Membrane Cleaning Under the Microscope Successful Cleaning Means Knowing the Foulant

(September, 1995, Water Technology) By Stephen R. Dunham and David L. Kronmiller, Ph.D.

Membrane fouling occurs in nearly all reverse osmosis systems. The frequency of fouling varies from one RO unit to the next and depends on a number of variables. including system recovery rate, RO feedwater characteristics. pretreatment and system operation. Fouling may occur as frequently as every week or as infrequently as once a year. In any case, it is important to have a good understanding of what membrane foulants are, how they occur and accumulate on the membrane, and when and how they may be most effectively removed.

Types of Fouling

There are four major categories of membrane foulants which may be classified by their physical type and their location on the membrane: dissolved solids, suspended solids, biological organisms and nonbiological organics.

Dissolved solids are scale-forming materials such as calcium and barium, which are soluble in feedwaters. They are either cations (positively charged ions) or anions (negatively charged ions), which may complex and precipitate in the brine stream as their concentrations increase in the RO. Examples of such precipitated cation/anion compounds include calcium carbonate, calcium sulfate, barium sulfate, and strontium sulfate.

Suspended solids maintain their suspension through a process of repulsion by a double layer of charge. Examples of suspended solids include colloidal forms of metal oxides such as iron. aluminum or silica. The charge-repulsion characteristics of suspended solids also stabilize particulates such as carbon fines which may inadvertently leak from mixed media or carbon filters. Suspended solids tend to agglomerate and settle onto the membrane surface when concentrated past the point of their charge related stability.

Biological foulants are aerobic and anaerobic living materials such as bacteria, fungus, algae, and the metabolic waste they generate. Such foulants tend to be present in low concentrations and literally grow into massive quantities that effectively block flow through the membrane surface.

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Non-biological organic foulants are substances that contain carbon-based chemical structures, but which are not living organisms. Examples of non-biological organic foulants are materials such as oil, plant materials, cationic surfactants, and hydrocarbons.

Foulant Misconceptions

A common misconception is that membrane foulants are a culmination of various constituents into a single heterogeneous mass. Depending on the chemical and physical composition of the foulants, they tend to form distinct layers between the membrane leaves, in the spacers and on the membrane surface.

Dissolved solids form and attach to the membrane in layers according to chemical type. Calcium carbonate forms in the brine spacers above the membrane surface and thus impedes flow. Sulfates form on the surface of the membrane in small pools. Silicate gels «wet out» the membrane surface, spreading over the surface in a thin layer and slowly blinding off the membrane. Suspended solids (colloids and particulates) agglomerate at the membrane surface, usually in the leading membranes of an array, whereas biological growth occurs in areas where «food» is available. Iron reducing bacteria, for example, grow in areas containing iron fouling. Fungus tends to grow in areas such as silica-phosphate gel, which provides both protection from flow and food for additional growth.

Organic foulants are carbon based molecules which have a natural affinity for the membrane surface. Because of this affinity, organic foulants such as oils wet out the membrane, spreading directly onto the membrane surface.

How Fouling occurs

Dissolved solids contribute to membrane fouling when water constituents become concentrated and precipitate onto the membrane. When constituents are concentrated in the RO past the point of supersaturation, a nucleus is formed. The nucleus may then either precipitate onto the membrane or become attached to the membrane at a previously fouled area on the membrane surface, known as a site of nucleation.

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With RO, higher recovery rates increase the concentration of the salts in the brine. Similarly, the calcium and bicarbonate ions, or the barium and sulfate ions, combine to form a nucleus which precipitates onto the membrane.

Calcium carbonate is one of the most common membrane foulants. Its potential for membrane fouling may be measured using the Langelier Saturation Index, or LSI. (Two other measures -- the Ryznar or stability index, and the Stiff and Davis modifications of the LSI -may also be used). A positive LSI, which is characteristic of feedwaters with greater hardness, indicates the potential for calcium carbonate scaling. Reducing the feedwater pH with acid reduces the LSI.

Lowering the pH decreases the formation of calcium carbonate, but increases the potential of other foulants, such as silica. In natural water, silica exists in two physical forms: soluble (or reactive) silica, and colloidal silica. Decreasing the pH to less than 7.0 will decrease the solubility of silica, encouraging precipitation onto the membrane. In the presence of metal ions such as magnesium, aluminum, or iron, silica will also form complexes and precipitate onto the membrane. Plus, in the presence of phosphate or phosphonates, silica may form a gel which thickens, retarding flow and eventually blinding the membrane.

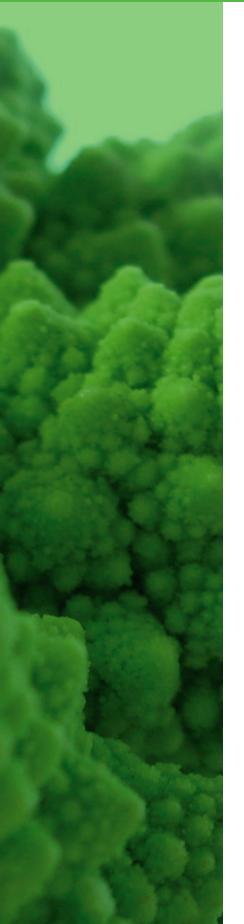
Pretreatment Strategies

Adjusting feedwater pH is only one of several RO pretreatments that can help minimize membrane fouling and cleaning. Other RO pretreatment methods include multimedia filters for large particulates, softeners for hardness reduction, and prefilters for smaller particulates. For waters with a positive LSI, deionization by ion-exchange resin columns may be used to reduce scaling potential.

Antiscalants are also capable of controlling waters with a positive LSI. They can stabilize the supersaturated precrystalline «soup» and retard the growth of crystals. Some high-performance antiscalant/ dispersants also control the formation of calcium sulfate, calcium phosphate, barium sulfate, strontium sulfate, silica scale, and iron and aluminum.



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Carbon filters are often used as a pretreatment method to remove chlorine and non-biological organics. However, you should have a preventative maintenance plan for the control of biological foulants, since carbon filters encourage biological growth. Chemical pretreatment may be applied to remove or control organics in solution. Biological fouling may be controlled by chemical injection, in conjunction with routine maintenance of mixing tanks and RO feed lines.

Another consideration affecting membrane cleaning frequency is system operating procedures. If RO production is temporarily interrupted or if the RO is periodically shut-down, first rinse the membranes at low pressure with RO permeate water. The objective is to minimize the concentration of salts in the membranes while there is no flow. Fewer salts are at the point of supersaturation, so most will remain in solution.

Particulate foulants should also be rinsed before shutdown or they may also settle onto the membrane surface and result in severe and often irreversibly fouled membranes. If the membranes are expected to remain idle for a longer period of time, an appropriate preservative should be used to inhibit biological growth.

When to Clean

Whether the foulants are biological, organic or inorganic, their presence on the membrane results in a decreased permeate flow, increased feed pressure to maintain the same flow, and/or an increase in the pressure differential (delta P) across the array. Closely monitor pressures and permeate flow rates and maintain them within the membrane manufacturer's specifications.

When a 10% decrease in system performance occurs, either as a 10% reduction in permeate flow at unchanged pressures or as a 10% increase in feed pressure to maintain the same flows, cleaning should be promptly initiated. Failure to clean according to the 10% rule can result in serious and irreparable damage to the membranes.

For example, silica may crystallize into a membrane surface pore. As the crystal grows, it expands and tears the membrane pore, reducing membrane salt rejection and compromising permeate quality. Inorganic scale accumulation in the membrane may also physically damage the membranes resulting in permanent salt rejection loss and/ or fouling which may be difficult or impossible to completely remove.

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The Order of Cleaning

When possible, conduct a foulant analysis to determine which foulants exist, what cleaners should be used and in which order cleaners should be applied. Foulant layers differ from one RO to the next, depending on feedwater characteristics and the hydration level of the foulants (absorbed water associated with the chemical form of the foulant).

When planning a membrane cleaning, it is important to consider the order in which the required cleaners should be used. In general, remove biological growth and colloidal silt first. A second cleaning removes the metals and scale from the membrane. Layers, such as silica and barium sulfate which tend to exist at the lower level of the stratus (closest to or directly on the membrane), may be removed in a final procedure.

Pros and Cons of Cleaners

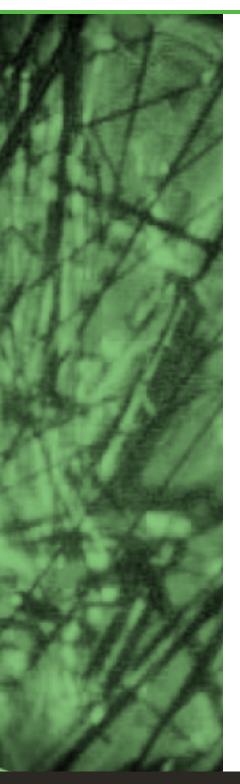
Generic membrane cleaners -- such as acid and caustic solutions -- and higher technology specialty cleaners have advantages and disadvantages. Generic membrane cleaners are relatively inexpensive, and in cases of minimal fouling, reduce feed pressures and increase product water flows. In more difficult feedwaters, operators will find it beneficial to use some types of higher technology specialty cleaners. Although higher in price, some specialty cleaners will remove the complete foulant mass from the membrane surface, reducing residual foulants which can serve as sites of nucleation, causing more rapid fouling. (Cleanings are required more frequently as the sites of nucleation become more numerous.)

While some foulants may be successfully solubilized or dispersed by generic cleaners, the foulants tend to fall out of solution and are redistributed onto other areas of the membrane, causing what is called «setback». Some specialty cleaners will maintain the foulant's solubility or stability once dispersed so the foulants cannot redeposit on the front end of a membrane or array.

In addition to the use of some types of specialty cleaners, two other techniques may prove beneficial. During the cleaner recirculation and rinsing procedures, pressures should be reduced so permeation is avoided. By reducing pressures, the membrane foulants are no longer being forced toward the membrane by the water flowing through it. Instead, foulants may move away from the membrane surface, into solution and out of the membrane element.



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Another method of foulant removal from spiral-wound membranes is the injection of compressed air into the cleaning solution feedline. This procedure is best suited for cleaning a few membranes at a time. The injection occurs during the recirculation process. By injecting minute amounts of air into the low-pressure cleaning solution feedline, air bubbles create a physical turbulence near the membrane surface which can «float» foulants. Such turbulence. used in conjunction with chemical cleaning, may aid in cleaning foulants from the membrane surface. However, when done improperly, this technique can have significant adverse effects on membranes, including extrusion or telescoping of the membrane element and delamination of the glue seams: it may also affect O-ring seal integrity. Compressed air injection is often only resorted to when normal clean-in-place (CIP) or skid cleaning procedures fail to restore membrane performance.

For Best Results

Understanding the basic principles of membrane fouling allows operators to more effectively prevent premature membrane fouling. Though fouling will occur in nearly all RO systems, proper maintenance procedures and good membrane cleaning methods can improve system operations in the long-term. Ultimately, proper prevention and a regular maintenance plan increases the useful life of RO membranes and improves the efficiency and economy of RO operations.

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