

MEMBRANES

PROCESS SIMPLIFICATION THROUGH THE USE OF ANTISCALANTS AND ANTIFOULANTS

The world's increasing need for economically purified water and the advent of 50 to 100 million gallons per day (mgd) reverse osmosis (RO) plants capable of producing potable water at competitive prices demand the simplest possible pretreatment processes. Recent advances in antiscalant and antifoulant design and applications now allow for significant simplifications in pretreatment steps necessary for RO feedwaters (1-3).

We are driven to innovate by the current realities that membrane fouling is accepted despite sometimes elaborate pretreatment schemes. The need for stopping production to clean periodically seems universal. Efforts at prolonging membrane service life in difficult-to-treat waters to beyond 2 to 3 years underlie much effort to resolve fouling problems (4-12). Retrofitting existing processes by the elimination of problematic pretreatment steps has solved numerous RO plant problems. This was made possible by the judicious selection of antiscalant and antifoulant and dosages used. Not only were these problems resolved, but also the resulting cost savings have been substantial.

Our successes in these efforts have led us to the conclusion that controlling the fouling potentials of scales and colloids in RO feedwaters with minimum dosages of chemicals is far better than the strategy involving the removal of

these objectionable contaminants from the RO feedwater.

In advance of case study publication with greater detail, we wish to present in Table A an overview of the comparison of traditional pretreatments to remove contaminants compared to current capabilities of antiscalant and antifoulants to control the fouling tendencies by continuous injection into the feed at parts per million (ppm) (milligrams per liter [mg/L]) concentrations. The long-range goal of these developments is to eliminate membrane fouling entirely, and make water purification by RO a truly continuous process with little or no maintenance cleaning, and prolonged membrane service life.

Antiscalants and Antifoulants

Antiscalants acts as threshold inhibitors of growth of crystals (scales) from supersaturated brine. In minute concentrations, they complex with the surfaces of seed crystals, preventing them to grow in the super-saturated brine. Some antiscalants also inhibit the precipitation of inorganic gels such as hydroxide/oxides of aluminum, iron, manganese, other heavy metals, and silica and silicates.

Antifoulants is a term that has been used for pretreatment chemicals that prevent RO membrane fouling in general. In the context of our article and our work, we choose to reserve this name for anticoagulant and dispersant chemicals that control colloidal fouling. Colloids are different from dissolved salts that crystallize or precipitate from solution. They are pre-existing particles that range in particle sizes of between 0.1 to 0.005 microns (μm), invisible to naked eyes but having the properties of particles. These particles can pass 0.45- μm filters used in the measurement of Silt Density Index (SDI), and are thus not detected in that measurement. They can also pass microfiltration and ultrafiltration membranes. Due to the extremely large surface areas relative to its mass, when destabilized from its equilibrium state in water, colloids can coagulate and flocculate in infinite complexities of composition. In the RO when

concentrations and salinity suddenly increases, the affinity of destabilized colloids towards the membrane surface is increased, leading to accelerated membrane fouling. Antifoulants inhibit coagulation of colloids, disperses associated particles, and reduce their affinity for membrane surfaces.

Saturation Values

To define saturation values in the context of this article, it is necessary to state that in contrast to the applications to cooling systems and boiler waters, the saturation thresholds of sparingly soluble salts in the RO process is very different (13). Water being concentrated during passage through the brine channels of membrane elements is out of equilibrium, and will not reach an equilibrium state until long after discharge.

When out of equilibrium, factors regulating the crystallization rate of low solubility salts from the super-saturated brine include concentration of ions, the presence of seed crystals, the intrinsic crystallization rates of each salt, common ion effects, ionic strength, and temperature. No reliable, commonly accepted models for calculating scaling potentials in RO systems exist. The Langelier Saturation Index (LSI) and the Stiff and Davis Stability Index (S&DSI) modification of LSI for high salinity water are used as approximations of calcium carbonate scaling potential in RO systems.

No such conventional model exist for all the other scales and gels seen in RO systems such as calcium, strontium and barium sulfate, calcium fluoride and phosphate, iron and manganese oxide/hydroxides, aluminum hydroxide, and silica and silicates. In the absence of convention, proprietary formulae are used in the various computer software from membrane and chemical suppliers with resulting variations in the projection of fouling potential for each of the scales commonly experienced in RO systems.

As imperfect as such projections might be, quantitative values are needed to calculate antiscalant dosages needed to control scaling. They are also re-

By Robert Y. Ning, Ph.D.
King Lee Technologies

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TABLE A
RO System Design Advances Made Possible by New Antiscalant and Antifoulant Chemicals

<i>RO Foulant</i>	<i>Traditional Pretreatment</i>	<i>Current Capability</i>
1. Calcium carbonate	acidification to lower LSI, then with antiscalant to maximum LSI=2.5	antiscalant alone: LSI=3.2; S&DSI=>4.5
2. Iron, manganese	oxidation/filtration: Greensand, manganese dioxide, catalytic oxidation	antiscalant alone: Fe and Mn at > 8 ppm
3. Silica: reactive non-reactive	lime, ion-exchange (OH) none	antiscalant: >280 ppm antifoulant: variable
4. Calcium sulfate	lime, ion-exchange	antiscalant: >400x saturation
5. Strontium sulfate	ion-exchange	antiscalant: >43 x saturation
6. Barium sulfate	ion-exchange	antiscalant: >51 x saturation
7. Calcium fluoride	lime, ion-exchange	antiscalant: >16,000 x saturation
8. Colloidal organic matter and sulfur	UF, MF, coagulation/clarification/ MMF. slow sand and carbon filter	antifoulant alone

quired for the documentation in databases for correlation with actual data obtained from model test systems performed in the laboratory and data from the field. However, to communicate current control capabilities, we use in Table A the conventional LSI and S&DSI for calcium carbonate scaling, and solubility product constants for the saturation values of calcium, strontium and barium sulfate, and calcium fluoride. The nature of solubility product constants as saturation values of these salts needs to be qualified and defined.

Solubility Product Constant

For sparingly soluble salts with solubilities of less than 0.1 mole per liter, it is an experimental fact that the product of the total molar concentrations of the ions is a constant at constant temperature. The solubility product is the ultimate value that is attained by the product of the ionic concentrations when equilibrium has been established between the solid phase of a troublesome soluble salt and the solution in low salinity waters. An increase in water salinity increases not only the ionic concentration, but also the ionic strength of the solution.

This will, in general, lower the activity coefficients of both ions. Therefore, the ionic concentrations (and therefore the solubility) must increase in order to maintain the solubility product constant. This effect, which is most marked when

salts present in solution, does not possess an ion in common with the sparingly soluble salt (14). This is the reason seawater has much lower scaling potential than similar concentrations of sparingly soluble salts in low salinity well waters.

Available compilations of solubility products illustrate that measurements are not trivial, and values given by different authors for the same solubility products often differ markedly. Differences of a few orders of magnitude are not uncommon (16). For uniformity with other workers, we use the solubility product values for the sulfate scales and calcium fluoride shown in Table B.

Process Simplification

Following a development program that resulted in the introduction of nine differentiated antiscalants and four antifoulants, the control limits in RO processes have been greatly extended. The capabilities of these new formulations coupled with the needs for economical and reliable processes have led us to successful retrofitting of numerous existing RO pretreatment processes. Often these modifications were made necessary due to severe fouling of the RO system due to insufficient removal of feedwater contaminants by the pretreatment unit-operations or by the surprise introduction of unintended foulants arising from the pretreatment

units.

High success rate in the implementation of antiscalant and antifoulant treatments in the resolution of RO process problems has led us to the conclusion that contaminants in feedwater entering the RO systems are not of concern as long as they are not retained as foulants. The best strategy in designing the process is to practice minimal intervention with small dosages of chemicals, than to provide pretreatment for the removal of contaminants. This would avoid pretreatment steps as contributors to RO fouling, and the necessity of adequately maintaining this equipment and the disposal of additional waste streams.

For applications in the food and drug, and other industries increasingly responsive to the universal good manufacturing practice guidelines, documentations for design, validation, monitoring, maintenance, and quality assurance of every step of the process in water purification is desired. There is a great benefit in having the simplest possible process to attain the desired product water quality. We will briefly discuss below the various process simplifications made possible by the use of antiscalants and antifoulants as listed in Table A.

Calcium carbonate. Traditionally RO feedwater is acidified to lower calcium carbonate scaling potential. Due to the usual buffering capacities of bicarbon-

ate ions in natural waters, concentrated sulfuric acid and in some locations hydrochloric acid, are used in large amounts. The capability of the newer antiscalants to control LSI values of 3.2 and an S&DSI of greater than 4.5 has in our experience completely eliminated the need for acidification of RO feedwater from natural sources (2). This increased ceiling also allows for the injection of caustic into RO feedwater (3) to ionize weakly acidic contaminants such as silicic acid (silica), boric acid, hydrogen sulfide, and phenolics, and of more recent importance, arsenous acid (17).

Iron and manganese. Well waters with up to 8 ppm of iron and comparable levels of manganese have been fed directly to RO systems fully controlled with just an antiscalant. This has greatly benefited municipal water departments of small remote communities in Central North America. Standard removal pretreatment strategies involving manganese greensand and other forms of oxidation-filtration in existing plants have been found to foul RO systems downstream with incompletely filtered iron complexes, manganese dioxide and even colloidal greensand. Case studies with more details will be published. The limits of control of iron and manganese have not yet been reached in the field.

Reactive and non-reactive silica (18). Reactive silica is primarily a silicic acid monomer measurable by molybdate colorimetric assay. Traditional pretreatment involves lime softening or ion-exchange with strong anion-exchange resins. With antiscalant alone, greater than 280 ppm in RO concentrate can be controlled.

Fouling tendencies of non-reactive (colloidal) silica and silicates like other colloids are less predictable. Due to its affinity towards humic and other natural organic matter, and carry-over of colloids from iron or aluminum coagulation/clarification treatment upstream, control can only be addressed empirically on-line with different anti-coagulant and dispersant antifoulants. Historically, there has been no effective pretreatment for colloidal silica and silicates that escape the coagulation clarification and filtration process.

Calcium, strontium and barium sulfate, and calcium fluoride. In recent years, with more effective usage of an-

Salt	mg/L Solubility Product
CaSO ₄	96,300
SrSO ₄	5,300
BaSO ₄	2.64
CaF ₂ *	723

*The fluoride concentration is squared when calculating the solubility product (taken from Reference 15, originally from Stumm and Morgan, 1981).

tiscalants, scales in this category are seen much less than colloidal fouling. Using solubility products listed in Table B as saturation values, current control capability for calcium sulfate is greater than 400 times saturation, strontium sulfate greater than 43 times, barium sulfate greater than 51 times and calcium fluoride greater than 16,000 times saturation. From among all the available antiscalants, a single formulation is chosen that would control all potential scales in any single RO feedwater at the maximum % recovery. With antiscalants, it is a rare case that any other pretreatment like lime softening or ion-exchange deionization would be necessary. Ion-exchange and electrodeionization units are more appropriate as polishing units post-RO for high-purity water production.

Colloidal Organic Matter

Fouling by colloidal organic and inorganic matter is the most serious challenge to the continuous operation of RO systems. Colloidal fouling needs to be dealt with in all surface brackish, sea and wastewaters. In aquifers near oil deposits such as in the Persian Gulf region, colloidal elemental sulfur being lipophilic, is a severe foulant for the RO membranes and even for the prefilter cartridges. Antifoulants have been shown effective in many large and small RO plants. Significant RO fouling potential exist in RO feedwaters with SDI values of less than 3, even after pretreatments with ultrafiltration (UF), microfiltration (MF), slow-sand filtration, coagulation/clarification/multimedia filtration, and activated carbon. Antifoulant alone with feedwater of turbidity of less than 1 Nephelometric Turbidity Units has a good chance of performing well without other pretreatment. It can certainly be used as an adjuvant to control RO fouling post MF or UF. Accumulat-

ing field experiences will allow us to eventually develop more precise application guidelines for the different formulations of antifoulants.

Conclusion

Improved capabilities of antiscalants and antifoulants provide a vista of an ultimately simple pretreatment process for RO using minute dosages of chemicals. In addition to simplicity and economy in equipment, continuous operation of RO plants with no stoppages for cleaning and very long membrane service lives is a worthy and viable goal. ■

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Author Robert Y. Ning, Ph.D., is vice president of science and business development at King Lee Technologies. He holds a Ph.D. in organic chemistry from the University of Illinois, Urbana, Ill. His work has involved research and process development in pharmaceuticals, biotechnology and water chemistry.

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