



**Chemical Pretreatment  
For  
RO and NF**

**January 2008**

**401 Jones Road, Oceanside, CA 92058  
Phone: 760.901.2500 • Fax: 760.901.2664 • 1.800.CPA.Pure  
www.membranes.com**



There are a number of chemicals that can be introduced into the RO feed to enhance the operation of the RO system.

- Acids
- Caustic
- Dechlorination Chemicals
- Antiscalants and Dispersants

## **Acids**

Acids, typically hydrochloric [HCl] or sulfuric [H<sub>2</sub>SO<sub>4</sub>], are fed to lower the feed pH.

Sulfuric acid is used more often than hydrochloric acid, based on a lower operating cost, reduced fuming to the atmosphere which can corrode surrounding metal components, and a better membrane rejection of the sulfate ion than the chloride ion. Technical grade sulfuric acid, with no other additives, is suitable for use with a RO system. Sulfuric acid is commercially available as a 20% and 93% solution. The 93% solution is also referred to as 66° Baume solution. Caution is required in diluting 93% sulfuric acid, since the maximum heat of dilution of approximately 280°F occurs around 60%. It is critical that the concentrated acid is added slowly to the top of dilution water that is being agitated to minimize the buildup of heat and boiling of the makeup solution.

Hydrochloric acid is preferred when there is a concern for scaling by calcium sulfate, barium sulfate or strontium sulfate. Sulfuric acid increases the sulfate ion level in the RO feed, which directly increases the potential for sulfate-based scaling. Technical grade hydrochloric acid (with no additives) typically is suitable for use with a RO system. Hydrochloric acid is typically available as a 30% to 37% solution. It is sometimes referred to as muriatic acid.

The primary purpose for reducing the feed pH is to reduce the potential of calcium carbonate scaling in the RO concentrate as measured by using the Langelier Saturation Index [LSI]. LSI is a method of reporting the scaling or corrosive potential of low TDS brackish water based on the level of saturation of calcium carbonate [CaCO<sub>3</sub>]. LSI is important in RO water chemistry in determining whether a water will or will not form calcium carbonate scale. Water with a negative LSI is considered corrosive to metal

pipings and will not form calcium carbonate scale. Water with a positive LSI is not corrosive, but it will tend to form calcium carbonate scale.

The LSI value is calculated by subtracting the calculated pH of saturation of calcium carbonate from the actual feed pH. Calcium carbonate solubility decreases with increasing temperature (as evidenced by the liming of a tea kettle), higher pH, higher calcium concentration, and higher alkalinity levels. The LSI value can be lowered by reducing pH by the injection of an acid (typically sulfuric or hydrochloric) into the RO feed water. A recommended target LSI in the RO concentrate is negative 0.2 (which indicates that the concentrate is 0.2 pH units below the point of calcium carbonate saturation). A negative 0.2 LSI allows for pH excursions in actual plant operation. A polymer-based antiscalant can also be used to inhibit the precipitation of calcium carbonate. Some antiscalant suppliers have reported the efficacy of their product up to a positive LSI value of 2.5 in the RO concentrate (though a more conservative design LSI level is +1.8).

## **Caustics**

Caustics, for a few process applications, can be injected to increase the RO feed pH. Typically, the only caustic injected is sodium hydroxide [NaOH] based on cost, availability and its solubility in water.

Most of the time the quality of the NaOH can be technical grade (and free of any additives). If the technical grade NaOH is not clear in color (e.g. has a blackish tint), then a higher grade of NaOH may be desirable such as rayon or nylon grade. NaOH is commercially available as 100% solid flake or as 20% or 50% solution. Caution is required in storing 50% caustic since it can freeze at temperatures just below 60°F (15.5°C), with a special concern for cold air drafts.

Caution is required in raising the feed pH as it can decrease the solubility of CaCO<sub>3</sub>, as measured by an increasing LSI, iron and manganese.

The most common process application that uses a caustic feed involve 2<sup>nd</sup> pass RO systems. In a 2-Pass RO, the permeate from a 1<sup>st</sup> pass RO becomes the feed to the 2<sup>nd</sup> pass. The 2<sup>nd</sup> pass RO “polishes” the 1<sup>st</sup> pass permeate to quality levels as good as 4 megohm-cm. Caustic is introduced into the 2<sup>nd</sup> pass feed for 4 reasons.

- At a pH of 8.2 and higher, all carbon dioxide gas is converted into the bicarbonate ion. The bicarbonate ion will be rejected by the RO. Carbon dioxide, being a gas, would pass through the RO into the permeate stream unimpeded. The carbon dioxide would become an undesirable load to downstream polishing mixed beds.
- Certain TOC constituents are better rejected at a higher pH.
- Silica rejection and solubility are higher at higher pH levels (particularly above a pH of 9).
- Boron rejection is higher at higher pH levels (particularly above a pH of 9).

One special process application, frequently referred to as the HERO™ process, institutes a caustic feed to raise feed pH to 9 or 10. The RO operates in a 1<sup>st</sup> pass mode and uses a brackish quality feed water. Brackish waters can contain potential foulants that become more of an issue at higher pH (e.g. hardness, alkalinity, iron, manganese, etc.). Pretreatment frequently uses a weak acid cation exchange system and a degasifier to remove these potential foulants.

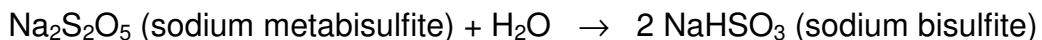
## **Dechlorination Chemicals**

At no time should there be a Free Chlorine residual in the feed water. Even very low levels of chlorine in the feed stream will result in irreparable oxidation damage of the membrane. Therefore, operators should ensure that oxidant does not enter the RO system. The two most common pretreatment methods for reducing chlorine levels are by absorption onto granular activated carbon filter media or by the use of a chemical reducing agent such as sodium bisulfite.

Pressurized carbon filters are typically used on small systems (50 gpm to 100 gpm or less) due to capital cost considerations. It is recommended that a premium grade of carbon is used that has been acid-washed for the removal of heavy metals and hardness and has very low levels of carbon fines that can foul the RO. Anytime new carbon media is installed, the carbon filter must be thoroughly rinsed until all carbon fines are absent from the effluent (this can take a few hours to days). One cannot rely on a 5-micron cartridge filter to protect the RO element from fouling due to carbon fines. The advantages of a carbon filter are their ability to remove organics from the feedwater that could foul the RO and that they are more reliable in treating all the feed water than a chemical feed system. The disadvantage is that carbon filters are notorious for breeding

bacteria that can result in a biological fouling of the RO. Carbon filters have been known to see a doubling of viable bacteria counts in 24 hours, with capital intensive and operator intensive periodic steam sanitization the only answer for controlling microbial populations. Steam sanitization for critical applications (like USP Water production for the pharmaceutical industry) can be as frequent as 1 to 7 days.

Sodium Bisulfite [SBS] is the typical chlorine reducing agent of choice for larger RO systems. **Note:** SBS should not be cobalt catalyzed. A SBS solution is made by dissolving solid sodium metabisulfite into water and has a pH of 4.6 at 1.0% (by weight) solution strength. A 10% (by weight) SBS solution will require the addition of 0.51 pounds of solid sodium metabisulfite into one gallon of water. The sodium metabisulfite is commercially available at 97.5% to 99% purity and can be stored safely up to six months in a dry storage area. The SBS solution is not stable to air and reacts with oxygen as well as chlorine, therefore it is recommended that batches less than 2% by weight be used within 3 to 7 days and batch solutions less than 10 % be used within 7 to 14 days. Theoretically, 1.47 ppm of SBS (or 0.70 ppm of sodium metabisulfite) will stoichiometrically neutralize 1.0 ppm of chlorine. Designers have been known to use a dosing rate of 1.8 ppm to 3.0 ppm of SBS per 1.0 ppm chlorine so as to include an industrial safety factor for brackish water RO systems. SBS needs to be added far enough upstream of the RO elements to insure at least 20 seconds of reaction time. Proper in-line mixing is required which preferably includes a static mixer.



The advantages of SBS dechlorination are that it is less capital intensive than carbon filters for large systems, the reaction by-products are readily removed by the RO, and residual SBS is readily removed by the RO.

The disadvantages of SBS can be the need to handle and mix a small volume of chemical and an increased risk in chlorine making it to the membranes if sufficient monitoring and controls are not designed into the dechlorination system. In a few cases where Sulfur Reducing Bacteria [SBRs] are present in the feed supply, the bisulfite functions as a nutrient and enhances their growth. SBRs are usually found in anaerobic (low oxygen content) shallow wells in regions such as Florida. Frequently hydrogen sulfide (H<sub>2</sub>S) is also present as a by-product of the SBR metabolic process.

Monitoring for dechlorination can be performed by the use of an Available Free Chlorine monitor, monitoring for a residual bisulfite concentration, or by an ORP meter. Hydranautics recommends that the feed to the RO/NF system is equipped with a ORP (Oxidation-Reduction Potential) meter. The feedwater can then be continuously monitored for the presence of oxidant. Except in wastewater applications where chloramines are used, the ORP meter reading should always be below 300 mV. If it exceeds 300 mV, the plant operator should receive a warning that a dangerous level of oxidant is getting to the membrane and should take action, such as adding or increasing the dose of SBS, to reduce the oxidant concentration. If the ORP value reaches 350 mV, the plant should be shut down until the oxidant concentration can be reduced to a safe value (ORP < 300 mV).

CPA membranes have an estimated chlorine tolerance of 1,000 ppm-hours to 2,000 ppm-hours before a doubling in salt passage occurs. The 1,000 ppm-hours level correlates to a chlorine level in the RO feed of 0.038 ppm for an operating period of 3 years. RO designers are cautioned that it has been observed that this chlorine tolerance can be dramatically reduced by the catalytic effects of increasing temperature (90° F or higher), increasing pH (7 or higher), or by the presence of transition metals on the membrane surface (e.g. iron, manganese, zinc, copper, aluminum, etc.).

CPA membranes have an estimated chloramine tolerance of 50,000 ppm-hours before a noticeable increase in salt passage occurs. The 50,000 ppm-hours level correlates to a chloramine level in the RO feed of 1.9 ppm for an operating period of 3 years. RO designers are cautioned that it has been observed that chloramine tolerance can vary due to the catalytic effects of high temperature, low pH, or presence of transition metals. One application at a tertiary waste water plant in California indicated a reduction of system salt rejection from 98% to 96% in 2 to 3 years with chloramines at 6 to 8 ppm. The designer must also be aware that dechlorination after chloramination may be required. Chloramines are produced by mixing chlorine and ammonia. Residual free chlorine, which can deteriorate membranes much more quickly than chloramines, can be present if insufficient ammonia is used. Therefore, it is vital that there is always an excess of ammonia, and the system should be monitored to ensure this. For more details on chloramines, please contact Hydranautics Technical Support Department.

## **Antiscalants and Dispersants**

There are a large number of chemical suppliers who supply a variety of proprietary antiscalants and dispersants to improve the operation of RO and NF systems.

Antiscalants are a family of chemicals designed to inhibit the formation and precipitation of crystallized mineral salts that form scale. Most antiscalants are proprietary organic man-made polymers (e.g. polyacrylic acids, carboxylic acids, polymaleic acids, organo-phosphates, polyphosphates, phosphonates, anionic polymers, etc.). Molecular weight of these polymers can range from 2,000 Dalton to 10,000 Dalton.

Antiscalant technology for RO systems initially was derived from chemistries used in cooling water and boiler water applications. It should be duly noted that the large number of different antiscalant chemistries that have evolved have produced a wide variety of results and efficacy depending on the application and organic polymer used.

Caution should be used in the use of antiscalants made of polyacrylic acid. They are susceptible to the formation of a foulant that settles on the membrane surface if there are high levels of iron. This foulant will increase feed pressure requirements, but typically can be cleaned using a low pH cleaning.

Caution should also be used in the use of antiscalants that are anionic in nature (e.g. polyacrylic acids) when a cationic-based coagulant or filtering aid is used in the pretreatment. A very viscous, sticky foulant can be produced that will increase feed pressure requirements, and it can be very difficult to clean off.

An antiscalant that was popular in the early days of RO was sodium hexametaphosphate (SHMP), but its use has been greatly reduced with the advent of proprietary antiscalants. SHMP has a number of limitations. Batches of diluted SHMP has to be made every 2 to 3 days due to hydrolysis by exposure to air, which would dilute its efficacy and create a potential calcium phosphate scaling risk. SHMP has a reduced protection to calcium carbonate scaling with a maximum LSI rating in the concentrate of +1.0.

Antiscalants retard the growth of crystalline salt structures in the RO feed and concentrate streams, thereby allowing a concentration of sparingly soluble salts in excess of the normal solubility limits. Antiscalants can be used to replace, or can be used

in conjunction with, acid feed to control calcium carbonate scaling.

A number of factors can affect the rate of mineral scale formation. Lower temperatures reduce the solubility of mineral scales (the exception here is calcium carbonate scale formation is enhanced when temperature increases). The solubility of sparingly soluble salts increase with higher TDS levels (this is due to the increased interference by all the ions in the seeding process of scale formation).

Most common mineral scalants of concern:

- Calcium carbonate [CaCO<sub>3</sub>]
- Calcium sulfate [CaSO<sub>4</sub>]
- Strontium sulfate [SrSO<sub>4</sub>]
- Barium sulfate [BaSO<sub>4</sub>]

Less common mineral scalants are:

- Calcium phosphate [CaPO<sub>4</sub>]
- Calcium fluoride [CaF<sub>2</sub>]

Dispersants are a family of organic man-made polymers designed to inhibit the agglomeration and deposition of foulants onto the membrane surface. Dispersants are sometimes referred to as anti-foulants. Foulants tend to be a softer, non-crystalline deposit. Dispersant chemicals frequently have antiscalant properties. The efficacy of differing dispersants can vary for different foulants, so one needs to know what foulant they are treating for.

Foulants treated by dispersants:

- Mineral Scales
- Metal Oxides and Hydroxides [iron, manganese, aluminum]
- Polymerized Silica
- Colloidal material [defined as very small particles that stays in an infinite suspension and can be composed of clay, iron, aluminum, silica, sulfur and/or organic matter]
- Biological matter

Predicting the maximum solubility of super-saturated silica can be difficult. In particular, iron present in the feed water can readily produce iron silicates and dramatically reduce the allowable concentration of silica in the RO concentrate stream. Other major factors are pH and temperature.



Predicting the maximum levels of metals (e.g. iron, manganese, aluminum) can also be difficult. The soluble forms of the metal ions allow for higher levels of saturation. The insoluble forms tend to act more like particles and colloids.

Optimal dosing and allowable maximum saturation levels of scalants and foulants for antiscalants/dispersants are best determined by the chemical supplier who utilizes a proprietary software package. Hydranautics utilizes conservative estimates in its IMSDesign software for alarm purposes in estimating the allowable level of super-saturation of sparingly soluble salts.

Maintaining proper dosing levels of an antiscalant/dispersant is important. Under-dosing can cause scaling or fouling. Over-dosing can cause a deposition of the antiscalant/dispersant onto the membrane, creating a fouling problem.

It is important that the antiscalant/dispersant be thoroughly flushed from the RO elements at shutdown, as it can settle onto the membrane and cause a fouling problem. The injection of antiscalant/dispersant should cease during low pressure flushes when the RO feed water is the source of flush water.

The design of the antiscalant/dispersant injection system into the RO feed stream needs to make sure that it is properly mixed before it enters the RO elements. The use of a static mixer is the most effective mixing method, but adds cost to a system. Most systems have the injection point just before the RO feed cartridge filter(s) and rely on the cartridge filter residence time and RO feed pump agitation to affect the mixing.

It is recommended that if there is an acid pH adjustment of the RO feed water, the acid should be injected upstream and thoroughly mixed before it reaches the antiscalant/dispersant injection point. Concentrated pockets of low pH acid may destroy the efficacy of the antiscalant/dispersant.

The chemical metering pump used for the injection of antiscalant/dispersant should be adjusted to maximize the frequency of injection. A suggested minimum stroking frequency is once every 5 seconds. Typical dosing rates of antiscalants/dispersants are 2 to 5 ppm. To achieve a reasonable stroking frequency of the metering pump, a dilution of the antiscalant/dispersant may be required.

Antiscalants/dispersants are supplied as either a concentrated liquid or in a powder form.

Dilution water should be hardness-free and preferably be of RO permeate quality. Diluted antiscalant/dispersants can become biologically fouled in the day tank depending on temperatures and how much it has been diluted. A suggested residence time for a diluted solution is 7-10 days. Normally, undiluted antiscalant/dispersant solutions do not suffer from biological fouling.

The table below reflects the upper operating limits of saturation reported by chemical suppliers and the typically conservative alarm points used in the Hydranautics RO design program. These values are based on the concentrate stream, with normal saturation limit of 100% without use of an antiscalant/dispersant. Hydranautics will always recommend that you contact the chemical supplier to confirm the efficacy of a product.

Scalant or Foulant	Maximum Reported	Hydranautics Alarm
LSI (calcium carbonate)	+ 2.9	+ 1.8
Calcium Sulfate	400%	230%
Strontium Sulfate	1,200%	800%
Barium Sulfate	8,000%	6,000%
Calcium Fluoride	12,000%	Not alarmed
Silica	300 ppm or more	100%
Iron	5 ppm	not alarmed
Aluminum	4 ppm	not alarmed

Another major issue in selecting an antiscalant/dispersant is the assurance that it is compatible with the RO membrane being used. There are incompatible chemicals that can irreversibly foul or damage a RO membrane. Hydranautics relies on the supplier of the chemical to have performed all RO membrane compatibility and process efficacy tests.

Some recommended questions to ask chemical suppliers of antiscalants and dispersants are:

- Is it compatible with the RO membrane type in question?
- Is there an installation list of end-users with over 1000 hours of successful operation?
- Does it react adversely with any other constituents in the RO feed water (e.g. iron, heavy metals, cationic polyelectrolytes, etc.)?

- What are the recommended dosing rates and maximum dosing rates?
- What are the projected limits of solubility for individual scaling and fouling components?
- Are there any special discharge concerns?
- Is it suitable for potable water applications (if required)?
- Does the supplier offer other RO chemical feeds like antiscalant-compatible coagulants, biocides and cleaning chemicals?
- Does the supplier offer off-site technical support services like membrane autopsies or cleaning of elements?

## **Glossary**

**Alkalinity:** Alkalinity is comprised primarily of carbon dioxide, bicarbonate, carbonate and hydroxides. Naturally occurring alkalinity is the earth's natural buffering system in that small doses of strong acids (e.g. acid rain) react with alkalinity and result in relatively small changes in pH. Carbon dioxide and bicarbonate are in a balance between the pH range of 4.4 and 8.2. At a pH of 4.4 or lower, all alkalinity is in the form of carbon dioxide. At a pH of 8.2, there is no carbon dioxide and all alkalinity is bicarbonate. Bicarbonate and carbonate are in a balance between the pH range of 8.2 and 9.6. At a pH of 9.6, there is no carbon dioxide or bicarbonate and all alkalinity is carbonate. As the pH increases above 9.6, hydroxyl alkalinity due to the presence of the hydroxide ion starts to occur. Most naturally occurring water sources have a pH between 6 and 8.4, so the presence of hydroxides is the result of man-made activity. Alkalinity, especially by boiler water chemists, can be reported as M-Alkalinity and P-Alkalinity. M-Alkalinity measures the Total Alkalinity in a water in terms of "ppm as calcium carbonate" based on an acid titration to a pH of 4.2 using a Methyl orange indicator endpoint. P-Alkalinity measures the amount of bicarbonate, carbonate and hydroxyl alkalinity based on an acid titration to a pH of 8.2 using a Phenolphthalein pink indicator endpoint.

**Barium (Ba):** A divalent cation. The solubility of barium sulfate ( $BaSO_4$ ) is low and can cause a RO scaling problem in the back-end of a RO. Barium sulfate solubility is lower with increasing sulfate levels and decreasing temperatures. Typically, barium can be found in some well waters, with typical concentrations less than 0.05 ppm to 0.2 ppm. It is important that barium be measured with instruments capable of 0.01 ppm (10 ppb) minimum detection levels. With saturation at 100%, super-saturation up to 6000% is typical with an antiscalant.

**Bicarbonate ( $\text{HCO}_3$ ):** A monovalent anion. The solubility of calcium bicarbonate is low and can cause a RO scaling problem in the back-end of a RO. Calcium bicarbonate solubility is measured using LSI (Langlier Saturation Index) for brackish waters or the Stiff-Davis Index for seawaters and is lower with increasing temperature and increasing pH. Bicarbonate is one component of alkalinity and its concentration is in a balance with carbon dioxide between the pH range of 4.4 and 8.2 and in a balance with carbonate between the pH range of 8.2 and 9.6.

**Calcium (Ca):** A divalent cation. Calcium, along with magnesium, is a major component of hardness in brackish water. The solubility of calcium sulfate ( $\text{CaSO}_4$ )(gypsum) is typically limited to 230% with the use of an antiscalant. The solubility of calcium carbonate is typically limited to a LSI (Langlier Saturation Index) value of positive 1.8 to 2.5.

**Carbon Dioxide ( $\text{CO}_2$ ):** Carbon dioxide is a gas that when dissolved in water reacts with the water to form weak carbonic acid ( $\text{H}_2\text{CO}_3$ ). If a pure water was completely saturated with carbon dioxide, its concentration would be about 1600 ppm and the pH would be about 4.0. A typical source for carbon dioxide in natural waters is the result of a balance with bicarbonate alkalinity based on the pH of the water. The concentration of carbon dioxide in water is typically indirectly determined by graphical comparison to the bicarbonate concentration and pH. Carbon dioxide and the bicarbonate ion are in a balance between the pH range of 4.4 and 8.2. The alkalinity is all carbon dioxide at pH 4.4 and is all bicarbonate at pH 8.4. The RO design program calculates the carbon dioxide level based on the bicarbonate level and pH of the water. Carbon dioxide, being a gas, is not rejected or concentrated by a RO membrane, therefore its concentration will be the same in the feed, permeate and concentrate. Acidifying the RO feed water will lower pH by converting bicarbonate to carbon dioxide.

**Carbonate ( $\text{CO}_3$ ):** A divalent anion. The solubility of calcium carbonate is low and can cause a RO scaling problem in the back-end of a RO. Calcium carbonate solubility is measured using LSI (Langlier Saturation Index) for brackish waters or SDSI (Stiff-Davis Index) for seawaters and is lower with increasing temperature and increasing pH. Carbonate is one component of alkalinity and its concentration is in a balance with bicarbonate between the pH range of 8.2 and 9.6. At a pH of 9.6 and higher, there is no carbon dioxide or bicarbonate, with all alkalinity being in the carbonate form.

**Ionic Strength:** The solubility of sparingly soluble salts increases with increasing feed

TDS. To account for this effect in calculating the solubility of a salt (e.g. calcium sulfate, barium sulfate, strontium sulfate or SDSI), the Ionic Strength of a water is calculated. The Ionic Strength of each ion is derived by taking the ppm concentration of each ion (as calcium carbonate) and multiplying each monovalent ion by  $1 \times 10^{-5}$  and each divalent ion by  $2 \times 10^{-5}$ . Summing the Ionic Strength of each ion then derives the total Ionic Strength of the water.

**Iron (Fe):** Iron is a water contaminant that takes two major forms. The water-soluble form is known as the ferrous state and has a + 2 valence state. In non-aerated well waters ferrous iron behaves much like calcium or magnesium hardness in that it can be removed by softeners or its precipitation in the back end of the RO system can be controlled by the use of a dispersant chemical in an RO feed water. The water-insoluble form is known as the ferric state and has a + 3 valence state. Typically, RO manufacturers will recommend that combined iron levels be less than 0.05 ppm in the RO feed. If all iron is in the soluble ferrous form, iron levels up to 0.5 ppm in the feed can be tolerated if the pH is less than 7.0 (though an iron dispersant is recommended). The introduction of air into water with soluble ferrous iron will result in the oxidation to insoluble ferric iron. Soluble iron can be found in deep wells, but can be converted into the more troublesome insoluble iron by the introduction of air by being placed in tanks or by leaky pump seals. Soluble iron can be treated with dispersants or can be removed by iron filters, softeners or lime softening. Insoluble ferric iron oxides or ferric hydroxides, being colloidal in nature, will foul the front end of the RO system. Sources of insoluble iron are aerated well waters, surface sources, and iron scale from unlined pipe and tanks. Insoluble iron can be removed by iron filters, lime softening, softeners (with limits), ultrafiltration (with limits) and multimedia filtration with polyelectrolyte feed (with limits). Precautions are required with the use of potassium permanganate in manganese greensand iron filters in that potassium permanganate is an oxidant that could damage any polyamide membrane. Precautions are also required with a cationic polyelectrolyte in that they can irreversibly foul a negatively charged polyamide membrane. Corrosion proof vessels and piping (e.g. FRP, PVC or stainless steels) are recommended for all RO systems, RO pretreatment, and distribution piping coming to the RO system. Iron as foulant will quickly increase RO feed pressure requirements and increase permeate TDS. In some cases, the presence of iron can create a bio-fouling problem by being the energy source for iron-reducing bacteria. Iron-reducing bacteria can cause the formation of a slimy biofilm that can plug the RO feed path.

**LSI (Langlier Saturation Index):** LSI is a method of reporting the scaling or corrosive potential of low TDS brackish water based on the level of saturation of calcium carbonate. LSI is important in RO water chemistry in determining whether a water will or will not form

calcium carbonate scale. Water with a negative LSI is considered corrosive to metal piping and will not form calcium carbonate scale. Water with a positive LSI is not corrosive, but it will tend to form calcium carbonate scale. LSI is important to RO chemists as a measurement of the scaling potential for calcium carbonate. The LSI value is calculated by subtracting the calculated pH of saturation of calcium carbonate from the actual feed pH. Calcium carbonate solubility decreases with increasing temperature (as evidenced by the liming of a teakettle), higher pH, higher calcium concentration, and higher alkalinity levels. The LSI value can be lowered by reducing pH by the injection of an acid (typically sulfuric or hydrochloric) into the RO feed water. A recommended target LSI in the RO concentrate is negative 0.2 (which indicates that the concentrate is 0.2 pH units below the point of calcium carbonate saturation). A negative 0.2 LSI allows for pH excursions in actual plant operation. A polymer-based antiscalant can also be used to inhibit the precipitation of calcium carbonate. Some antiscalant suppliers have claimed the efficacy of their product up to a positive LSI value of 2.5 in the RO concentrate (though a more conservative design LSI level is +1.8). Sodium hexametaphosphate, an inorganic antiscalant, was used in the early days of RO but the maximum concentrate LSI was + 0.5 and it had to be made in short-lived batches as the air easily oxidized it.

**Magnesium (Mg):** A divalent cation. Magnesium can account for about a third of the hardness in a brackish water, but can have a concentration five times higher than calcium in sea water. The solubility of magnesium salts is high and typically does not cause a scaling problem in RO systems.

**Manganese (Mn):** Manganese is a water contaminant present in both well and surface waters, with levels up to 3 ppm. Manganese, like iron, can be found in organic complexes in surface waters. In oxygen-free water, it is soluble. In the oxidized state, it is insoluble and usually in the form of black manganese dioxide ( $MnO_2$ ) precipitate. An alert level for potential manganese fouling in a RO aerated RO feed waters is 0.05 ppm. Drinking water regulations limit manganese to 0.05 ppm due to its ability to cause black stains. Dispersants used to control iron fouling can be used to help control manganese fouling.

**pH:** The pH of the feed water measures the acidity or basicity. A pH of 7.0 is considered neutral. A pH between 0.0 and 7.0 is acidic. A pH between 7.0 and 14.0 is basic. To the analytical chemist, pH is a method of expressing hydrogen ion concentration in terms of the power of 10 with the pH value being the negative logarithm of the hydrogen ion concentration. To the water chemist, pH is important in defining the alkalinity equilibrium levels of carbon dioxide, bicarbonate, carbonate and hydroxide ions. The concentrate pH is typically higher than the feed due to the higher concentration of bicarbonate/carbonate ions relative to the concentration of carbon dioxide. The RODESIGN program allows the

user to adjust the pH of the feed water using hydrochloric and sulfuric acid. Lowering the feed pH with acid results in a lower LSI (Langlier Saturation Index) value, which reduces the scaling potential for calcium carbonate. Feed and concentrate (reject) pH can also affect the solubility and fouling potential of silica, aluminum, organics and oil. Variations in feed pH can also affect the rejection of ions. For example, fluoride, boron and silica rejection are lower when the pH becomes more acidic.

**SDSI (Stiff Davis Saturation Index):** SDSI, in similar fashion as LSI, is a method of reporting the scaling or corrosion potential of high TDS seawater based on the level of saturation of calcium carbonate. The primary difference between SDSI for high TDS seawater and LSI for low TDS brackish water is the effect that increasing ionic strength has on increasing solubility. The solubility of sparingly soluble salts increase with higher TDS and ionic strength, based on the theory that a denser ion population interferes in the formation and/or precipitation of the sparingly soluble salt.

**Silica (SiO<sub>2</sub>):** Silica (silicon dioxide), in some cases, is an anion. The chemistry of silica is a complex and somewhat unpredictable subject. In similar fashion as TOC reports the total concentration of organics (as carbon) without detailing what the organic compounds are, silica reports the total concentration of silicon (as silica) without detailing what the silicon compounds are. The “Total Silica” content of water is composed of “Reactive Silica” and “Unreactive Silica”. Reactive silica (e.g. silicates SiO<sub>4</sub>) is dissolved silica that is slightly ionized and has not been polymerized into a long chain. Reactive silica is the form that RO and ion exchange chemists hope for. Reactive silica is the form of silica to be used in RO projection programs. Reactive silica, though it has anionic characteristics, is not counted as an anion in terms of balancing a water analysis but it is counted as a part of total TDS. Unreactive silica is polymerized or colloidal silica, acting more like a solid than a dissolved ion. Silica, in the colloidal form, can be removed by a RO but it can cause colloidal fouling of the front-end of a RO. Colloidal silica, with sizes as small as 0.008 micron can be measured empirically by the SDI (Silt Density Index) test, but only that portion that is larger than 0.45 micron or larger. Particulate silica compounds (e.g. clays, silts and sand) are usually 1 micron or larger and can be measured using the SDI test. Polymerized silica, which uses silicon dioxide as the building block, exists in nature (e.g. quartzes and agates). Silica, in the polymerized form, also results from exceeding the reactive silica saturation level. The solubility of reactive silica is typically limited to 200-300% with the use of a silica dispersant. Reactive silica solubility increases with increasing temperature, increases at a pH less than 7.0 or more than 7.8, and decreases in the presence of iron which acts as a catalyst in the polymerization of silica. Silica rejection is pH sensitive, with increasing rejection at a more basic pH as the reactive silica exists more in the salt form than in the acidic form.

**Strontium (Sr):** A divalent cation. The solubility of strontium sulfate is low and can cause a RO scaling problem in the back-end of a RO. Strontium sulfate solubility is lower with increasing sulfate levels and decreasing temperatures. Typically, strontium can be found in some well waters where lead ores are also present, with typical concentrations less than 15 ppm. With saturation at 100%, super-saturation up to 800% is typical with an antiscalant.

**Sulfate (SO<sub>4</sub>):** A divalent anion. The solubility of calcium, barium and strontium sulfate is low and can cause a RO scaling problem at the concentrate end of a RO. The solubility of these sparingly soluble salts is lower with decreasing temperature. The recommended upper limit for sulfate in potable water is 250 ppm based on taste issues.