

WHITE PAPER

RO Membrane Cleaning – explaining the science behind the art.

Authors: *Stephen P. Chesters*
Matthew W. Armstrong

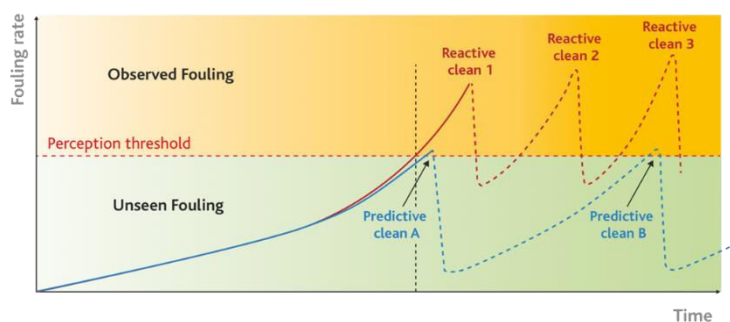
Introduction

Reverse Osmosis membrane cleaning is essential for efficient plant operation and yet there has been very little innovation or development in over 30 years. This paper reviews best practice on reverse osmosis (RO) membrane cleaning. It challenges preconceptions and describes novel approaches for the removal of foulants and scale deposits from membrane surfaces.

Abstract:

Over the last ten years there have been significant developments in new devices for energy recovery, new membrane materials, and new sizes and orientations of reverse osmosis (RO) plants, all designed to reduce costs and improve efficiency. The fundamental issue of keeping membrane surfaces clean to ensure efficient RO plant operation has seen relatively few new ideas. This is surprising as any fouling of the membrane surface will have a dramatic effect on energy consumption and plant efficiency. This paper demystifies RO membrane cleaning which is often described by practitioners as an art as much as a science. The more science that is applied the better results will be. Current best practice is reviewed and practical suggestions are given to improve results: These include:

When to clean – waiting for a 15% loss in performance before cleaning allows deposits to become compressed and difficult to remove. It is advocated that cleaning is conducted as soon as fouling is perceived and deposits are less compacted and easier to remove. A more effective clean results so the underlying fouling rate is slower and frequency of cleaning reduced.



What to clean with – by carrying out simple inspection of filtration and membrane systems indications of the nature of the deposit on the membrane can be established. Inspection should be combined with autopsy and deposit identification from filter media, sacrificial and actual membranes. Different cleaning formulations can be tested in the lab and the most effective used for full scale cleans. The different chemistries commonly used and their effectiveness against different deposits is described.

How to clean – hints and tips on how to apply the cleaning chemistries to maximize cleaning effectiveness are discussed.

Innovations – some new approaches on membrane cleaning including natural osmosis through high ionic strength cleaners and use of effervescent are outlined. Results from a case study using micro-bubbles to enhance deposit removal are presented.



I. INTRODUCTION

Many researchers have focused on identifying and studying the foulants in great detail but there have been few studies in how to remove it. Commodity acid and alkali compounds are still widely used due to the perceived lower application costs. Specialty blended cleaning chemicals incorporating detergents, surfactants and chelants are also in wide use and are increasingly accepted by the market to be economically and environmentally viable. “Strategically pairing chemical agents that have complementary cleaning mechanisms so a higher cleaning efficiency can be attained” has been described by Wui.[1] This white paper outlines current thinking and common practice and attempts to demystify the process of membrane cleaning. The authors set out the benefits of early autopsy and cleaning, explain some key chemistries to remove different deposits, present best practice on carrying out cleaning. The use of recent innovative methods for membrane cleaning is reviewed and a case study presented. New approaches are described and the mechanisms of enhanced cleaning explained. These include use of a cleaning suspension of bubbles, effervescent and high ionic strength cleaners. Enhanced cleaning is observed as a result of agitation of deposits on the membrane surface by different mechanisms which assist foulant removal. Small bubbles are generated during the cleaning process by a combination of different chemical and physical methods. The use of high ionic strength cleaners creates a small flow of permeate across the membrane to the feed side during the soaking period of cleaning. This flow is sufficient to help dislodge foulants on the membrane surface. This simple technique could easily be applied to existing RO plant restoring efficient RO plant operation.

II. WHEN TO CLEAN?

The decision of when to clean is often made when a change in operation is noticed. Either normalized permeate flow or quality has decreased, or the differential pressure across the plant or one of its stages has increased. Membrane manufacturers typically say that when one of these parameters changes by 10-15% membranes should be cleaned.

In addition they advise that “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.” [2] Another membrane manufacturer comments that “Heavy fouling can impair the effectiveness of the cleaning chemical by impeding the penetration of the chemical deep into the foulant and in the flushing of the foulant out of the elements.” [3]. Bearing this advice in mind it therefore important to clean membranes as soon as a change in operation is noticed, but preferable to clean as soon as an increase in relevant measured parameters is identified. Any delay will result in deposits being compacted under pressure on to the membrane surface and the deposit will be more difficult to clean.

An increase in differential pressure across a stage of the RO plant is a clear indication of either:

- a. fouling – on lead elements cause by suspended solids
- b. scaling – on last stage elements where salts exceed their solubility and form mineral scale.

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 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.

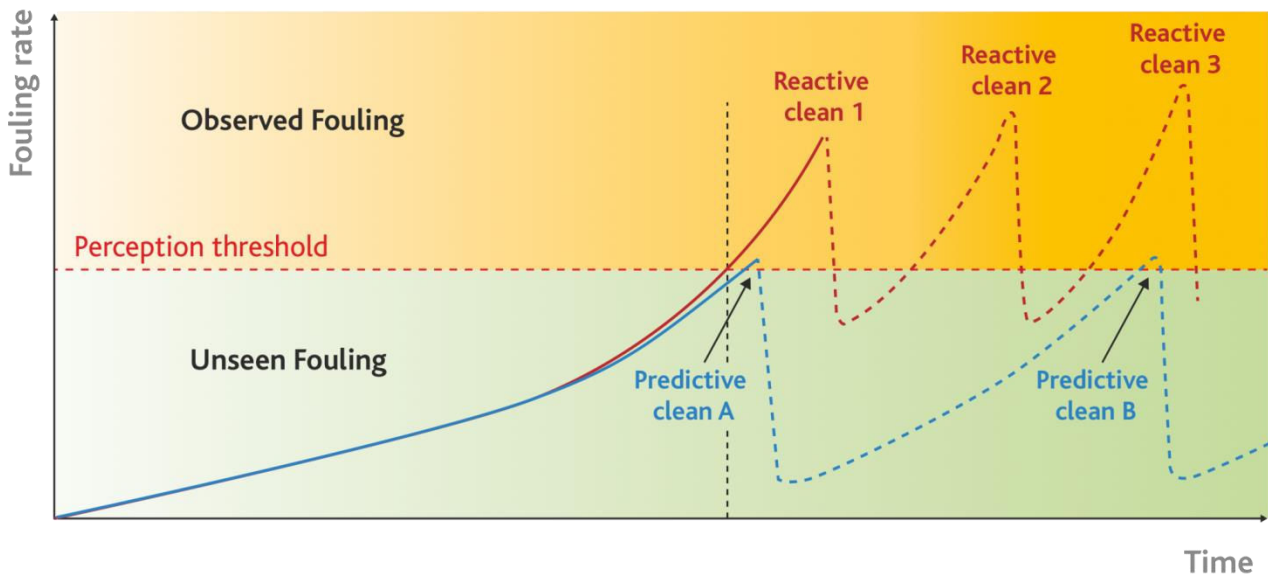


Figure 1. Membrane fouling rate and advantage of Predictive cleaning

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 become thicker and more compressed into the membrane surface and be much more difficult to clean. Predictive 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.

III. INSPECTION

Various methods may be employed to help us to understand the nature of a foulant and to plan the CIP procedure accordingly. Examination of the cartridge filters and inspection of the lead elements gives an indication of the foulants which may be present on the first stage. Suspended solids passing through the pre-treatment and filtration system will deposit here. If deposits are slimy and/or malodorous, then microbiological fouling could be an issue. A red/brown coloration indicates Iron (III) oxide or ferric oxide (hematite) Fe_2O_3 . Clay (aluminosilicates) can be identified as a very fine grey brown deposit. figure 2



Figure 2: Iron fouling feed of a lead element



Figure 3: Calcium sulphate last stage element

It is not uncommon to detect filtration media on the membrane element feed inlet. This could be anthracite or sand from the dual media filter or activated carbon.. If the lead element and cartridge filters appear clean, then the fouling could be as a result of scaling in the end membranes. This is where soluble ions are at their most concentrated and can exceed their solubility, precipitate and form crystalline scale. In this case, the final element(s) from the last stage should be removed and weighed. Visual inspection may reveal deposits such as calcium carbonate which will appear as an off- white powdery chalk deposit, whereas calcium sulphate will be hard and crystalline. Fig.3. The weight of the element compared with a new wet membrane will give an indication to the extent of the problem.

IV. IDENTIFICATION

The excerpts below from membrane manufacturers, confirm that they agree that identification of the deposit on the membrane surface is key to optimum cleaning.

“Each cleaning situation is different; therefore specific cleaning recommendations are dependent on the foulant” [2].

“The appropriate solution to use can be determined by chemical analysis of the fouling material. A detailed examination of the results of the analysis will provide additional clues as to the best method of cleaning” [4].

Different chemistries are required to remove different foulants and scalants. The preferred method of analysis is membrane autopsy which uses various scientific methods to accurately identify the individual types and amounts of foulants present. Different cleaning chemicals are tested against the membrane with characterization of flux and salt rejection (SR) used to establish the most efficient cleaning procedure. Autopsy of cartridge filters and SDI filter papers can identify likely deposits

present on lead elements. A small sacrificial 2” element could also be installed to simulate operating conditions; an autopsy is performed after a suitable time to establish the fouling nature of the main system. Feed water analyses, scaling prediction software and normalized data can all be used to help give clues to the foulant.

V. CLEANING CHEMISTRY

Basic cleaning chemistries are described in the table below and are referenced by membrane manufacturers in their cleaning guides.

Type	Action	Typical Chemical
Acid	Solubilisation	Hydrochloric, nitric, sulphamic, citric
Non Oxidising Biocide	Biocidal	DBNPA, Isothiazolin
Caustic	Hydrolysis, Solubilisation	NaOH,
Chelant	Chelation	EDTA
Detergent	Emulsifying, dispersion, surface conditioning	STPP
Oxidant	Oxidation, disinfectant	Hypochlorite, ozone, hydrogen peroxide
Surfactant	Emulsifying, dispersion, surface conditioning	SDS

The selection of the appropriate cleaning chemicals has a major effect on the success and, most importantly, frequency of the CIP procedure. Many different chemical formulations are commercially available. The choice of which to use is often made on cost/kg of the individual product, although in reality the cost of any effective product in terms of operational costs of a fouled system is extremely low, and pay-back will be quickly achieved. When selecting a suitable chemical it is therefore of greater importance to consider different evaluation criteria; application rates, performance of the individual products against your specific foulants (availability of documented scientific evidence) and onsite technical support. Overall evaluation of the success of a cleaning chemical should be performed over a longer period to give an indication of the change in required cleaning frequency of the RO system. Experience shows that employing a successful cleaning regime can reduce required cleaning frequency by several times per annum. Many researchers have shown that the use of speciality formulated cleaners combining different chemistries incorporating detergents, chelants and surfactants have an enhanced cleaning effect on membranes when compared to the use of commodity acids and alkalis.[1] Commodities also tend to have transition metal impurities which can damage the membranes and leave them prone to subsequent catalysed oxidation reactions. Membrane manufacturers’ recommendations must always be followed.

VI. CHEMICAL APPLICATION

Foulant identification and chemical selection are vital. Since all cleaning situations and RO systems are different, it is not possible to produce a generic cleaning procedure for all membrane plants. All of the factors below must also be considered when designing a suitable cleaning procedure:

- a. Temperature is vital for removal of organic foulants, generally 35-40°C is acceptable. For removing inorganic scales, temperature of the CIP water may affect solubility and therefore removal. Lower temperatures are generally required.
- b. Contact time is also vital; in a highly fouled system, cleaning cycle times should be maximized to ensure efficient removal. Speciality chemicals will reduce the time required for cleaning. Sufficient time for optimum cleaning must be allowed, with additional cycles added if necessary, by emptying and refilling with the same chemical.

- c. pH is important for removal of both MAIN groups – organic based foulants and scales. Monitoring pH changes during the CIP will help to evaluate success.
- d. RO permeate should be used to prepare CIP solutions and to flush the system between application of different chemicals.
- e. Pressures and flow rates can be altered in line with membrane manufacturers’ guidelines to help remove foulants physically.
- f. The system should be thoroughly flushed after the CIP procedure to ensure traces of CIP chemicals are removed before returning to service.

VII. FUTURE INNOVATIONS

The use of products formulated with multiple cleaning mechanisms offers enhanced cleaning performance. Conducting an effective clean rather than multiple partial cleans is a gentler and more efficient process to help extend membrane lifespan and reduce operational costs. New cleaners have recently been developed incorporating effervescent chemistries. It is claimed that the bubbles generated agitate deposits at the membrane surface which assists their removal. On-line cleaning methods have been developed using a concentrated salt solution which passes quickly (10secs) across the membrane element causing direct osmosis of permeate to the feed thus lifting deposits from the membrane surface. There are powder high ionic strength cleaners which, when used during an off-line clean, cause normal osmosis to occur during periods of soaking; permeate water passes through the membrane surface to the feed side breaking up layered deposits. This allows the cleaning chemicals improved penetration to dislodge deposits. These powdered products have proven particularly effective against clay, biofilm and organic removal which make up 85% of the foulants in lead elements. The next generation of membrane cleaning could include use of generated microbubbles which will cause further agitation of deposits at the membrane surface. The bubbles can be introduced using a specially designed microbubble generator. If a pump forces a fluid flowing into the microbubble generator tube an increase in velocity occurs in the constricted part simultaneously with the decrease in pressure which leads to air being sucked in through the tube. Pressure recovery takes place further downstream and the air bubbles drawn in collapse forming bubbles which then have a tendency to coalesce into larger bubbles around the microbubble generator. In order to optimize cleaning it is preferable to have micro and macro bubbles. This can be achieved using specially formulated cleaning agents which minimize the coalescing of micro, mini and midi bubbles into larger bubbles. The cleaning reagents create a suspension of bubbles and cleaning solution which distribute evenly over the membrane surface in a pulsed fashion. Figure 4 shows the large range of bubble size achieved in the feed spacer of a fouled membrane.

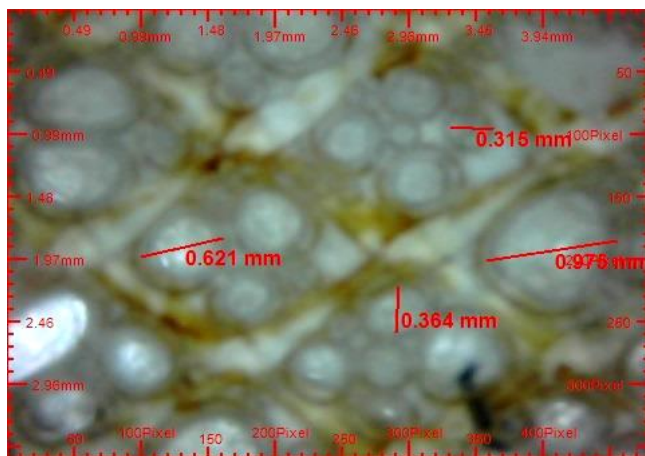


Figure 4: Macro and microbubbles in feed spacer of a membrane element

VIII. CASE STUDY

An RO plant having a history of rapid and consistent fouling was chosen to trial the new microbubble multi-mechanism RO membrane cleaning approach. The site is a major salads producer in the UK. The salad wash water is recycled and contains bacteria, soil and clay. All the factory process water is also recycled and is contaminated with bacteria and detergents and cleaners used in the wash-down and factory cleaning in place systems. The wastewater treatment and reuse plant incorporates an advanced membrane bioreactor ultra-filtration and RO plant to treat and purify the water for reuse and discharge.

System description – The treatment plant is based on pre-treatment and aerated flow balancing followed by an advanced membrane bioreactor (AMBR), reverse osmosis (RO) and ultraviolet (UV) disinfection. (Figure 5) A total of 1,400 m³/day of waste water to be treated can be produced by the factory all of which is pumped to the AMBR. After RO and UV disinfection up to 450m³/day of treated water is fed to the incoming mains water tank for blending prior to entering the factory for salad washing and process water.

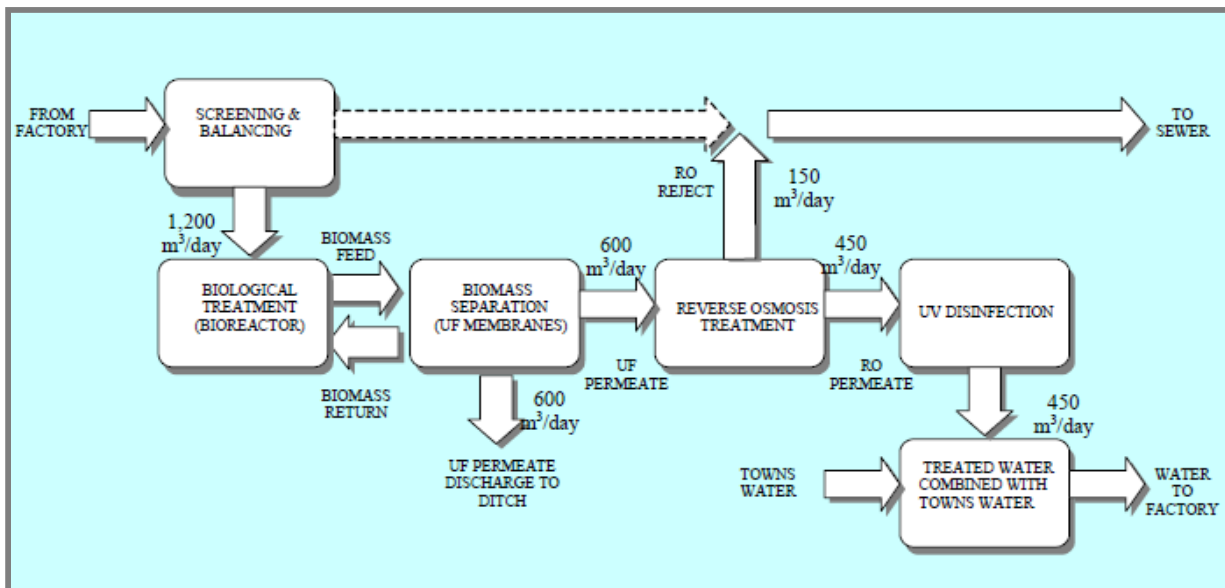


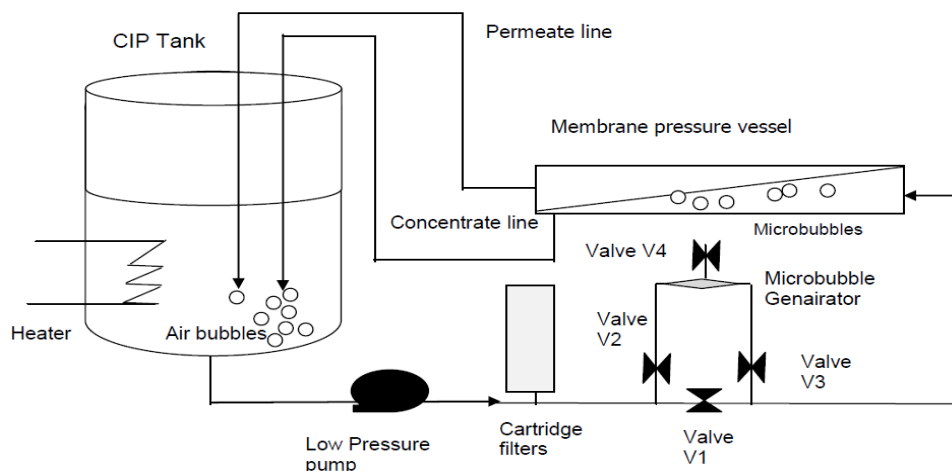
Figure 5: process flow diagram

The plant treats an influent COD total to the balancing tank of up to 480kg/day depending on factory production. In order to effectively separate biomass three banks of ultra-filtration modules are used fed by a recirculation system from a single bioreactor tank. An intensive aerobic environment is created in the AMBR using a JETOX aeration system allowing a high quality final effluent to be achieved in a small footprint.

System operation – The RO plant was commissioned in 2004 and has been prone to fouling under periods of peak production. The results of autopsies on membrane elements and cartridge filters indicated that foulant is mainly organic and microbiological in origin. There is also aluminium silicate present as clay and soil from the salad washing process and calcium phosphate deposits. In 2006 there were three incidences of the plant tripping out on high pressure due to calcium phosphate scale formation. Membrane cleaning was conducted using a biocide followed by conventional formulated acid and alkaline cleaners. Cleaning was conducted every 7-14 days for seven years and membrane elements

were replaced every 18-24 months. In 2013 two new acid and alkali effervescent cleaning products A & B with high ionic strength were introduced. From October 2013 only the new alkaline cleaner B plus inducted air to create microbubbles was used.

Methodology - In order to further enhance the cleaning effect, speed up the process and increase the periods between cleans an air induction device was installed which in combination with the cleaning product B produces a suspension of very small mini, midi and microbubbles between 5 and 500µm in size. The microbubble generator device is installed on a bypass loop of the CIP system after the recirculating pump and cartridge filters on the inlet to the pressure vessels as shown in Figure 6. Initially a similar cleaning procedure was followed to that described above but the timescales for recirculation and soaking were reduced substantially following findings in the laboratory and on our test plant. The procedure has been fine tuned to a 20 minute warm water flush, 20 min recirculation of 1% cleaning solution warmed to 35-40°C followed by a 20 min soaking period during which permeate flows back across the membrane due to normal osmosis lifting deposits from the feed side membrane surface. The microbubble generator is then put on line by partially opening valves 2,3 and 4 and partially opening valve 1. The cleaning solution is then circulated for 20 minutes with microbubbles to dislodge the cake layer on the membrane surface. The recirculation, soaking and microbubble stages are repeated twice maintaining the cleaning solution temperature at 35- 40 °C and pH between 11.5 and 12.0 followed by flushing with permeate. This procedure is carried out using alkaline Cleaner B only and the whole cleaning process now only takes 2 hours and 40 minutes.



Key
 Valve V1 = Valve in CIP line
 Valve V2 = Bypass valve for inlet to Microbubble Genairator
 Valve V3 = Bypass valve for outlet from Microbubble Genairator
 Valve V4 = Air control valve for Microbubble Genairator

Figure 6: Installation schematic for the CIP microbubble generator

Results – The graph in Figure 7 shows the reduction in normalised differential pressure on stage 1 of the RO plant. From January 2013 to 1st June 2013 conventional cleans were carried out. Permeate production and normalised differential pressure (ndP) was temporarily restored but rapid refouling occurred. Cleans were conducted every 10.5 days on average over this period. On the second of March all 30 of the membrane elements in five pressure vessels were replaced. The ndP was initially recorded at 1.5 bar but rose rapidly to 2.5 bar the next day and then to over 4 bar on the 22nd March when a clean was conducted. The clean was not very successful as the plant had not been cleaned for 20 days so cleans were repeated on the 26th March and 31st March. Regular 10 days cleans were reinstated but after

only 3 months the ndP was above 4 bar so it was decided to install a new set of membrane elements and change the cleaning reagent to Cleaner A & B. The first clean was conducted 7 days after installation and because ndP was low the period between cleans was extended to 13 days. After one month of operation with new membranes the ndP had increased but stabilised at 2.5 bar using cleaners A & B with additional effervescent and high ionic strength. This was a significant improvement on using the conventional cleaners, however fouling was still rapid and cleans conducted every 11-13 days. On the 3rd October the air induction combined with Cleaner B to produce microbubbles was started. After 3 cleans a significant improvement in ndP was observed with a cleaning frequency of 12.5 days on average. After three months and six cleans the ndP had been reduced from 4.5 bar at the beginning of the year to consistently less than 1 bar on the first stage and on the whole plant. From January to April 2014 the frequency of cleans has been extended from every 10.5 days to 31.6 days and latterly the period between cleans has increased to over 50 days. The reason for the sudden increases in dP is thought to be due to the presence of biofilm and clay which was only partially removed using conventional cleaners. Cleaners A & B worked more effectively getting the membrane surface cleaner. When inducted air and cleaner B to create microbubbles were used the membranes were significantly cleaner, reducing surface roughness and hence the underlying fouling rate is much slower. Furthermore it is thought that biofilm removal and disruption will significantly reduce the surviving microbial population which will not then replicate at the same rate despite the on-going nutrient source. The initial results are very encouraging showing a distinct improvement in the ability to clean these rapidly fouling membranes in a significantly shorter timescale. No loss of salt rejection has been detected and permeate flow has improved from 15m³/hr at the beginning of 2013 to 24 m³/hr from Jan to April 2014.

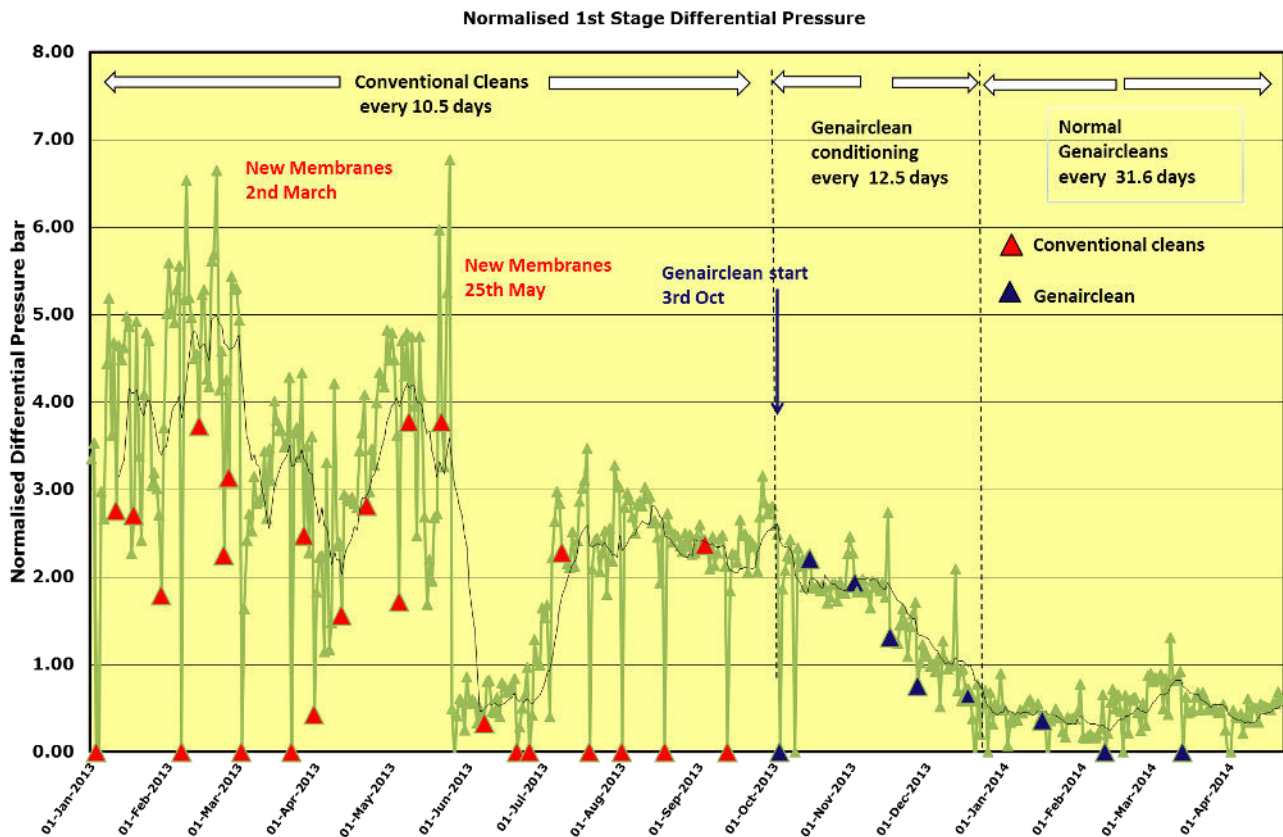


Figure 7: Graph of normalised differential pressure over time using different cleaning methods.

IX. CONCLUSIONS

Applying science to identifying the membrane foulant, cleaning membranes early and using effective chemistries are simple techniques to improve membrane cleaning. Innovative advances in membrane cleaning need to focus on a reduction of environmental impact and minimization of potential membrane damage, both by using gentler “greener” chemicals and by applying physico-chemical techniques. Using high ionic strength cleaners to create permeate flow across the membrane during periods of soaking helps dislodge layered deposits of clay and biofilm. There are encouraging results that the creation of micro-bubbles using air induction and specially formulated cleaning chemicals helps dislodge clay and biofilm foulants in the front elements of a membrane plant without damaging the polyamide layer. Incorporating multiple cleaning mechanisms increases the chances of removing mixed deposits from membrane surfaces.

References

- [1] Wui Seng Ang, Ngai Yin Yip, Alberto Tiraferri, Menachem Elimelech. Chemical cleaning of RO membranes fouled by wastewater effluent: Achieving higher efficiency with dual-step cleaning. *Journal of Membrane Science* 382 (2011) 100– 106
- [2] Page 122 Technical Manual The Dow Chemical Company ("Dow") Form No. 609-00071-0808
- [3] Page 2 Hydraulics Technical Service Bulletin October 2011 TSB107.21
- [4] Page 4 Hydraulics Technical Service Bulletin July 2009 TSB102.06