

RO ANTISCALENT

Introduction - History and Development

The demand for scale inhibition increased tremendously with the advent of membrane treatment for water purification. The application of scale inhibitors (also called threshold inhibitors) in the reverse osmosis (RO) water treatment process is the primary focus in this article. Most of the information is applicable to scaling as it occurs in electro dialysis treatment of water. The development of synthetic polymers to control scaling aided the acceleration of RO as an economically and technically feasible process.

Necessity and Application of Scale Inhibitors

Fouling and Scaling

One of the major causes of reverse osmosis system failure is membrane fouling. The terms fouling and scaling are often confused or misapplied. Technically, fouling is defined as the accumulation of scale or foulants on the surface of the membrane resulting in impaired performance. Therefore, the definition of fouling includes mineral scaling from the precipitation of sparingly soluble salts. More commonly, the term fouling is used primarily to refer to biological or colloidal fouling. This paper addresses the phenomena of mineral scaling and its prevention or control. A quick, rule-of-thumb indicator of whether a system is primarily experiencing colloidal fouling versus mineral scaling is to evaluate whether the loss of flow is in the lead elements or vessels of the system or the tail-end elements or vessels. Colloidal or particulate fouling tends to cause loss of performance in the front-end of a system due to plugging of the feed-brine spacer or the membrane surface. Scaling tends to cause loss of performance in the tail-end of a system because the level of scaling minerals becomes higher as the feed brine flow becomes more concentrated and concentrate flows become less, providing less flushing capability. Biological fouling can cause loss of performance throughout a system, although, more commonly it is exhibited at the front of a system.

Silica solubility is well known both pH & temperature dependent. Polymerization and precipitation of amorphous silica at various super saturation is critical. The precipitation and deposition of amorphous silica and silicate influences consequential RO membrane fouling and loss of efficiency. Once formed Silica deposit/ fouling is very difficult to remove. The precipitation of Magnesium silicate is dependent on pH & Temperatures.

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Biocides versus Scale Inhibitors

The means for controlling fouling and scaling are varied and complex, and more are being developed constantly as membrane treatment processes are becoming more commonly applied on high organic surface waters. Biological fouling may be minimized by the injection of chlorine, if the membrane is chlorine-tolerant, or through the addition of a non-oxidizing biocide such as sodium bisulfate or a proprietary biocide. Proprietary organic scale inhibitors often contain a biocide to preserve and protect the scale inhibitor from biological growth, but it does not enable the scale inhibitor to act as a biocide in the RO system

Dispersant Activity of Select Scale Inhibitors

Several of the new generation of proprietary scale inhibitors have a dispersant capability that enables them to reduce suspended solids and colloidal fouling. These dispersant/antifoulants keep particles suspended so that they will be discharged in the brine stream prior to being deposited on the membrane surface. A dispersant is adsorbed on the surface of particles, preventing them from agglomerating. [2] A case study on the application of one of these scale inhibitors is presented below.

General Description of Scaling Potential and Activity

Water Chemistry (Scaling Ions)

Scaling concerns primarily arise in the application of membrane treatment technology to brackish water or seawater sources, as opposed to surface water sources. As mentioned above, it is also of concern in the electro dialysis treatment process. Most of the information presented in this paper is also applicable to the chemistry of the concentrate produced by the electro dialysis process. Brackish waters and seawater contain varying levels of sparingly soluble salts that will come out of solution if concentrated above a certain level. As water passes through a membrane and the limiting salts do not, the remaining water and salts become concentrated until a salt precipitates and scaling occurs. A thorough ion analysis of the feed water is the starting point for determining the scaling potential. A list of the parameters that should be measured is shown in Table 1. The sparingly soluble salts that will cause scaling are not indicated directly on an ion analysis because they are compounds. Therefore, the designer must review the analysis for possible combinations of detrimental compounds. The most common scale-forming salts are calcium carbonate, calcium sulfate, barium and strontium sulfite, and silica. Note that several of the ions critical to predicting scaling potential, such as barium, strontium and silica, are not commonly analyzed in preliminary water testing. Therefore, if a membrane treatment plant is under consideration for implementation on a new water source, these ions should be included in the raw water analysis.

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Concentration polarization

Concentration polarization is often discussed in conjunction with membrane scaling. Concentration polarization occurs because the concentration of dissolved species rejected by the membrane is always higher at the membrane surface than in the bulk feed stream. At the boundary layer of the membrane there is laminar flow, as opposed to turbulent flow, therefore, the concentration of the dissolved ions in the layer next to the membrane surface is higher than the mixed, turbulent feed stream. The concept of concentration polarization is important to many aspects of membrane process design, including the prediction of scaling. With increased levels of concentration polarization, the osmotic pressure of the solution next to the membrane surface increases, resulting in higher required feed pressure to permeate water. Also, higher salt passage occurs with increased concentration polarization due to increased diffusion of salt through the membrane. Most membrane manufacturers calculate and report a parameter in their design projections that indicates the level of concentration polarization that might be expected for the conditions given. This parameter is usually called the beta (β) number. The recommended acceptable beta number can be different for different manufacturers, however. It is an important parameter to review when designing an RO system. [3]

Definitions and Calculation of K_{sp}

Another term commonly used in discussion of scaling potential is the solubility product constraint, K_{sp} . It is necessary to calculate the solubility product constant for the sparingly soluble salts in the concentrate stream to determine if they present a potential scaling problem. The concentration of the salt in the concentrate stream depends on the recovery of the system. The concentration can be calculated by the following (assuming a typical level of salt rejection of 97% to 98%):

$$\text{Concentration factor} = 1/(1-\text{recovery})$$

Thus, if the level of chloride in a raw water stream was 100 mg/l and it was supplied to an RO system that operated at 75% recovery, the level of chloride in the concentrate stream would be:

$$(1/(1-0.75))*100 \text{ mg/l} = 400 \text{ mg/l}$$

The solubility product constant is defined as an equilibrium constant for the dissociation of a sparingly soluble, highly ionized electrolyte. K_{sp} is generally expressed in molar concentrations and is dependent on ionic strength and temperature. Most water chemistry texts contain charts and graphs that demonstrate solubility products versus ionic strength for specific ionic compounds.

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More simply, the solubility product constant indicates the level of salts that may be allowed in the concentrate before precipitation may be expected. This is commonly referred to as the saturation level. Most membrane manufacturers design projections will calculate and predict the levels of sparingly soluble salts in the concentrate as a function of the solubility product. The level of salts in the concentrate is called the ion product (IP). Some manufacturers express the level as a factor, or as a percentage, that is, if the level of CaSO_4 in a concentrate stream is supersaturated four times above the solubility product, it may be expressed as $4 \cdot K_{sp}$ or 400% K_{sp} .

Calculation or Modeling of Scaling Potential

The scaling potential of a raw water can generally be calculated from the water quality analysis and RO system design. For specific ions, the scaling potential should be evaluated as described above, utilizing the ion product versus the solubility product for each ion. For modeling CaCO_3 scaling potential the following parameters should be calculated from the water quality analysis and RO system design. Membrane manufacturers design projections will also model and predict the parameters. The most useful criteria are the Langlier Saturation Index (LSI). The LSI is calculated from the alkalinity, calcium, total dissolved solids, and pH of the concentrate stream, utilizing LSI curves available in most water chemistry text. Similarly, the Stiff-Davis Index predicts CaCO_3 scaling, but is less commonly referenced. For either index, a negative value indicates the potential for CaCO_3 to dissolve; a positive value indicates CaCO_3 will precipitate.

Other Methods for Scale Control

Recovery

As described above, the level of scaling ions in the concentrate stream is directly related to the RO system recovery. The most direct way to reduce the level of salts in the concentrate is to lower the recovery. This reduces the concentration factor of the ions. This method of scale control dramatically affects the design of the RO system, however. To obtain the same quantity of permeate production more raw water must be supplied, which may mean additional raw water supply facilities, larger raw water piping, larger cartridge filters, etc., or a reduced quantity of RO permeate must be allowed. Therefore, adjusting the recovery as a means for scale control is a method that should be evaluated during the initial design phase of a facility, and is not generally cost effective.

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pH Adjustment

A review of the LSI calculation and curves demonstrates that the concentrate LSI is directly affected by pH. Therefore, adjusting the pH of the feed water is a simple and direct means of controlling the CaCO₃ scaling potential of the concentrate. If no scale inhibitor is going to be used, the pH should be adjusted to maintain a concentrate LSI of 0.5 or lower. However, it is usually more efficient and cost effective to incorporate pH adjustment in conjunction with scale inhibitor application. The scale inhibitor manufacturers typically present information in their literature that states what level of LSI can be accepted with the proper application of the scale inhibitor. A common design practice is to use scale inhibitor and adjust the pH of the feed water to obtain a concentrate LSI of 1.5 to 1.8. As even more effective scale inhibitors are developed, permitting operation at higher concentrate LSI levels, the use of acid may be eliminated entirely in certain cases.

Adjusting the pH does not typically affect or reduce the scaling potential of sparingly soluble salts. Lowering the pH may help reduce other potential fouling problems, such iron or manganese particulate fouling. The reduced pH may help keep the metals in a soluble form.

The most common method for pH reduction is the addition of sulfuric acid, H₂SO₄. This acid is easily and cost effectively obtained in concentrated liquid form in different strengths. It is fairly easy to store, handle and feed. Unfortunately, the addition of sulfuric acid contributes sulfates to the raw water which may be undesirable if the raw water already has high sulfate levels, contributing to the potential for calcium sulfate, barium sulfate, or strontium sulfate scaling. Hydrochloric acid, HCl may be used for pH adjustment but it is more difficult to store and handle due to its tendency to fume. As a result of fir volatility of the HCl, it is usually obtained at lower strengths and therefore storage, handling and feeding facilities must be sized for higher volume. In addition, HCl contributes chlorides to the raw water.

How Scale Inhibitors Work

Mineral scale formation occurs through the following steps: 1. super saturation of sparingly soluble salts, 2. formation of crystal nuclei, and 3. growth of crystal nuclei into crystals. [4-5] Scale inhibitors control mineral scale formation by inhibiting the formation of crystalline precipitates under supersaturated conditions. The inhibitor affects the growth rate and changes the form or shape of the crystals. Exactly how the crystals are modified by the scale inhibitor is not entirely known, but it is believed the crystals are weakened by internal stresses, causing them to fracture. [2] Additionally, certain scale inhibitors are a good stabilizer for metal ions, keeping metals such as aluminum, iron and manganese in solution. A few of the newest generation of scale inhibitors also provide a dispersant capability, maintaining suspended solids and colloids in suspension until discharged from the membranes.

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(Formerly Known - ALTRET Performance Chemicals Guj.Pvt.Ltd)

Products Currently Available

Polyphosphates

The first chemicals to be employed as scale inhibitors for calcium carbonate scaling were polyphosphates: potassium pyrophosphate and **sodium hexametaphosphate**. Sodium hexametaphosphate, used in conjunction with acid, was the scale inhibitor of choice for many years in RO Systems. Typically, early RO systems incorporated cellulose acetate membranes that required an operating pH below 6.5 to avoid hydrolysis. Thus, the combination of the lowered pH and the sodium hexametaphosphate was suitable for controlling calcium carbonate scaling in most RO Systems. With the development of the low-pressure, thin film composite membranes, operating pH levels did not have to be lowered for protection of the membrane. Therefore, a greater level of scale formation control was desired from the scale inhibitor. Also, a drawback of sodium hexametaphosphate results from the tendency of the polyphosphates to hydrolyze to form orthophosphate which could then react with calcium to form insoluble calcium phosphate scale. [1] Another disadvantage of sodium hexametaphosphate is its ineffectiveness in inhibiting the precipitation of other sparingly soluble salts.

Proprietary Scale Inhibitors

In 1970's, synthetic polymers, polyacrylates, were developed which provided good calcium carbonate and calcium sulfate control. Polyacrylates also provided limited metal ion stabilization and dispersant activity. They had excellent hydrolytic and thermal stability. [1] The next development in scale inhibitors incorporated proprietary copolymers that provided excellent scale inhibition, enhanced metal ion stabilization, and colloidal dispersant properties.

Specialty Product Development

Iron/Manganese Dispersant Capabilities

Metal oxides and hydroxides can be a problem in RO Systems. In a strictly anaerobic condition, dissolved iron concentrations of 5 or 10 mg/l or greater can be tolerated and will be well-rejected by the membranes. However, if the iron is allowed to contact air it will precipitate to iron hydroxide or iron bicarbonate and will foul the membranes. In fact, if the feed water contains dissolved oxygen, iron levels of 0.05 to 0.5 mg/l may be troublesome. [6] Unfortunately, maintaining feed waters in a perfect anaerobic state is often not realistic or practical. Historically, scale inhibitors have had limited ability to stabilize metal ions (i.e., iron, aluminum, manganese), however, more recently developed products have demonstrated promising capabilities in keeping metals and metal hydroxides in solution and/or in suspension with the dispersants. A briefcase study on an application that demonstrates the remarkable effectiveness of the new generation of scale inhibitors is presented below.

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Silica Fouling

Silica fouling has been a topic of much discussion in the reverse osmosis industry. Relatively high levels of silica, SiO_2 are commonly found in groundwater's. Silica can form an insoluble colloidal silica or silica gel that will foul the membrane surface. Comparing the level of silica in the concentrate to the solubility limit for amorphous silica will indicate if silica fouling may be a problem. Historically, the guideline has been to limit the level of silica in the concentrate to 120 to 150 mg/l. However, this limit may be exceeded in certain cases, depending on other factors such as temperature or the presence of metals.

Silica solubility chemistry is very complex and difficult to predict. Silica has two forms in natural waters, colloidal and soluble. Both forms can cause problems in RO Systems. Soluble silica can deposit as an impervious glassy film on the membrane, and soluble silica can polymerize to form colloidal particles. Colloidal silica particles can deposit on the membrane surface or plug the membrane feed spacer.

Problems of Generics Chemicals for R.O. Scale Control

Some generic pretreatments are known to promote biological growth. An inorganic Antiscalants, sodium hexametaphosphate (**SHMP**) is not only the source of microorganisms but also a source of nutrients for biofilm to occur. In addition, the instability of SHMP in the stock solution inhibits its effectiveness in an RO system. Sodium thiosulfate used to neutralize chlorine can also be a nutrient for bacteria. Sodium metabisulfite also can contribute to biological growth and sulfate scale.

The use of crystal modifying Antiscalants is also problematic. By absorbing polymer onto the surface of the growing crystal, growth is disrupted by the adsorption and redistribution on the surface of the material. Large pristine crystal growth may be inhibited but new planes form by surface deposition and migration on the edges of the crystal. This causes a chemical dynamics shift that yields a large number of smaller crystals instead of fewer greater-sized crystals. A higher concentration of smaller but growing crystals has greater overall crystal surface area. The result is more crystal precipitation over more of the membrane surface thus creating more sites of nucleation. The sites then become larger as other constituents have an affinity for the preexisting foulants and fouling accelerates.

Some Antiscalants, which rely solely on the substoichiometric control of cations as a method of controlling crystal growth may also, prove problematic. Although some cations are scavenged by the polymer's functional groups, metal ions such as iron or aluminum cause the formation of an insoluble compound, which precipitates onto the membrane.

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Limitation of HEDP Based Antiscalants for RO Scale Control

HEDP is moderate moderately effective as scale inhibitor for RO system. Its having limited threshold inhibition capacity. As per the data under low super saturation HEDP inhibition is sufficient but under high super saturation situation PBTC outperform than HEDP.

Under certain condition of Total hardness, pH and temperature phosphonate can react stoichiometrically with calcium ions which leads the precipitation of Calcium phosphate. Calcium phosphate is troublesome deposit itself.

Features of Altret 818 KP

It is a blends of PBTC and polymer base chemical does not contain any phosphate or generic phosphonate. The polymerization is well controlled to the desired chain length so as to get a uniform structural configuration and functionality. As a result, ALTRET 818 KP has very good performance as scale inhibitor and dispersant. It can widely use in reverse osmosis system, desalination processes and sugar mill evaporators.

Property of PBTC

It is low content of phosphoric, has structural features of both phosphoric acid and carboxylic acid group, which enable its excellent scale inhibition properties. PBTC's antiscaling property under high temperature is far better than that of phosphonates. Phosphonate PBTC can improve zinc salt solubility, has good chlorine oxidation tolerance and good composite synergy. PBTC can be use where situations of high temperature, high hardness, high alkali and high concentration index. It's generally blend with polymer for synergistic result.

Property of Polymer

Polymer provides the best dispersancy of inorganic particles commonly found in water that requires membrane treatment. Excellent dispersancy properties of polymer for calcium carbonate, iron oxide, and clay. The higher the turbidity, the better the polymer as a dispersant. It is particularly effective on calcium carbonate, calcium sulfate, barium sulfate and other low solubility salts. Polymer being used in ALTRET 818 KP is thermally stable and very high silica tolerance.

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ALTRET 818 KP excellent inhibitor of hard scales through dispersion and threshold inhibition, and also controls the effect to presence of silica. It is particularly effective in presence of insoluble inorganic salt such as calcium carbonate, magnesium carbonate, Sulphates and reactive or non-reactive (polymeric) silica.

ALTRET 818 KP prevent Silica polymerization in RO system.

ALTRET 818 KP disperses colloidal matter.

The presence of suspended solid does not affect the silica deposit inhibition property of ALTRET 818 KP.

ALTRET 818 KP provide iron oxide dispersant property and comparable against commercially available co polymer based inhibitor.

The polymeric dispersant base Antiscalants, effectively control silica /silicate deposition in R.O. system.

Altret 818 KP is biodegradable hence ecofriendly.

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