IDA-DWR-97

RO SYSTEMS
Current Fouling Problems and Solutions

by

Zahid Amjad, Ph.D.
Noveon, Inc.
(formerly The BFGoodrich Company, Performance Materials)
9911 Brecksville Road, Cleveland, Ohio 44141

This paper was originally published in ***Desalination and Water Reuse**,* Feb/Mar-1997, Vol. 6/4, 55-60.

noveon

RO SYSTEMS
Current Fouling Problems and Solutions

By Zahid Amjad, Ph.D.

The advent of semipermeable membranes as a viable separation technique has prompted a virtual explosion in the number of processes that use these separation steps in the purification of a final product. During the last two decades, reverse osmosis (RO) has become an integral and vital process in the desalination of sea, brackish, and ground waters for potable water and industrial needs. RO applications in the food processing industry are developing broadly to include fruit and vegetable juices, processing of milk, sugar, fats and meat by-products. The RO membrane separation process also plays a useful role in cleaning industrial effluents including those from pulp and paper, metals recovery from electroplating wastes, and municipal wastewater reclamation. In addition, RO processes are used widely in the production of high purity water for pharmaceutical, cosmetics, semiconductor, and power industries.

RO membranes typically remove greater than 99% of the dissolved salts, microorganisms, and colloids, and in some cases, more than 90% of the soluble silica and total organic carbon from the feed stream. A fundamental problem facing RO users today is the persistence of "fouled" membrane surfaces. The term fouling implies the deposition of any material on the surface of the semipermeable membrane. In many cases, fouled membranes have a reduced flux and lower operating efficiency which may lead to poor water quality, unscheduled shutdowns, and premature membrane replacement resulting in increased operating cost. The long term success of an RO system largely depends on three factors: design, pretreatment (including chemical conditioning), and operation and maintenance.

Figure 1 illustrates a typical RO system. An RO system is comprised of pretreatment, RO, and post treatment units. The pretreatment unit adjusts the water chemistry of the feed for optimal performance of the RO system which also adjusts the feed water chemistry to optimize the post treatment. The primary consideration is the quality and quantity of the water entering the system as well as leaving the treatment process. RO systems design and operation have been reviewed in detail elsewhere (1). This paper reviews the current status of membrane fouling and pretreatment, especially the application of antiscalants and dispersants.

Membrane Fouling: Causes and Cases

The major cause of performance deterioration in RO processes is the deposition of undesirable materials on membrane surfaces. The fouling of an RO membrane is a complex phenomenon involving the deposition of several different but related types of foulants on the membrane surface. RO system fouling problems are becoming more prevalent as the use of low quality feed water increases. In addition, surface water treated with cationic

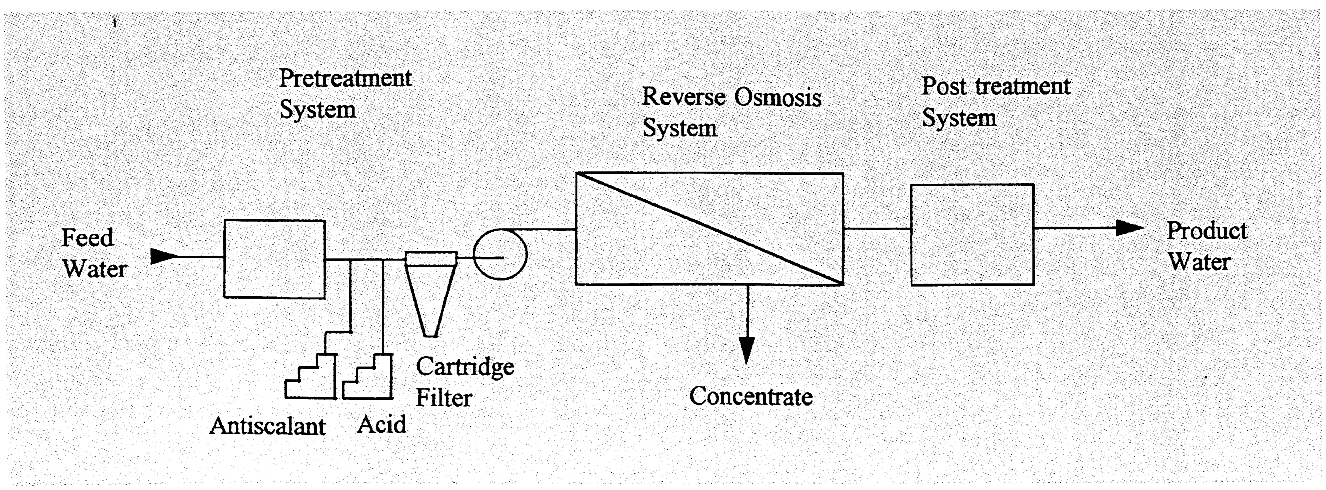

Figure 1. *Reverse osmosis system*

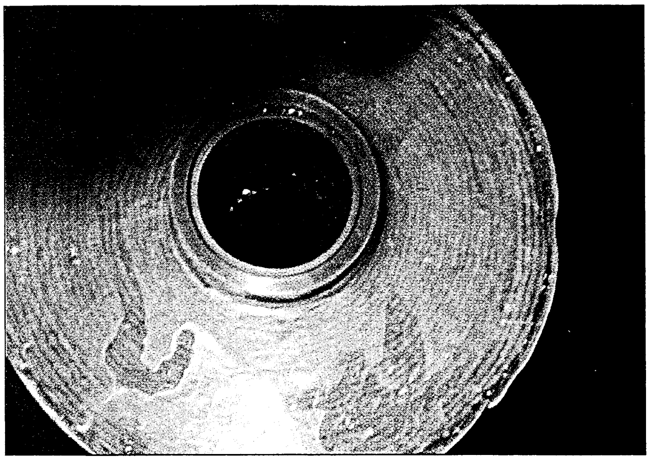

Figure 2. *RO membrane fouled with iron and copper sulfides.*

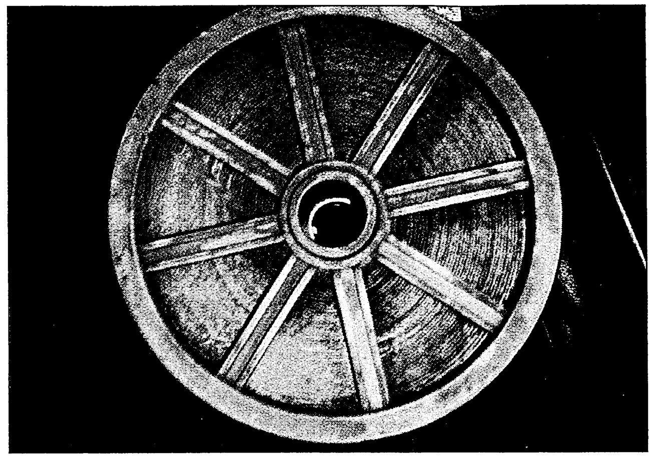

Figure 3. *RO membrane fouled with iron oxide.*

organic flocculants poses very different and challenging fouling problems. A brief discussion of four commonly encountered foulants e.g., inorganic, particulate, microbial, and organic, is presented below.

Inorganic Fouling (Scaling)

The precipitation and deposition of sparingly soluble salts as the feed water is concentrated causes membrane scaling. The major components of these precipitates include calcium carbonate; sulfates of barium, calcium, and strontium; calcium fluoride; and calcium phosphates. Occasionally, sulfides of copper and iron are also encountered.

Scaling normally begins in the latter stages of an RO system. Fouling of membranes with scale-forming salts will cause increased resistance, thereby increasing feed pressure necessary to produce the same amount of product water. As scaling progresses, a reduction in salt rejection ability occurs as a result of increased concentration polarization in the boundary layer, and the feed-to-brine pressure drop increases. *Figure 2* demonstrates heavy copper and iron sulfides scaling of RO element resulting from inadequate pretreatment.

Colloidal Fouling

The fouling of RO membranes by suspended matter is a critical concern for the RO industry and perhaps the major constraint in the efficient use of RO systems. Certain feed waters, especially surface waters, normally require far more extensive pretreatment than other sources such as deep wells. Changes in feed water composition can occur due to seasonal variations of a surface water supply. Feed waters containing suspended matter such as clay, silt, etc., are typically treated with coagulating / flocculating agents before entering the RO system. The effectiveness of surface water treatment to reduce suspended matter is dependent upon the proper selection and concentration of coagulants, pH, mixing, and residence time (2). Commonly used water clarification chemicals include: aluminum chloride, ferric chloride, and cationic polymers such as dillayldimethyl ammonium chloride (DADMAC). These chemicals have been known to "carry over" from the water clarification process to RO system and can potentially interfere with the performance of the RO water treatment program. *Figure 3* shows severe iron oxide fouling on RO membrane.

Organic Fouling

Certain surface-active chemicals such as surfactants, detergents, high molecular weight polymeric flocculants may irreversibly adsorb onto the membrane surface and impair performance. Other natural organics such as fulvic, humic, and tannic acids present in surface waters may also affect membrane properties such as salt rejection and water flux (3). These organic compounds are known to damage the membrane characteristics at very low concentrations (a few part per million). In our previous study, it was demonstrated that the presence of low levels of DADMAC can significantly reduce the performance of cooling water treatment programs. It was also shown that the composition of the antiscalant / dispersant plays a key role in the overall performance of the water treatment program (4). In addition, it has also been reported that in high hardness waters polyacrylate based antiscalant can form an insoluble salt with calcium, thus leading to membrane fouling. The presence of Ca-acrylate salts in the RO membrane deposit clearly illustrates the poor use of antiscalant (5).

Biological Fouling

Fouling by microbiological slimes is a constant threat to the efficient operation of an RO system. Microorganisms which cause the slime deposits are living organisms capable of exceedingly rapid reproduction. Biological fouling can occur when the feed water contains sufficient nutrients to sustain rapid growth of organisms. In the boundary layer, the nutrients present in the feed water are concentrated. Since microorganisms attach to the surface, these are ideal conditions for optimum growth. In most water systems, a thin biofilm is formed on the membrane surface that does not interfere with the performance in the short term. However, over a long period of operation, a biofilm accumulates thereby affecting the product flow sufficiently to require cleaning. Fouling associated with microbiological activity not only includes fouling associated with the aggravation of suspended microbes on the membrane boundary layer and the subsequent loss of flux but also includes irreversible membrane deterioration and product water contamination. Oil and other hydrocarbons are not usually present in significant quantities but can enter into the RO systems through leaks or spills. Even in low quantities, oil serves as a nutrient for accelerated microbiological growth, or can agglomerate other suspended particles into a sticky mass. In November 1993, in a joint conference on fouling and module design workshop sponsored by NSF (National Science Foundation) and NWRI (National Water Research Institute), biological fouling was rated as one of the most prevalent and least understood phenomena (6).

Pretreatment

Pretreatment is a key to the successful long-term performance of an RO system; its importance in system design cannot be overemphasized. The pretreatment techniques used to alleviate fouling problems are nearly as varied as the problems themselves. A short description of some of the more common means of pretreating a given feed water stream to make it suitable for further treatment by RO is given below. It is often necessary to pilot test the pretreatment unit operations to verify the efficacy of the process in a particular application.

Media Filters

The most common (and oldest) means of removing solids from feed stream is media filtration. Included in this category are: slow sand filtration; rapid downflow or upflow sand filtration; single media anthracite, garnet, or green sand filtration; or, more recently, multimedia filtration. Multimedia filters often feature layered beds of anthracite coal, various sands, finely crushed garnet, pumice, walnut shells, or other media. Each type has distinct advantages and disadvantages which must be weighed carefully when designing a system.

Because suspended matter of a colloidal nature is often too small to be removed efficiently, and the particles may be charged and actually repelled by the media itself, the media filter alone may not be sufficient. In these cases, a coagulant / flocculant may be added as a filter aid. The primary function of a coagulant is to adsorb onto the surface of a colloid and to neutralize the surface charge allowing small particles to agglomerate or coagulate. A flocculant will bridge between smaller particles to form larger particles which will settle faster or may be more easily retained by the filter.

Cartridge Filters

Nearly every RO system in use today is equipped with cartridge filters before the high pressure pumps to prevent suspended matter from entering the system. Cartridge filters are available in a variety of sizes, configurations, and materials of construction. Cartridge filters may be surface (often absolute filters) or

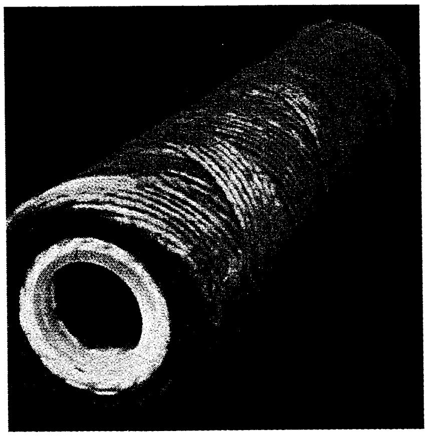

Figure 4. *Cartridge filter fouled with iron hydroxide.*

depth configurations. They may be made of cotton, cellulose, or polypropylene. These filters come in a variety of physical sizes from six inches to five feet long and have pore size cutoff (or retention sizes) of 0.2 to 200 microns. Most membrane manufacturers suggest 5 micron or smaller filters to provide adequate protection. In some cases, it is beneficial to use decade filtration. The use of larger filters followed by smaller ones to reduce individual filter loading by better filtration in depth. *Figure 4* shows an iron fouled cartridge. Iron is formed on the outer surface, little or no iron broke through the filter.

Ultrafilters

Ultrafiltration (UF) membranes have been introduced in recent years. These UF filters are not nearly as tolerant as media filters to suspended solids. They are also expensive and require additional equipment for their operation. However, UF membranes provide consistent, good quality low SDI (Silt Density Index) water which may, in many cases be fed to an RO with little or no other pretreatment. Additionally, they are fairly rugged (compared to an RO). It is often beneficial if the fouling problem can be transferred from the RO to the UF membranes. UF membranes can usually tolerate a wider range of harsher cleaning chemicals. Some ultrafilters may be backwashed.

Pretreatment Chemicals

Every RO water treatment program used today can benefit from the use of suitable pretreatment chemicals (i.e., antiscalant / dispersant). Depending on the system and treatment program, the pretreatment chemicals can be hexametaphosphate, a simple homopolymer or a copolymer comprised of several monomers of varying functional groups (multifunctional). In some cases, blends of polymers and other scale control agents may be used to provide well balanced treatment technology. These antiscalants offer the following modes of action:

Scale inhibition

- Sequestration
- Particulate dispersion
- Crystal modification

Scale Control

The high levels of dissolved scale forming ions in most feed waters necessitate some form of pretreatment to control scale formation on membrane surface. Sodium hexametaphosphate (SHMP) in conjunction with sulfuric acid (H_2S0_4) addition to maintain the pH below 6.5, was used for years, primarily as a pretreatment for cellulose acetate membrane systems. However, the use of SHMP has lost favor since the advent of low-pressure thin film composite; polymeric antiscalant / dispersant (which facilitate operating RO system above pH 7.0); phosphate effluent discharge limitations and safety concerns about the use of H_2S0_4. The performance of multifunctional antiscalants (i.e., AQUAFEED® 1000 Antiscalant (AF 1000)) to control various scales has been reviewed in previous publications (7,8). This paper presents our recent results on the effect of low levels of DADMAC on the inhibitory power of the commonly used antiscalants. The $CaCO_3$ inhibition data presented in *Figure 5* clearly show that the presence of 1.0 ppm of DADMAC affects the performance of polyacrylic acid antiscalants (i.e., AQUAFEED 600 Antiscalant (AF 600), competitive products) far greater than for multifunctional AF 1000. From a practical point of view, if low levels of DADMAC are encountered in RO feed water, incorporation of high performance antiscalant in RO treatment program will ensure better overall performance of the system.

Metal Ion Stabilization

There are a number of metal ions (e.g., aluminum, iron, manganese, zinc, etc.) that are particularly bothersome in RO systems. The most prevalent in this group is probably iron. There are several methods commonly used to control iron fouling. These methods include the following:

- Maintain a reducing environment to keep the iron in the ferrous form. This can be achieved either by addition of a reducing agent (e.g., sodium bisulfite) to eliminate oxygen and / or pH via acid (e.g., H_2SO_4) addition.
- Removal of iron ahead of the RO system by oxidation, to form ferric hydroxide, and filtration.
- Addition of sequestering / stabilizing agent - These agents can be either polymeric or non - polymeric acids such as citric acid, ascorbic acid, gluconic acid, or a multifunctional antiscalant / dispersant (e.g., AF 1000). Although non-polymeric acids are effective iron sequestering agents, these compounds exhibit poor scale inhibition and dispersancy properties.

Figure 6 illustrates the performance of various products for iron stabilization. As shown in Figure 6, stabilization of iron is strongly dependent upon the composition of the stabilizing agent. Poor to moderate improvement in stabilization of iron (III) when either SHMP or polyacrylic acid - based antiscalant (e.g., AF 600) was added to the system as seen by the intensity of color (the darker the yellow color more iron hydroxide precipitated from solution). The addition of AF 1000 under similar dosage conditions provided almost complete stabilization of iron. The excellent performance exhibited by AF 1000 is extremely important in the successful operation of RO system where presence of metal ions in feed water can cause serious fouling problems. For many years, the RO industry relied primarily on SHMP or PAA in controlling the deposition of various types of foulants. However, to control the formation of iron, manganese or aluminium - based foulants, the RO user needs a much higher level of performance than the SHMP or PAA can provide.

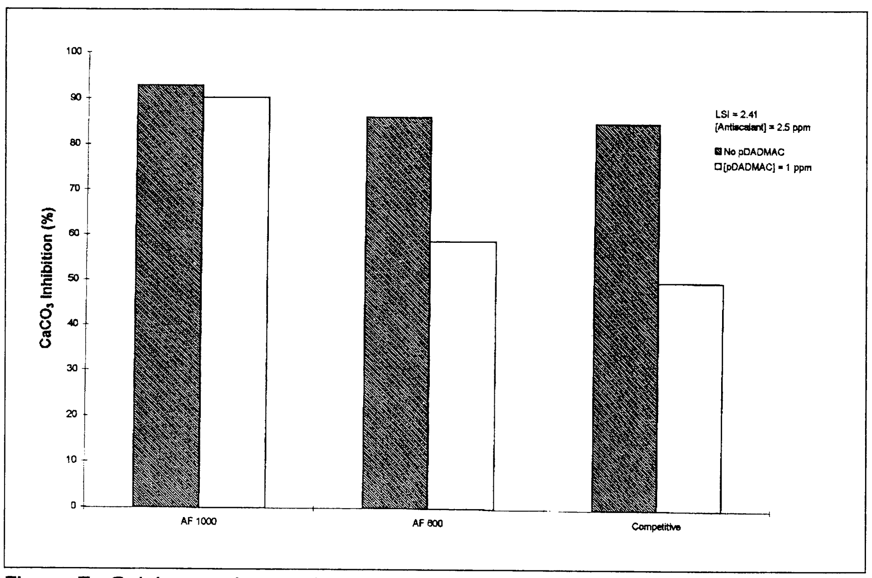

Figure 5. *Calcium carbonate inhibition by various antiscalants in the presence of DADMAC.*

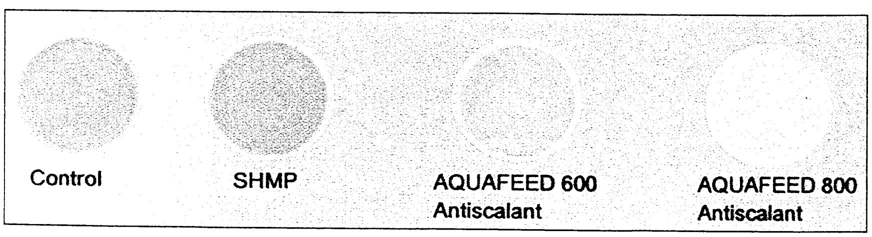

Figure 6. *Stabilization of iron hydroxide by various antiscalants.*

Colloidal Fouling Control

Severe membrane fouling can occur in RO systems due to the presence of colloidal / suspended matter in the feed water. The control of suspended solids can be done mechanically, chemically, or by a combination of both. Mechanical control methods include side stream filtration, pretreatment of the feed water by clarification or filtration, or softening. Many RO systems using the mechanical method operate with only limited success and require planned periodic downtime for cleaning. Some RO systems experience brief, unexpected increase in suspended solids. This may be due to a disturbance in the well supplying the feed water, or to an upset in an auxiliary process in an industrial or waste stream application. Incorporation of an effective dispersant into an RO pretreatment program can provide improved operating reliability to handle upsets due to suspended solids and to reduce the need for routine cleaning. Dispersants function in RO colloidal foulant control applications by keeping solid particles suspended so that they can be removed without settling out. The performance of a dispersant strongly depends on nature and level of colloidal materials. Photomicrographs of clay and iron oxide dispersed by AQUAFEED 800 Antiscalant (AF 800) are shown in *Figure 7*. The excellent dispersancy power exhibited by AF 800 for commonly encountered mixed suspended matter will reduce the rate of membrane fouling and can extend the operation time between membrane cleaning cycles. Any decrease in frequency of cleaning will have a direct impact on increasing the overall RO system performance

Biofouling Control

Biological control is a subject of considerable dispute mainly due to disagreement on the priority given to control biological population. It is generally agreed that bacterial population should be reduced. However, improperly applied biocides can adversely affect downstream processing. Biofouling is generally controlled by the use of chemical agents that kill or slow down the growth of microorganisms. The oxidizing biocides include: chlorine, chloramine, and hydrogen peroxide. Even though the chlorine is known to be effective in controlling microorganism growth, it oxidizes many membrane surfaces resulting in a permanent damage. There are proprietary non-oxidizing type biocides available for use with RO systems. The use of these biocides is relatively recent and their proponents are still gathering data about their efficacy. Additionally, continuously feeding a non-oxidizing biocide may prove expensive and discharging the RO system reject can be a limiting factor.

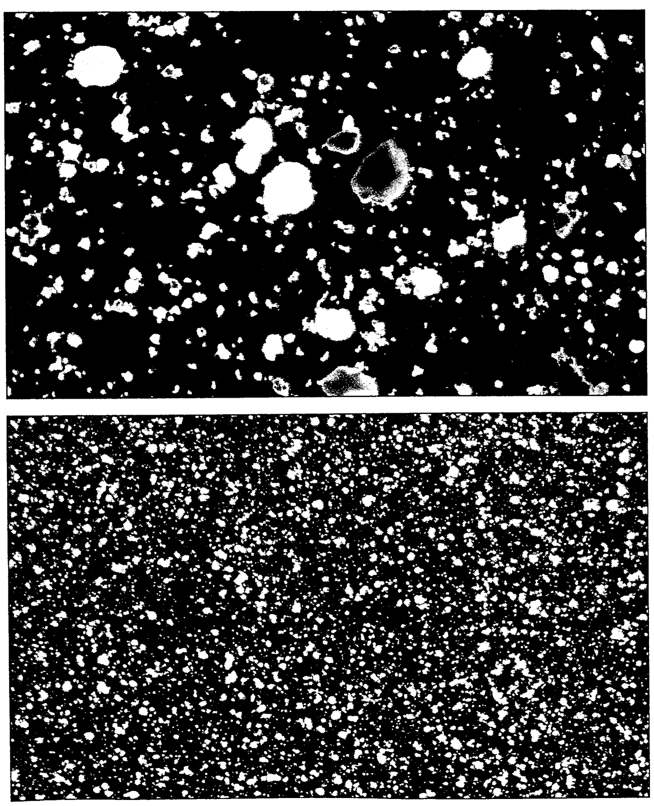

Figure 7. *Dispersion of iron oxide and clay in the absence (a) and presence (b) of AF 800.*

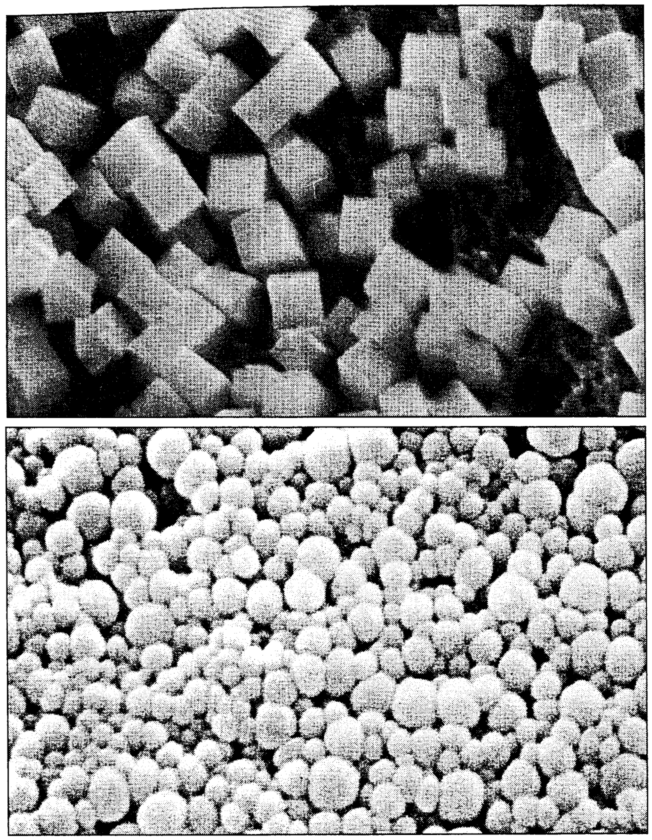

Figure 8. *Calcium Fluoride crystals grown in the absence (a) and presence (b) of AQUAFEED 1000 Antiscalant.*

Crystal Modification

It has been reported that the antiscalants used at low concentrations not only influence the growth rate but also the morphology of the scalant crystals. In some cases, such as calcium carbonate, calcium phosphates, calcium sulfates, and calcium oxalates, the presence of antiscalants also affects the nature of the phase that forms. The influence of a multifunctional antiscalant on the crystal morphology of calcium fluoride was studied by scanning electron microscopy. *Figure 8* (a) shows cubic calcium fluoride grown in the absence of AF 1000. The crystals are reasonably large and offer substantial surface area to adhere to membrane surface. Figure 8 (b) shows crystals grown in the presence of 1 ppm AF 1000. The crystals are spherical in shape and are markedly distorted and would have less tendency to adhere to the membrane surface.

Summary

RO systems frequently experience operational problems due to membrane fouling, the most common cause of lost production, reduced membrane life, and higher operating costs. This paper has attempted to provide an overview of the causes of membrane fouling. It has been shown that RO foulants such as mineral scales, colloidal matter, and metal hydroxides can be controlled with the application of high performance multipurpose antiscalants / dispersants. ■

References:

1. *Z. Amjad (Ed.), " Reverse Osmosis: Membrane Technology, Water Chemistry, and Industrial Applications", Van Nostrand Reinhold Publishing Company, New York, December 1992.*
2. *K. M. Jackson, Industrial Water Treatment 28, 24, 1996.*
3. *M. Nystrom, K. Ruohomaki, and L. Kaipia, Desalination, 106, 79, 1996.*
4. *Z. Amjad, J. Pugh, J. Zibrida, and R. Zuhl, CORROSION/96, NACE Int'l., Houston, TX, 1996.*
5. *F. H. Butt, F. Rahman, and U. Baduruthamal, Desalination, 101, 219, 1995.*
6. *Fouling and module design workshop, National Water Research Institute and National Science Foundation, University of Delaware, November, 1993.*
7. *Z. Amjad, J. Pugh, and J. Harn, UltraPure Water, 48, November, 1996.*
8. *Z. Amjad, UltraPure Water, September, 1987.*

About the Author:
ZAHID AMJAD, ***Ph.D.*** *is a Research Fellow with the Advanced Technology Group, B.F. Goodrich, 9921 Brecksville Road, Brecksville, OH 44141-3289.*

Noveon, Inc.
9911 Brecksville Road
Cleveland, OH 44141-3247, U.S.A.

Phone: 1-800-380-5397 or 216-447-5000
FAX: 216-447-6315 (Customer Service USA)
216-447-6144 (Customer Service International)
216-447-5770 (Marketing & Technical Service)

http://www.noveonsolutions.com

1997 (updated Apr 2003)