



Scale Inhibition in Desalination Applications: An Overview

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ABSTRACT

Desalination is a process in which dissolved impurities are removed from water. Three processes commonly employed include: distillation, electrodialysis, and reverse osmosis. This paper provides a general discussion of various desalination processes including advantages and disadvantages of each, performance comparisons, and problems encountered in the operation of the process. An in-depth discussion of fouling by mineral scales, colloidal matter, and metal hydroxides is also included. The role of the foulant control agent in treating a desalination system is also presented. Basic chemistry and efficacy of the individual scale inhibitors is summarized.

KEY WORDS: Antiscalant, Desalination, Dispersant, Distillation, Electrodialysis, Membranes, Reverse Osmosis, Scaling

INTRODUCTION

Water is the wellspring of life. It is the most important liquid in the world to maintaining the plant and animal life. It fills lakes, streams, the vast oceans, and flows under the ground. Water is a remarkable chemical, an excellent solvent capable of dissolving, to varying degrees, almost anything with which it comes in contact. Water picks up suspended matter as it runs across the ground and absorbs gases from the atmosphere. Impurities in the water come from many sources. It is important to understand the role of these impurities in desalination processes. This chapter presents an overview of scale inhibition in desalination processes. It starts with a brief introduction of various desalination processes, types and performance expectations, and comparative analysis of the desalination techniques. This is followed by a detailed presentation on types of foulants encountered in desalination processes and their effects on process performance. The last section deals with the application of pretreatment chemicals to prevent the deposition of foulants on heat exchanger and membrane surfaces.

OVERVIEW OF DESALINATION PROCESSES

Water may be purified by a number of desalination techniques in which the dissolved impurities are removed from water or, more correctly, pure water is removed from the impurities. Feed waters suitable for desalination are generally classified into four categories namely: sea water, brackish water (a mixture of sea water and fresh water), surface water, and ground water. Sea water is highly corrosive to iron pipes because of the high dissolved salt concentrations, especially sodium chloride which accounts for 60 to 70% of the total dissolved solids (TDS). River, lake, and pond waters may be classified as surface waters. Surface waters contain high levels of dissolved gases, such as carbon dioxide and oxygen, and suspended matter, both organic and inorganic in nature. Among the dissolved solids form the inorganic type suspended matter impurity. The quality of surface water varies with the season. Pollution from industrial waste and sewage is frequently present. Ground water sources include springs, wells, and bore wells. The quality of ground waters depends upon the strata through which the water has passed. Ground waters normally contain both carbonate and bicarbonate hardness. Iron, present mainly as ferrous carbonate, is sometimes found in large amounts in ground water.

The desalination of water can be achieved by a variety of techniques. These techniques, and the types of feed waters on which they are typically used, are reviewed below and summarized in Table 2.

Distillation

Distillation, the oldest type of desalination, is the process whereby a phase change is induced in the feed stream from which the pure water fraction may be separated by physical means.

<u>Thermal.</u> Though distillation may be accomplished by any process which invokes a phase change, evaporative, or thermal distillation, is the most common distillation process. In this process, the feed stream is temperature and pressure treated until the water boils. The steam is then collected and condensed. A single step distillation is not very efficient. The efficiency of these systems may be increased by increasing the number of times pure water is removed from the brine. Figure 1 shows the schematic of a multistage thermal distillation system. The efficiency may be further increased by duplicating the entire multistage process to make a multi-effect, multi-stage (MEMS) system. MEMS distillation has been the dominant technology used for large sea water desalting plants around the world. Today, hybrid systems taking advantages of reverse osmosis (RO) and MEMS technologies can offer new opportunities to expand water production by blending the RO permeate water with multistage flash (MSF) distillate to meet World Health Organization (WHO) standards of less than 500 mg/L TDS.

<u>Crystallization.</u> Crystallization, or freeze distillation, takes advantage of the lower energy toll for freezing water as opposed to boiling it. Freezing is also a phase change and, therefore, pure water frozen from a brine may be physically separated. The energy cost for raising the temperature from ambient to boiling is approximately 1 BTU (British Thermal Unit) per pound of water per °F and the boiling process itself requires approximately 980 BTU per pound of water. Lowering the temperature of water to its freezing point requires the same 1 BTU / lb °F but, in most cases, ambient temperature is closer to freezing temperature than to boiling. The energy toll to freeze water is only 144 BTU / lb, significantly less than for boiling. The crystallization distillation process (Figure 2) includes freezing part of the feed stream to form an ice slurry. This is accomplished by passing the sea water around cooling coils. The ice crystals are then separated from the brine, rinsed with small quantity of pure water (to remove any salts from the unfrozen surface), and then melted. Desalination by crystallization, compared to other processes, is not always economically attractive, largely due to difficulties involved in solids-handling and separating the ice crystals from brine, and is not commonly used.

<u>Solar Evaporation</u>. Solar distillation is a method which takes advantage of the sun's energy to produce fresh water from brackish or sea waters. In this process solar energy heats a black plate over which the feed stream flows. As the plate heats, the water flowing across it also heats. Some of the water evaporates. As the steam rises, it contacts the optically clear, cool encasement. Pure water is collected as illustrated in Figure 3. Although the process appears rather simple (utilizing solar energy in place of another energy source), this technology is not yet fully developed.

Ion Exchange

Ion exchange (IX), as the term implies, is a process by which undesirable ions of dissolved inorganic salts are exchanged with the more desirable ions. This process has been used for years for the pretreatment of waters fed to distillation columns and boilers in order to minimize scaling and carry-over. Complete desalination is achieved by exchanging the cations (i.e., Na^+ , Ca^{++} , Mg^{++} , and other metal ions) and anions (i.e., Cl^- , $S0_4^{--}$, etc.) with H^+ and OH^- ions, respectively.

At low salinity (<200 mg/L) IX is more economically attractive than RO to produce high purity water. For water containing high salt concentrations (such as brackish and sea waters), IX technology becomes prohibitively expensive because of increased need for regeneration and potential issues with waste disposal regulations. Currently, IX is used as a polishing aid in the production of high purity water. Figure 4 shows the cost comparison (\$ US / 1000 gallons of water produced as a function of salinity) of IX and RO. As illustrated in Figure 4, RO becomes more cost effective when the salinity of feed water exceeds 200 mg/L. IX resins are also prone to fouling by colloids, metal hydroxides, silica, and dissolved organics. The long exhaustion step allows the adsorption of suspended foulants deep into the resin that cannot diffuse back out in the short regeneration.

Membrane

<u>Electrodialysis and Electrodialysis Reversal.</u> Dialysis is a natural physiological process by which a body relieves itself of contaminants by allowing the passage of those contaminants through a membrane into a sweep stream which is flushed away. The main difference between this process and membrane separation processes such as reverse osmosis (RO) or nanofiltration (NF) is that the contaminants are the passing species not the solvent (in fact, the solvent usually cannot pass through the membrane at all). In this process, the concentration gradient is the driving force. An enhancement of this process involves inducing a magnetic field in the membrane cell via electrodes placed on either side of a cell which contains a membrane through which anions may pass and cations may not (the "anodic" membrane) and a membrane through which cations may pass and anions may not (the "cathodic"). By placing many of these cells in a parallel configuration (every second cell being a "concentrating" cell and the other of the pair "depleting"), the unit can exhibit energy savings on the induced current. The electrodialysis process is illustrated in Figure 5. The attraction of the anions for the anode and the attraction of the cations for the cathode provide for enhanced separation through enhanced driving force of the induced current.

One of the major limiting factors of this process is the build-up of foulants on the surface of the membranes due to the current polarity. Periodically reversing the polarity of the induced current (EDR, Electrodialysis Reversal) reduces fouling potential. When the polarity of the current is reversed, a concentrating cell becomes depleting. This allows for pseudo on-line cleaning. Of course, a certain amount of the product water must be sent to drain after a polarity reversal. The polarity of the applied direct current potential is usually reversed at regular 15 to 30 minute intervals. In the ED or EDR process, the amount of electricity consumed is directly proportional to the amount of salt removed. Desalination of sea water by this process is therefore not economical. Pretreatment is required for EDR, although perhaps not to the same extent as for distillation or RO. Typically, sulfuric acid and/or SHMP (sodium hexametaphosphate) is used to control scaling.

<u>Reverse Osmosis.</u> A dissolved substance in water will tend to migrate through the water until its concentration is equal in all regions of its confinement. If a semi-permeable membrane (that is, permeable by one material but not by another) were to impede the flow of the dissolved salt but not the water, the water would flow from the lower concentration through the membrane to the higher concentration area to achieve concentration equilibrium. This process is called osmosis. Osmotic pressure is the measure of how strongly a water wants to be diluted by pure water. Reverse Osmosis (RO) is a process whereby pressure is exerted on the more concentrated side in excess of the osmotic pressure to cause the natural osmosis to reverse. The water is forced by this pressure to flow through the semi-permeable membrane from the more concentrated side to the less concentrated side. The pressure required to cause the water flow against its natural tendency is equal to the osmotic pressure (plus any other fractional losses in the system). This process typically reduces the dissolved inorganic salt content of the product water by 90 to 99% as compared to the feed water. In RO process, the salt and other contaminants in the water are concentrated in the waste stream called the brine or reject. Desalination of ground, brackish, or sea water by RO is dependent upon the osmotic pressure of the feed stream. For example, in sea water RO systems, high pressures are necessary to overcome the high osmotic pressure of sea water (375 to 500 psi) compared to <100 psi needed for desalting of brackish water.

There are three major membrane types on the market today: cellulose acetate (CA), polyamide, and thin film composites (TFC). Table 3 compares relative performance of CA and TFC membranes. As shown in Table 3, the TFC membrane, from operational perspective, offers better overall performance in treating surface/brackish waters.

A typical RO system is shown in Figure 6. The system consists of the pretreatment system, cartridge filters, the RO system, and the post treatment system. The pretreatment to the RO system may include a clarifier, sand filters, multi-media filters, softener (hot or cold process lime or sodium cycle cation exchange), chemical injection, degassifier, decade filtration, or other membrane processes depending on the quality of the feed water. The purpose of the pretreatment is to protect the RO membranes from being damaged by the feed water. There is almost always a cartridge type pre-filter immediately upstream of the high pressure pump. This filter serves the dual role of protection for the pump from particles that may damage the impellers and final protection for the membranes. The post treatment may include ion exchange, ultraviolet sterilization, ultrafiltration, pH adjustment or other chemical addition, or even distillation. The post treatment used will depend on the quality of the water required for the end use. The heart of the system is, of course the membranes. All membranes are prone to fouling and therefore great care must be taken in selecting the membranes, designing and building the RO system, and operating the system to avoid membrane fouling. This is the reason why correct and adequate pretreatment is so very important to RO plants.

Table 4 summarizes some of the advantages and disadvantages of these various desalination processes. The selection of membrane versus thermal distillation for various feed water sources is an economic decision dependent upon several factors including, quality and quantity of product water, overall system performance, user friendliness, pretreatment chemicals requirement, environmental and disposal regulations related to brine disposal, etc.

CAUSES OF HEAT EXCHANGER AND REVERSE OSMOSIS MEMBRANE FOULING

The economics of desalination suggests that the more pure water that can be recovered from a stream, the higher the efficiency of the process. Any time that water is removed from the bulk feed stream, the brine becomes more concentrated. As the concentration of the salts in the brine increases, the potential for fouling also increases resulting in the precipitation of scale forming salts from brine. The density of a colloidal material may also increase during desalting of feed stream allowing coagulation and deposition of colloidal matter from brine.

The major cause of performance deterioration in distillation and RO processes is the deposition of materials on heat exchanger (Hx) and RO membrane surfaces. The fouling of Hx and RO membrane is a complex phenomenon involving the deposition of several different but related types of foulants on the surfaces. The fouling problem in these processes is becoming more important as the use of lower quality feed water increases. Membrane and Hx fouling via deposits results in decreased production, unscheduled shutdowns, poor product water quality, and premature equipment failure.^{1,2}

FOULANT TYPES

Commonly encountered foulants in desalination processes fall into the following three basic categories:

- Scale
- Suspended/colloidal matter
- Biological material

Each will be looked at separately with a review of the causes, prevention, and restoration of performance.

Scaling

Scaling of equipment surfaces is caused by the precipitation of sparingly soluble salts dissolved in the feed water. During the desalination process, the solubility of the sparingly soluble salts can be exceeded which will lead to precipitation. Common scales encountered include calcium carbonate, calcium sulfate, silica, metal silicates, oxides/hydroxides of aluminum, iron, and manganese. Other less commonly encountered scales include calcium fluoride, barium sulfate, strontium sulfate, and cupric sulfide.

<u>Calcium Carbonate</u>. Calcium carbonate is an important naturally occurring compound. It occurs in colloidal and amorphous states as well as in at least three polymorphs: calcite, vaterite, and aragonite. Many feed waters contain high concentrations of calcium bicarbonate. The primary mechanism leading to the deposition of calcium carbonate

on equipment surface is the conversion of soluble calcium bicarbonate salt into sparingly soluble calcium carbonate due to pressure drop and /or increase in temperature. The scale may be easily removed by cleaning with an acid.

<u>Calcium Sulfate.</u> Calcium sulfate is another mineral scale frequently deposited by brines. Calcium sulfate can crystallize from solution in three forms: dihydrate (CaSO₄•2H₂O, gypsum), hemihydrate (CaSO₄•1/2H₂O, plaster of Paris), and anhydrite (CaSO₄). Most calcium sulfate deposits in the RO systems are gypsum (the predominant form at temperatures below 40°C) whereas anhydrite and hemihydrate are the sulfate deposits commonly found on heat exchangers in the distillation processes. Though this scale is more soluble than calcium carbonate, once it has formed it is more difficult to remove. The predominant method of removing this scale involved the use of chelating agents. Figure 7 shows heavy gypsum scaling on an RO membrane. In this case the amount of gypsum deposited on the membrane was almost 60% of the virgin membrane weight.

<u>Silica/Silicate Compounds.</u> Silica, a common constituent of most natural waters, can occur at extremely high levels in well water supplies. At present, solubility is used to predict silica scaling. The precipitation of silica from solution is strongly affected by insoluble metal hydroxides/oxides present in the feed water. Silica, once deposited on the membrane, is difficult to remove and should be treated with caution. Two approaches which are often used to control silica in RO include lime softening and running the RO system at low recovery to keep the soluble silica concentration in the brine below the saturation point.

<u>Iron, Aluminum, and Manganese Hydroxides/Oxides.</u> Iron in feed water may be present as colloidal or soluble species. The ferrous (Fe⁺⁺) form is quite soluble at pH ranges commonly encountered in RO. Ferrous iron is not a problem as long as it remains in that form. Upon oxidation to the ferric form, iron hydroxide can deposit on the membrane. It has been reported that iron present in feed water, if not properly controlled, can co-precipitate with soluble silica present in water which poses a completely different type of fouling problem.

Aluminum based compounds have been used for years as coagulant aids to clarify RO feed waters. Depending on the pH and mode of operation, high concentrations of aluminum ions can be present in the feed water. Aluminum hydroxide precipitation can occur when its solubility is exceeded or when an acid is used to eliminate calcium carbonate scaling potential.

Manganese, although not as common as iron, is often found in iron-containing water. Like iron, manganese can cause fouling problems when oxidized and precipitated in RO systems. Iron and manganese bacteria are not common and are usually not correctly identified, but where they occur, they may be factors in deposition of iron and manganese-based foulants.

Suspended/Colloidal Matter Fouling

The fouling of RO membrane by suspended/colloidal matter is an important problem in RO industry and is perhaps the major constraint in the efficient use of RO systems.³ This type of fouling occurs due to the deposition of solids (e.g., clay, silt, mud, corrosion products, organic colloids, etc.) which were in suspension in feed water. As the feed water is concentrated in the desalination process, coagulation of colloids may occur resulting in plugging of the membrane and/or forming a deposit layer on the membrane surface. Figure 8 illustrates a membrane surface coated with a layer of silt. This RO system was operating on river water and the fouling occurred due to ineffective filtration preceding the RO module. This type of fouling is quite typical of RO systems operated on surface water.

Biological Fouling

Biological fouling is a serious problem if not properly controlled. Biofouling is a special case of particulate fouling in that it involves living organisms. The initial fouling is similar to other particulate foulants but once the organism has impacted on the surface of the membrane, it has the ability to grow and proliferate. Small amounts of biological materials present in desalination systems may rapidly grow and deposit on equipment surfaces. The biological material growing on membrane surface not only causes loss of flux but may physically degrade certain membranes. The removal of a biomass is difficult and simply killing it is not sufficient. A dead biomass will adhere as well as, and sometimes better than, a living one. Biofouling of membrane surfaces is invariably accompanied by other fouling. Scaling is common, however the types and the concentrations of mineral salts may vary greatly, depending on the specific chemical and microbiological characteristics of the feed water.⁴ Particulate matter is also often trapped in a bacterial glycocalyx. A biologically fouled membrane is shown in Figure 9. Fouling of heat exchangers by biological mass is also a serious problem in distillation process. Certain species of bacteria thrive at the temperatures seen in

distillation. Additionally, because of the range of temperatures encountered in a typical MEMS system, the prevalent species may differ greatly from stage to stage making the sterilization and removal process very difficult.

Physiochemical Degradation

<u>Oxidizing agents.</u> Oxidizing agents, such as chlorine, are commonly used in water supplies as bacteriastats. In municipal supplies in this country, federal and local regulations require the use of a biostat for the health of the public served. Certain composite membranes do not tolerate the presence of oxidizing agents. These membranes undergo an oxidative de-crosslinking by which the membrane literally falls apart. Even the "chlorine tolerant" cellulose acetate/triacetate membranes have limit to their tolerance and will slowly degrade in an oxidizing environment. The rate of oxidation is increased at higher temperatures and pH levels.

<u>Hydrolysis.</u> The acetyl groups in a CA membrane are susceptible to hydrolysis. The rate of hydrolysis is increased at higher temperatures and pH above 6.5 and below 3.5. This is the reason for the narrow temperature and pH range for CA membranes (as shown in Table 2).

<u>Physical Damage.</u> An example of physical damage can be seen in Figure 10. This membrane was damaged by excessive pressure drop due to heavy fouling. The layer of particulate material in this membrane obstructed the feed flow causing a high differential pressure. Each time the system was cycled, the outer layers of the membranes moved in the direction of the brine flow, whereas the inner layers of the membrane remained stationary (attached to the permeate tube). Eventually, telescoping, the conical profile at both ends of the module, occurred. This displacement can, and often does, result in the tearing of the membrane (Figure 10) which allows direct passage of brine into the product water.

The fouling of Hx and RO surfaces has a pronounced effect on the cost of the produced water. If the fouling of an RO membrane is allowed to go unchecked, the membrane may become irreversibly damaged which will necessitate replacement. According to Graham⁵ membranes can account for approximately 20 % of the installed costs of a typical brackish water plant and 30 % of a sea water plant. This is significant enough to compel the operator to maintain the membranes in their best condition. The heat exchangers in a distillation system can usually be cleaned more rigorously when they foul, but the economic penalty for operating a fouled heat exchanger may be greater. This, again, suggests that vigilance is always warranted.

FOULANT IDENTIFICATION

Literature includes excellent sources of analytical techniques suitable for identifying and analyzing mineral scales, organic material, biological foulants, etc. The following is a brief overview of some of the techniques used to determine the nature of a foulant and the extent of the problem.^{6,7}

Water Analysis

All feed waters, regardless of purification technique, should be analyzed regularly to assure that the system is being operated efficiently. The frequency of the analysis will depend on the water to be analyzed. Ground waters and open sea waters are typically more stable than surface or coastal waters. In RO, it is often beneficial to periodically analyze the permeate and concentrate streams as well. This can be a valuable tool in maintaining the system and may point out problems before they become serious.⁸⁻¹⁰

Digestions/Extractions

Samples of cartridge prefilters or filter media can be removed and foulants extracted chemically to determine how well the pretreatment is working. Even whole membrane may be autopsied to determine exact cause(s) of failure or to determine the nature of foulants on the surface.

Physicochemical Techniques

There are many analytical techniques available today to assist in the identification of foulants encountered in water treatment systems. Physicochemical techniques such as X-ray diffraction spectroscopy (XRD), infrared spectroscopy (IR), optical microscopy, scanning and tunneling electron microscopies (SEM and TEM), energy-dispersive Xray spectroscopy (EDX), elemental dot mapping (EDM), and atomic spectroscopies (absorption, AA, and emission, AES) can be extremely valuable in accurately identifying the cause of a failed surface. Though these methods may not be used often, they are often highly definitive. These techniques are able to identify the foulant composition, foulant-membrane surface interactions, and other physical characteristics that are necessary before making recommendations to correct the fouling problems. Figure 11 shows a scanning electron micrograph and EDX spectrum of a fouled membrane. The details seen here are indispensable in formulating a cleaning protocol.

SCALE CONTROL

Scale formation in desalination systems can be effectively controlled. Following is a discussion of several of the various approaches used in this endeavor:

System Recovery

In RO systems, membrane fouling by mineral scale can be controlled by operating the system under conditions where solubility of scale forming salts is not exceeded, i.e., running the RO system at low recovery. This technique is not always viable due to the decreased efficiency and may not be effective due to a concentration gradient within the membrane. In distillation, the temperature gradient across the Hx can be controlled in a similar fashion to limit the recovery and maintain solubility. In distillation systems, as in RO, the true concentration gradient may be difficult to predict and reducing the recovery may not be truly advantageous.

Acid Feed

Acids are among the oldest treatment chemicals used by industry to control calcium carbonate scale formation. Acid is injected into the feed water to reduce alkalinity to prevent calcium carbonate precipitation:

$$Ca(HCO_3)_2 + H_2SO_4 ----> CaSO_4 + 2 CO_2 \uparrow + 2 H_2O$$
 (1)

Normally sulfuric acid is used because it is easy to use (compared to HCl) and is relatively inexpensive. The use of sulfuric acid for alkalinity reduction increases the potential for sulfate scale (such as calcium sulfate, strontium sulfate, or barium sulfate) formation. Though calcium sulfate is relatively soluble, strontium sulfate is becoming a problem in certain areas of the world and barium sulfate is extremely difficult to remove once it has formed. When acid is used to control pH, the product water is often degassified to remove the resultant carbon dioxide. Gases are not rejected by RO membranes and will pass directly into the permeate stream, which will decrease product water quality. In distillation, gas on a Hx surface can lead to poor heat exchange and may cause localized corrosion of the tube.

Softening

Hot and cold process lime softening and sodium cycle cation exchange are commonly applied methods to remove hardness ions from RO feed water. Sodium (which replaces the hardness ion) salts are rarely scale forming and, therefore, can be tolerated.

Antiscalant

Antiscalants can prevent the precipitation of scale forming salts by preventing formation of crystals larger than the critical size (preventing nucleation) and by surface modification of those crystals which do form. The surface modification of the crystals causes them to distort as they grow. This distortion can slow and actually stop the growth of the usually highly-ordered crystals. Several types of antiscalants are commercially available now and the proper selection of an antiscalant depends upon the water chemistry and system design.

FOULANT CONTROL

Equipment fouling by suspended solids can be controlled mechanically, chemically, or by a combination of the two. Mechanical control methods include sedimentation, side-stream filtration, pretreatment of feed water by clarification (i.e., coagulation and flocculation) or filtration.

Chemical control is achieved by the dispersion of suspended matter such that it does not coagulate and settle out of solution. The role of chemical agent (i.e., dispersant) in such desalination systems is to keep the solid particles suspended so **h**at they can be removed from an operational desalination system without settling out. Various factors including pH, temperature, and settling time as well as particle size, water chemistry, and ionic charge are known to affect the performance of a dispersant.

Metal Ion Stabilization

Metal ions (i.e., iron, manganese, copper, zinc) can be stabilized by the use of chelating agents. Common chelating agents are gluconic acid, citric acid, ethylenediaminetetraacetic acid (EDTA), and polymeric antiscalants/dispersants such as polyacrylic acid, or acrylic acid, maleic acid-based copolymers.

FOULANT CONTROL AGENTS

The use of foulant control agents (antiscalants / dispersants) is the key to the successful long-term performance of a desalination system and its performance in system design should not be underestimated. The role of antiscalant/dispersant in water treatment program is to prevent the deposition of unwanted materials on Hx and membrane surfaces. For optimum system performance, equipment manufacturers, consultants, or systems designers, should be consulted so that the correct treatment program can be designed for a given feed water. The following section discusses the types and characteristics of several antifoulants.

Commonly used foulant control agents fall into the following four categories:

- Polyphosphates
- Phosphonates
- Synthetic polymers
- Proprietary, formulated blends

Polyphosphates

In 1939, Hatch and Rice¹¹ reported that low levels of polyphosphate prevented the precipitation of calcium carbonate from aqueous solution. According to Hatch and Rice, "threshold treatment" using sodium hexametaphosphate (SHMP) in the range of 1 to 5 mg/L was found to be very useful in preventing the formation of calcium carbonate scale in many industrial applications.¹¹ The term "threshold inhibition" describes the mechanism of scale inhibitor at sub-stoichiometric ratios. This threshold effect is explained by an adsorption of the inhibitor onto the crystal growth sites of sub-microscopic crystallites which are initially produced in the supersaturated solution, interfering with crystal growth and altering the morphology of those that grow. This process can prevent crystal growth or at least delay it for prolonged periods of time. Therefore, scale inhibition by threshold inhibitor is based on kinetic and not thermodynamic effects.

Numerous papers have been published and several patents have been issued since the earlier work regarding the control of scale forming salts by threshold agents.¹² In addition, polyphosphates in the 2 to 10 mg/L range have been reported to exhibit particulate dispersion, stabilization of metal ions such as iron and manganese, and control of aqueous corrosion of metals.¹³

Application of polyphosphates as scale control agents offers several advantages including high solubility in water, cost-effectiveness, and low order of toxicity. However, the major problem with the use of polyphosphates is hydrolysis of the phosphorus-oxygen (P-O) bond resulting in the formation of orthophosphate, an ineffective scale inhibitor. Further, orthophosphate can react with calcium ion to form relatively insoluble calcium phosphate scale. In addition, polyphosphates, when reverted to orthophosphate, are a potential nutrient for algae.⁸ Several factors influence the reversion of polyphosphate, including temperature, pH, concentration, and water chemistry.¹³

Organophosphonates

Organophosphonates are a class of compounds which contain a phosphorus-carbon bond (P-C). Unlike the P-O bond present in polyphosphates, the P-C bond is not as susceptible to hydrolysis. The structures of commonly used polyphosphates and organophosphonates are given in Table 5.

Phosphonates have been successfully used as scale inhibitor in desalination systems where the Langelier Saturation Index or the Ryzner Stability Index indicated scaling conditions. However, it has been recently recognized that, under certain conditions of calcium hardness, pH, and temperature, phosphonates can react stoichiometrically with the calcium ion which leads to the precipitation of calcium phosphonates. The calcium phosphonate can be a troublesome deposit itself, but precipitation of calcium phosphonate can deplete the solution phosphonate concentration to such an extent that severe CaCO₃ scaling can occur.¹⁴

Chlorine is a prevalent biocide in the desalination applications and, therefore, its influence on the stability of phosphonates has been examined. There is a general agreement in the literature that amine-containing phosphonates are susceptible to chlorine attack. Other, non-amine based phosphonates are still the subject of rigorous testing.

Synthetic Polymers

The development of synthetic polymers for controlling foulants in industrial water systems led to their evaluation as foulant control agents in desalination applications. These polymers contain a variety of functional groups along the polymer chain and are generally anionic in nature. Among the most commonly used polymers as scale control agents are: poly(acrylic acid), PAA; poly (methacrylic acid), PMAA; poly (maleic acid), PMA, and proprietary polymer-based formulated blends. The structures of these polymers are illustrated in Table 5.

<u>Poly (acrylic acid)</u>. Low molecular weight polyacrylic acids (PAAs) are the most widely used of the synthetic polymers in desalination feed water pretreatments. As shown in Table 5, PAA contains only one functional group (carboxyl, -COOH) and is generally used as a scale control agent. PAA also exhibits some activity in dispersing particulate matter. The performance of PAA has been shown to be strongly dependent upon the molecular weight^{2,15,16} of the molecule.

<u>Poly (methacrylic acid).</u> Polymethacrylic acid (PMAA) is another synthetic polymer commonly used as a dispersant. As shown in Table 5, PMAA contains both methyl and carboxyl groups.

<u>Poly (maleic acid).</u> Table 5 shows the structure of polymaleic acid (PMA). This polymer contains 2 carboxyl groups on the adjacent carbon atoms, and has been used for scale and suspended matter control. The performance of PMA as a dispersant is somewhat lower than that of PAA.

Unlike polyphosphates, PAA, PMAA, and PMA are not subject to a loss of activity due to hydrolysis. These polymers are more hydrolytically stable in highly alkaline formulations. The tolerance is due to the absence of labile hydrolyzable functional groups in the molecular structure.

<u>Proprietary Polymer-Based Formulations.</u> Although effective in many applications, synthetic polymers such as PAA, PMAA, PMA like other scale control agents (e.g., phosphonates, polyphosphates, etc.) have low calcium tolerance, i.e., they will react with calcium ion to form the insoluble calcium-polymer salt. In many instances, the water to be treated is high in hardness because of high recovery within desalination system which becomes a potential problem. Under these conditions, PAA, PMA, phosphonates, and polyphosphate cannot always be safely used. The poor calcium tolerance of these inhibitors has been overcome with the development of new proprietary products (Table 6). Figure 12 compares the calcium tolerance of various commercial products.

ANTIFOULANT EVALUATION

This section presents a review of the literature and laboratory/field data on the performance of various antifoulants in desalination systems:

Polyphosphate and Phosphonates

Monsanto has tested various phosphonates¹⁷ (Table 5) and has shown that, for calcium carbonate scale control, the order of effectiveness among various phosphonates is HEDP > AMP > DETMP. Ralston¹⁸ showed that AMP was more effective than polyphosphate for waters containing calcium carbonate at 3.9 times saturation. Increasing the temperature or increasing the degree of saturation necessitated an increase in AMP concentration.

Nancollas et al.¹⁹ have reported on their extensive studies of the effect of various phosphonates on the crystal growth of sparingly soluble salts. For calcium sulfate crystal growth inhibition under similar experimental conditions, the EDTMP showed superior performance compared to DETMP.

The inhibition of calcium carbonate by various phosphonates, e.g., AMP, HEDP, PBTC (Table 5), under harsh conditions has been investigated. The inhibition data on these phosphonates reveal that at low supersaturation the order of effectiveness is HEDP >> AMP = PBTC. However, at high supersaturation, PBTC outperforms AMP and HEDP.²⁰

Pervov²¹ evaluated the performance of various polyphosphates and phosphonates on the deposition of gypsum on cellulose acetate and composite membranes at different recovery ratios. The results of his investigation show that compared to phosphonates (i.e., AMP, HEDP), polyphosphates (i.e., sodium tripolyphosphate, STPP, and SHMP) exhibit superior performance. Similar observations were also reported in a study on the inhibition of gypsum scale growth for RO applications.²²

Polymer Composition

Numerous studies have been reported on the precipitation of calcium sulfate in the presence of antiscalants. McCartney and Alexander²³ have examined the effect of a number of polyelectrolytes on the growth rate of calcium sulfate dihydrate. It was found that polymers containing carboxyl groups such as carboxymethyl cellulose, alginic acid, PMA, and PAA were particularly effective as gypsum growth inhibitors.

Smith and Alexander²⁴ in their study on the evaluation of polymers as gypsum scale inhibitors reported that PAA was more effective than PMAA. Furthermore, growth inhibition results for a series of experiments with styrene/maleic anhydride polymers suggest an optimum effectiveness at a molecular weight (MW) of 1600.

Amjad and Hooley²⁵ investigated the influence of polymer composition containing acrylic acid (AA), 2-acrylamido-2methyl propane sulfonic acid (SA), and acrylamide (AM) on the precipitation of gypsum from aqueous solutions. The kinetic data show the following order of polymer effectiveness: PAA > AA:SA > AA:AM >>PAM (polyacrylamide) indicating that carboxyl group in the polymer plays a key role in the inhibitory activity of the polymer. A surface adsorption mechanism was proposed to explain gypsum inhibition by polymers.

Amjad²² in another study on the effect of various antiscalants (Tables 5, 6) on the crystal growth of gypsum reported the following order (in terms of decreasing effectiveness), of antiscalants:

AF 600⁽¹⁾ (PF-1) > SHMP >> PYP (pyrophosphate) > Polystyrenesulfonate ~ Polyacrylamide ~ control (no antiscalant)

Weijnen and van Rosmalen²⁶ studied the inhibition properties of polymers on the precipitation of gypsum. The polymers studied included: PAA, PMA, copolymers of AA:styrene sulfonate, AA:acrylamide, and AA:vinyl sulfonic acid. Their results indicate that polycarboxylic acids (PAA and PMA) are effective gypsum growth inhibitors. In a study on the evaluation of various polymers for scale control in sea water evaporators, it was demonstrated that the order of effectiveness among polymers of similar molecular weight (5000) is PMA > PAA > PMAA.²⁷

Polymer Molecular Weight

Amjad and Masler¹⁴ in a seeded growth on the evaluation of PAA of varying molecular weight showed that the molecular weight of polymers plays an important role in the inhibition of gypsum crystal growth from solution. The optimum effectiveness, determined by induction period duration, occurred with a PAA molecular weight of 2100. Amjad,²⁷ in another study involving the deposition of gypsum on heat exchanger, also reported that the amount of

⁽¹⁾ AF 600 is an acronym for AQUAFEED 600 Antiscalant a formulated polyelectrolyte available from The BFGoodrich Company.

gypsum scale deposited on the heat exchanger was found to be higher in the case of high molecular weight polyacrylates (240 000) than that obtained in the presence of lower (2100) molecular weight PAA.

Flesher et al.,²⁸ in their study on the evaluation of a variety of polymers at high temperatures as calcium sulfate scale inhibitors, showed that the efficacy of the polyacrylates decreases with increasing molecular weight in the range 2000 to 750 000. Jones²⁹ in his study on the effect of molecular weight (50 000 to 400 000) of carboxymethyl cellulose (CMC) reported that high molecular weight CMC polymers are the least effective and the effectiveness increases as the molecular weight of the polymer decreases. Similar observations were also reported by Sexsmith and Petrey³⁰ on the evaluation of PAA, PMAA, and PMA. In addition, the inhibition data on these polymers also show that at similar molecular weight PMA is a better inhibitor than PAA and PMAA.

Solution pH

Several studies have been reported on the influence of solution pH on the performance of polymeric and nonpolymeric inhibitors on the crystal growth of sparingly soluble salts. Griffith et al.³¹ have shown that the performance of phosphonic acids as gypsum growth inhibitors improves with increasing pH and have attributed this to an increase in the degree of deprotonation. Leung and Nancollas,³² using seeded growth technique, arrived at similar conclusions after studying the effect of benzene polycarboxylic acids on the crystal growth of gypsum. Recently, Amjad using the seeded growth technique has investigated the influence of solution pH in the range 2.5 to 9.0 on the performance of PAA as gypsum growth inhibitors.³³ The results show that solution pH has a marked effect on the induction period. The observed improvement in inhibition with increasing pH was interpreted in terms of degree of deprotonation of PAA with increasing pH.

Recently, Smith and Hulin³⁴ evaluated the influence of various factors on the performance of gypsum scale inhibitors for RO applications. The results of this investigation reveal that the effectiveness of antiscalants (i.e., PAA and SHMP) increases with increasing pH in the range of 4 to 8. In addition, the kinetic data also show that the performance of antiscalants is decreased more in the presence of ferric ions than in the presence of zinc ions. This effect was presumably caused by the antiscalant preferentially chelating ferric ions, and becoming unable to be adsorbed onto the growing gypsum crystal faces.

Weijnen and van Rosmalen³⁵ in their investigation on the influence of pH for PAA and PMA as gypsum crystal growth inhibitors reported that at pH 5 both antiscalants exhibit equal inhibitory activity. However, at relatively high pH values greater than 7, PMA, being a stronger acid, is a better antiscalant than PAA.

Proprietary Formulated Blends

During the last several years, a large number of proprietary formulated blends have been developed for desalination applications especially for RO and distillation processes. These formulations range from simple homopolymer (e.g., PAA, PMA, etc.) to acrylic acid-, maleic acid-based copolymers, and blended products containing copolymers and phosphonates. Table 6 provides the list of some of the formulations used in desalination processes. The following section summarizes the performance of these products in RO and MSF applications.

Smith et al.,³⁶ in their study on the evaluation of EL-5600⁽²⁾ (PF-2) at Roswell Test Facility in Roswell, New Mexico, using well water and a pilot facility using brackish water, reported that the blend provides good dispersion of silt, clay, and metal oxides.

Logan and Kuroda³⁸ in the field testing of EL-2438⁽³⁾ (PF-3) showed that the deposition of alkaline scale on the heat exchanger surfaces can be prevented by the use of the high performance product. A physical inspection of the heat exchanger after 2 months of operation revealed only minor accumulation of deposits. The analysis of the deposit confirmed that the scale in the unit was principally calcium carbonate, as aragonite, with lesser amounts of magnesium hydroxide and absence of sulfate scales.³⁷ In another study on the evaluation of PF-3 and SHMP as gypsum scale inhibitor for RO application, Logan and Kimura established the superior performance of PF-3 against SHMP.

⁽²⁾ EL-5600 is a formulated blend of polycarboxylates and phosphonates available from the Calgon Corp.

⁽³⁾ EL-2438 is a formulated blend of an AA:SA copolymer and a phosphonate available from the Calgon Corp.

Butt et al.³⁹ carried out field trials using Albrivap- $G^{(4)}$ (PF-4) and the Albrivap-DSB⁽⁵⁾ + (PF-5) acid (hybrid) treatments on an MSF unit at 112.8 °C brine temperature. The results of these trials show that compared to PF-4 treatment, hybrid treatment is overall ~50% more cost effective. In a field test conducted at Cape Coral, Hatch et al.⁴⁰ demonstrated that the acid feed can be eliminated by the application of AQUAFEED 100 Antiscalant⁽⁶⁾ (PF-6) at high calcium carbonate scaling conditions.

Recently, Fukumoto et al.⁴¹ reported that a new copolymer based antiscalant called Aquakreen KC-550⁽⁷⁾ (PF-7) showed good performance in MSF applications especially in the presence of multivalent ions. Amjad et al.⁴² in a field test demonstrated the efficacy of AQUAFEED 1000 Antiscalant⁽⁸⁾ (PF-8) at a Southwestern United States site. The test data shows that, compared to SHMP/acid feed and PAA, PF-8 prevented the calcium carbonate and calcium sulfate scaling of RO membrane under adverse operating conditions, i.e., recycle of brine stream (Stiff & Davis Index = +1.7) and calcium sulfate supersaturation at approximately 1.7X. Other significant benefits provided by PF-8 are excellent stabilization of iron, manganese, zinc, and dispersion of iron oxide and clay.

Metal Ion Stabilization

The stabilization of metal ions (e.g., AI, Fe, Mn, etc.) in desalination systems can be achieved by the use of sequestering agents. These agents can be either inorganic or organic such as citric acid, ascorbic acid, gluconic acid, polyphosphate, PAA, PMA and copolymers containing acrylic acid and/or maleic acid.. The term sequestration, chelation, complexation, and stabilization are generally referred to phenomena where metal ions or complexed species are maintained in a soluble form.

Figure 13 illustrates the performance of products for aluminum stabilization. The stabilization of aluminum is strongly dependent upon the composition of stabilizing agent. Poor to moderate improvement in stabilization of aluminum was obtained when either SHMP or PAA was added to the system. The addition of a AQUAFEED 800 Antiscalant⁽⁹⁾ (PF-9) provided almost complete stabilization of aluminum.

Amjad and Masler⁴³ evaluated various types of copolymers as iron stabilizing agents in high salinity water. Under the test conditions of their test, they found copolymers of AA:itaconate esters, AA:SA:vinyl acetate, and AA:substituted acrylamide, are more effective in stabilizing iron (III) than SHMP, PAA, citric acid, and ascorbic acid. Boffardi⁴⁴ also showed that copolymers of AA:SA were more effective than PAA in stabilizing iron (III).

Figure 14 illustrates the performance of several commercial products used in desalination applications. The excellent performance properties of PF-8 and PF-9 are extremely important in the successful operation of desalination systems 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, aluminum, or manganese based foulants, the RO user needs a much higher level of performance than the SHMP or PAA can provide.

Suspended Matter Dispersion

An antifoulant must exhibit good dispersancy properties to prevent the settling of colloids and particulate matter on membrane and heat exchanger surfaces. The dispersancy power of an antifoulant can be measured by adding the antifoulant to a suspension of iron oxide particles. After a time, the amount of material in the dispersion may be measured colorimetrically. Figure 15 shows the effectiveness of different dispersants at 1 mg/L of product dosage. The data clearly indicates that copolymer based products (such as PF-8 or PF-9) exhibit superior performance as compared with SHMP, PAA, PMA, citric acid, and ascorbic acid. It is noteworthy that good iron stabilizing agents such as citric and ascorbic acids, are ineffective as iron oxide dispersants. Figure 16 shows photographs of iron oxide particles dispersed by PF-9, a highly effective dispersant. The incorporation of high performance dispersants in the desalination water treatment programs will help ensure that the optimum performance of the system is achieved.

⁽⁴⁾ Albrivap-G is a proprietary polymeric product available from Albright & Wilson UK Ltd.

⁽⁵⁾ Albrivap-DSB is a proprietary polymeric product available from Albright & Wilson UK Ltd.

⁽⁶⁾ AQUAFEED 100 Antiscalant (AF 100) is a discontinued formulated polyelectrolyte from The BFGoodrich Company

⁽⁷⁾ Aquakreen KC-550 is a copolymer based antiscalant.

⁽⁸⁾ AQUAFEED 1000 Antiscalant (AF 1000) is a formulated polyelectrolyte available from The BFGoodrich Company.

⁽⁹⁾ AQUAFEED 800 Antiscalant (AF 800) is a formulated polyelectrolyte available from The BFGoodrich Company.

SUMMARY

Water is used in more processes than any other chemical known to man. In its natural state, water contains too many impurities to be used for many applications and must be purified. Electrodialysis, distillation, and reverse osmosis are the three commercially applied desalination processes used to treat surface, brackish, and sea waters for industrial applications. The build-up of deposits such as mineral scales, colloidal matter, corrosion products, and biological growth on heat exchanger and membrane surfaces can severely reduce the performance and efficiency of the system. The long term success of a desalination system is largely dependent on three factors: system design, pretreatment, and operation and maintenance of the system.

Fouling considerations currently set the upper limits of systems recovery in the case of RO process, and temperature and brine concentration for the distillation process, thus controlling their efficiency. Three commonly employed methods to control fouling include application of acid, antiscalant, and acid plus antiscalant. Currently, various types of antiscalants such as polyphosphates, phosphonates, acrylic, maleic homopolymers, copolymers, and blended products containing phosphonates and copolymers are employed to control foulants. The performance data based on both lab and field evaluation of several products show that the copolymer-based blended products offer the best overall performance in preventing the deposition of foulants on heat exchanger and membrane surfaces.

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Table 1Typical Characteristics of Various Water Sources

Salinity Range	Colloidal Material	<u>рН</u>	<u>Biological</u>
<600 ppm	high	6.5 to 8.0	high
<1100 ppm	usually none	variable	usually low
2000 to 15 000 ppm			
20 000 to 50 000 ppm			
	.600 ppm .1100 ppm .000 to 15 000 ppm	GOO ppm high c1100 ppm usually none c000 to 15 000 ppm	600 ppmhigh6.5 to 8.0c1100 ppmusually nonevariablec000 to 15 000 ppm

Table 2Desalination Techniques and Their Typical Naturally Occurring Waters

Desalination Processes	Feed Waters
Distillation	<60 000 ppm (as NaCl)
Solar Evaporation	<60 000 ppm (as NaCl)
Freezing	<60 000 ppm (as NaCl)
Ion Exchange	<300 ppm (as NaCl)
Membrane	<45 000 ppm (as NaCl)

Table 3Comparison of Operational Parametersfor Cellulose Acetate (CA) and Thin Film Composite (TFC) Membranes

Parameter	<u>CA</u>	<u>TFC</u>
Pressure (to produce similar flux)	400 psi	250 psi
Temperature	<95°F	<115°F
pH Range	4 to 6	2 to 10
NaCI Rejection	95%	97.5%
Cl ₂ Stability	1 ppm continuous	none
Compaction	yes	no
Cost	low	medium

Table 4 Advantages and Disadvantages of Various Desalination Processes

Desalination Process	Advantages	<u>Disadvantages</u>
Distillation	Produces good quality product water	Very energy intensive
	Can effectively treat a wide range of feed streams	Equipment corrosion and scaling means that antiscalants and corrosion inhibitors are needed
Solar Evaporation	Solar energy is free	High initial costs
	Minimal scaling	Process is still relatively inefficient
Ion Exchange	Produces good quality product water	Handling and storage of regeneration chemicals
	Produces large waste streams	Efficient operation possible
		Inefficient for treating high salinity streams
Electrodialysis (ED) and Electrodialysis Reversal (EDR)	Limited chemicals requirements for normal operation	Single stage does not produce high rejection
	Produces fairly good quality water	Increased operational cost for high recovery systems due to need for antiscalants
	Membrane can operate over wide range of pH	
Reverse Osmosis	Inexpensive - both capital and operating costs	Susceptibility to fouling requires operator vigilance
w	Can effectively treat a ide range of feed streams	Filtration needed for high SDI water
Ρ	roduces good quality product water	

Table 5Commonly Used Antiscalants

Inhibitor	<u>Acronym</u>	Structure
Sodium Tripolyphosphate	STPP	$Na_5P_3O_{10}$
Sodium Hexametaphosphate	SHMP	(NaPO ₃) ₆
Amino tri (methylene phosphonic acid)	AMP	N(CH ₂ PO ₃ H ₂) ₃
1-Hydroxyethylidene-1,1- diphosphonic acid	HEDP	$CH_3C(PO_3H_2)_2OH$
Ethylenediaminetetra (methylene phosphonic acid)	EDTMP	$(PO_{3}H_{2}CH_{2})_{2}N(CH_{2})_{2}N(CH_{2}PO_{3}H_{2})_{2}$
Hexamethylenediaminetetra (methylene phosphonic acid)	HMTMP	$(CH_2PO_3H_2CH_2)_2N(CH_2)_6N(CH_2PO_3H_2)_2$
Diethylenetriaminepenta (methylene phosphonic acid)	DETMP	$N(CH_2)PO_3H_2[(CH_2)_2N(PO_3H_2)_2]_2$
2-Phosphonobutane 1,2,4- tricarboxylic acid	PBTC	CH ₂ COOHC(PO ₃ H ₂)COOH(CH ₂) ₂ COOH
Poly (acrylic acid)	PAA	(CH ₂ CHCOOH) _n
Poly (methacrylic acid)	PMAA	(CH ₂ C(CH ₃)COOH) _n
Poly (maleic acid)	РМА	(CHCOOHCHCOOH) _n

Table 6 Commercially Available Proprietary Formulated Antiscalants

<u>Acronym</u>	Composition
PF-1	Polyelectrolyte
PF-2	Blend of polycarboxylates and phosphonates
PF-3	Blend of AA:SA copolymer and phosphonate
PF-4	Proprietary phosphonate blend
PF-5	Proprietary phosphonate blend
PF-6	Polyelectrolyte blend
PF-7	Copolymer based antiscalant
PF-8	Polyelectrolyte blend
PF-9	Polyelectrolyte



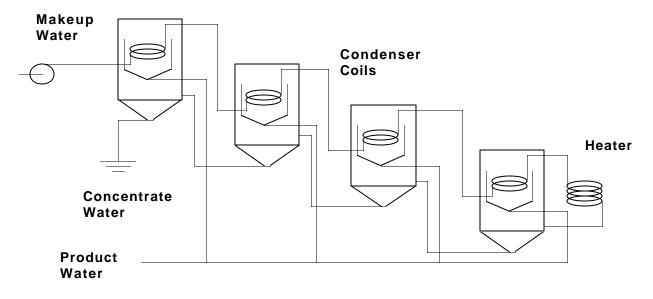


Figure 1. Multi-stage thermal distillation process

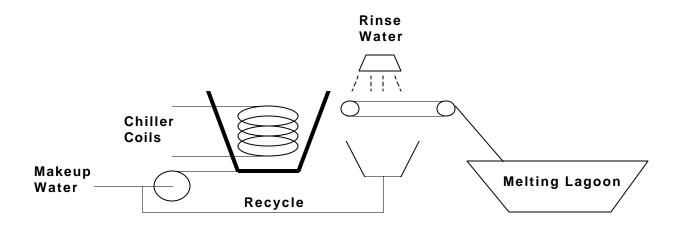


Figure 2. Crystallization distillation process

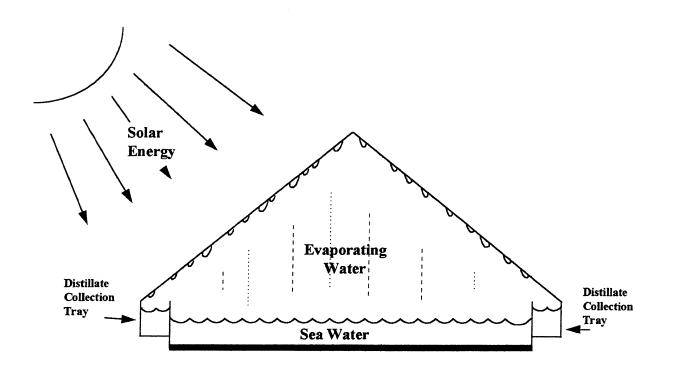


Figure 3. Solar evaporation still

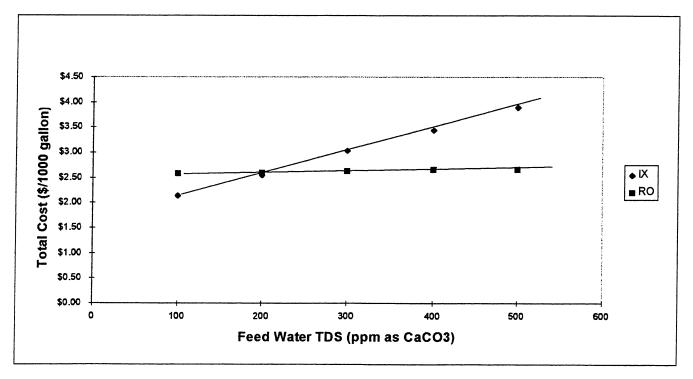


Figure 4. The economics of reverse osmosis and ion exchange based on 1 000 000 gallon-per-day systems

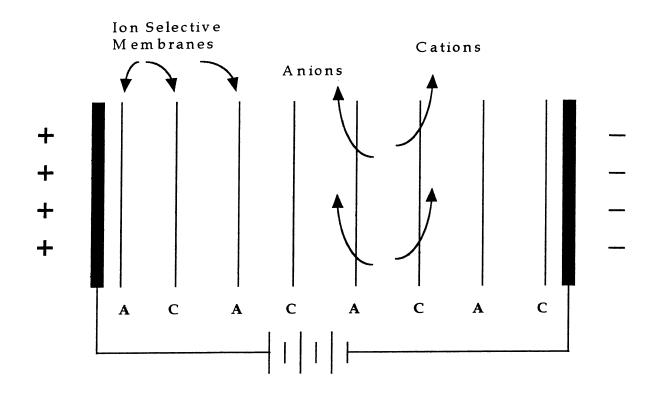
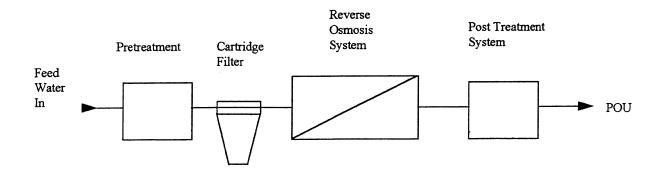
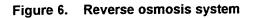


Figure 5. Electrodialysis process





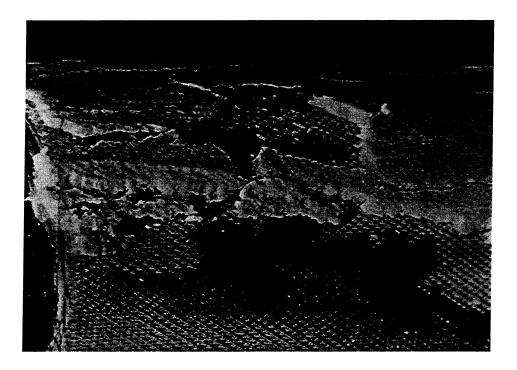


Figure 7. Calcium sulfate (gypsum) scaling on an RO permeator



Figure 8. Surface of membrane covered with silt

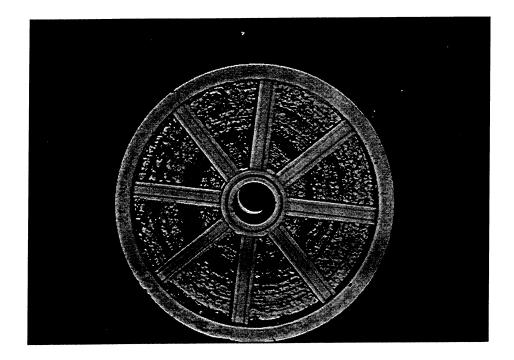


Figure 9. Feed end of biofouled membrane

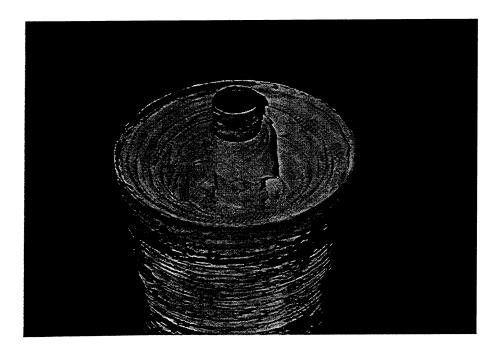


Figure 10. Telescoped membrane

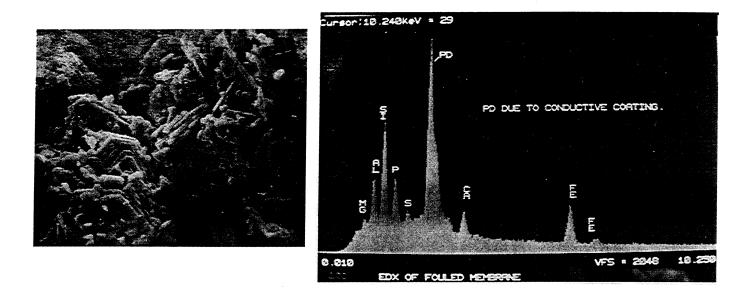


Figure 11. Electron photomicrograph and EDX spectra of a fouled membrane

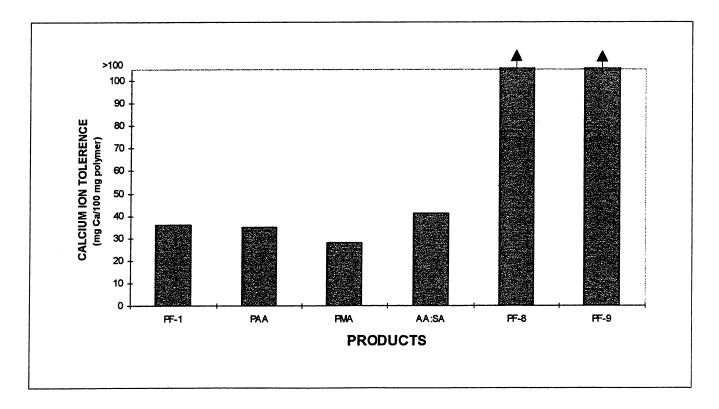


Figure 12. Calcium ion tolerance of various antiscalants

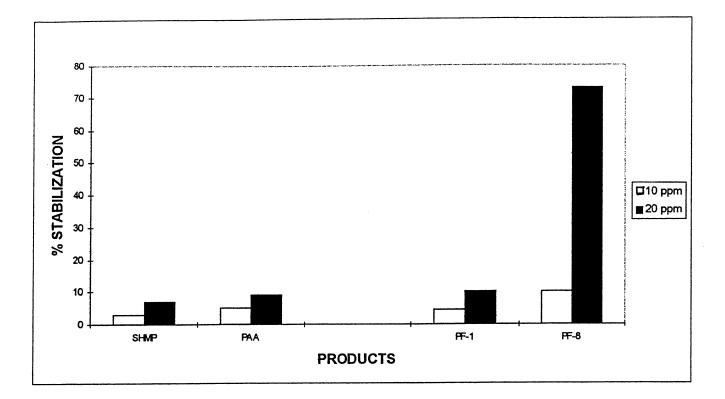


Figure 13. Aluminum stabilization versus product dosage. Synthetic water containing 60 ppm calcium, 30 ppm magnesium, and 195 ppm chloride. Test conditions include 22 °C, pH 6.6, 3 hours.

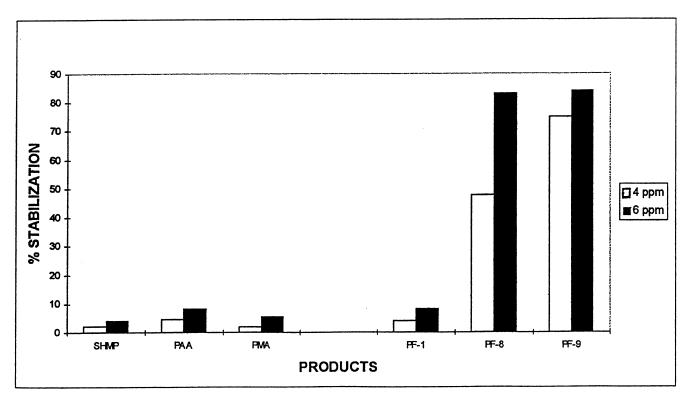


Figure 14. Iron stabilization versus product dosage. Test conditions include pH 7.0, 3 hours, 2.5 ppm iron (III).

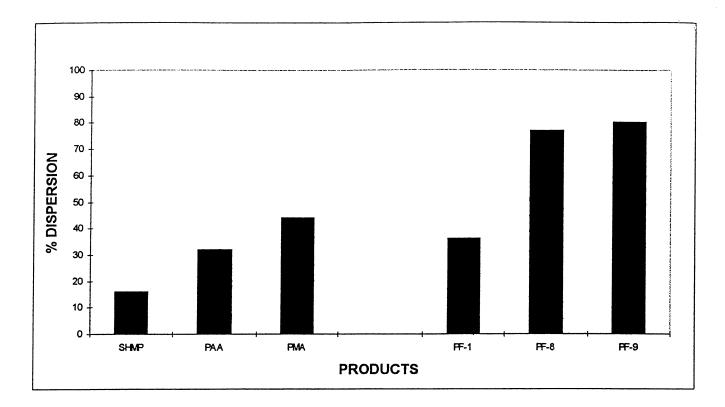


Figure 15. Dynamic iron oxide dispersancy for various products. Test conditions include pH 7.8 to 8.0, 22°C, 3 hours, 1 ppm product.

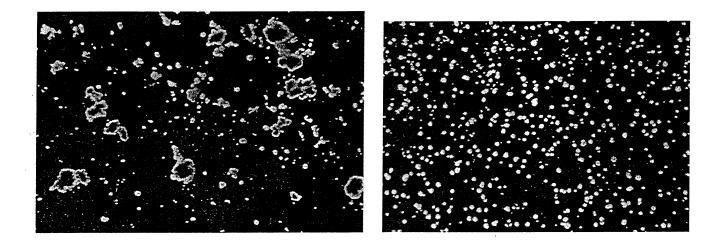


Figure 16. Dispersion of iron oxide particles in the absence (left) and the presence (right) of PF-9 Antiscalant.