

# The Evolution of Pretreatment Chemicals in Membrane Processes

## An Analysis of Innovations in Chemical Pretreatment Practices

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Several advances have been made since scale inhibitors were first put to use for membrane processes. Today's pretreatment chemicals, which are often proprietary in nature, offer solutions for many challenging applications, in contrast to the first chemicals that were used for membrane pretreatment.

In some cases these advancements have increased the required feed pH going into the membrane process, increased the time between cleaning events, extended the life of membrane elements, and reduced operating costs at treatment facilities. Since using the correct type of pretreatment chemical can often mean the difference between a well-functioning facility and a problematic one, it is imperative that proper planning and research are incorporated into the bidding and procurement process.

This article will refer to RO processes throughout the text. The term RO is intended to represent both reverse-osmosis and nanofiltration technologies. The practice of feeding a scale inhibitor as a method of RO pretreatment is by no means a new concept; however, recent advancements in the pretreatment chemical industry and subsequent operational data have shown that certain scale inhibitors may be best suited for a particular feed-water quality or process. The many variables that affect scale inhibitor selection include raw-water source and quality, RO system recovery, feed-water temperature variations, membrane material, and the presence of biological contaminants in the source water.

A treatment facility can be built and operated using the best practiced methods in the industry and still have operational difficulties if the pretreatment chemicals are not chosen and applied correctly for the conditions of service. Using the wrong chemical can result in higher feed pressures, more frequent cleaning, decreased water quality, reduced membrane life, and ultimately higher O&M costs.

### **Bidding of Pretreatment Chemicals**

Given the political climate in municipal purchasing departments and the current trend of going to bid for large commercial

contracts, it is critical that a method for selecting an appropriate pretreatment chemical is in place. This effort should be led by the membrane plant staff and/or a process consultant to ensure process performance is given highest priority.

Whenever possible, scale inhibitor selection should be based on quality and not cost alone. The request for bids should include technical specifications with requirements for the acceptable chemical characteristics and the acceptable methods of handling and injection.

Pilot testing is also recommended when there is not a history of operating conditions available for consideration. Many larger utilities run a pilot system in conjunction with their treatment facility so that new pretreatment chemicals, adjustments to dosing, and skid operating parameters can be tested prior to full-scale implementation. Prequalification can also be used to insure that an acceptable pretreatment chemical is submitted. If time allows, pilot testing of multiple types of chemicals is the preferred method for prequalifying scale inhibitors.

For those designing or operating new treatment facilities, a starting point in this process can often be meeting with personnel from other local facilities that have similar feed-water sources and process characteristics. Operators at facilities with a successful operational history can share the successful methods they employ, while operators at facilities with a high occurrence of cleaning events due to scaling or fouling can share lessons learned. In either case, these existing facilities can also be sources of additional information on feed-system design and ranges for chemical dosing.

For both new and existing facilities, appropriate time should be spent gathering information on the chemicals that are available for the proposed application. Today there are a number of companies offering multiple lines of chemicals to address the growing RO marketplace.

To get the best competitive pricing, it is important to make an effort to gather information from all known manufacturers who provide a product that meets the known requirements. If available and reliable, sub-

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mit the water quality to each for a recommendation. Many, if not all, chemical manufacturers will provide such a recommendation at no cost to the purchaser.

While these methods for determining the appropriate chemical are not a substitute for conducting pilot testing, they do provide an improvement over taking the "low price" bid without a performance specification.

### **Membrane Fouling/Scaling**

One of the main causes of membrane system degradation or failure is membrane fouling. The phenomenon of fouling results from the accumulation of scale or foulants on the surface of the membrane and/or in the feed channel, resulting in impaired performance; however, in practice the term fouling is commonly used to describe either biological, particulate, or colloidal fouling, while mineral scaling (also technically a form of fouling) is commonly referred to as scaling.

Mineral scaling is the result of the precipitation of a sparingly soluble salt that occurs when the solubility of that salt is exceeded.<sup>1</sup> Colloidal or particulate fouling can often be differentiated from biological fouling by the loss of performance in the lead end of a membrane system. Biological fouling can often cause a loss of performance throughout a membrane system, but it may be most noticeable in the lead elements. Scaling can often be differentiated from the other forms of fouling through a loss of performance in the tail end of a membrane system.

### **Pretreatment Chemical Water Chemistry**

Solubility and the chemistry of slightly soluble salts (also referred to as sparingly soluble salts) were initially and still are the driv-

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ing force for most pretreatment chemicals in RO membrane processes. Since calcium is more commonly found in natural waters, the most frequently referenced salt that falls into this category is calcium carbonate (CaCO<sub>3</sub>). Calcium carbonate can best be kept in a soluble state by reducing the feed-water pH, which decreases the concentration of carbonate species available for formation with calcium ions.

The most common method for determining the solubility of calcium carbonate in water is the Langelier Saturation Index (LSI). Waters that are negative on this index indicate an undersaturated condition with respect to calcium carbonate (tendency to dissolve CaCO<sub>3</sub>), while waters that are positive indicate an oversaturated condition (tendency to precipitate CaCO<sub>3</sub>). The LSI equation is:

$$LSI = pH - pH_s$$
$$pH_s = pCa + pAlk + C$$

Where:

- pCa = negative logarithm of the calcium molarity.
- pAlk = negative logarithm of the alkalinity in equivalents per liter.
- C = constant to account for the change in calcium carbonate solubility with temperature and ionic strength.

Other equations used for determining the solubility of calcium carbonate include the Stiff and Davis Scaling Index (SDSI). The SDSI equation is:

$$SDSI = pH - pCa - pAlk - K$$

Where:

- pCa = negative logarithm of the calcium molarity, as in LSI.
- pAlk = negative logarithm of the alkalinity in equivalents per liter, as in LSI.
- K = different empirical constant from LSI to account for temperature and ionic strength.

### Sulfate Salts

The solubility product (K<sub>sp</sub>) is used to determine the solubility of calcium sulfate (CaSO<sub>4</sub>) in a water. If calcium sulfate or another sulfate is the limiting salt of concern, using sulfuric acid for pH adjustment will often increase the potential for scale formation by increasing the sulfate (SO<sub>4</sub><sup>-2</sup>) concentration in the water; therefore, typical means for preventing calcium and/or other forms of sulfate scale include using a scale inhibitor.

The K<sub>sp</sub> for any given salt is influenced by the water temperature and the ionic strength of that salt, and can be determined using the follow equation:

$$K_{sp} = [cation]^n \times [anion]^m$$

Where:

- K<sub>sp</sub> is a value for the solubility product.
- [cation] is the cation concentration

(mol/L).

- [anion] is the anion concentration (mol/L).
- # is the number of the particular ion present within the salt molecule.

Barium sulfate (BaSO<sub>4</sub>) and strontium sulfate (SrSO<sub>4</sub>) are other sparingly soluble salts that are formed with sulfates. Similar to calcium sulfate, the K<sub>sp</sub> is used to determine the solubility of these salts in the concentrate. Most RO membrane manufacturers' projection software will estimate solubility levels for slightly soluble salts in either a decimal or percentage form, so that a concentrate containing SrSO<sub>4</sub> at concentrations two times above its solubility product would be expressed as 200% K<sub>sp</sub> or 2\* K<sub>sp</sub>.<sup>1</sup>

### Silica

Silica fouling can be more difficult to predict and control than other types of fouling. Silica (SiO<sub>2</sub>) is expressed in terms of mg/L concentration, rather than the solubility product method used for sparingly soluble salts. Silica is commonly found in groundwaters and typically exists in the weakly ionized soluble form. As soluble silica is concentrated to insoluble levels in the RO process, insoluble colloidal silica or silica gel can be formed through a process of polymerization.

Methods used to prevent silica from reaching insoluble concentrations include limiting the RO system recovery and increasing the feed-water temperature—neither of which are easily or cost-effectively practiced in municipal treatment facilities. Similarly, removing silica through a pretreatment process can be cost prohibitive. Silica solubility is increased at high feed-water pH values; however, this method of pretreatment can hinder the control of calcium carbonate scaling.

With these methods dismissed as effective solutions, the development of new antifoulants has brought an alternative which allows silica polymerization to be inhibited while also dispersing particulate matter. While traditional scale inhibitors allow maximum concentrations in the order of 120 to 150 mg/L of silica, the latest technological achievement in scale inhibitors has been found to allow RO concentrate streams containing as much as 500 mg/L of soluble silica.<sup>6,7</sup>

### Controlling Organic Fouling

In some cases where the feed water contains significant levels of humic acids, dosing of a scale inhibitor or dispersant has caused operational problems, including organic fouling. In one particular case, testing showed that the raw-water characteristics allowed for successful operation in the absence of any type of chemical pretreat-

ment.<sup>5</sup>

During testing performed without a scale inhibitor, it was found that decreasing the pH increased the attraction of the humic acids to the membrane surface; therefore, a pretreatment acid feed was not required. When designing a system to treat raw water containing high levels of TOC, pilot testing should be utilized to help design the correct pretreatment system and to reduce complications at startup.

### Other Possible Foulants

Hydrogen sulfide, if oxidized, can precipitate elemental sulfur, which can cause particulate fouling; therefore, for a feed water that contains levels of dissolved hydrogen sulfide, utmost care should be taken in the design and construction of pumping and transmission facilities to insure that air is not introduced into the system.

Other constituents that should be considered when designing an RO pretreatment system include iron, manganese, and aluminum. Any significant presence of these metals in the feed water should be evaluated to minimize particulate fouling. In some cases, lowering the feed-water pH may provide a means of reducing the fouling by these metals.

### Effects of RO System Recovery

The recovery of a membrane process has a direct impact on the tendency for a slightly soluble salt to become insoluble and begin scale formation. While limiting the recovery can insure that solubility limits are not exceeded, this practice can waste a significant portion of the raw-water resource. For this reason, dosage of a scale inhibitor (threshold antiscalant) and/or dosage of a mineral acid to lower the feed-water pH are often the most technically effective, cost-effective, and commonly used methods to prevent scale formation on the membranes.

### Temperature Effects

The temperature of the feed water can also have a significant effect on solubility. As temperature increases, the solubility product increases for a water of the same ionic strength. For this reason, cleaning a scaled membrane system is more effective when performed at a higher temperature.

Since it is not practical to control the temperature of a feed water, consideration should be taken when selecting a scale inhibitor or designing an acid-feed system to insure that slightly soluble salts will not become insoluble at the lower range of feed-water temperatures; however, since groundwater is the predominant source for membrane facilities in Florida, such seasonal tem-

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perature variations are low in significance, if present at all.

### **Scale Inhibitors (Antiscalants) & Dispersants**

Scale inhibitors (antiscalants) are required where the concentration of a salt exceeds its solubility. Precipitation of salts may begin to occur with the formation of crystal, which acts as a catalyst to the formation of more of the crystal on the crystal surface until the crystals reach a size and density that causes them to fall out of suspension. This process will continue until the ions left

in solution are at their solubility limit.<sup>1</sup>

Scale inhibitors are effective in preventing the fouling of RO membrane elements due to the formation of scale. These chemicals slow the precipitation process and inhibit salt growth by their adsorption onto the surface of the forming salt crystal, which in turn slows its expansion and prevents the attraction of more supersaturated salt to the crystal structures.

Some scale inhibitors have some dispersive qualities, which involve surrounding particles of suspended salt or organic solids with the anionically charged scale inhibitor. These anionically charged particles will repel each

other to prevent the agglomeration of the particles to larger particles that may precipitate.

Typical scale inhibitors consist of molecules that contain carboxylic acid or phosphate functional groups. Polyacrylate molecules (molecular weight distribution from 1,000 to 5,000) contain multiple carboxylic acid functional groups and are commonly used in many inhibitors for inhibiting carbonate and sulfate formation.<sup>1</sup>

### **Polyphosphonates**

Polyphosphonates have been used for scale control in boilers and other industrial processes and were among the first scale inhibitors used in reverse-osmosis membrane processes. The functional groups most often used in scale inhibitors contain carboxylic acid or phosphate.<sup>3</sup>

Polyphosphonates consist of sodium hexametaphosphate (SHMP) or sodium hex and potassium pyrophosphonate. SHMP is inexpensive when compared with other scale inhibitors and has been commonly used in conjunction with a mineral acid for scale control.

While SHMP has a history of successful operation in membrane processes, care must be taken in order to avoid hydrolysis of SHMP in the dosing feed tank (a fresh solution should be made every three days).<sup>3</sup> Hydrolysis can not only decrease the scale inhibition efficiency, but also can lead to formation of calcium phosphate scaling, which causes fouling in the membrane system. Also, because it is not as effective for scale control as newer polymeric scale inhibitors, SHMP typically requires a higher dose. For these reasons, its use has decreased significantly in recent years.

Organophosphonates are another form of phosphonates that offer an improvement over SHMP. They are more expensive than SHMP but are more resistant to hydrolysis and offer scale inhibition and dispersion capabilities similar to those of SHMP.

### **Polyacrylates**

The development of polymeric scale inhibitors has been a significant catalyst to the expanded applications of RO technology. Perhaps the most significant among the polymeric offerings available are polyacrylates, or polyacrylic acids (PAA).

Polyacrylates can be divided into two categories: lower molecular-weight polyacrylates and higher molecular-weight polyacrylates. Lower molecular-weight polyacrylates typically have a molecular weight distribution in the range of 1,000 to 5,000 and contain multiple carboxylic acid functional groups. These polyacrylates are most effective

at inhibiting carbonate and sulfate formation.

Higher molecular-weight polyacrylates typically have a molecular weight distribution in the range of 6,000 to 25,000 and are most effective at dispersion but not as effective at scale inhibition as the lower molecular-weight polyacrylates.

In general, polyacrylates are more effective than SHMP; however, precipitation reactions may occur with cationic polyelectrolytes or multivalent cations such as aluminum or iron to foul the membrane.<sup>3</sup>

Blend inhibitors are a combination of low and high molecular-weight polyacrylates or a blend of low molecular-weight polyacrylates and organophosphonates for excellent dispersive and inhibitor performance. Blend inhibitors can offer advantages over monochemical inhibitors, which if over-injected can cause the inhibitor itself to fall out of solution with a multivalent cation. Many of the latest developments in scale inhibitor and dispersant technology are proprietary chemicals that fall into this category. As technology continues to push the limits of today's RO systems, blend inhibitors appear to possess the highest potential for future developments.

### **Scale-Inhibitor Feed Facilities**

RO permeate should be used when diluting concentrated scale-inhibitor products or mixing solution from powdered chemical, since calcium or other contaminants present in the feed water, in combination with scale inhibitors at high concentrations, may form a precipitate. Precautions must also be taken to prevent microbial growth in the inhibitor dilution tank. Make certain that no significant amounts of cationic polymers are present when adding an anionic scale inhibitor.

### **Mineral Acid pH Adjustment**

The addition of a mineral acid to lower the pH of RO feed water is one of the most effective ways to prevent calcium carbonate from forming. Since the formation of calcium carbonate salt is dependent on the total inorganic carbonate concentration and pH, converting the carbonate ion into bicarbonate ion and carbon dioxide by lowering the pH will decrease its formation.

Adding a mineral acid can also be a method of controlling biological fouling in an RO system. It should be noted, however, that the carbon dioxide converted from total inorganic carbonate is present in the feed water as a dissolved gas and as such is not rejected by the RO membranes.

The most common mineral acid used for this purpose is sulfuric acid; however,

injection of hydrochloric acid (HCl) is also a viable method for pH adjustment. When acid is fed as the sole form of pretreatment, the acid dosage must be sufficient to produce a negative Langlier index in the concentrate. When acid and scale inhibitor are added for pretreatment, the acid dose can be reduced to provide a Langlier index within the range controlled by the scale inhibitor.

As noted previously, sulfuric acid was among the first pretreatment chemicals used for RO technology, and as such has a well-documented history of successful use in treatment facilities. Acid was first used on cellulose acetate (CA) membrane systems as a

necessity to reduce the hydrolysis rate of the membranes.

While the injection of sulfuric acid does reduce the scaling potential for calcium carbonate, as it is injected the concentration of sulfate ions is accordingly increased in the feed water. This can further contribute to scale formation such as the calcium, strontium, or barium sulfate salts and should be accounted for when providing water-quality data to a pretreatment chemical manufacturer for a product recommendation.

It should also be noted that sulfuric acid is classified as a strong acid. As such, it

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requires high levels of safety precautions by operating personnel who handle the acid and maintain the acid storage and feed facilities. Currently 93 to 98 percent concentrations of sulfuric acid are commercially available; however, recent trends indicate that acid supply is moving toward 98 percent as the most commonly available.

The recent switch by some suppliers to high-strength (>98 percent) acid has become an issue that affects several facilities throughout the state, primarily because in some cases the higher-concentration acid has been found to cause failure of the acid-feed system components. In most cases the traditional materials of construction used for piping, valves, storage tanks, and pumping equipment known to be compatible with the lower-strength (93 to 96 percent) acid may not be adequate to handle the higher-strength acid. Since the materials that are compatible with the higher-strength acid are high-grade stainless and thermoplastic materials, the facilities that switch from the lower-strength acid will likely be faced with the costly replacement of their existing chemical feed systems.

Alternates to the expensive materials, such as carbon steel piping and tanks, can be used with the high-strength sulfuric acid, but they require a great deal of maintenance to keep in good operational condition. For HCl acid systems, attention should be given to feed-system design to insure that the storage and feed facilities are well vented to handle the fuming that is characteristic of volatile (high-strength) HCl, or that they have sufficient capacity to handle the increased storage and pumping volumes required for lower-strength HCl.<sup>1</sup>

In all cases, the planning and design of new or modified acid facilities should include a study of commercially available concentrations. Once the acid concentration basis of design has been confirmed, the availability of compatible materials should be evaluated for acid-feed system equipment, valves, and piping to insure a trouble-free system.

In addition, the consideration of acid pretreatment should also include the effects on water quality throughout the process. As mentioned previously, sulfuric acid contributes sulfates to the feed water when used for pH adjustment, which should be considered when sulfate-based salts are in excess of their solubility limits. Similarly, the use of HCl for pH adjustment contributes to the chloride levels in the feed water and should be carefully considered when chlorides are the limiting constituent of concern in the product water.

Since sulfates are divalent ions, they are

typically rejected at a higher percentage than the monovalent chloride ions from HCl; therefore, the same product-water concerns do not apply when dosing sulfuric acid, but concentrate water quality may become a concern, depending on disposal methods.

### ***No-Acid Membrane Treatment Systems***

Due to immense improvements in scale inhibitor capabilities and the relatively low levels of alkalinity and calcium found in some brackish groundwater supplies, some facilities have incorporated a scale-inhibitor-only or no-acid pretreatment approach for RO processes. Some advantages to the no-acid pretreatment include reduced costs of operation, improved rejection of chlorides and TDS, and possible elimination of an on-site hazardous chemical. While the reduced operation costs have most likely been the key issue driving the effort to eliminate acid pretreatment, there is yet to be a study confirming the significance of the annual cost savings for such a system that includes chemical cleaning frequencies, membrane life, and their associated costs.

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face-water sources contain microorganisms such as bacteria, algae, fungi, viruses and higher organisms. The potential for biological fouling is higher with surface water than groundwater. Microorganisms can be regarded as colloidal matter and removed by the pretreatment; however, complete removal of all microorganisms in a raw water is difficult if not impossible to achieve. If conditions are favorable, those that pass through pretreatment filters may begin to reproduce and form a biofilm downstream.

As described above, the symptoms of the biologically fouled RO system are an increase of the differential pressure and a decline in membrane flux or production. The concentration of bacteria in water is directly related to the biological fouling potential.

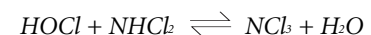
The total bacteria count (TBC) is a common method utilized to determine the total number of viable microorganisms in a water sample. This count is sampled by filtering a measured quantity of water through a membrane filter. Subsequently, the organisms retained on the filter surface are cultured on the proper nutrient medium for several days

to develop colonies, which are then observed and counted at low-power magnification. This culture technique can be applied to monitor the microbial activity from the intake through the subsequent treatment steps up to the concentrate stream and permeate.

In addition to the issues related to removing and controlling microorganisms, scale inhibitors which provide organic substrate and/or phosphorous may promote growth in biologically active feed waters. This potential problem increases the importance of pilot testing of the membrane and pretreatment processes when biological fouling microorganisms are known to be present in the water supply.

### Chlorination

Free chlorine has often been the biocide of choice for CA membranes; however, polyamide (PA) membranes are not tolerant to free chlorine. The germicidal efficiency of free residual chlorine is directly related to the concentration of undissociated HOCl, which is 100 times more effective than the hypochlorite ion OCl<sup>-</sup>. Chlorine can react with ammonia to produce chloramines in a series of stepwise reactions:

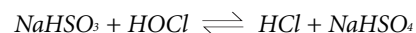
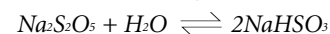


Chloramines also have a germicidal effect, albeit lower than that of chlorine. In some cases disinfection using chloramines has been found to have little or no significant effect on RO membranes; however, there will be always some residual unreacted HOCl, which can still oxidize the membranes. Thus, care must still be taken when chloramines are used as a disinfectant.

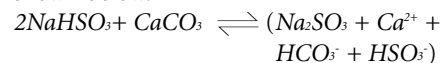
### Dechlorination

As a strong oxidizing agent, residual chlorine must be dechlorinated prior to the RO membranes to prevent damage. While some RO membranes may initially exhibit tolerance to chlorine, eventual degradation may occur after continuous exposure to 1 ppm or higher levels of free chlorine, depending on the pH, temperature, and residual transition metals such as iron in the feed water. Under alkaline pH conditions, chlorine degrades the membrane faster than at neutral or acidic pH. At an acidic pH, chlorine becomes more effective as a disinfectant.

Sodium metabisulfite (SMBS) or sodium bisulfite (SBS) is most commonly used for removal of free chlorine and as a biocide, as shown in the following reaction:



Other uses of SBS include dosing in the pretreatment as an effective agent to control biological fouling. Colloidal fouling has also been reduced by this method. SBS is also helpful in controlling calcium carbonate scaling by supplying hydrogen (H<sup>+</sup>) ions as shown below.



### Summary

With the continually increasing demands on our natural water resources, RO membrane water treatment processes provide the best available technology to meet the increasing needs of municipal water utilities throughout Florida. With the advent of new pretreatment chemicals and the continuation of efforts to optimize their use, the future holds much promise for new and more challenging applications to come.

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