

# Membrane Pre-Treatment and Scale Control

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## ABSTRACT

*Over the last 15 years, membranes have become an established technology worldwide for the production of good quality water for potable and process applications. Although the use of membranes within the UK is small compared to many other countries, they are rapidly becoming an acceptable alternative to more traditional processes as a means of water purification.*

*Pre-treatment design and the use of the correct chemical additives is an essential aspect in maintaining trouble-free operation and keeping operating costs to a minimum.*

*This paper considers the impurities found in feedwaters such as organic matter, bacteria, iron and humic acids, which are the primary causes of membrane fouling. It also reviews the principal scale-forming mechanisms that take place along the membrane surfaces and reviews the mechanisms of the scale inhibitors in everyday use.*

*We conclude by looking at causes for system failure and review the recommended monitoring practices that should be implemented by the plant operator. Although some level of membrane fouling is 'a fact of life,' this can easily be contained. There is no reason why membrane systems cannot be operated continuously 'trouble-free' and at an acceptable cost.*

## INTRODUCTION

Reverse osmosis membranes are extensively used worldwide for the desalination, softening and purification of brackish, sea and other surface waters for potable, industrial and agricultural use. Although there has been an upsurge in interest in membrane technology within the UK over the past 5 years, in global terms, the British membrane market is considered small.

Apart from their prime use as a boiler feedwater treatment, membranes are used by a number of UK industries to provide process water for applications in the micro-electronic, pharmaceutical, beer and beverage industries. Several types of membrane are used including micro-filtration (MF), ultra-filtration (UF), nano-filtration (NF) and RO membranes. In recent years, membranes have been used by the UK water utilities. It has been predicted that within the next 30 years most of our drinking water will have passed through a membrane during at least one stage of its passage to 'the tap.'

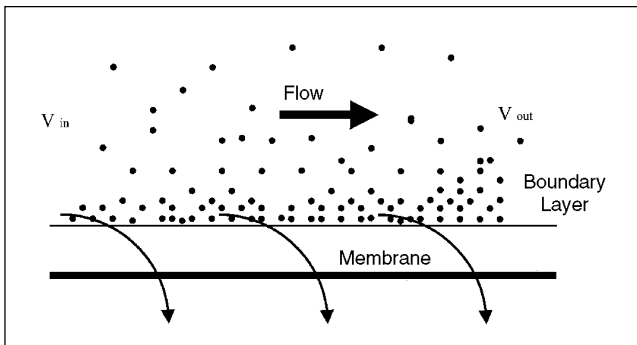
Poor chemical pre-treatment can lead to a failure to control scale formation, organic fouling and bio-growth. Microbiological contamination in any part of the feedwater system can cause bacteria and other microorganisms to enter the membranes, causing bio-film formation, which leads to restricted flows through the plant. Biofouling on the separating surface can significantly reduce output and product quality. Maintaining constant output under these conditions leads to an increased energy consumption and higher running costs. For this reason, RO systems invariably require chemical and physical pre-treatment irrespective of the feedwater source.

Inadequate pre-treatment and/or poor plant maintenance has often resulted in membrane failure. This has tarnished the reputation of RO as a cost-effective alternative to traditional water treatment processes.

## CAUSES OF MEMBRANE FOULING

Any deposit that attaches to the membrane or spacer material is referred to as a 'foulant.'

The build-up of foulants on the membrane are due to the concentration gradient that occurs at the separating surface. As product water passes across the membrane, it leaves behind an ever-increasing level of dissolved and suspended solids in the boundary layer at the membrane surface as shown in Figure 1.



**Figure 1 — Concentration polarisation at the membrane surface**

Common foulants that affect the performance of RO membranes are:

- calcium carbonate and calcium sulphate scales
- organic matter
- iron
- colloidal material
- biofilm
- silica
- humic acids

Other contaminants such as barium and strontium sulphate, calcium fluoride, aluminium silicate, manganese salts and cationic flocculants have been recorded, but fortunately these are comparatively rare.

The type and severity of fouling potential is determined by feedwater quality and feedwater source. It can be assessed by a chemical analysis of the micro-foulants including iron and metal oxides/hydroxides, silt, colloids, bacteria and organic matter and by the Silt Density Index (SDI) measurement. An SDI <3 is recommended for spiral wound membranes and an SDI <5 for hollow fibre elements.

Bacteria, filamentous fungi and yeasts frequently contribute to membrane biofouling and are a major component of the biomass that builds up at the membrane surface. There are a number of biocidal products available that are generally used as 'off-line' cleaning and sanitising agents, although for non-potable applications, 'on-line' dosing programmes have been successfully used in recent years. Fortunately, the colder ground waters of Northern Europe tends to give minimal biofouling, whilst the higher temperatures of the Middle East leads to endemic biofouling.

## PREVENTION OF FOULING USING CHEMICAL PRE-TREATMENT

### MICROBIOLOGICAL CONTROL

Most large membrane systems are located in the warmer areas of the world where membrane biofouling is a continuous problem. There is probably more on-

going research in membrane biofouling than any other segment of the technology. Although numerous papers have been written on the subject, biofouling remains a major problem to many plant operators.

It is impractical to prevent a biofilm forming on a polyamide membrane unless the membrane is continuously treated with a microbicide. It has been reported that in some large RO systems the use of chlorination followed by de-chlorination is aggravating the problem. Some of these plants have now removed the chlorine with significantly improved results. Although biofilm prevention is difficult, the biofilm can be 'conditioned' such that the problem is contained.

Accumulation of biofilms has been shown to occur in four stages:

1. Adsorption of organic matter resulting in a 'conditioned' surface
2. Transport of microbial cells to the 'conditioned' surface (reversible attachment)
3. Adhesion of microbial cells (irreversible attachment)
4. Biofilm development

Once a few microorganisms have entered the membranes, there is a rapid growth and a biofilm layer quickly forms. The biofilm consists of the organisms themselves and their polysaccharide excretions, known as 'glycocalyx.' The biofilm layer then becomes an excellent medium for attachment of other particulate matter and precipitated salts present in the incoming feedwater. The narrow water channels between the membrane surfaces containing the plastic spacer material are particularly prone to blockage.

The following microorganisms have regularly been identified by our laboratory in foulant samples obtained from the surfaces of autopsied membranes:

**Bacteria:** *Corynebacterium*, *Pseudomonas*, *Bacillus*, *Arthrobacter*, *Actinomyces*, *Flavobacterium*, *Aeromonas*, occasionally sulphate-reducing bacteria (SRB's)

**Fungi:** *Penicillium*, *Trichoderma*, *Mucor*, *Fusarium*, *Aspergillus*

**Yeasts:** occasionally enumerated in high numbers

**Algae:** occasionally identified

It is usual to find high bacteria counts on both the plastic spacer and the membrane. Although bacteria cannot pass through the membrane separating layer because of their molecular size, they have regularly been identified on the product water carrier. This is due to slight leakage of the brine seals or membrane imperfections or back-contamination from pipework on the product water side. In Table 1, cfu/cm<sup>2</sup> refers to the number of colony-forming units enumerated per cm<sup>2</sup> of sample.

**Table 1— Typical bacterial counts found in membrane foulants**

Fouled sample	Range of viable counts enumerated (cfu/cm <sup>2</sup> )
Membrane	1 x 10 <sup>2</sup> to 1 x 10 <sup>8</sup>
Plastic spacer	4 x 10 <sup>2</sup> to 5 x 10 <sup>6</sup>
Permeate carrier	0 to 1 x 10 <sup>6</sup>

### BIOCIDE SENSITIVITY TESTS

A quantitative suspension test can be used to determine biocidal efficacy against bacteria and fungi isolated from foulant samples obtained during membrane autopsy. This technique is used to select the most appropriate biocide and the concentration required to control the microorganisms. Samples of sessile organisms are obtained from the membrane surface and spot or pour plate counts used to determine the efficacy of each biocide being tested. The biocidal performance of each product can then be expressed as % kill at a known application concentration.

There are a number of commercially available non-oxidising biocidal formulations that have membrane compatibility approvals from the leading membrane manufacturers. When used as part of a structured biocontrol programme, these are effective in minimising the effects of biofouling to a manageable level. Ideally, these products should be non-oxidising, fast-acting, biodegradable and easily deactivated for disposal purposes.

### REMOVING BIOFILM

There are many factors influencing the ease of removing biofilm from a fouled plant. Good cleaning procedures require a combination of surfactants and a broad-spectrum microbicide. It is recommended that a non-oxidising membrane biocide is periodically used off-line to clean membrane systems and to control microbiological growth.

A three-stage cleaning and sanitising procedure is recommended as follows:

1. Conditioning clean to break down the accumulated fouling layer
2. Sanitising step to kill the sessile organisms
3. Surfactant clean to break up and remove all organic debris

### SCALE CONTROL

Scale is another foulant caused by the concentration of lowly soluble ions in solution. Feedwater analysis gives a good indication of scaling potential. Computer

predictions can determine the risk and rate of scale formation that may occur if the pre-treatment system and antiscalants are not correctly selected.

### SCALE-FORMING MECHANISMS

Scale formation occurs when the solubility of a particular salt is exceeded. Most natural waters will deposit calcium carbonate on the membrane surface if untreated. Calcium sulphate is another common scale and consideration should also be given to barium and strontium sulphate and calcium fluoride although their occurrence is rare.

Scale forms in three stages:

1. As the water passes along the membrane, the ions in solution concentrate, in the boundary layer adjacent to the separating surface. As the ionic strength increases, the distances between the ions decreases and they start clustering as a loosely formed *proto-nuclei* of up to 1000 atoms. This reaction is reversible and the ions readily pass back into solution.
2. As the *proto-nuclei* further develops, the ions become more 'ordered' and regular shaped *nuclei* start forming. This stage is also reversible; but as these nuclei form, reversibility is less likely.
3. The final stage is the irreversible growth of *crystals*. Once formed, the crystals continue to grow indefinitely as long as the respective salt exceeds its solubility coefficient.

All scaling salts develop and grow in this way; the only difference is their greatly variable solubility products. Scale inhibition is dependent on the ability of the inhibitor to interfere with this growth mechanism.

### SCALE INHIBITORS

The first commercial membranes were made of cellulose acetate, which required operation in an acidic environment. By using pH control, the bicarbonate molecule is destroyed, thus reducing or eliminating the calcium carbonate scaling potential.

The advent of polyamide membranes meant the use of hazardous acid was no longer necessary and other 'antiscalant' products could be used. Foremost of these was sodium hexametaphosphate (SHMP) [(NaPO<sub>4</sub>)<sub>6</sub>], which functions as a threshold inhibitor. Although still widely used, SHMP is losing ground to more effective antiscalants, particularly phosphonate-based products, which function as 'super threshold inhibitors'.

There are other ways of inhibiting scale formation such as ion exchange, cold or hot lime soda softening or by simply limiting recovery rates.

Today, the most widely used scale inhibitors are based on an extensive range of organic compounds. They work by three closely related mechanisms that interfere with one or more of the stages of crystal growth.

1. *Crystal Distortion Effect* interference with the normal crystal growth produces an irregular crystal structure with poor scale-forming ability.
2. *Threshold Effect* sub-stoichiometrical levels of inhibitor retard the precipitation of salts that have exceeded their solubility products.
3. *Dispersancy* a charge is placed on the surface of the crystal. Similar charges cause the crystals to repel one other.

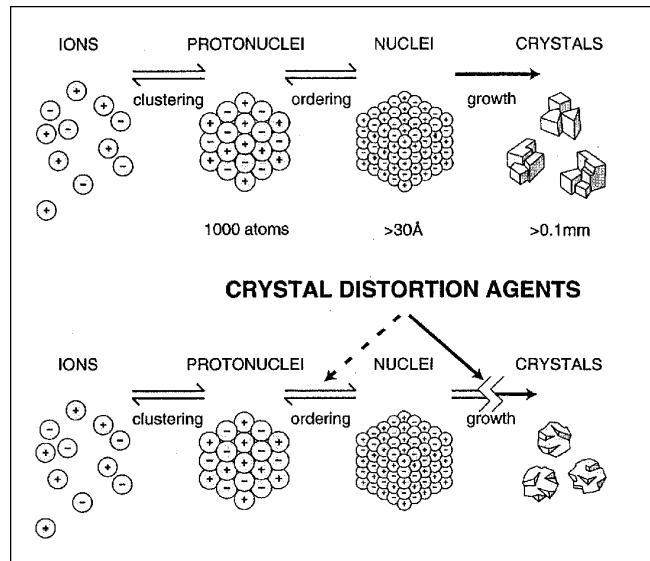
Numerous polymers are commercially available, the most common of which is polyacrylic acid  $[\text{CH}_2\text{CHCOOH}]_n$  with molecular weights in the 1,500 to 2,500 range. These polymers function as crystal distortion agents; at higher molecular weight, they exhibit dispersancy properties (Figure 2). Although it is debatable how effective dispersancy and crystal distortion properties are within a tightly packed membrane element, many of these polymeric substances exhibit good threshold properties against calcium carbonate and calcium sulphate so that scale inhibition occurs by more than one mechanism (Figure 3).

Phosphonates, as typified by the stable C-P bond, overcome the tendency of hydrolysis to the O-P chain, which is typical of polyphosphates. Phosphonates are widely used in water treatment formulations as scale and corrosion inhibitors and are used in membrane systems as 'super-threshold' agents. These products have the ability to hold highly supersaturated solutions in a stable condition during the finite time it takes the water to exit the membrane system.

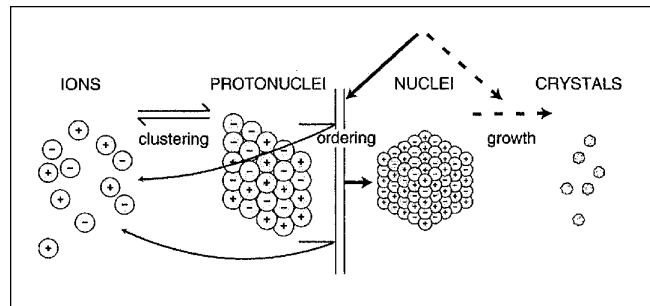
## OTHER MEMBRANE FOULANTS

Three other common foulants are iron, silica and humic acids. All of these foulants can enter the membrane system in the feedwater and they can all be present in a variety of forms.

Iron exists in two states, soluble ferrous ( $\text{Fe}^{2+}$ ) and insoluble ( $\text{Fe}^{3+}$ ) salts. Owing to the risk of ferrous salts oxidising to ferric salts after the micron filter, it is advisable to reduce the total iron loading in the feedwater to as low a level as possible. This may be done by oxidising the ferrous salts with chlorine and filtering the insoluble ferric salt. Some phosphonate-based inhibitors are effective iron sequestrants used to prevent iron fouling, but this may be an expensive solution. General advice is to remove iron from the feed if the total iron level in the concentrate reaches 0.8 mg/l.



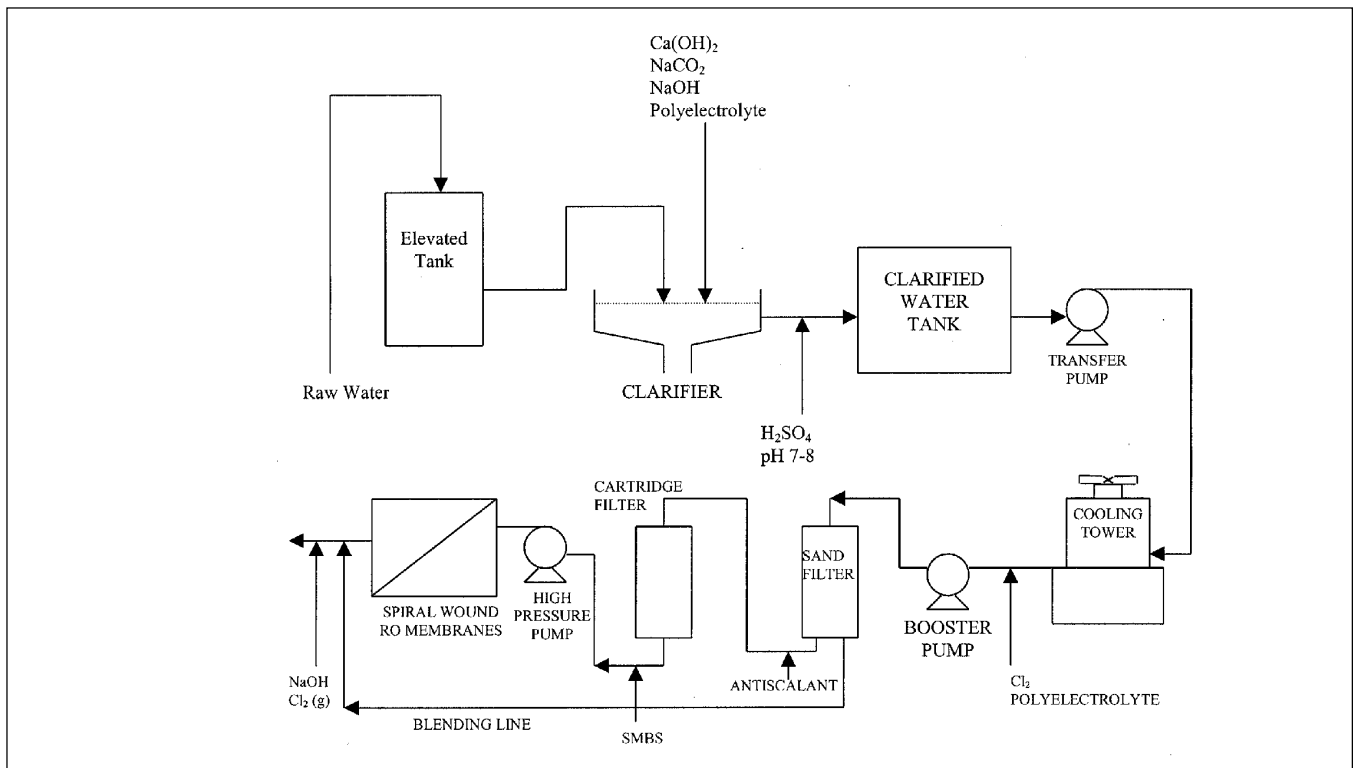
**Figure 2 — Crystal growth and scale inhibition mechanisms**



**Figure 3 — Threshold agents (antiprecipitants)**

Silica is a problem in certain areas of the world, particularly in volcanic and geothermal regions. Much has been written about it in recent years. Traditionally, silica control has been achieved by limiting the recovery rate to keep the silica level below the silica concentration ratio (SCR) for the temperature and pH concerned, which is around 125 mg/l in the concentrate. In recent years, the levels of acceptable silica in the concentrate has been increasing due to the availability of silica antifoulants and better operating techniques. Although brine silica levels of 200-250 mg/l have been experienced without adverse effects being recorded, specialist advice should be sought from chemical suppliers.

Humic acid is present at various concentrations in a wide range of surface waters. Humic acids are complex organic structures that may provide a food source for bacteria and may also cause severe membrane fouling. It is possible to remove humic acids by carbon filtration or an organic trap, but care should be taken to ensure a high level of removal. There have been recorded cases where feedwater treatment by



**Figure 4 — Pre-treatment system for Middle East plant**

**Table 2 — Common causes for system failures**

Effect	Failure	Recommended monitoring practice
Scale formation, usually at the concentrate end of the membranes	Antiscalant	Check dosing equipment and monitor changes in water quality, softener failure
Biofouled pipework, cartridge filters and membrane	Ineffective sanitisation procedures	Sand filters, GAC, microbiological analysis, chlorine dosing, dosing tanks
Iron loading on cartridge filters, reduced membrane performance	High iron content	Pipework corrosion, ferric breakthrough from media beds, failure of media filters
Humic substances and organic fouling on membrane	High organic content	Feedwater composition, review TOC, flocculation procedures, feedwater colour
Colloidal particles foul micron filters and membranes	Colloidal breakthrough	SDI, condition of cartridge filters, eliminate media fines
Carbon fines foul micron filters and membrane	Granular activated carbon filters	Check washing procedure to remove fines
Cationic flocculant irreversibly fouls membranes	Overdosing of flocculant	Check dosing levels and detect excess traces
Membrane damage, high conductivity and increased flux	Overdosing chlorine	Dosing equipment, Redox meters, bisulphite dosing levels and bisulphite activity and positioning of injection point, chlorine test kit
High bacterial and fungal counts in water samples	Ineffective biocide	Biocide adsorption on GAC, check contact time and dose rate, select broad-spectrum biocide
Colloidal and bacterial fouling of micron filters and membranes	Breakthrough of sand filter	Check back wash procedures
Rapid scale formation, CaCO <sub>3</sub> only	Acid dosing	pH monitor, plant pressure drop
High microbiological loading, biofilm, severe cartridge filter fouling	Seasonal blooms	Microbiological counts in water samples, evidence of biofilms, check algae counts

acid or by chlorine has resulted in a fouling problem worse than if the feedwater were untreated.

## **SELECTION AND CONTROL OF PRE-TREATMENT PLANT**

Feedwater quality dictates the performance of the membrane system, which in turn limits system recovery, plant output and water quality.

The most appropriate pre-treatment system is dependent on the source and analysis of the feed stream and the size of the membrane system involved. This can vary from a simple micron cartridge filter to a sophisticated system which may include ozonation, DAF, lime/soda softening, claro-flocculation, mixed media filtration and cartridge filters. Figure 4 shows the pre-treatment system for a Middle East plant.

The minimum pre-treatment required for a 'clean' well water with a low SDI <2 and a temperature acceptable to the membrane is a 10 micron cartridge filter and antiscalant dosing to prevent scale formation.

Larger systems often use surface or sea water where additional flocculation and filtering procedures are required to remove suspended solids. With surface waters, it is standard practice to control microbiological growth by chlorination. It is often necessary to de-chlorinate with sodium bisulphite.

As a general rule, well water usually has a higher TDS than surface water but a lower suspended solids and organic content; sea water is an exception to this

rule. For this reason, the limiting factor for membrane fouling in ground water is the quantity of calcium, alkalinity and iron present, whilst in surface waters membrane fouling is dictated by the level of particulate, organic and humic acid matter present.

## **MONITORING AND SYSTEM FAILURE**

To maintain system efficiency, it is essential to continuously monitor feedwater quality and the performance of the individual components of the pre-treatment system. Table 2 gives some recommended monitoring advice.

## **CONCLUSIONS**

Good pre-treatment design and the use of correct chemicals are essential to protect the membrane, which is at the heart of the water purification system. Even with a well-designed pre-treatment system in a well-run plant using effective antiscalants, some degree of membrane fouling is inevitable over a period of time. Membrane fouling is a fact of life. Regular cleaning will not damage the membranes provided they are cleaned at a reasonably early stage of fouling with approved products. Expert advice is available to the plant operator from a number of sources.

With the support of the chemical supplier, the plant operator will be able to maximise operating conditions so as to make system operation 'hassle free' at the same time ensuring that running costs are kept to a minimum.