

# The Role of Antiscalants and Cleaning Chemicals to Control Membrane Fouling

By L. Y. Dudley and J. S. Baker, PermaCare®

## ABSTRACT

*Membrane systems have been widely adopted in the industrialised and developing world as an efficient and cost-effective technology for the production of quality municipal and industrial grade water. Membrane process technology is also becoming more frequently selected for use in wastewater treatment applications. These cases often demand specialised control of membrane fouling.*

*The primary aim for plant operators and owners is to maintain good performance and minimise operating costs. This paper highlights how the selection of appropriate proprietary chemicals and their use in conjunction with good pre-treatment design can ensure cost-effective and efficient operation. It outlines membrane fouling and how the use of effective antiscalants, membrane cleaning chemicals and biocides can optimise membrane performance as part of a tailored treatment programme.*

## INTRODUCTION

The most commonly used reverse osmosis (RO) membranes in water treatment applications are spiral wound and hollow fibre thin film composite type. These consist of a polyamide salt-rejecting film on a polysulphone base. The very thin surface layer of polyamide (up to 3 µm) provides the semi-permeable and salt-rejecting properties of the membrane.

Fouling potential is an inherent characteristic of membrane module design. The high membrane packing density required for good production rates results in low voidage for feedwater flow. However, this need not result in detrimental performance. Fouling has been widely documented and researched since the first commercial use of membrane separations. It is important that this subject is addressed because membrane replacement is a considerable expense in the operation of an RO plant. In the case of large municipal and industrial systems, this cost can be prohibitive.

The structural design and functional characteristics of a spiral wound and hollow fibre element, particularly the narrow feedwater channel and the concentration polarisation effect occurring during operation, create an ideal environment for the accumulation of foulants. This may include the colonisation of microorganisms and the build-up of organic and inorganic foulants, leading to blocking of the flow channels and consequently increased pressure drops.

In cases where fouling has not been controlled or prevented adequately, this will result in higher energy consumption, greater operating costs, reduced water production and quality, and the need for more frequent cleaning.

Pre-treatment design and the use of the suitable chemical treatments are essential aspects in maintaining 'trouble-free' plants and keeping operating costs to a minimum.

## MEMBRANE FOULING

Pre-treatment systems for RO plants are designed to produce a feedwater with a reduced fouling potential by removing potential fouling species prior to membrane treatment. Common foulants include:

- Calcium carbonate and calcium sulphate scales
- Organic matter
- Iron
- Colloidal material
- Biofilm and microorganisms
- Silica
- Natural humic and fulvic acids

Other contaminants such as barium and strontium sulphate, calcium fluoride, aluminium silicate and manganese salts have been identified but are comparatively rare. It is also possible for surface-active chemicals such as cationic surfactants or polymeric flocculants to result in irreversible fouling.

Fouling potential is determined by feedwater quality and feedwater source and is dependent on the pre-treatment used. It can be assessed by a chemical analysis of the microfoulants and by the Silt Density Index (SDI), an empirical measurement widely used by on-site operators. An SDI <3 is ideal for spiral wound and hollow fibre elements. The two most important types of fouling to be controlled are scale formation and biofouling.

## SCALE INHIBITION

The primary fouling risk in untreated water treatment systems is scale formation that occurs when the solubility of any low solubility salt is exceeded. The scaling mechanism at the membrane surface is due to a concentration gradient that occurs as product water continuously passes through the membrane, leaving behind an ever-increasing level of dissolved and suspended solids (Figure 1). These concentrate at the membrane-separating surface creating a boundary layer, an effect known as concentration polarisation. Within this boundary layer, salts may precipitate and suspended solids can start to deposit on the membrane surface and within the spacers, leading to scaling and fouling.

Many natural waters will deposit calcium carbonate on the membrane surface if untreated. Calcium sulphate is another common scale. The scaling usually begin in the latter stages of the plant. This results in increased pressure drop and the need for greater feed pressure to maintain constant product water output.

Scale forms in three stages:

1. Ions in solution concentrate as the water passes along the membrane, particularly in the boundary layer near the separating surface. The ions start clustering as a *proto-nuclei* of up to 1000 atoms, a reaction that is readily reversible.
2. As the proto-nuclei grows, the ions start ordering themselves and a regular-shaped *nuclei* develops. This stage is also reversible; but as the nuclei grows, reversibility is less likely.

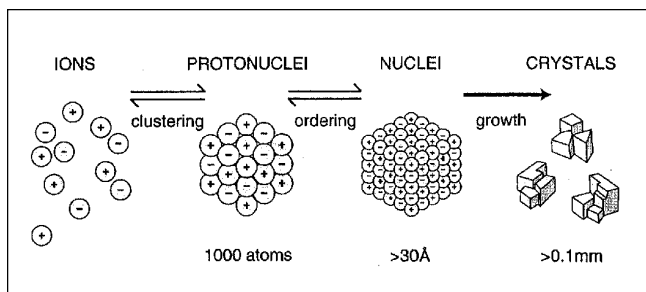


Figure 1 — Scale formation mechanism

3. The final stage is the irreversible growth of *crystals* from the nuclei. Once formed, the crystals continue to grow indefinitely as long as the respective salt exceeds its solubility coefficient.

The formation of the solid phase for all scaling species proceeds in this way, the only difference being their variable solubility products ( $K_{sp}$  values).

## TYPES OF ANTISCALANT

Early membranes were made of cellulose acetate requiring pH control, which also reduced or eliminated the calcium carbonate scaling potential. Polyamide membranes are now almost exclusively used in water treatment. Their rejecting surface requires a better means of scale control.

In the absence of a bulk softening process, there are several methods of inhibiting scale formation such as pH control (suitable for calcium carbonate only), antiscalants like sodium hexametaphosphate (SHMP) and a wide range of proprietary products. Today, the most widely used scale inhibitors are based on an extensive range of organic compounds. These work by three closely related mechanisms that interfere with one or more of the stages of crystal growth:

1. **Threshold Effect** — These inhibitors retard the precipitation of salts that have exceeded their solubility products, e.g., phosphonate-based products.
2. **Crystal Distortion Effect** — These inhibitors distort normal crystal growth and produce an irregular crystal structure with poor scale forming ability, e.g., polyacrylic acid  $[\text{CH}_2\text{CHCOOH}]_n$  with molecular weights in the 1,500–2,500 range.
3. **Dispersancy** — Dispersants work by placing a surface charge on the crystal. Comparable charges cause the crystals to repel one other and are dispersed into the water bulk.

Numerous polymers are commercially available, the most common of which is polyacrylic acid. These polymers function as crystal distortion agents; but at higher molecular weight, they also exhibit dispersancy properties. Although it is debatable how effective dispersancy and crystal distortion properties are within a tightly packed membrane element, many of these polymeric substances can exhibit good threshold properties against calcium carbonate and calcium sulphate so that scale inhibition occurs by more than one mechanism.

Phosphonates, as typified by the stable C-P bond, overcome the tendency of hydrolysis to the O-P chain, which is typical of polyphosphates such as SHMP. Phosphonates are widely used in water treatment formulations as scale and corrosion inhibitors and

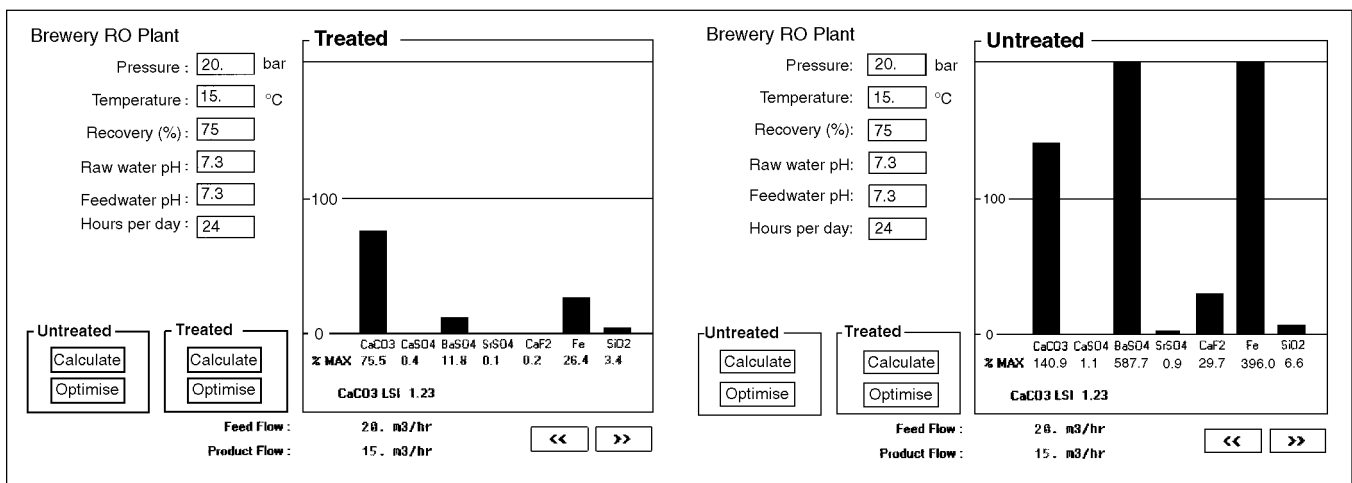
**Table 1 — Scale inhibition characteristics of a proprietary phosphonate antiscalant**

Foulant	Index	Maximum inhibition limits for Antiscalant A	Typical dose rate in feedwater
Calcium carbonate <sup>(a)</sup>	LSI	<+2.6	1.0 to 4.0 mg/l
Calcium sulphate	$Ip_b:K_{sp}$	<3.0	1.5 to 2.5 mg/l
Barium sulphate	$Ip_b:K_{sp}$	<50	0.5 to 2.5 mg/l
Strontium sulphate	$Ip_b:K_{sp}$	<12	N/A
Calcium fluoride	$Ip_b:K_{sp}$	<120	N/A
Silica	SCR <sup>(b)</sup>	<1.32	0 to 4.0 mg/l
Iron	IFI <sup>(c)</sup>	<1.2	0 to 6.0 mg/l

<sup>(a)</sup> Where the Stiff and Davis Saturation Index is calculated and Antiscalant A is used, the maximum S&DSI limit has never been reached.

<sup>(b)</sup> Saturation Concentration Ratio (SCR) at 25°C, pH 7.5 with 165 mg/l SiO<sub>2</sub> in the concentrate.

<sup>(c)</sup> Iron Fouling Index (IFI) developed by PermaCare restricts the total iron level in the concentrate stream to 1.2 mg/l.



**Figure 2 — Scaling potential with phosphonate antiscalant dosing (left) and without (right)**

iron sequestrants. In membrane systems, they act 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.

### SUPERIOR PERFORMANCE OF THRESHOLD SCALE INHIBITORS

Selection of an appropriate antiscalant will reduce the risk of scaling and often eliminates the use of hazardous acids, at the same time maintaining efficient plant operation with optimum conversion rates. It can also be a cheaper alternative for membrane protection than pH control or ion exchange softening.

Super-threshold agents, such as phosphonates, are able to stabilise a wide range of supersaturated salt solutions, allowing the engineer to design systems with maximum recovery rates. Phosphonate-based products are excellent inhibitors for a wide range of scaling species. Although minority scalants such as

calcium fluoride and strontium sulphate must be considered when designing a system, they have rarely been seen in practice.

Table 1 demonstrates the inhibition characteristics of a proprietary phosphonate product (Antiscalant A). Use of this product can enable safe plant operation at much higher % recovery limits than that allowable with dosing of acid and SHMP. It should also be observed that the phosphonate product has the unique capability of sequestering low level of iron still remaining in the feedwater after pre-treatment and will also inhibit silica fouling with up to 165 mg/l SiO<sub>2</sub> present in the brine.

The use of an effective antiscalant will permit plant recovery to be increased to an LSI of +2.6 compared to LSI +1.0 when using a commodity antiscalant such as SHMP. Performance can be predicted using an antiscalant computer prediction programme. The effect of antiscalant on scaling potential is illustrated in Figure 2 for a brine of LSI+1.23. The graph for the treated brine conditions indicates that the plant

recovery of 75% could be increased further if plant design limitations allow.

**Why use a proprietary phosphonate-based antiscalant?**

**Advantages over acid dosing**

*Handling:* Safer to handle than either sulphuric or hydrochloric acids.

*Cost advantage:* The dose rate is much lower than the acid dose rate and is a cheaper treatment option when the disadvantages and risks of acid treatment are considered.

*Technical:* Sulphuric acid is only effective against carbonate scale and increases the calcium sulphate scaling potential, whereas Antiscalant A is an effective calcium sulphate inhibitor. With Antiscalant A, the product water has a higher pH and is of better quality due to enhanced bicarbonate rejection.

*Corrosivity:* At natural pH, the operating environment is less corrosive.

**Advantages over sodium hexametaphosphate (SHMP) dosing**

*Handling:* SHMP has a short shelf life and solutions must be made up daily.

*Technical:* Antiscalant A is a far more effective antiscalant than SHMP, maintaining salts in solution at high LSI and  $I_{p_i}/K_{sp}$  values, which means systems can operate at higher recovery rates.

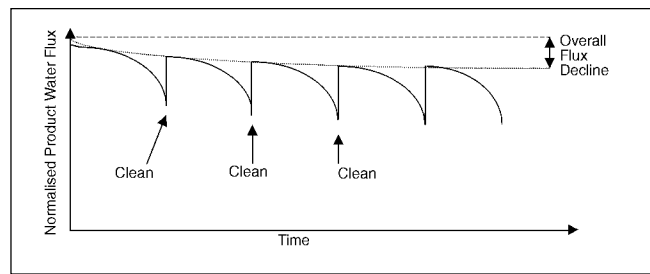
*Cleaning:* Antiscalant A is far more stable than SHMP and is unlikely to cause any calcium or iron-based phosphate deposition. For this reason, the interval between cleaning is significantly longer.

*Dosage:* The dose rate is significantly lower than for SHMP

**MEMBRANE CLEANING PRACTICES**

Inevitably membranes require periodic maintenance cleaning to remove micropollutants from the membrane surface after prolonged periods of operation. This is an accepted practice that is often required despite the wide use of quality antiscalants and other means of fouling inhibition. If regular maintenance cleaning is not carried out, there may be a significant reduction in product output and quality over time (Figure 3).

The type and frequency of cleaning anticipated should be based on the fouling potential of the pre-treated feedwater entering the system. The selection of appropriate cleaning products is dictated by the most common fouling species. It is usually necessary to use a combination of products in at least two cleaning steps to effectively clean a plant. Procedures usually require a combination of both an alkaline surfactant and an acidic cleaning solution to remove common fouling species and hence recover membrane flux.



**Figure 3 — The effect of maintenance membrane cleaning**

Both acidic and alkaline formulations are able to pass through the membrane during the cleaning process, thus allowing removal of foulant within the membrane structure in addition to adsorbed sessile foulants. Chemical properties of membrane cleaning formulations will dictate the ease and speed of foulant removal. Key characteristics are summarised in Table 2.

In the majority of cleaning schedules, the use of a proprietary surfactant is recommended, which facilitates the breakdown of organic material and the effective removal of all fouling particles from within the elements. The primary function of a surfactant is to decrease the contact angle between the foulant species and membrane, reducing adhesion to the membrane surface. Some surfactant formulations contain enzymes capable of digesting specific foulants. However, these products are very specific and are only suitable for systems where the precise nature of the foulant is known and a specific enzyme has been identified to break down the species present.

There are three main types of surfactant product: non-ionic, anionic and cationic. Due to the negative surface charge characteristics of polyamide membranes, cationic products are unsuitable for use. Both anionic and non-ionic formulations are widely used in the industry; however, the performance of non-ionic products can vary with the type of membrane material.

**Table 2 — Types of chemical suitable for foulant removal**

Product Characteristic	Foulant removed
Strong acidic	Calcium carbonate and heavy scaling
Weak acidic	Light scales and iron oxide
Alkaline surfactant	Organic debris and biofilm
Chelating agent	Colloidal material, sulphate scales
Microbicide (non-oxidising)	Bacteria, fungi and yeasts
Enzyme	Foulant specific



**Figure 4 — Laboratory technical support – membrane autopsy**

Anionic products are highly effective in the majority of organic fouling problems.

The most appropriate choice or order of applying the products, in some cases, can be critical. When complex fouling is experienced, it may be beneficial to perform a membrane autopsy (Figure 4) to identify the nature of foulants deposited on the membrane surface. Chemical and microbiological analysis will identify the foulant characteristics and will enable the best recommendations for cleaning. Flat sheet samples of the fouled membrane can also be obtained following an autopsy and tested in a flat sheet crossflow cell (Figure 5). This technique is a valuable tool to evaluate the performance of the membrane, in terms of flowrate and salt rejection before and after cleaning. The most effective cleaning programme can be easily identified in this way. This apparatus is also used to evaluate the membrane compatibility of chemical products used in RO systems.

Our laboratory research has found that in certain fouling situations, in particular where there are natural organic foulants, the application of an acid cleaner before the use of an alkaline product may result in an irreversible flux decline. It is believed that this phenomenon is due to the stability of humic acids. For this reason, it is always advisable to perform alkaline cleaning first.

Cleaning practices should include periodic soaking of the membrane and using warm cleaning solutions of up to 30°C. Ideally, the total cleaning solution volume for a standard 8" x 40" spiral element should be 40 litres per membrane, as recommended by the membrane manufacturers. However, existing cleaning tank volumes can often limit these guidelines. In such cases, a minimum of 25–30 litres cleaning solution per membrane element (excluding pipework volume) is advised.



**Figure 5 — Laboratory technical support – flat sheet crossflow cell**

Procedures may take between 4 and 12 hours to perform, depending on the severity of fouling and may require a cleaning duration of up to 24 hours incorporating overnight soaking. Frequency may range from monthly cleaning cycles to an annual maintenance clean. Cleaning requirements may be dictated by the feedwater quality, effectiveness of the pre-treatment, plant recovery and plant operating conditions.

## CLEANING PROGRAMME EXAMPLE

### Stage 1 – For removal of organics, colloidal material and biofilms

- Prepare a 2% v/v solution of **Product A (alkaline surfactant)** at pH 11 and 30°C.
- Add 2% v/v **Product B (chelating agent)**. (It may be necessary to adjust pH to 11 with HCl.)
- Flush 20% of solution through membranes to drain.
- Circulate and soak remaining solution for 15-minute intervals for 4 hours.
- Discard and flush thoroughly with good quality, chlorine-free water.

If cleaning solution shows heavy discolouration, discard and make up new solution *and* repeat cleaning stage.

*Acid cleaning should only be carried out after all organic material has been removed.*

### Stage 2 – For removal of iron oxide and light inorganic scales

- Prepare a 4% v/v solution of **Product C (weak acid)** at 20–25°C.
- Flush 20% of solution through membranes to drain.

- Circulate and soak remaining solution for 15-minute intervals for 2 hours.
- Discard and flush thoroughly with good quality, chlorine-free water.

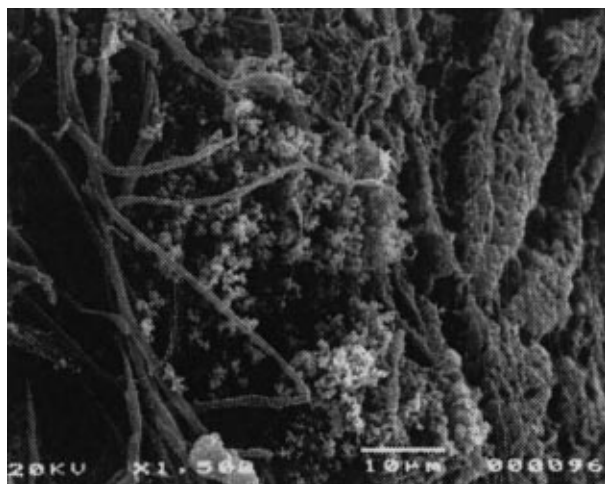
It must be stressed that membrane manufacturers' guidelines must always be followed with respect to pH, temperature, flow rate and differential pressure. The pH restriction for cleaning of polyamide membranes is within the limits of pH 3–11. In severe fouling cases, the standard guidelines may occasionally be exceeded, but this should only be performed with written permission from the membrane supplier.

## BIOFOULING CONTROL

Biofouling is a common cause of poor performance of RO systems. This is primarily due to the accumulation of extracellular polysaccharide substances (EPS) secreted by microorganisms entering the membrane plant.

Microbiological contamination in any part of the pre-treatment system can cause microorganisms to enter the membranes, assisting biofilm formation (Figure 6). It is extremely difficult to prevent this and many microbes can survive free-chlorine environments when enveloped within a protective EPS slime. Biofouling can significantly reduce product output and quality. Our laboratory studies have shown that a typical membrane biofilm has the following characteristics:

- >90% moisture content
- Of dried deposit, >50% total organic matter
- Up to 40% humic substances as % of total organic matter in high coloured waters
- Low inorganic content
- >5% Fe as iron oxide when treating brackish water
- High microbiological counts ( $>10^6$  cfu/cm<sup>2</sup>) including bacteria, fungi and yeasts



Cleaning programmes to remove biofilms require a combined sanitisation and cleaning procedure. This includes the use of an alkaline surfactant and an effective microbicide. The effectiveness of the biocide at killing bacteria, fungi and yeasts can be determined by performing biocide sensitivity tests (BSTs) using microorganisms isolated from the pre-treatment system, feedwater or the membrane surface.

The use of oxidising biocides requires caution since they are incompatible for long-term contact with polyamide membranes. Where compounds like chlorine are used in the pre-treatment system, it is essential to remove any residual chlorine with sodium bisulphite well in advance of the membranes, and preferably after the cartridge filters. When chlorine or ozone are dosed to sea water, hypobromous acid is formed, which will eliminate bacteria but may also cause oxidative membrane damage.

It has long been standard practice to control biological growth in the feedwater by the use of chlorine. However, current theory and practical experience indicate that this is not always successful in controlling biofouling. In fact, it has been found on occasions to worsen the biological activity.

Several proprietary non-oxidising biocides have been developed for use in membrane systems. These are membrane compatible and easily deactivated for discharge and have good biocidal properties. Many of these compounds can be dosed intermittently at low dose rates in non-potable applications, and are a cost-effective means of maintaining a clean membrane surface. Low molecular weight compounds can pass through the membrane and can thus sanitise the product water side. This is advantageous as it is common to find evidence of microorganisms on the product water carrier, normally due to slight membrane imperfections or poor post-membrane sanitisation.

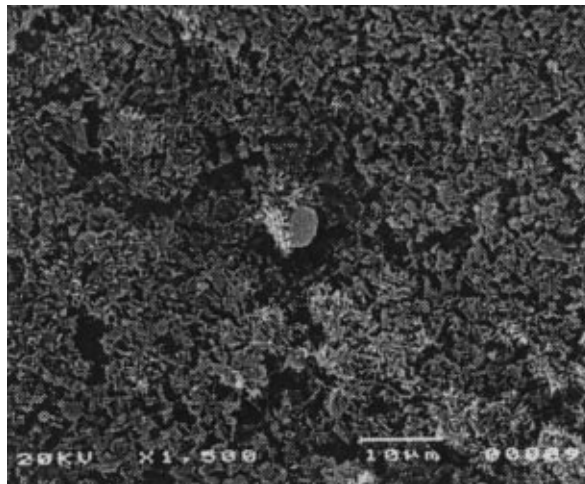


Figure 6 — Scanning electron micrographs of biofouled membranes

In potable plants, it is recommended that a broad-spectrum non-oxidising membrane biocide is periodically 'shock dosed' off-line to clean membrane systems and to control biogrowth. A three-stage cleaning and sanitising procedure is recommended as follows:

- A conditioning clean to breakdown the accumulated biofilm
- A sanitising step to kill all sessile organisms
- A surfactant clean to break up and remove all organic debris

It is often beneficial to periodically use a secondary non-oxidising biocide to prevent the emergence of resistant bacterial and fungal strains. The majority of systems with a high risk of biofouling can be treated by using an integrated approach to biogrowth control including regular maintenance cleaning, biocide treatments and optimised pre-treatment. In the majority of cases, a trade-off between plant efficiency and chemical costs is necessary. It is likely that biofilm formation may not be eliminated but can be maintained to within tolerable 'threshold' levels.

## CONCLUSIONS

This paper highlights the advantages of an integrated approach to fouling control with the use of proprietary chemical products.

1. Many years' experience of dosing proprietary phosphonate-based antiscalants have demonstrated that scale formation can be successfully inhibited. Such practices allow plant operation at improved recovery rates and with brine LSI's of up to LSI+2.6.

2. It has been shown that regular maintenance cleaning of membrane systems will optimise plant performance and ultimately increase the overall membrane lifetime. The use of proprietary cleaning formulations and structured cleaning schedules proposed in conjunction with laboratory test results and knowledge of potential foulants will prevent and control severe fouling.
3. Biofouling is the greatest potential fouling risk in the majority of RO systems. The use of microbicides by intermittent 'shock' on-line dosing (in non-potable applications) or as off-line cleaners can inhibit biogrowth to within tolerable levels. A broad-spectrum non-oxidising product is preferable. It is advantageous if the product can be easily de-activated for disposal.
4. Technical support services such as membrane autopsies provided by chemical suppliers can provide invaluable information that can be used to make recommendations that significantly improve plant performance.
5. Membrane compatibility is essential for antiscalants, biocides and cleaning products used in these applications. Compatibility can be established in the laboratory using a membrane cross-flow test cell.