

MEMBRANES

OPERATIONAL CHARACTERISTICS OF REVERSE OSMOSIS PROCESS CHEMISTRY

The application of membranes in the purification of water provides a powerful means of producing high-purity water. In the total treatment of raw water, reverse osmosis (RO) is an important midstream process for fractionating feedwater into high-purity water and brine. The brine may be used to feed cooling towers and evaporators. The RO process is sensitive to upstream treatments and itself impacts downstream operations. The almost infinite variety of contaminants entering the membrane systems with the feedwater and the economic necessity to expend minimal resources on raw water pretreatment pose a major challenge to RO process chemistry design and control. The RO process chemistry characteristics are important towards the understanding and control of the quality of the product permeate water that may be further polished to meet the high-purity specifications needed in industries such as pharmaceuticals, microelectronics and power generation.

Overview

In this article, we survey the factors that affect the operational characteristics of RO systems. The factors include the chemistry of the feedwater, membrane fouling mechanisms, composition of foulants found in membrane elements from many plants and examples of antifoulants and their application. Current approaches towards the development of

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

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antifoulants to prevent fouling and membrane cleaners for plant maintenance are discussed in this context.

Feedwater Chemistry

Water that enters RO systems comes from all imaginable sources. Table A includes a list of sources that are differentiable by their quality and significant chemistry occurring in these waters that impact the performance of RO systems. The oceans are the most abundant source, amounting to 99.37% of water on earth (1). This includes 2.24% in ice form at the poles and in glaciers. Only 0.02% of the total water in the world is in rivers, while 0.61% is on the ground (as surface waters in the lakes and the majority underground in aquifers).

Major physical occurrences in these natural waters are the processes of erosion of rocks to generate sand (50 microns [μm] to 2 millimeters [mm]), silt (5 to 10 μm), clay ($< 5 \mu\text{m}$) and submicron colloidal particles. Just as active a physical process is the growth, excretion, death, and decay of animals and microorganisms. In simplified form, we can identify some significant chemical processes occurring in these waters. The rain extracts oxygen, oxides of carbon, sulfur, and nitrogen, and organic aerosol particles from the atmosphere. The spring waters dissolve soluble matter

and the acidity of the rain water is neutralized with alkaline rocks such as limestone. Ponds and lakes are biotic reactors in which biomass is produced and accumulated and complexation interaction of organic matter with inorganic particles occur. Much of these particulate matter are retained in upper zones of the ground as water enter the aquifers. The large surface areas of contact and the long times available for dissolution and precipitation allows the waters in the aquifers to be equilibrated and fully saturated with respect to the composition of the minerals they are in contact with. Thus, it is from the deep well source waters that the greatest scaling potentials from foulants such as calcium carbonate, calcium sulfate, strontium sulfate, barium sulfate, silica, iron, and aluminum exist. We can view the water in the lower sections of rivers with municipal and industrial waste streams in which complexation interactions of organic and inorganic particles predominate.

The chemistry of seawater is particularly interesting to note. It reflects the equilibrated endpoint of the processes that began in the surface waters that we just considered and in a manner that happens within the RO system that serves to accelerate these processes. The quantity of the different compo-

TABLE A
Sources of Feedwaters and Significant Chemistry that Impact RO

<i>Source Waters</i>	<i>Significant Chemistry</i>
1. Rain	Oxidation-reduction (e.g., $\text{O}_2 + \text{NO}_x$), acid base (e.g., $\text{CO}_2 + \text{H}_2\text{O}$)
2. Springs	Dissolution acid-base (acid rain + carbonate rocks)
3. Ponds	Complex interactions of living and non-living matter
4. Wells, aquifers	Dissolution-precipitation (e.g., CaCO_3 , CaSO_4 , SrSO_4 , BaSO_4 , silicates, iron, and aluminum salts, sulfides), relatively low in organic matter
5. Rivers, municipal and industrial wastewater	Complexation interaction, precipitation
6. Oceans (99.4% of earth's water, including 2% as ice)	Biotic life, complexation interactions, precipitation

TABLE B
Colloidal Matter in Natural Water

Microorganisms
Biological Debris (plant and animal)
Polysaccharides (gum, slime, plankton, fibrils)
Lipoproteins (secretions)
Clay (hydrated aluminum and iron silicates)
Silts
Oils
Kerogens (aged polysaccharides, marine snow)
Humic Acid/Lignins/Tannins
Iron and manganese oxides
Calcium carbonate
Sulfur and sulfides

nents in seawater is not proportional to the quantity of the components that river water pours into the sea, but is inversely proportional to the facility with which the components in the seawater are made insoluble by chemical actions in the sea (2). When river water meets the highly saline seawater, much of the suspended colloidal matter coagulate and deposit as organic matter — rich silt in the delta regions. This is the same mechanism as the deposition of coagulated colloidal matter in the RO system with the increase in salinity of the brine. Complexation interactions and precipitation of particles that began in the ponds and lakes continue in the ocean.

Despite the high salinity, biotic life abound. Some of the types of colloids that exist in the natural waters, especially in the sea, are listed in Table B. Polyphenolic complexes like humic acid, lignins and tannins are decay products of woody tissues of plants and are particularly noticeable in surface waters due to their tendency to foul RO membranes by themselves or coagulated with other foulants (3). Polysaccharides that constitute cell walls of microorganisms and plants and excreted variously as gums, slimes, and biofilms are prominent players in membrane fouling. In the ocean, they are added to polysaccharides from sea organisms, especially planktons (4), which upon aging become kerogens. It is believed that a white material called "marine snow" that has been observed to fall in the deep oceans are these aged and ubiquitous polysaccharides (5).

Membrane Fouling Mechanisms

Feedwaters to RO systems typically are concentrated by a factor of 2 to 10 (50% to 90% recovery) during production of

high-purity permeate water. For simplicity in classification, three classes of fouling (6 to 12) can be said to occur.

First, the solubility limits of various dissolved salts in the brine stream may be exceeded, leading to deposition and growth of crystals in the flow channels and membrane surface of the RO elements. This type of fouling is referred to as scaling. Most common examples of scales are calcium carbonate, sulfates of calcium, strontium and barium, and calcium fluoride. In the examination of foulants (3) under the microscope, crystals have well defined shapes. Inhibitors injected into feedwaters to suppress crystallization are called antiscalants.

Secondly, particulate matter preexisting in feedwater can agglomerate and adhere to the membrane and brine flow channels due to increased concentration, salinity, compaction, flocculation, surface interactions, and other physical and chemical factors. The particles may be large enough to be removed with 1 to 5 μm RO prefilters, such as silt, carbon fines, coagulants, and microbial clusters. There may also be colloidal particles that escape filtration even with 0.45- μm filters used in silt density index (SDI) measurements. The colloids can be organic, inorganic or composites. Ferric, aluminum and manganese hydroxides, and silica grow through increasing particle sizes by polymerization and cross-linking with organic and inorganic polymers to become gels and amorphous foulants commonly seen on membranes (3, 13). Biotic debris such as polysaccharide and dead cellular matter contribute largely to this type of foulants. We have found that anticoagulants and antideposition agents show promise in inhibiting this fouling pro-

cess. Antifoulants then can be a term applied specifically in this particular fouling context. In a broader sense, the term antifoulant is used in the field to include antiscalants as well (7).

Thirdly, a prominent source of fouling, as is true of all water treatment or distribution systems, is the growth and anchoring of microorganisms. Moderate temperatures and minimal nutrient levels in RO waters can support at times explosive growths of microorganisms. Bacteria with cell division times of 20 minutes can grow from a normal count per unit volume of water to a too numerous count in the period of an 8-hour shift. Due to the tendency of bacteria to secrete polymers that anchor themselves to surfaces to facilitate growth as the biofilm, this fouling mechanism is unique and poses a serious threat to the operation of RO systems (14). This threat is compounded by the great difficulty of completely removing biofilm from membrane surfaces.

Composition of Foulants

Through analysis of the composition of foulants on RO membrane elements sent from plants across the country, we have seen examples of simple scales and, more frequently, the more difficult to clean composites of foulants and biomass (3). Inorganic scales are relatively easy to identify by qualitative tests and quantitation by ion emission spectroscopy using inductively coupled plasma (ICP) or by scanning electron microscopy with energy diffusive X-ray analysis (SEM-EDX) methods. Our experience confirms the limited set of calcium carbonate, sulfate of calcium, strontium and barium, and calcium fluoride as the common scales found in RO systems. Known responses to specific cleaning formulations also allow us to confirm the identity of the scale.

Elemental gravimetric analyses of carbon, hydrogen, and nitrogen along with quantitation of residual ash after combustion allowed us to examine the organic components of foulants (in the limited sense of coagulated particulate matter) and biomass. Through the correlation of the results of these analytical data on foulants with feedwater chemistry, plant design, and operations data, we have made the following observations (3). These observations have been helpful in guiding process improvements to minimize fouling and improve cleaning strategies.

1. Organic matter contribute more than 10% of the mass of foulants in all recent samples, with the majority of the samples containing 50% to 100% of organic matter.
2. Biomass constituted the major part of the organic contents of the foulants.
3. Synthetic polymers used in water pre-treatment can often be differentiated from biomass in the foulants.
4. Anionic polymers used as antiscalants and dispersants can deposit on membranes and act to concentrate high valence metal ions (Fe, Al, and Ca) on the membrane surface.
5. Colloidal silica and clays have complex and variable contents of iron, aluminum, and calcium.
6. Elemental phosphorous is associated with biomass, phosphate, and phosphonates.

These six aspects of fouling can each occur alone or frequently as two or more aspects simultaneously. Discernment and differentiation of the contributing fouling mechanisms is a developing science. This science is vital to the development of antifouling chemicals and effective cleaning methods.

Antifoulant Design and Application

The term antifoulant used here is in its broadest meaning covering scaling, particulate fouling, and microbial fouling—the three classes of fouling mechanisms discussed above. We will briefly discuss strategies aimed at each of these three areas.

For scale control, the development and application of antiscalants is well known and reviewed in the field of boiling water and cooling water chemistry (1, 7, 15, 16), and applied to boilers, evaporators, cooling towers, and cooling systems. Anionic polymers, polyphosphates, and organophosphorous compounds, sometimes referred to as threshold inhibitors and dispersants, are used in substoichiometric amounts, usually in the range of 1 to 5 milligrams per liter (mg/L) concentrations. By binding to surfaces of growing crystal nuclei, the rates of crystallization from supersaturated solutions are retarded, and crystal packing orders are modified. By this mechanism, crystallization rates are so retarded that although supersaturation of solutes in the water will eventually equilibrate through crystallization, within the residence time of the water in the

system, there is little or no scale formation. The uniqueness of RO among water conditioning systems is that the residence time is very short (a few seconds), concentration of seed crystals is low and the temperature is constant. For this reason, higher levels of supersaturation without crystallization are possible. On the other hand, the limits of saturation and rates of scaling are hard to model, measure and predict. Interferences come from other solutes in the water, organic or inorganic (17). Assumptions of RO fouling limits vary considerably among practitioners.

For controlling fouling by preexisting particulate matter, the task is much more challenging due to the variety of types of potential foulants and the complexity of their interactions (2, 3, 9, 11, 13), with each other in the same water and with the membrane. Stability and agglomeration of colloidal particles is a subject of major importance in natural waters (2) as well as in the treatment of process waters (1). Drawing on the basic science of colloids and testing of model foulants suggested by our RO foulant analysis data (3), progress is made steadily with the development of antifoulants. Case studies from various plants will be presented in the near future.

Concerning the prevention and management of biofouling in water treatment systems, the literature is extensive. Much of the art and science found useful, generally is applicable to RO systems as well. Several factors peculiar to the RO system can be mentioned. Chemicals used to sanitize and clean the system have to be chemically compatible with the thin, salt-rejecting, barrier membrane. Of prime concern is that accumulation and exponential growth of the microorganisms that should not be allowed to occur within the system. Pretreatment of feedwater, adequate maintenance of upstream unit operations, continuous flow of water through the RO unit, good monitoring and sanitization program, and use of preservatives during downtime (18) are important to this end. Normalized flow and differential pressure in the system are sensitive indicators of biofouling. To prevent irreversible fouling, trend charting and readiness to perform adequate cleaning are important aspects of the system operation. Immediate assistance should be sought where cleaning has been inadequate. Powerful new cleaners are now available, providing alterna-

tives to membrane replacement in the worst cases of biofouling.

Conclusions

This article provides the conceptual framework in which contributions to the RO process chemistry is being made. By reviewing the chemistry profile of water quality from rain, to springs, lakes, wells, rivers, and the ocean, the natural processes that lead to deposition of solids are instructive for the control of the same or similar processes within the RO system. Known membrane fouling mechanisms are reviewed. Analysis of the composition of foulants sampled from membranes from RO plants provided insight on the specific contributors to fouling. Such knowledge provides the basis for designing antifouling strategies and testing methodology for developing antifoulants. We look forward to the expansion of this conceptual framework and reporting on advances towards the day when RO plants can be uniformly sturdy in operation and predictable in performance. ■

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Author Robert Y. Ning, Ph.D., is vice president of science 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 pharmaceutical, biotechnology, and water chemistry.

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