

# Membrane Fouling and Autopsy

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## ABSTRACT

*Fouling in reverse osmosis (RO) plants can be caused by a number of common foulants such as inorganic scales, organic matter and biofilm. Foulants are commonly problematic in membrane systems with inefficient pre-treatment or ineffective scale inhibition. Build-up of foulants usually results in reduced output and declining water quality.*

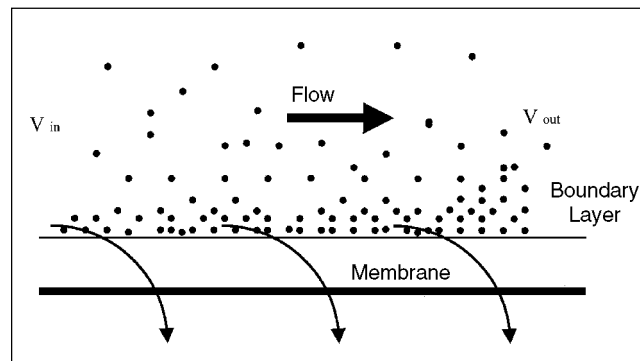
*In the case of severe membrane fouling, it is recommended that thorough investigation is performed on a fouled membrane element taken from the affected plant. This technique is commonly known as 'membrane autopsy.' This paper describes the major fouling problems encountered and the analytical procedures that can be used to identify the cause of fouling. This enables recommendations to be made for additional pre-treatment, plant modifications or membrane cleaning procedures.*

## INTRODUCTION

The reverse osmosis (RO) process uses either spiral wound or hollow fibre membranes. Plants consist of pressure vessels containing several membrane elements in series. RO technology is applied to treat surface water, well water and sea water.

The membrane type generally used for potable water treatment applications are thin film membranes made from polysulphone with an ultra-thin (3 micron) polyamide salt rejecting layer, which provides the essential semi-permeable and salt rejecting properties. The pore size of these membranes is less than 0.001 microns, and they typically reject >98% of dissolved salts and all organic particles, microorganisms and other nutrients.

The design of spiral wound membrane elements makes them an ideal environment for the growth of microorganisms, which form as biofilms on the membrane surface and on the spacing material in the narrow feed channels. This biofilm acts as a 'trap' for other particulate matter that quickly builds up as a biomass.



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

A spiral wound membrane element consists of membrane material with a mesh spacer wound around a plastic product water carrier, all sealed in a fibreglass casing. Although this design of membrane is efficient, it can be very difficult to clean due to the narrow feed channels and the mesh spacer that can result in dead areas once any degree of fouling has been established. The design of hollow fine fibre membranes is also susceptible to the accumulation of foulants due to the close proximity of the fibres within the module casing.

## MEMBRANE FOULING

The fouling mechanism at the membrane surface is due to a concentration gradient that occurs at the separating surface as product water continuously passes through the membrane leaf, leaving behind an ever-increasing level of dissolved and suspended solids. These concentrate at the membrane separating surface creating a boundary layer, an effect known as concentration polarisation (Figure 1). 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.

It is necessary to make a full and detailed water analysis to identify all major anions and cations that contribute to scale formation and general fouling. The

major scaling/fouling ions are calcium, magnesium, bicarbonate, sulphate, silica, iron and barium. The fluoride and strontium levels should also be measured, although these are rarely a problem.

The following inorganic scales may be present in fouled RO membranes: calcium carbonate ( $\text{CaCO}_3$ ), calcium sulphate ( $\text{CaSO}_4$ ), and barium sulphate ( $\text{BaSO}_4$ ). Calcium carbonate is the most likely inorganic scale to be deposited; however, use of an effective antiscalant will inhibit scale formation in brines with LSI's up to +2.6. Other common fouling species include: biofilms, microbiological species, ferric oxide/hydroxide, silica, organic debris, colloidal particles and humic acids.

Membrane biofouling is the most commonly encountered cause of poor performance in water treatment membrane plants. This is primarily due to the accumulation of extracellular polysaccharide substances (EPS) secreted by microorganisms entering the membranes in the feedwater. This adhesive polysaccharide material can act as a trap for other organic debris and as a source for further microbiological growth.

To ensure acceptable feedwater quality to the RO, plant operators must measure SDI and scaling potential in order to control membrane fouling. The membrane manufacturers recommend operation at SDI levels of <5 for hollow fibre and <3 for spiral wound elements. The SDI is a guide to the colloidal fouling potential. A 'clean' brackish water will typically have an SDI <3, whereas sea water will have significantly higher SDI with values of 6 – 20. With sea water, it is common practice to use beach wells rather than surface intakes to provide a 'cleaner' water source. With surface waters, SDI levels above 150 are common.

The total dissolved solids (TDS) is also measured. For brackish water, the TDS will be less than 15,000 ppm and for sea water 40,000 – 55,000 ppm. The TDS (or ionic strength) dictates the natural osmotic pressure and hence the system operating pressure. It also affects the scaling potential of all the scaling species present.

Inorganic and organic foulants may accumulate at the membrane surface restricting crossflow through

the modules. This deposition can cause a reduction in product water flow and changes in the salt rejection characteristics of the membrane. It has been observed that different types of fouling may be found at different locations along the length of an element and in membranes at different stages of the plant. This due to the nature of the foulant and the concentration factors at each stage. For example, scale will deposit first at the outlet end of the plant, whereas suspended matter will settle out in the early stages of membrane filtration.

The key indicators of loss of membrane performance are:

- low product flows
- poor product quality (increased salt passage)
- high pressure drops ( $\Delta P$ )
- a need for more frequent cleaning

The influence on each of these factors is determined by the types of fouling present (Table 1).

## MEMBRANE AUTOPSY

Membrane autopsy is a technique used to identify the cause of poor membrane performance (Figure 2). This requires a sacrificial membrane element to be removed from the plant for destructive analyses. Analytical techniques are used to determine the nature of membrane foulant present on the membrane surface.

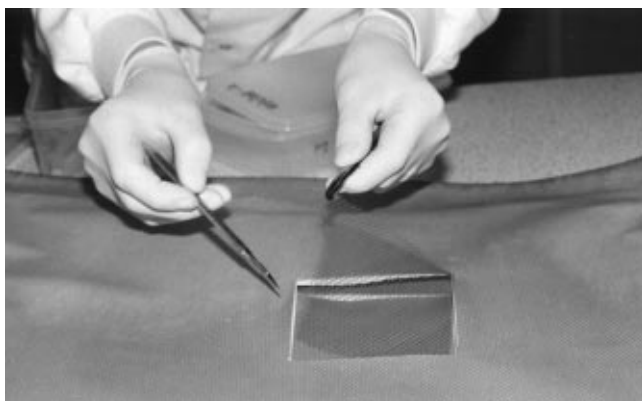
Standard autopsy investigation involves the dissection of a fouled membrane element taken from the problem plant. The membrane is unrolled to reveal the membrane leaves and plastic spacer material. If a hollow fibre module is being autopsied, the fine fibres are removed from the fibreglass casing for investigation. Foulant sample is then obtained from a known surface area of membrane or quantity of hollow fibres for chemical and microbiological analysis.

The key steps of membrane autopsy procedure are:

- selection of representative element (or elements)
- dissection
- analysis
- identification
- remedy

**Table 1 — Effect of common foulants on plant performance**

Foulant Type	Salt Passage	Pressure Drop	Product Flow
Calcium and inorganic salts	10-25% increase	10-40% increase	<10% decrease
Metal oxides hydroxides	>2 x rapid increase	>2 x rapid increase	20–40% decrease
Colloids	>2 x gradual increase	>2 x gradual increase	>50% gradual decrease
Organic matter	increase or decrease	small increase	>50% decrease
Biofouling	>2 x rapid decrease	>2 x rapid increase	>50% decrease



**Figure 2 — Membrane autopsy**

Where possible, a fouled element should be selected from each stage of the plant. If this is not possible, obtain an element from the final stage. Feedwater, product water and reject samples should be obtained in addition to historical plant operating data taken prior to plant shutdown and element removal.

After removal of the element, it should be kept wet and wrapped immediately in a plastic bag and sent to the autopsy laboratory. It is important that no preservative is added at this stage otherwise microbiological investigations cannot be carried out. On receipt of the membrane, it is weighed to give an initial indication of the quantity of foulant present. This is particularly significant when scale formation has occurred.

The membrane is visually inspected for evidence of telescoping or damage of the fibreglass casing. Such damage indicates a high degree of fouling caused by excessive pressure drops across the membrane. At this stage, any observation of organic matter at the inlet or outlet end of the element is recorded. A slimy deposit may also be seen on the outer casing as a result of biofouling.

The membrane should be dissected as soon as possible after removal from the plant. If the element is not to be dissected immediately, it should be kept wet, wrapped in a plastic bag and stored in a cool place. The next stage is to transfer the element to a laboratory area and to remove the fibreglass casing and plastic end-pieces with a cutting tool. The membrane can then be unrolled, revealing the membrane separating surface and plastic spacer material. When the membrane has been unrolled, the glue lines at the edge of the membrane should be checked for damage or signs of leakage.

On visual inspection, heavy scaling and foulant may be observed by the naked eye, but light fouling and membrane damage may not necessarily be visible. It is important to take samples for analysis immediately

after the membrane has been exposed. The foulant layer should not be allowed to dry. The following samples should be taken from two or three positions along the length of the element:

- fouled membrane material
- foulant sample
- plastic spacer material

A range of analytical techniques can then be carried out to identify and quantify the major membrane foulants.

## **ORGANIC AND INORGANIC ANALYSIS**

Moisture content and chemical composition of dried deposit is determined. Standard analytical techniques are used to quantify inorganic and organic content of foulant samples. This determines the percentage composition of moisture, scale, organics, silica and iron.

In some fouling situations, humic acid analysis is required; this is necessary when treating highly coloured surface waters such as those found in the Scottish Highlands or in areas of Northern Europe.

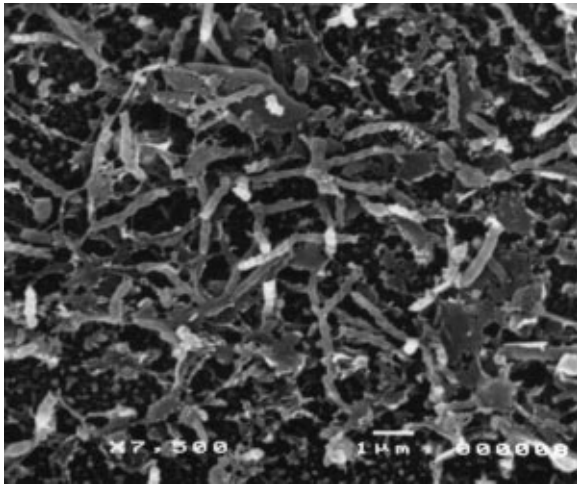
## **MICROBIOLOGICAL IDENTIFICATION**

A large number of reverse osmosis systems have been investigated by the PermaCare laboratory to quantify and characterise biofouling. The main objective is to gain information to recommend procedures to remove accumulated biofilm and prevent re-contamination.

Samples of foulant can be scraped from a known area of membrane for microbiological analysis, which consists of basic identification and enumeration of bacteria, fungi and yeasts. Microbiological counts should be expressed as cfu/cm<sup>2</sup> of membrane. Biocide Sensitivity Tests (BST's) can be used to evaluate the performance of selected biocides on sessile microorganisms.

Membrane biofilms have been characterised by our laboratory to provide enough basic information to evaluate the cause, degree of accumulation and ease of removal.

The following bacteria are regularly identified on the membrane surface: *Corynebacterium*, *Pseudomonas*, *Arthrobacter*, *Actinomyces*, *Flavobacterium* and *Aeromonas*. One or more of the following fungal genera have also been found in the **majority** of samples, sometimes in significant numbers: *Penicillium*, *Trichoderma*, *Mucor*, *Fusarium* and *Aspergillus*. It is not common practice in the industry to enumerate or identify planktonic fungal species, but our studies have found this to be a significant contributor to sessile fouling. In some cases, yeasts have also been identified in significant numbers.



**Figure 3 — SEM of microbiological fouling on a polyamide membrane**

Typically, the bacterial counts found on a biofouled membrane will range between  $10^6$  and  $10^8$  cfu/cm<sup>2</sup>. Theoretically microorganisms should not be present on the permeate side of the membrane due to their size, but it is common to find significant counts on the product water carrier. This is due to either membrane imperfections or back-contamination downstream of the RO.

### **MICROSCOPIC EXAMINATION AND MEMBRANE SURFACE ANALYSIS**

Samples of fouled membrane can be examined using Scanning Electron Microscopy (SEM). This technique produces pictures that can clearly show scale deposits and biofilm layers on the separating surface. Micrographs are usually produced at x7,500 magnification (Figure 3).

Surface analysis techniques are useful when the cause of fouling is complex and cannot be fully determined by routine chemical analysis. This may be due to trace quantities of unusual foulants such as heavy metals present in wastewater streams, causing poor performance or membrane damage. X-Ray Photoelectron Spectroscopy (XPS) has been successfully used to detect small quantities of species present on the membrane surface. When using this technique, a new membrane sample of the same material should be analysed as a blank reference sample.

### **MEMBRANE CLEANING**

Frequent and appropriate cleaning procedures are vital in order to maintain the performance of RO membranes. It is necessary to follow a structured cleaning programme that has been designed to suit the cleaning needs of each plant. Although the proce-

dures may be similar in many cases, the cleaning solution concentrations, volumes of solution and stages of cleaning will differ. The frequency of cleaning will be determined by the rate of fouling.

The need for cleaning is indicated by a reduction of the product water output. In some instances, fouling of the membrane results in a marked increase in salt passage.

The recommended cleaning programmes must be selected according to the specific fouling potential of the treated feed entering each plant. This is determined by analysis of the microfoulants in the incoming feedwater stream. In cases of severe membrane fouling, chemical analysis may be carried out on surface foulants obtained from membrane autopsy techniques. The main factors that will influence the effectiveness of membrane cleaning are:

- Type of cleaning chemicals used
- Cleaning solution volume must be appropriate for the size of plant
- Contact time, soaking of membranes in solution can aid cleaning
- Temperature, cleaning chemicals are most effective at warm temperatures
- Design of the cleaning circuit and operating parameters

There are a variety of different cleaning chemicals available for membrane cleaning. The properties of some chemicals are not suitable or compatible with some membrane materials. For example, cellulose acetate membranes can only be cleaned with chemicals that are within a restricted pH range, and thin film composite membranes are easily oxidised.

A cleaning procedure can be devised based on anticipated or identified foulants. As a general guide, cleaning is recommended when any of the following change by 10 to 15%:

- an increase in salt rejection
- an increase in pressure drop ( $\Delta P$ )
- an increase in feed pressure
- a decrease of product flux

The major types of cleaning agents suitable for a range of common foulants are detailed in Table 2. A combination of these chemicals is usually required to give effective membrane cleaning. Procedures may consist of a three-stage clean with provision for soaking in between recirculation of the cleaning solution.

Bench scale cross-flow equipment can be used to evaluate recommended cleaning programmes using fouled membrane samples obtained from an autopsy.

**Table 2 — Cleaning agents for membrane fouling**

Foulant Type	Chemical Characteristics	Recommended Product
Inorganic scale	Acid based	PermaClean® 88
Sulphate scale	Chelating agent	PermaClean® 33
Iron and metal oxides	Weak acid	PermaClean® 77
Organic matter	Alkaline surfactant	PermaClean® 99 or PermaClean® 67
Biofilm	Alkaline based cleaner	PermaClean® 99
Silica	<i>*Very difficult to remove: Demin water, pH11, 40°C</i>	<i>*Use a silica antiscalant PermaTreat® 510</i>
Silt/colloids	Chelating agent	PermaClean® 33
Microorganisms	Non-oxidising biocide	PermaClean® 11 or PermaClean® 55
Cleaning CA membranes	Mild acidic and alkaline	PermaClean® 78 PermaClean® 67

The results of these tests have been reliable and give a good indication of the predicted effectiveness of tested cleaning schedules.

Cleaning solutions are most effective when circulated at elevated temperature, preferably 30°C. The following procedure has proven highly effective in removing biofouling. However, biofouling often recurs and plants require repeated use of the procedure to maintain plant operation with a tolerable level of biofilm.

#### **EXAMPLE: CLEANING SCHEDULE FOR REMOVAL OF BIOFILM**

The membranes were rinsed with chlorine-free water between each stage of the cleaning procedure.

##### **Step 1 :**

Alkaline surfactant and chelating agent, to condition and break down organic fouling

Cleaning conditions: pH 10.5, 30°C, 4 hour recirculation and soaking

##### **Step 2 :**

Broad-spectrum non-oxidizing biocide, to stop microbiological growth

Cleaning conditions: 30°C, 30 minute recirculation and soaking

##### **Step 3:**

Alkaline surfactant, to remove microorganisms and organic debris

Cleaning conditions: pH 10.5, 30°C, 4 hour recirculation and soaking

##### **Step 4:**

*Optional:* acidic clean, to remove traces of inorganic scale and iron oxide

Cleaning conditions: pH 3.6, 25°C, 2 hour recirculation and soaking

Suitable biocides must comply with a long list of specifications which includes: broad-spectrum, membrane-compatible, non-filming, anionic or non-ionic, non-oxidising and preferably fast acting. The industry is in need of new effective biocide formulations compatible with polyamide membrane systems, but the likelihood of identifying new formulations is low due to the impending European Biocidal Products Directive.

## **CONCLUSIONS**

- Assume that some fouling will occur in all membrane systems.
- Good pre-treatment design, biogrowth control and adequate antiscalant dosing minimises fouling.
- Membrane autopsy is a useful technique when fouling is complex and poorly understood.
- Periodic maintenance cleaning is recommended.