

METHODS FOR ENHANCED CLEANING OF FOULED RO ELEMENTS

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Abstract

Reverse Osmosis (RO) membranes have been successfully used on a variety of applications from well waters, to surface waters, to wastewaters. One of the chief concerns in the application of the membranes is fouling. This is still the primary reason for poor plant performance, and can lead to shortages of product water from the plant. Proper pretreatment design and operation are still the most effective ways to minimize fouling of the membranes. In many cases, however, fouling is not controlled and can lead to serious plant problems and shorter membrane life. In such cases, more aggressive approaches to cleaning the membranes is required to recover as much of the membrane performance as possible.

This paper reviews limitations of cleaning membranes and looks at a few more aggressive ways to clean membranes without prematurely damaging the membranes. Firstly, it is important to analyze and understand the type of fouling that is occurring. By doing this, it is possible to better target the best cleaning strategy. For cases where fouling is due primarily to organic material, it is best to use high pH cleaners. A laboratory study showed that at pH 13 and one month of exposure, the membrane rejection was unchanged, while the membrane strength greatly decreased. This shows that RO membranes lose performance at very high pH due to limitations of the polyester support degrading at these conditions.

A case study was presented where generic cleaners were used at aggressive conditions to recover much of the lost performance of an element that was heavily fouled while treating surface lake water. This study showed that very high pH cleaning was needed before the performance started to recover. Also, it showed that low pH cleaning was key to quickly returning the rejection to expected levels.

If the fouling is primarily on the front part of the system, the user may also consider reverse flushing/cleaning. This is a practice where the chemical or flush liquid is circulated in a direction opposite to the normal flow of feedwater. This is shown in a real plant experience, where this method was found to be more effective than using cleaning chemicals in a normal flow direction.



I. INTRODUCTION

The treatment of wastewaters and surface waters by reverse osmosis (RO) is often complicated by fouling that is common with these difficult waters. The fouling can consist of fine colloidal particles, bacteria, biofilm, dissolved organic matter and inorganic precipitates. In most cases, the fouling has resulted from inadequate pretreatment or variable water quality. Many papers have been published which give useful guidelines to properly design pretreatment to minimize these problems, and these are followed with successful results. In other cases, fouling is uncontrolled and causes excessive downtime, higher operating costs, and poor membrane performance. When fouling is experienced, there are many reports and guidelines in literature to effectively restore membrane performance. This can consist of the use of generic chemicals and proprietary chemicals, depending on the nature of the foulant and the user's approach.

Whenever cleanings are done, it is important to follow the cleaning restrictions specified by the membrane supplier. This ensures the longest life of the product. Due to recent advances in membrane technology it is possible to be more aggressive in cleaning the membranes, without damaging the membranes themselves. This paper will look at the materials of construction in the RO element and discuss what can damage the individual components.

II. TYPICAL CLEANING GUIDELINES AND PRACTICES

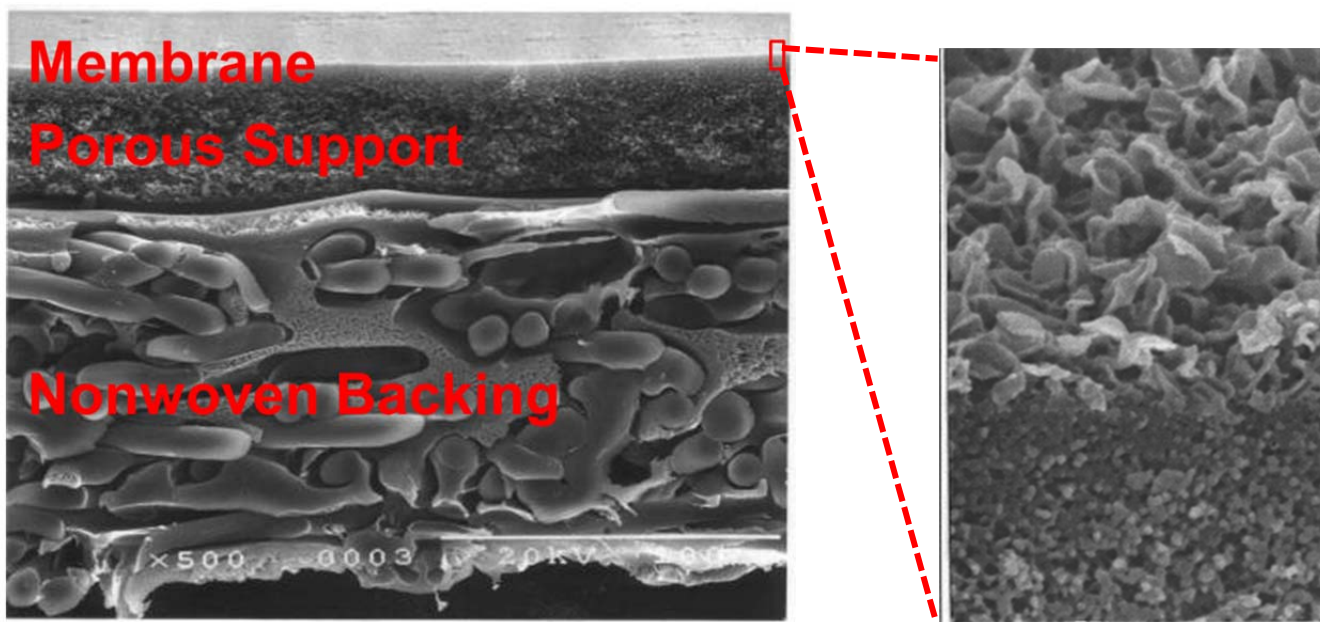
RO membranes are generally cleaned separately at low and high pH, depending on the type of foulant on the membrane. Scale minerals, and inorganic colloidal material are best removed by low pH cleaners, while organics and biofouling are best removed by high pH cleaners. Biocides are used to minimize and control the growth of bacteria and resulting biofilms. Typical composite polyamide membranes in a spiral element configuration are quite resistant to acid cleaners, but are more susceptible to damage by high pH. This is reflected in the upper limitations of pH allowed by the membrane companies. The allowed range is usually around pH 10-12, while low pH cleaning can be done at pH as low as 2. This allowed high pH exposure also depends on the temperature, since chemical reactions with the membrane materials are accelerated at higher temperatures. The chemical limitation for membranes and elements depends on the various materials used in the membrane or element. This is explained in more detail below.

II. CHEMICAL LIMITATIONS AND CLEANERS FOR POLYAMIDE MEMBRANES

The standard membrane used in the industry is a composite polyamide membrane. It is made up of a three layer structure as shown in Figure 1. The top layer, which is not clearly distinguishable, is the polyamide membrane which is very thin, less than 200 nm. It is composed of the reaction product of m-phenylene diamine and tri mesoyl chloride. Although this is a very durable chemical structure, oxidants can especially cause damage to this material. This will of course limit one of the most common cleaners for organic foulants. One of the chief concerns is the effect of free chlorine [1], which can lead to chlorination of the aromatic ring and greatly reduce rejection (Formula 1). Thus, use of halogen-based oxidants such as chlorine, chlorine dioxide, and bromine are not allowed. Likewise, strong oxidants such as ozone and peroxides are also not allowed, as these can attack the amide bond as well. A recent investigation also pointed to the dangers of excess sodium bisulfite (SBS) at elevated pH and with the presence of transition metals. A recent study [2] showed that increased salt passage of polyamide

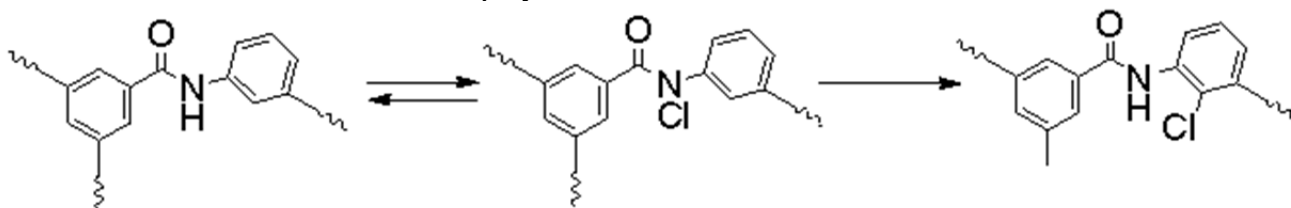
membranes could be correlated with this effect, and is likely due to the formation of hydroxyl radical. In summary, this layer limits the use of oxidants to clean membranes.

Figure 1 Structure of a composite polyamide membrane



The one exception which has been proven successful is the use of chloramines, particularly for wastewaters. Most wastewater RO plants run with 2-4 ppm of chloramines and can achieve 5 years or more of stable membrane performance. It is well-proven that continuous dosing of chloramines prevents biofouling of the membranes. [3] There have been some cases of chloramines oxidizing PA membranes, but this seems to be rare and related to certain catalyst components being present. [5]. While chloramination works well to control biofouling in most wastewater and many surface brackish water applications, it has been shown to have detrimental effects on the RO membranes for seawater applications due to the formation of bromide compounds that rapidly oxidize the membrane. It has been shown in literature [4], that chloramines can be formed in seawater, but that bromide ion in the seawater will react with the chloramine to form bromochloramine or bromamine, both of which are more aggressive oxidants than chloramine. This bromine oxidant has been shown to rapidly oxidize membranes. There is research underway to evaluate ways to preform chloramines to minimize this effect, but results have not yet been published.

Formula 1 Reaction of chlorine with polyamide material



It should also be noted that although the polyamide chemistry is stable toward high pH caustic solutions, some lower cross-linked polyamide membranes may be more susceptible to loss of rejection due to

caustic exposure. It is thought that this results from the dissolution of oligomeric materials which are filling or plugging the larger pores of these less cross-linked polyamide layers. Once the material is removed from these large voids in the PA film, there can be a great increase of salt passage.

The second or middle layer of a composite PA membrane (Figure 1) is typically polysulfone in an asymmetric UF porous structure. The formula for this layer is shown in Formula 2. This material is known to be stable against many chemicals (some alkanes and simple alcohols), and particularly stable for low and high pH solutions and oxidants. However, this material can be attacked by aromatics, ketones, esters, ethers and halogenated compounds. These should always be strictly avoided in the use of membrane cleaners. Thus, the chemical properties of this layer limit the use of most chemical solvents for the cleaning of RO membranes.

Formula 2 Polysulfone formula used in as the intermediate layer of the composite membrane

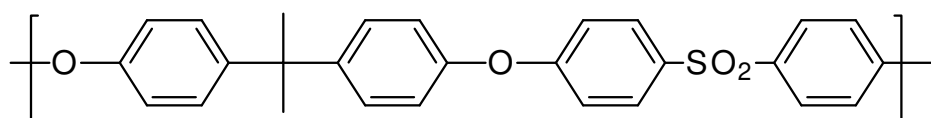


Table 1 Partial list of chemicals which can affect polysulfone porous materials

| Reagent | Effect on Polysulfone |
|-------------------------|-----------------------|
| n-Butane | G |
| Benzene/Toluene | SA |
| Ethanol | G |
| Methyl Ethyl Ketone | SA |
| Ethyl Acetate | SA |
| Methylene Chloride | SA |
| Dimethyl Formamide | SA |
| Hydrochloric Acid (20%) | E |
| Sodium Hydroxide (10%) | E |
| Hydrogen Peroxide | E |

E = Excellent / No Change

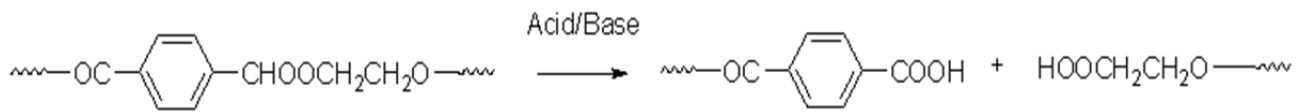
G = Good / Minor Attack, No Serious Loss of Properties

F = Fair / Some Attack, Some Useful Properties Retained

SA = Severe Attack or Rupture

The final layer and thickest layer is the non-woven support (Figure 1). This layer is responsible to impart physical strength to the separating layer and porous support. It is typically composed of polyester material as shown in Formula 3. This material is stable toward a variety of organic chemicals and against oxidants. However, it is susceptible to hydrolysis, or de-polymerization, when exposed to pH extremes. This causes the polymer to react to go back to the original acid and alcohol from which it was made. Naturally, this will result in a rapid loss of strength, and therefore, this material limits the pH extremes that can be used to clean membranes.

Formula 3 Polyester non-woven support and the hydrolysis reaction



2.1. High pH Laboratory Exposure Studies

Organic fouling and biofouling seem to be the most common types of foulant seen on RO membranes. These materials are most effectively cleaned by high pH cleaners which can saponify the organics (turn them into soaps) or kill the bacteria. A laboratory study was done to determine the effects that long term caustic exposure can have on membrane performance and strength.

The composite PA membrane (CPA5) was soaked in high pH NaOH solution for 1 day or for 1 month at 35 C. At the end of the soak period, the membranes were removed from the chemical solution and rinsed with distilled water so they could be salt tested. This test was done with 1500 mg/l NaCl, 225 psi pressure, at 25 C. The results are shown in Figure 2.

The salt rejection of the membrane was virtually the same, whether soaked at pH 7, 11, or 13. However, the samples soaked at these conditions, but then subjected to a mechanical elongation test, showed a much different result. At pH 7 and 11, the mechanical strength for 1 day and 1 month of soaking was unaffected. The sample soaked at pH 13 showed a slight loss of strength at 1 day of soaking, but as much as 40% loss in strength for a 1 month soak. Analysis of these results reveals the cause of the membrane failure. It is apparent that the high pH cleaner did not affect the polyamide layer, since the separation characteristic was not affected. However, the loss in mechanical strength indicates that the fabric backing is being damaged. Thus, as stated above the limit of long-term caustic exposure is limited by the polyester backing, which is common to most all RO membranes.

2.2. High And Low pH Cleaning Of Fouled Elements

With the understanding of these limits, it is possible to clean RO membranes with high pH chemicals. However, users should check on the pH limit for their particular membranes.

To further understand the effects of cleaning at high and low pH, we performed a cleaning study on a fouled element returned from a RO system that was treating surface lake water. The system had extensive pretreatment, but due to the high level of organics present in the water and the warm temperatures (in summer), it was believed that there was extensive biofouling of the membrane.

Elements were returned for cleaning studies to determine how aggressively the membranes could be cleaned, without damaging the membrane. The element was cleaned at 30 gpm feed flow and 40 psi feed pressure. The cleaning solution was adjusted to pH 13 with surfactants including sodium tripolyphosphate and sodium dodecylbenzene sulfonate at 40C. After treating the element with cleaning solution, the element was retested at 1500 mg/l NaCl, 225 psi, 25 C, and 15% recovery.

Figure 2A Effect of high pH soak on membrane rejection

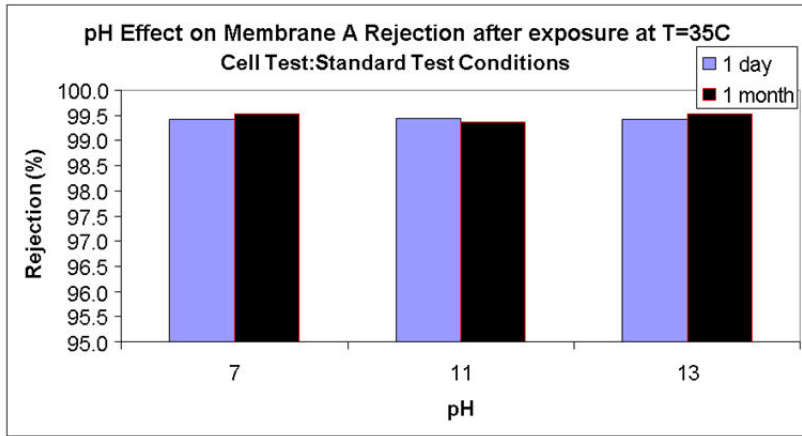
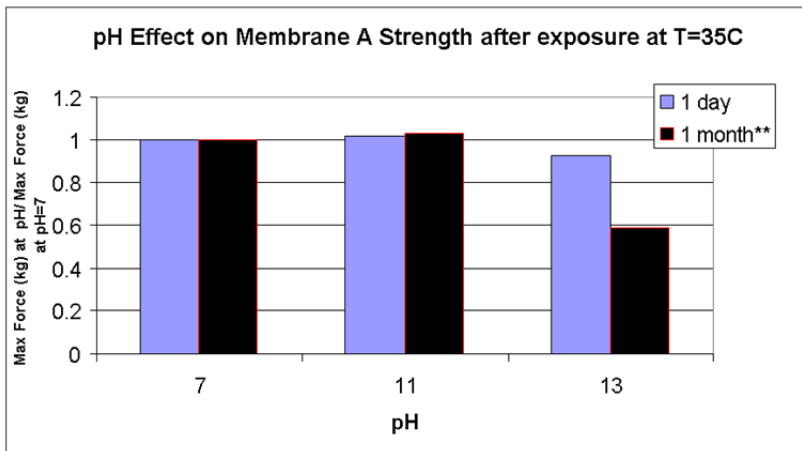


Figure 2B Effect of high pH on membrane strength



The results in Table 2 show that the “as-received” element had lost approximately 50% of its flow at standard test conditions. After the high pH cleaning, there was a substantial recovery of flow for the element. The flow increased 52%, from 5584 gpd to 8496 gpd. However, the salt passage was only moderately improved, going from 1.44 to 1.39%. It is known in the industry that polyamide membranes can be temporarily swollen by high pH solutions, but that extended rinsing will reverse this and recover some rejection. To speed this process, we elected to clean the membrane with a low pH cleaner. 2% citric acid (pH 2.17) at 40 C was used for this. The effect is shown in Table 2. The flow of the element was virtually unchanged, but the salt passage decreased by 55%, going to 0.63%. We conclude from this study that we can successfully clean the RO membranes at higher pH to enhance the effectiveness of the cleaning. Again, it is important that users operate within the temperature and pH range listed by the membrane supplier, but if the fouling is more advanced, it would be best to use a more aggressive cleaning approach than to allow the element to undergo mechanical damage that can be caused by excessive fouling.

Table 2 Cleaning of a fouled element from a surface water BWRO plant.

| Element | As Received Flow (gpd) & dP (psi) | As Received Rej (%) | After Clean Flow (% Change) | After Clean Salt Pass (% Change) |
|------------------------|-----------------------------------|---------------------|-----------------------------|----------------------------------|
| CPA5 LD | 5584 / 8.9 | 98.56 | | |
| CPA5 LD High pH Clean* | 8496 / 9.4 | 98.61 | +52% | -11% |
| CPA5 LD Low pH Clean^ | 8457 / 6.9 | 99.37 | -0.5% | -55% |

***High pH Cleaning Solution**

STPP 2%
(sodium tripolyphosphate)
Na-DDBS 0.025%
(Na-dodecylbenzene sulfonate)
pH 13
40C
1 Hour

Low pH Cleaning Solution

Citric Acid 2%
pH 2.17

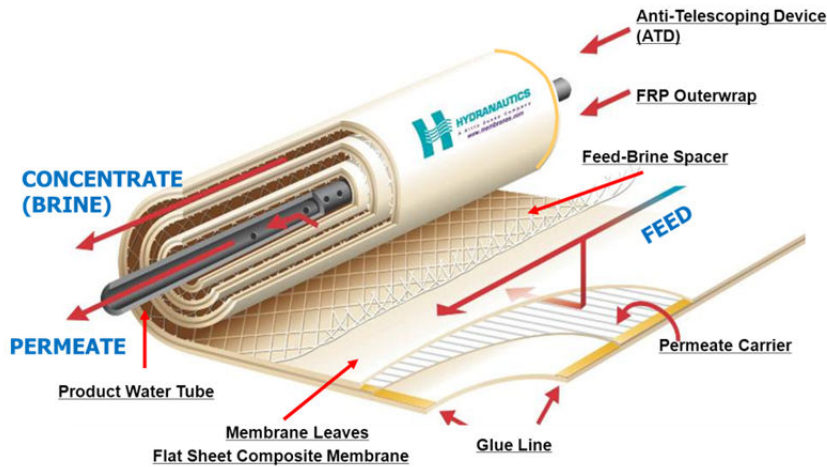
40C
1 Hour

For applications which are thought to be highly fouling, the user should select membranes with the highest pH tolerance for cleaning. If fouling is heavy, and particularly when the differential pressure is going up rapidly, the user should use the highest allowed generic cleaning pH to keep the element as clean as possible and prevent migration of the feed spacer. This will be discussed more later in the paper. Some new lower pH proprietary cleaning solutions have come onto the market which claim that they can keep the membrane and spacer cleaned as good or better than using high pH caustic solutions. As the lower pH would degrade the polyester less, it would be good to use such chemicals if the cost differential is off-set by the longer membrane life.

III. ELEMENT CLEANING

As with the membrane, the materials used in making the spiral wound element can have an effect on the limits of the cleaning, and the design of the materials can affect the fouling rate. Figure 3 shows the general construction of the spiral wound element. The material limits of the spiral are generally consistent with the membrane. For example the brine/feed spacer is made of polypropylene which is dissolved by high concentrations of aromatic solvents, like benzene. The permeate spacer is usually made of a bicomponent polyester material or a mono-component polyester which is then coated with epoxy to provide stiffness. These are chemically stable, but again, the polyesters can be readily damaged by high pH exposure, just like the membrane support fabric. The leaf adhesives are usually polyurethanes. These can be damaged at extremely high/low pH when the temperature is high. A variety of materials can be used in the product water tube. The most common is ABS, which is stable to a wide variety of chemicals and is rarely a limiting factor for chemical cleaning selection.

Figure 3 Spiral wound element construction



The plugging of the brine spacer is usually the biggest issue with the spiral wound element regarding cleaning. Many plants observe an increase in the differential pressure across the membrane vessel. This is due to plugging and if not corrected, can lead to migration of the spacer which can physically damage the membrane surface.

Figure 4 Fouled feedspacer from used element



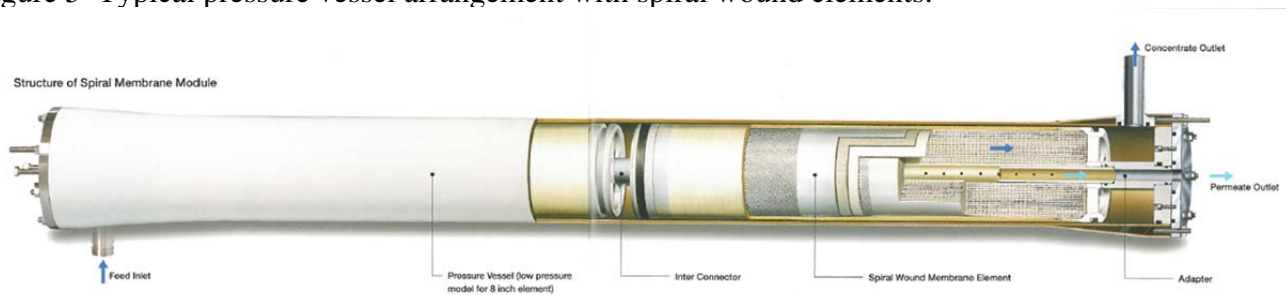
The fouling or plugging of this spacer can be extensive, especially when there is excessive biofouling or scaling. An example of biofouled feed spacer is shown in Figure 4. When this occurs, there is generally channeling in the foulant, which allows feed to pass to the brine side of the element through small channels. Due to the restricted size of these channels, there is a resultant, higher pressure drop for the

feed to pass through the element. These channels can be clearly seen in the spacer of Figure 4. This picture also demonstrates that the plugging of the feed spacer usually occurs at the feed side of the element, and we find it is most extensive in the first element of the vessel. Because of the increased differential pressure and greater forces on the spacer, it is possible that the spacer will start to push out the brine side of the element, and the leaves may start to telescope. This causes damage to the membrane material, and should be avoided.

IV. REVERSE CLEANING/FLUSHING

Another cleaning method which has been considered in some cases, but rarely applied is reverse cleaning. In most plants, the cleaning solution is piped to the RO train in the same direction as the feedwater. In this approach, the cleaning solution flows from the feed side of the pressure vessel to the brine side of the pressure vessel. Most RO systems are designed hydraulically for this, by the placement of the thrust ring on the downstream side of the vessel. This provides support to the outer diameter of a spiral element, to prevent telescoping of the element, in the case that there is high dP in the stage. If the cleaning solution is run in the opposite direction (brine side of the vessel to the feed side), there is no thrust ring to support the outer diameter of the element. This aspect and the need for special piping, need to be carefully reviewed before the application of reverse cleaning/flushing.

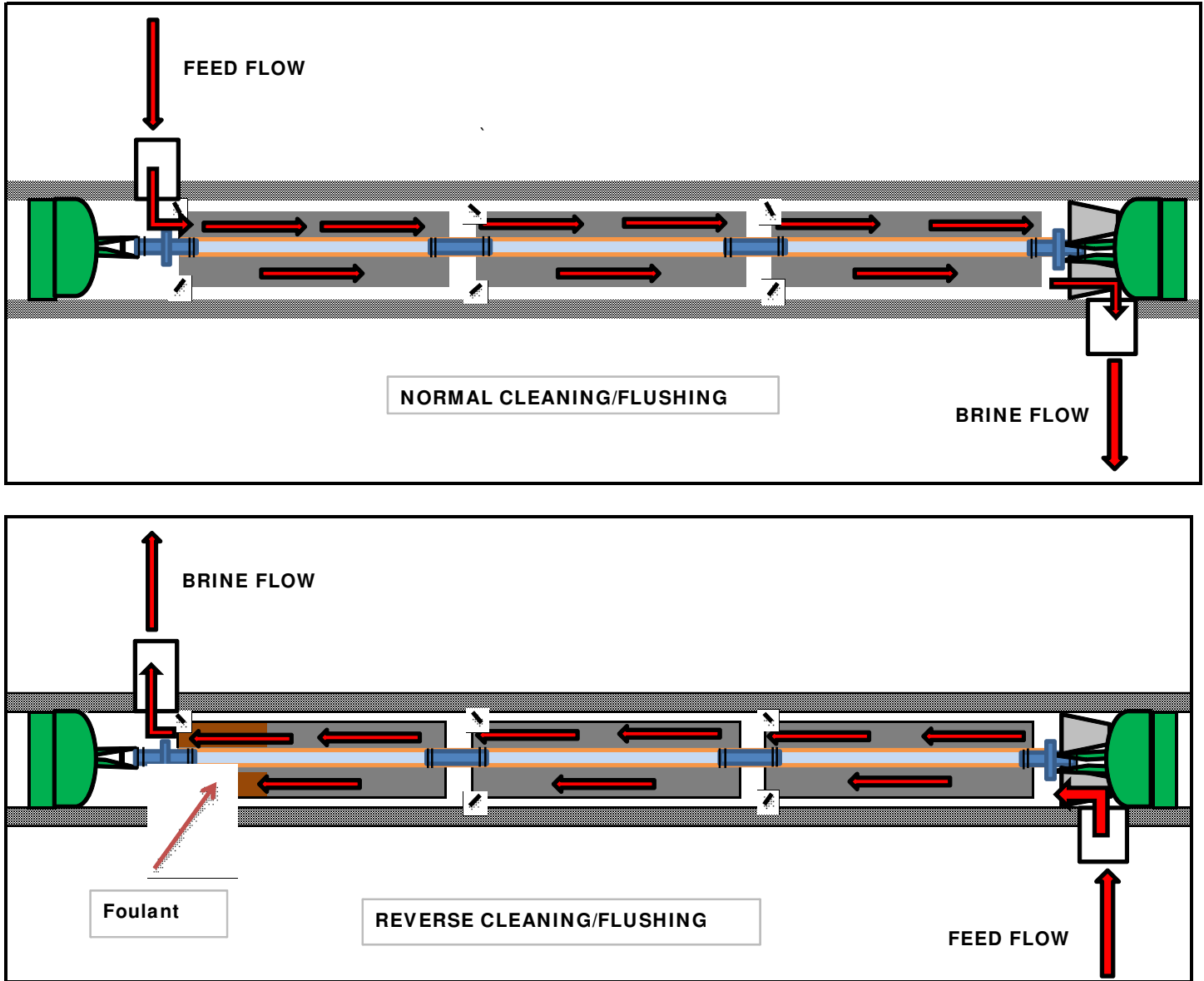
Figure 5 Typical pressure vessel arrangement with spiral wound elements.



The advantage of reverse cleaning is that certain types of foulants concentrate on the feed end of the lead membrane, as shown in Figure 4. Biological foulants, particulates, and colloidal matter are examples of foulants that usually are present on the lead end of the feed membrane. Normal cleaning must break up these foulants and push the foulant through all of the other membranes in the pressure vessel to exit out the brine side. With reverse cleaning, it becomes more of a physical process of “pushing” the foulant out through the feed end, the shortest path length to leave the element.

In the early days of RO when hoses and spools were used for cleaning systems, it was simply a matter of changing the feed and reject connections of the CIP (Clean-in-Place) skid. Nowadays, many cleaning systems are hard-piped into the RO system, without the ability to change the direction of the cleaning. Therefore, it is much easier (and cheaper) to design the RO system with ability to reverse clean before being built. For plants that do not have the ability to reverse clean, one option is to remove the lead membranes from the RO system and turn them around (while putting the brine seal on the other end of the element) and load the membranes into the tail end of the RO system. When you operate the RO system, any accumulated foulant (which is now at the tail end of the RO system) will more readily be flushed out of the element.

Figure 6 – Diagrams showing normal cleaning flow path and reverse cleaning flow path



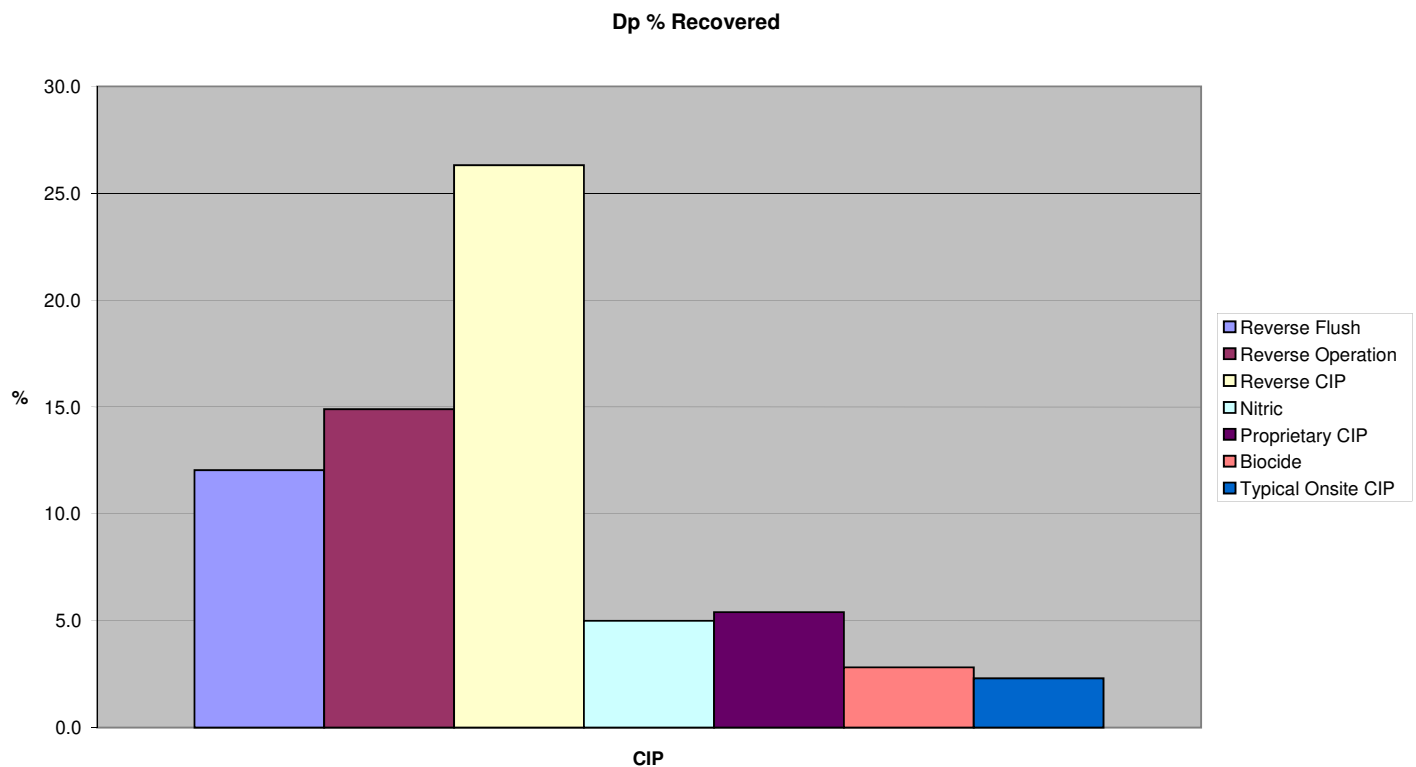
When designing the RO system to have the ability to reverse clean, it is important to remember that the ability to clean in either direction is required. If scaling occurs in the RO system, it will be primarily concentrated in the tail end. In this case, you would want to clean in the normal “forward” direction. If you were to clean scaled elements in a reverse direction, you could cause scaling particles (which can have very sharp edges) to pass through all of the membranes before exiting through the front of the RO system. This could end up damaging the membranes needlessly, so “forward” cleaning is recommended in cases where scaling has occurred. Cleaning should never be done from the permeate side as this will cause permeate backpressure and damage the RO elements. When doing reverse cleaning, it is important to limit the cleaning flow rates initially to prevent telescoping of the RO elements. As discussed previously, there is no thrust ring supplied on the feed side of most pressure vessels. This

leaves the feed membrane unsupported when doing reverse cleanings, and in cases of very high dP's this could lead to telescoping of the element if the cleaning flow rates are too aggressive. For this reason, we recommend limiting the cleaning flow rates to 2/3 the normal cleaning flow rates (at least initially). As the foulant get flushed out and the dP reduces, the cleaning flow rate can be brought back to normal cleaning flow rates.

Some plants use a modified “osmotic” reverse flushing with excellent results [6]. The Gold Coast SWRO plant employs osmotic flushing upon shutdown where permeate is drawn into the pressure vessels when the high pressure pumps are shut down. The permeate is drawn into the vessels due to osmotic forces since there is a high concentration of salts still on the membrane side of the elements. The permeate will want to dilute the high concentration of salts, so it will flow (from an elevated permeate holding tank installed on each train) into the feed channel of the elements and then out the feed side of the lead membranes. The plant has installed a dump valve on the feed header of each train, so that when the train shuts down, they do a very short (30 seconds or so) osmotic flush which helps push out any biological foulants, colloidal matter, particulates, etc. In addition, since the permeate flushing is being done osmotically from the permeate side of the membrane to the feed side of the membrane, it helps lift off any foulants that may have accumulated on the membrane surface.

A recent study was done by Nick Sheehy of the Water Corporation of Western Australia to compare the effectiveness of different cleaning regimens on biologically fouled elements from a wastewater reclamation site.

Figure 7 Study showing reverse flow cleaning effectiveness versus standard cleaning methods



The study showed that reverse cleaning (using CIP chemicals) was the most effective at removing the biological foulants. Reverse operation (without CIP chemicals), where the elements are turned around

and the brine seal moved to the other end and operated in this fashion for 24 hours, was the 2nd most effective cleaning method. Reverse flushing (using permeate for 1 hour), where the flows are much lower than reverse operation, was the 3rd most effective method.

V. CONCLUSIONS OR RESULTS

Thin film composite membranes, which are composed of three polymer layers, have a variety of chemical limitations which stem from the polymer properties of the individual layers. These have been documented and discussed, namely the polyamide layer which limits oxidant use, the polysulfone UF layer which limits exposure to petroleum hydrocarbons, and the polyester fabric layer which limits high pH exposure. The spiral wound element itself, also has some limitations, but no restrictions beyond those of the membrane. Studies have shown the success of high pH cleanings are best to restore performance of organically fouled membrane, and that short-term, high pH exposure is most effective. If used properly, these can lead to increased recovery of the membrane performance and minimize the damage to the RO membranes. The plant examples give real-world evidence to the effectiveness of these approaches. Additionally, trials with reverse flushing have been used in some plants. This cleaning procedure, where cleaning solution or flush water is flowed in the opposite direction of the normal feed flow, has shown a better propensity for removing the colloidal foulant from feed-end elements. This cleaning method should receive more attention as an alternative to conventional cleaning practices, but it must have some special piping to be implemented.

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