Foulants in reverse osmosis membranes

BY **ROBERT Y. NING, PH.D.**

Fouling is an accepted evil when dealing with reverse osmosis membranes. What are the substances that make up the foulants? By understanding the composition of foulants, it is possible to select the most appropriate cleaning process.

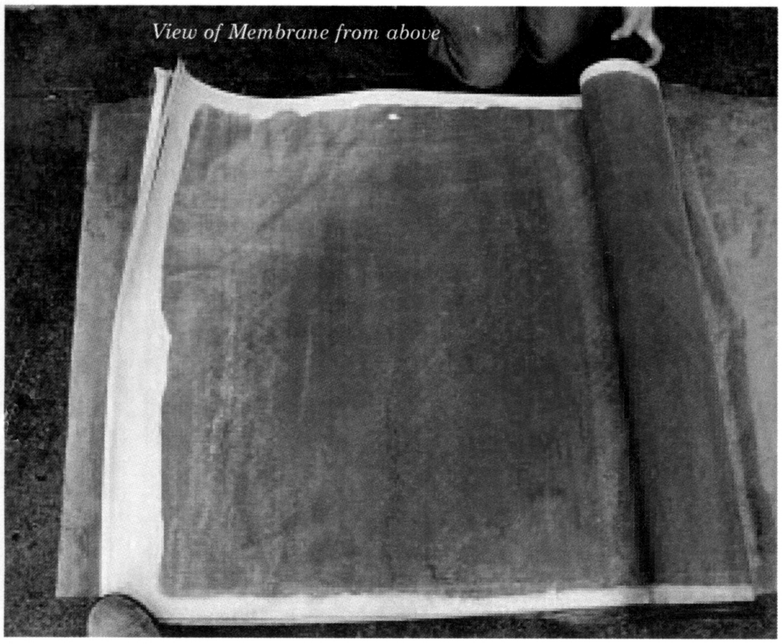
INTRODUCTION

Periodic cleaning of reverse osmosis (RO) membranes is generally accepted as a necessary routine maintenance operation in the running of water purification plants. Common foulants found in RO membrane elements include calcium carbonate, calcium sulfate, strontium sulfate, barium sulfate, calcium fluoride, calcium phosphate, ferric hydroxide, aluminum hydroxide, silica, silt and polymers from natural sources and synthetic polymers used in pretreatment. These foulants may occur singly, or in most cases in complex combinations. Single foulants are simpler to address in prevention and in dissolving (except for barium sulphate) during cleaning. The complex foulants, usually resulting from coagulation of colloidal particles, offer the greatest challenge in prevention and removal during cleaning.

Summarised here are the observations from a large body of data during the troubleshooting of RO systems. Complex foulants are extracted from membrane elements sent from plants needing assistance across the world. Qualitative tests and quantitative elemental analyses of these foulants, combined with thorough review of the pretreatment chemistry provide insights on the nature and the source of the foulants. Experiences with the pattern of responses to various cleaners, and successful resolution and elimination of fouling problems provide confirmation on conclusion regarding the source of foulants and the mechanisms of formation in each specific situation. Following generalisations have been helpful in solving fouling problems, and in selecting the most appropriate cleaning chemicals:

1. Organic matter usually contributes more than 10% of the mass of foulants, with the majority of the samples containing 50-100% of organic matter.
2. Biomass constitutes 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 (Fe, Al, Ca) on the membrane surface.
5. Colloidal silica and clays have complex and variable contents of iron, aluminum, calcium and magnesium.
6. Elemental phosphorous is associated with biomass, phosphate and phosphonates.

The six generalis ations separately 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 consistently been realised through their application.



View of Membrane from above

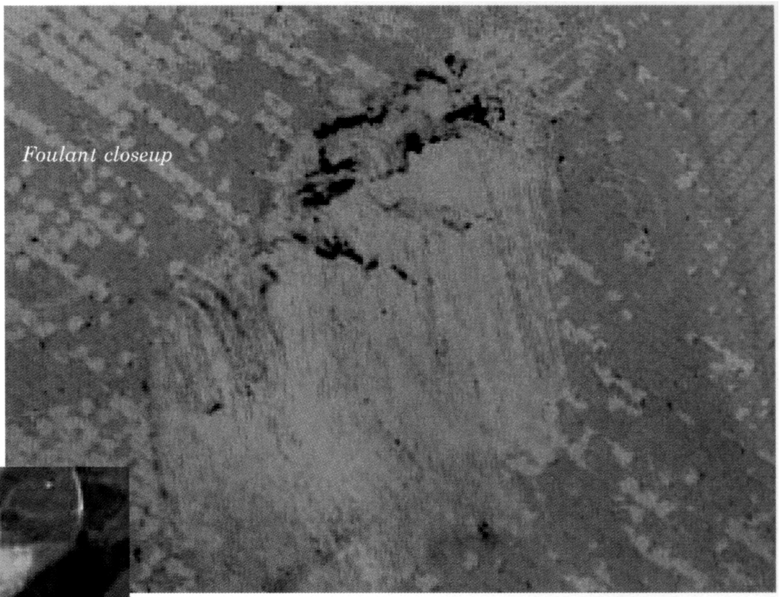
ORGANIC MATTER

Organic matter is defined as carbon-containing matter. Each foulant is washed by decantation with pure water, then dried at 120-130^{0}C. It is gravimetrically analysed for carbon, hydrogen and nitrogen (C,H,N) elemental content by standard methods of pharmaceutical analysis, along with a quantitative ash test (furnace at 400-450^{0}C) to determine the percent of inorganic matter. The percent total volatile or combustible elements (C,H,N and oxygen) from the ash test is considered Organic Matter, and it correlated well with C,H,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 analysed during a recent period have the values shown on Table 1.

Organic Matter (% by weight)	No. of Foulants Analysed	
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 1: Organic Matter in RO Foulant Samples

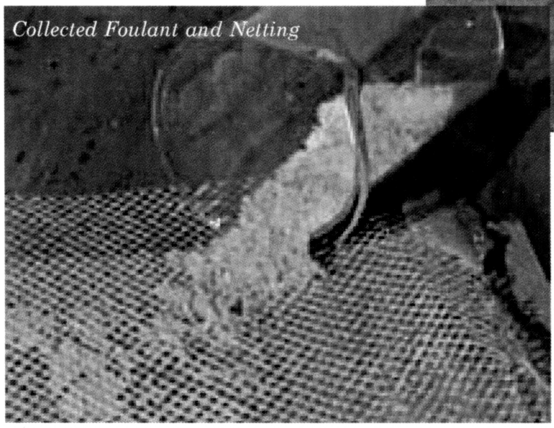
From the table, it is interesting to note that all samples contained at least 10% by weight of organic matter, and that 73 % of the samples contained 50-100% by weight of organic matter. It should be noted that these foulants analysed are representative of the more difficult to clean types of foulants. Foulants such as calcium carbonate, calcium sulfate and ferric and aluminum hydroxides that are readily cleaned with generic acid cleaners are not represented. Organic matter, which includes biomass and polymers used in pretreatment, usually makes the foulant difficult to remove.



Foulant closeup

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 and the accumulation of the biofilm in the system due to the difficulties in removal. Such accumulation is usually promoted by inadequate maintenance sanitisation procedures of the entire water processing system, and stagnation during frequent or prolonged downtimes without preservative.



Collected Foulant and Netting

Severe growths are often detectable by odour 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) 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 co-related 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. In the absence of the characteristics of biomass - odour, visual and microscopic appearance, colour, slime, microbial counts, enzyme activities, presence of phosphates, sodium and potassium in ash and the presence of usually thin and even coating of colourless to tan gel suggest synthetic polymers. Severe flux reduction accompanied by almost invisible film of organic material is the hallmark of poisoning by cationic polymers.

Using Fourier transform infrared spectroscopy (FT-IR), if reference spectrum of the suspect pretreatment polymer is available, and the foulant spectrum is uncluttered, positive identification through "finger printing" is possible. Carryover of high molecular weight synthetic cationic, anionic and non-ionic polymers used as coagulants in pretreatment often are flocculated with colloidal particles of complex compositions, carry more mass, and are 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 multivalant 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.

Table 2: Elemental Composition of An Iron Acrylate Foulant

Component	Percent by Weight
By gravimetric elemental analysis:	
Carbon	23.67 % (absolute)
Hydrogen	3.73
Nitrogen	3.26
Ash (inorganic)	48.08
By SEM-EDX (atomic no. 12-42, Mg-Mo):	
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
	Total: 98.4%

As an example, the elemental composition of such a foulant is given in Table 2. This sample contains 52% volatile organic matter (C,H,N,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 quantify elements between atomic numbers of 12-42, 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 magnesium. Bridging to phosphate, silicate and sulphate 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 reverse osmosis system and become deposited on the membrane as a foulant. Colloidal silica, also known as non-reactive silica, results in natural waters from the polymerisation of silica 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. Clays in feedwaters result mainly from the erosion of rocks however. Indeed it is stated (8) 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 (50 microns - 2mm), silt (5-10 microns) and clay (<5 microns), 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 0.45micron test filters. In practice, feedwaters with SDI values greater than 5 would lead to high fouling rates in the plants. Since the 0.45 micron filters are nominal filters, and particle size is a continuum through the nanometer (colloidal) range down to molecular sizes, 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 the 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 3.

Component	Percent by Weight
By gravimetric elemental analysis:	
Carbon	
1.15 % (absolute)	
Hydrogen	0.67
Nitrogen	0.02
Ash (inorganic)	92.46
By SEM-EDX (atomic no. 12-42, Mg-Mo):	
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%

Table 3: Elemental Composition of A Colloidal Silica Foulant

PHOSPHOROUS

Phosphorous is detected in foulant samples by SEM-EDX. Relative amounts in the inorganic portions of 20 recent foulants surveyed ranged from 0-58% of the elements measured in these samples (mean=14.6%, SD=15.7%). Sources of this phosphorous-containing matter can be correlated with a number of sources. Biomass generally contains measurable amounts of phosphates. Algal biomass in natural waters is reported to contain almost 1% of elemental phosphorous.

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 reverse osmosis system. 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 wastewaters have phosphate concentrations usually in the range of 15-30 mg/litre of phosphate ion (about 5-10 mg/litre as phosphorous). In addition to calcium phosphate, ferric and aluminum phosphates are particularly insoluble, and can enter the reverse osmosis 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 which 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. Even phosphonates can precipitate with high levels of calcium, iron and aluminum, and can participate in fouling.

These conclusions regarding the formation of RO foulants have been the basis of resolutions of many operation problems of RO plants. Hopefully they will serve as a framework for further insights on the way to making RO systems more stable in operation. ***AW***

***Dr Robert Y. Ning**, is Vice President of Science and Business Development at King Lee Technologies, San Diego, CA, USA. His training in chemistry has been at Rochester Institute of Technology (BS), University of Illinois (Ph.D.) and California Institute of Technology (Post-Doctoral research). He has published 19 papers and 17 US patents on pharmaceutical chemistry, and more than 20 papers on water treatment with reverse osmosis (RO) membrane plants.*

For his contact details, please email the editor of Asian Water at vikass@singnet.com.sg.