

MEMBRANES

OBSERVATIONS FROM ANALYSIS OF REVERSE OSMOSIS MEMBRANE FOULANTS

Periodic cleaning of reverse osmosis (RO) membranes is generally accepted as a necessary routine maintenance operation in the running of the water purification plants. The need for more effective cleaning methods is alluded to in recent reviews (1-3). The availability of a variety of proprietary cleaning formulations, and frequent premature replacement of membrane elements due to irreversible fouling attest to the need for systematic understanding of the composition, characteristics, and mechanism of formation of a variety of membrane foulants.

Perhaps in time, classes of foulants may be more definitively distinguished, and cleaner effectiveness be better correlated with the type of foulant. Just as important, is the prevention aspect of the fouling phenomenon. It is quite possible that economical pretreatment of feedwater with the appropriate anti-foulants in minute amounts would allow for continuous operations with no interruptions for cleaning. This indeed is already a reality in a few systems. In industries such as pharmaceutical manufacturing, process optimization, predictability, control, and documentation through an extensive validation program (4) is critical for product approval and facilities licensure. Much will be gained from understanding and controlling the membrane fouling phenomenon.

Overview

This article begins to summarize a large

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body of data and observations resulting from troubleshooting in RO systems. Foulants are extracted from membrane elements sent from plants across the country needing assistance. Qualitative tests and quantitative elemental analyses of these foulants provide insights on the nature of foulants that are more resistant to cleaning. Data will be presented below to illustrate the following conclusions that have been helpful in minimizing further fouling in the systems, and in selecting the most appropriate cleaning chemicals:

1. Organic matter contributes 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 pretreatment 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 (iron [Fe], aluminum [Al], and calcium [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 two or more aspects simultaneously. Such complexity necessitates the often observed needs in the development of cleaning strategies for use of multiple cleaners, and appropriate sequences of applications^a (1, 5, 6). Discernment and differentiation of the contributing fouling mechanisms of fouling is a developing science. This science is vital to the development of antifouling chemicals and more effective cleaning methods. Undoubtedly in time, with accumulation of data and correlations of foulant compo-

sition with feedwater analysis, pretreatment chemistry, responses to a variety of cleaners, and resulting plant process improvement and control, our understanding of fouling mechanisms will become more refined, and better established. The six observations presented below are derived from a synthesis of foulant analysis data and correlation with plant process chemistry and responses to cleaners. Positive outcomes in the plants have been realized through their application. By presenting these concepts with summary introductory data, refinements of our understanding and more in-depth case studies can be the subject of forthcoming reports.

Organic Matter

Organic matter is defined as carbon-containing matter. Each foulant is washed by decantation with RO permeate water, then dried at 120°C to 130°C. It is gravimetrically analyzed for carbon (C), hydrogen (H), and nitrogen (N) elemental content by standard methods of pharmaceutical analysis, along with a quantitative ash test (furnace at 400°C to 450°C) to determine the percent of inorganic matter. The percent total volatile or combustible elements (C,H,N, and oxygen [O]) from the ash test is considered organic matter, and it correlated well with C,H, and N values along with general oxygen atom contents of biological and synthetic organic polymers commonly used in water pretreatment.

By these methods, the organic matter in 22 foulant samples analyzed recently have the values shown in Table A. From the table, it is interesting to note that all samples contained at least 10% by weight of organic matter, and that 73 % of the samples contained 50% to 100% by weight of organic matter. It should be noted that these foulants analyzed are representative of the more difficult to clean types of foulants for which service assistance is needed. Foulants such as calcium carbonate, calcium sulfate, as well as ferric and aluminum hydroxides that are readily cleaned with generic acid cleaners are not represented. Organic matter which includes biomass

TABLE A
Organic Matter in RO Foulant Samples

<i>Organic Matter (% by weight)</i>	<i>Number of Foulants Analyzed</i>	
0-10 %	0	
10-20	3	
20-30	2	
30-40	0	
40-50	1	27%
50-60	3	
60-70	3	
70-80	4	
80-90	5	
90-100	1	73%
	Total: 22	100%

TABLE B
Elemental Composition of An Iron Acrylate Foulant

<i>Component</i>	<i>Percent by Weight</i>
<i>By gravimetric elemental analysis:</i>	
Carbon	23.67% (absolute)
Hydrogen	3.73
Nitrogen	3.26
Ash (inorganic)	48.08
<i>By SEM-EDX (atomic no. 12-42, Mg-Mo):</i>	
Iron	44.0% (relative)
Calcium	15.0
Phosphorous	13.0
Silica	9.9
Aluminum	8.8
Sulfur	4.2
Chromium	1.8
Magnesium	1.7

and polymers used in pretreatment, usually makes the foulant difficult to remove.

Biomass

Biomass refers to organic matter arising from living or dead organisms. In the colloidal form, it can enter the RO system with the feedwater, and then coagulates and accumulates on the membrane elements. More severe source of biomass is the exponential growth of viable organisms within the system (7) and the accumulation of the biofilm in the system due to the difficulties in removal (8). Such accumulation is usually promoted by inadequate maintenance sanitization procedures of the entire water processing system, and stagnation during frequent or prolonged downtimes without preservative. Severe growths are often detectable by odor or slime on the internal surfaces in contact with water. Milder growths are detectable by microbial culturing and enzyme activity tests. Natural surface waters

(lakes, rivers, and sea water), especially in warm regions, have very high levels of decaying or excreted plant and animal matter. High biomass contents of foulants in the samples examined could be correlated with the factors as mentioned, in the feedwater and in the plant.

Synthetic Polymers

Synthetic polymers used in water pretreatment can often be differentiated from biomass in the foulants. The characteristics of biomass include odor, visual and microscopic appearance, color, slime, microbial counts, enzyme activities, presence of phosphates, sodium, and potassium in ash. In their absence, the presence of a usually thin and even coating of colorless to tan gel will suggest synthetic polymers. Severe flux reduction accompanied by almost invisible film of organic material is the hall mark of poisoning by cationic polymers. Using fourier transform infrared spectroscopy (FT-IR), if reference spec-

trum of the suspect pretreatment polymer is available, and the foulant spectrum is uncluttered, positive identification through "finger printing" is possible.

The carryover of high-molecular-weight synthetic cationic, anionic, and non-ionic polymers that are used as coagulants in pretreatment will often be flocculated with colloidal particles of complex compositions. They can carry more mass and be less readily identifiable. Lower molecular-weight polymers used as antiscalants often participate in these complexes and are deposited as foulants. Indeed, even in the absence of polymeric coagulants, low molecular-weight polymers used as antiscalants and dispersants, can and will deposit on membranes at a slower rate (see following section).

Anionic Polymeric Antiscalants

Anionic polymers used as antiscalants and dispersants are known to be quite intolerant of multivalent cations such as ferric and aluminum ions. These ions act as ionic cross-linkers, causing even polymers in the molecular weights in the range of 1,000 to 2,000 daltons to flocculate. By a combination of gradual deposition and accumulation due to incomplete removal during routine cleaning, such foulants build up over several years, and gradually concentrate high valence cations as an ion-exchange resin would. As an example, the elemental composition of such a foulant is given in Table B. This sample contains 52% volatile organic matter (C, H, N, and O) and 48% of inorganic ash. The carbon and hydrogen contents of the foulant (23.67% and 3.73% respectively) are in reasonable agreement with the theoretical polyacrylic acid composition (at 52%) of 26.4% carbon, 2.9% hydrogen, and 23.4% oxygen. Smaller amounts of coagulated nitrogen-containing polymers or biomass can account for the nitrogen content.

The inorganic composition of the foulant is revealed by scanning electron microscopy with energy diffusive X-ray analysis (SEM-EDX). The instrument is calibrated to quantitate elements between atomic numbers of 12 to 42, which correspond to magnesium-molybdenum on the Periodic Chart. Since the lighter elements like B, C, H, N, O, and F are not measured, the % by weight values are relative for the range of atoms measured. As shown, the predominant cation is iron (44% relative), followed by calcium, aluminum, chromium and mag-

nesium. Bridging to phosphate, silicate and sulfate anions are apparent.

Colloidal Silica and Clays

Colloidal silica and clays refer to preexisting siliceous particles in the feedwater which coagulate during passage through the RO system and become deposited on the membrane as a foulant (1,9,10). Colloidal silica, also known as non-reactive silica, results in natural waters from the polymerization of silicic acid and reactive oligomeric species, which as a population is termed reactive silica. Reactivity is measured by and often referred to as reactivity towards molybdate ions by the same type of condensation reaction. Condensation of reactive silica with aluminum, iron, and calcium hydroxides form clays. However, clays in feedwaters result mainly from the erosion of rocks. Indeed it is stated (11) that the chemical analysis of most clays is similar to the composition of the earth's crust: oxygen, 49.9%; silicon, 26.0%; aluminum, 7.3%; iron, 4.1%; calcium, 3.2%; sodium, 2.3%; potassium, 2.3%; magnesium, 2.1%; all other elements, 2.8%. Following erosion, we have sand (2 microns [μm] to 50 μm), silt (5 to 10 μm), and clay (<5 μm). All are differentiated by particle sizes.

Depending on the extent of clarification and prefiltration of feedwaters, silt and clays often do end up on the membranes. Silt Density Index (SDI) is a means of measuring particle load in the feedwater by timing the fouling of 0.45- μm test filters. In practice, feedwaters with SDI values greater than 5 would lead to high fouling rates in the plants. Since the 0.45- μm filters are nominal filters, it is likely that a significant fraction of clays entering with the feedwater is not detected by SDI monitoring.

Colloidal silica and clays are often encountered in our analyses of foulants. They frequently appear in the presence of organic matter, and accumulate in the flow channels of the membrane elements with significant masses. Occasionally colloidal silica can severely foul membranes in amounts almost too minute to physically sample. The composition of one such example is given in Table C.

Phosphorous

Phosphorous is detected in foulant samples by SEM-EDX. Relative amounts in the inorganic portions of 20 recent foulants surveyed ranged from 0% to 58% of the elements measured in these sam-

TABLE C Elemental Composition of A Colloidal Silica Foulant	
Component	Percent by Weight
<i>By gravimetric elemental analysis:</i>	
Carbon	1.15% (absolute)
Hydrogen	0.67
Nitrogen	0.02
Ash (inorganic)	92.46
<i>By SEM-EDX (atomic no. 12-42, Mg-Mo):</i>	
Silicon	90.0% (relative)
Iron	3.6
Aluminum	2.7
Potassium	1.3
Sodium	0.8
Calcium	0.8
Magnesium	0.6
Sulfur	0.5
Chlorine	0.3
	Total: 100.6%

ples (mean = 14.6%, SD = 15.7%). Sources of these phosphorous-containing matter can be correlated with a number of sources. Biomass generally contain measurable amounts of phosphates. Algal biomass in natural waters is reported to contain almost 1% of elemental phosphorous (12). Phosphates except that of sodium, potassium and ammonium, are generally only slightly soluble in water. If phosphates are present in a feedwater to any appreciable extent, unless the water is acidified, phosphate scales will likely form in the RO system (2). Calcium phosphate has a limited solubility at neutral pH, and an even lower solubility at higher pH. Since phosphates are widely used in agriculture and in laundry products, it is common to find phosphate in silt and agricultural runoff. Municipal wastewater have phosphate concentrations usually in the range of 15 to 30 milligrams per liter (mg/L) of phosphate ion (about 5 to 10 mg/L as phosphorous) (11). In addition to calcium phosphate, ferric and aluminum phosphates are particularly insoluble, and can enter the RO system in the clay or colloidal form.

Other sources of phosphorous are found in the environment of the membrane itself. High pH membrane cleaners widely used for removing organic foulants are often formulated with trisodium phosphate and sodium tripolyphosphate[®]. Incomplete cleanings likely would deposit insoluble phosphates with the residual foulants that accumulate over time. Another source is the commonly used generic antiscalant sodium

hexametaphosphate (SHMP). Solutions of SHMP are hydrolytically unstable, generating phosphate ions and phosphate foulants (2). Even phosphonates can precipitate with high levels of calcium, iron and aluminum, and can participate in fouling.

Conclusions

We have begun to summarize a large body of data and observations. Our conclusions hopefully will form a framework for further insights and discussions on the way to making RO systems more rugged in operation. For us, these conclusions have been the basis of practical resolution of problems encountered in the plants, as well as the starting points for the development of improved antifoulants and cleaning chemicals to maintain efficient plant operation. While some plants exist today that operate continuously with no cleaning for many years, for many others, membrane fouling has become an increasingly challenging problem. This is especially so in areas of the world where technical services are less available. With the advancing science and art of foulant control, we see a day when all plants can be operated without cleaning. To that end, we look forward to presenting additional data and case studies, and welcome input from our readers.■

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Endnotes

*Combination cleaners used in selected sequences are routinely practiced by providers of off-line membrane cleaning services (private communications).
 *A survey of generic high pH cleaners recommended by all major membrane manufacturers contain one or both of these reagents.

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