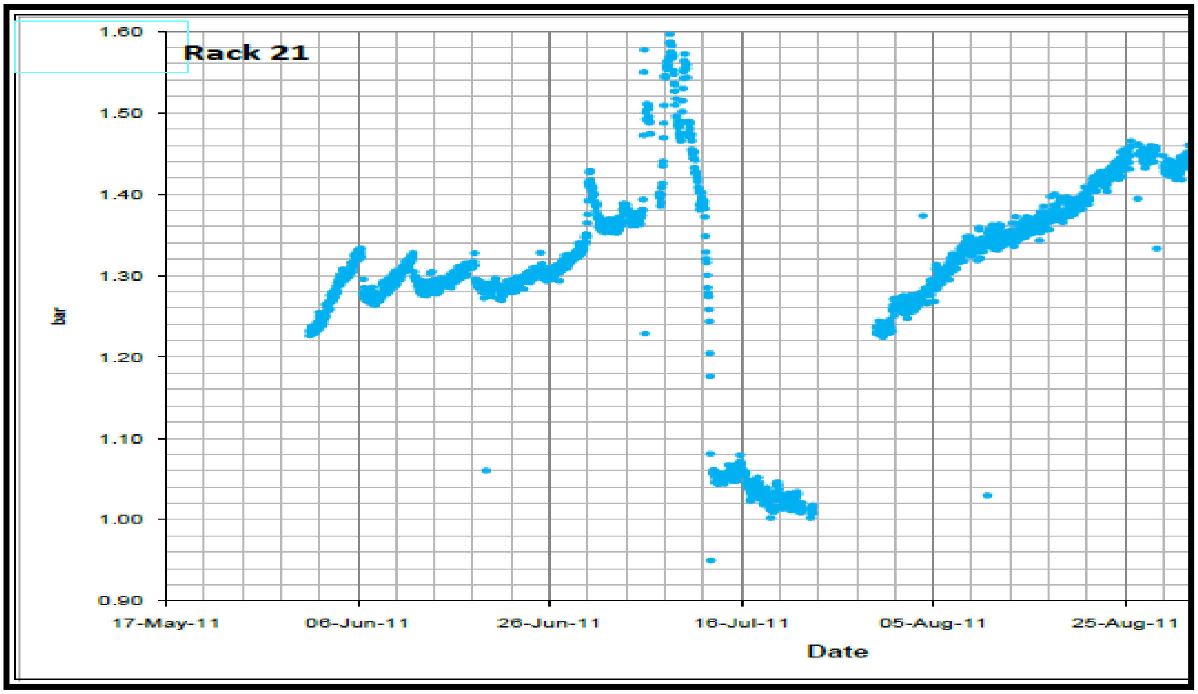

Figure 10. Differential pressure following cleaning May 2011 to Aug 2011

Conclusions

The recommendations by membrane manufacturers on when to clean and what chemistry to use have changed very little in the last 30 years. The authors question the logic in waiting for operating parameters to deteriorate by 10-15% before taking action. Results from a BWRO and SWRO autopsy, cleaning tests and actual site cleans allow the following conclusions to be drawn.

- If membranes are not cleaned early the deposit is very difficult to remove and may require high ionic strength cleaners and periods of extensive soaking to remove biofilm and clay.
- If predictive early cleaning is conducted then deposits are easier to remove and the underlying fouling rate is lower.
- A membrane element autopsy or cartridge filter analysis within 3 months of start up will identify typical and likely membrane foulants.
- Cleaning tests on the foulant enables a predictive cleaning protocol to be produced so the necessary equipment and cleaning reagents can be sourced in advance speeding up the reaction time to the first sign that fouling has taken place.

Predictive maintenance can now be adopted by the membrane cleaning industry to improve the effective and efficient operation of sea and brackish water RO plant.

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