MEMBRANE TREATMENTS

CHEMICAL KEYS TO OPTIMAL REVERSE OSMOSIS PROCESSES

Processes for the purification of water and wastewater incorporating reverse osmosis (RO) membranes are increasingly being used. The demand for stability and reliability of the processes has steadily increased as RO systems proliferate. Field experiences since the introduction of this technology in the 1970s have generally shown that RO, and indeed microfiltration and ultrafiltration membranes as well, are prone to fouling. Systems suffering from high cleaning frequencies, incomplete cleanings, and premature membrane replacements come into sharp contrast with smoothly performing systems that do not have to be stopped for cleaning, with membranes lasting 12 or more years.

Our business focus on the conversion of low-performance systems to high-performance systems has given us great opportunities to understand how feedwater quality and other parameters affect membrane fouling. A careful analyses of foulant composition (1), its source (2, 3), and development of efficient cleaning methods allow for the continued operation of problematic systems, while modifications to the process to avoid fouling are carried out. In this manner, the performances of systems are improved. Insights that we call keys on process design have been gained, providing feedback for the design of new processes and systems. Each key represents a factor that is critical in the solution of a problem or a significant contributor to the improvement of the process.

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In this article, we present an overview of 20 keys by which the performances of more than a thousand large RO plants have been improved around the world. Following the presentation of these keys in detail in future papers, we intend to publish illustrative cases for establishing the evolving limits of design and performance.

Keys to Improved Operation

Here are the keys we have found that can contribute to improved operation of water treatment membrane systems.

Elimination of acid injection (4). Continuous acid injection to lower pH and the associated Langelier Saturation Index (LSI) and Stiff and Davis Stability Index (S&DSI) is commonly used to control calcium carbonate scales. Bicarbonate ions in waters are converted to carbon dioxide with acid, requiring the consumption of large amounts of acids in RO plants. The availability of superior antiscalants today makes possible its singular use at low dosages to simultaneously control all scales, including calcium carbonate. Continuous acid injection can now be safely eliminated in RO plants not using cellulose acetate membranes.

Reactive silica control. Silica and silicate species in water that react with molybdate colorimetric assay reagent has a great tendency to polymerize and co-polymerize with hydroxide forms of aluminum, iron, magnesium, and calcium. We have introduced antiscalants that are also inhibitors of such polymerization, thus controlling fouling by reactive silica.

Colloidal silicate control. Non-reactive silica and silicates in the colloidal particulate form along with other types of colloidal particles such as bacterial slime that can be present in surface waters. Under the conditions of rapid concentration in the RO system, the colloids coagulated and deposit on membranes. We have introduced a series of anticoagulants and dispersants to counter this fouling mechanism, and have seen good results in the field.

Iron control. With appropriate antiscalants, we have entered an era of iron control without the traditional iron-removal pretreatments such as greensand filter and oxidation-filtration strategies. High levels of iron can be tolerated in the RO feedwater.

Colloidal humic and organic foulant control. As an alternative or adjuvant to ultrafiltration or microfiltration pretreatment, we have found success with the use of anticoagulant/dispersants that we call antifoulants, to distinguish this class of chemicals from antiscalants.

Colloidal sulfur control. Colloidal elemental sulfur present in aquifers associated with petroleum , sulfate-reducing bacteria, and hydrogen sulfide can severely foul RO elements and even prefilters. Antifoulants have been found effective when appropriately used.

Calcium sulfate control. We have introduced new antiscalants for very challenging scaling profiles as well as a new cleaner that would dissolve calcium sulfate crystals lodged inside the RO elements.

Barium sulfate control. To date, no cleaner has been developed to dissolve barium sulfate crystals that have a tendency to strongly anchor on surfaces inside of RO elements. An additional challenge comes from the very low equilibrium solubility product constant of barium sulfate. In the presence of often-high concentrations of sulfate ions in feedwater, even 0.01 ppm of barium ion is significant in projecting scaling potential. This situation is complicated by the often-poor precision and accuracy of routine water analyses. Antiscalants vary widely in their barium sulfate control capabilities, and should be selected carefully.

Calcium fluoride control. Excellent antiscalants are available as threshold inhibitors of calcium fluoride precipitation from RO brine. Pre-existing fine calcium fluoride in raw well waters can present difficult clarification problems leading to fouling of RO membranes as colloidal particles.

Phosphate scale control. In treatment of city wastewaters with RO, calcium phosphate scaling is often encountered. Full control often requires a carefully chosen antiscalant with some acidification of the feedwater with acid.

Effective microbial control. Most success has hinged on maintaining sanitary conditions in pretreatment equipment and biofilm control within the RO system. Sanitizers with biofilm penetration capabilities are used. Normally difficult to clean biofouled RO elements have been recovered with unique cleaning solutions by prolonged soaking or storage strategies.

Cleaning calcium sulfate scales. Until recently, calcium sulfate scales have been considered difficult to clean in RO systems. As mentioned in Key 7 (calcium sulfate control) above, we have developed a cleaner that can fully solubilize calcium sulfate crystals without damaging the membrane.

Debugging mechanical problems. Due to the physical sensitivities of RO membrane bundles operating under high hydraulic pressures, problems and deficiencies from mechanical origins need to be differentiated from chemical outcomes. Instrument calibration, control of concentrate valve, feed pressure changes, and automatic system flushing before stoppages are among the important potential sources of problems.

Trend charting. Like all processes, careful monitoring is required for success in operation. Trending Normalized Permeate Flow, Differential Pressure, and Salt Rejection is needed to initiate a cleaning when values deviate 10% to 15% from the reference startup values. A cleaning event should trigger, at a minimum, assurance that the cleaning method selected is sufficient to restore completely the performance of the system, and to develop a better cleaning procedure if performance is not fully restored. Partially cleaned elements foul more quickly and become increasingly resistant to cleaning. A systematic investigation at this point as to the composition of the foulant, its source and methods of avoidance usually leads to an adjustment in the pretreatment process or operation of the system to avoid repeated fouling.

Stabilization of brine concentrate. Rejects from large RO plants sometimes are stored and discharged through miles of discharge pipelines. Consideration needs to be given to the stabilities of the brine concentrate from crystallization or precipitation of solids in the discharge process. Concentrates sometimes are used in other applications for which the presence of antiscalant and antifoulants is selected and evaluated for acceptability and efficacy.

Cleaning biofilm. The refractile nature of biofilm on membranes to cleaners and sterilizing chemicals is well known. We have developed an online and offline method of cleaning irretrievably biofouled membranes.

Elimination of coagulant addition. Coagulants carried over from incomplete clarification processes often lead to severe fouling of RO membranes. The combination of effective physical filtration and antifoulants has eliminated the need for coagulants in many plants.

Minimization of pretreatment. The solution of RO problems through substituting pretreatment steps like acid injection, degasification, iron and manganese removal, clarification, carbon adsorption, and ion-exchange with low dosages of antiscalants or antifoulants or both has led to not only performance improvement but also major operating cost reductions.

Avoiding inappropriate antiscalants. Commercial antiscalants show a wide range of efficacies and liabilities. Efficacies should be qualified against the contaminants present in the RO feedwater. Compatibility must be assessed against the natural and added contaminants in the RO feedwater (1, 2).

Using high feedwater pH. The solubility and rejection of weakly acidic contaminants can be greatly enhanced by operating RO at very high pH. Common contaminants in this category include silicic acid, reactive silica and silicates, arsenous acid, boric acid, hydrogen sulfide, and humic acid. To overcome the scaling potential of calcium carbonate, and hydroxides of multivalent cations like those of iron, aluminum, and magnesium, among others, new antiscalants are now available (5).

Conclusion

We have presented an overview of key factors contributing to the optimal performance of RO processes for the purification of water and wastewater. Through our focus on solving operation problems of RO processes, and the introduction of necessary antiscalants and antifoulants to control scales and colloidal particles respectively, we have successfully retrofitted hundreds of existing RO processes and are actively collaborating with design engineers and system manufacturers to provide economical high performance systems.

This article serves as an evolving topic index under which we intend to publish case studies. By so doing, hopefully the cutting-edge of design and control limits can be more clearly defined.■

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