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Chemistry in the Operation and Maintenance of Reverse Osmosis Systems

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1. Introduction

Across the spectrum of industrial and municipal water utilization and treatment plants, extensive desalination and purification of water relies on the use of reverse osmosis (RO) membranes. Sustaining the productivity of RO plants as continuous processes for water purification has been since the late 1970s, and still is, a significant technological challenge. The challenge is magnified on the one hand by the increasing shortages of water thus driving down the quality of available raw waters, and on the other hand by the demand and the high cost of lost production that can result from insufficient productivity of RO systems. Reduced productivity of RO plants exerts serious economic impact on the downstream production of steam, power, microelectronics, pharmaceuticals and beverages among other products. Not only used in the front-end to provide supply of high quality process water, the loss of RO capacity to process wastewater at the back-end to allow regulated discharges can shut down production or operation of some industrial complexes. With all these requirements, efficient operation and maintenance (O&M) of RO plants based on an understanding of chemistry is essential.

The design and working of an RO system as a unit operation is widely described in articles, books, technical literature and design software of membrane manufacturers and updated versions of user association manuals, such as from the American Water Works Association [1] The sensitivity of RO membranes towards fouling however has presented great challenges and crises to O&M personnel [2]. Once a plant is built, changes in source water quality, inadequacies in pretreatment unit operations, and inappropriate O&M procedures lead to costly repairs to the RO. Even more serious, is the stoppage of water supply to the entire production plant of high value products. Insufficient attention to changing chemistry in raw water, and inadequate performance of pretreatment units result in our current industry

practice of expecting 2 to 4 years membrane service life along with frequent stoppages for membrane cleaning and system maintenance. When optimally controlled, RO membranes have lasted more than 12 years. Systems exist that have operated continuously, and not have to be cleaned for many years. In this article, we point to aspects of process chemistry peculiar to RO plants [3-21].

2. Membrane Fouling Mechanisms

Feedwaters to RO systems typically are concentrated by a factor of 2 - 10 (50%-90% recovery) during production of permeate water. For simplicity in classification, three classes of fouling can be said to occur [8-11].

2.1. Firstly, there is scaling

The solubility limits of various dissolved salts in the concentrate 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 and calcium phosphate. In the examination of foulants by naked eye or with magnifying glass, crystals have well defined shapes. Inhibitors injected continuously into feedwaters to suppress crystallization are called antiscalants. For scaling to occur, seed crystals from in the super-saturated concentrate. The seed crystals may grow into discernable shapes such as plates, flakes, prisms or needles, or remain as finely dispersed particles, visible or invisible to the naked eyes. Antiscalants work by inhibiting the growth of such seed crystals, and forcing the RO concentrate to remain for a time in a supersaturated state. This mechanism is known as threshold inhibition. This task of scale growth inhibition is efficiently accomplished by low concentrations of antiscalants maintaining high super-concentrations in the RO concentrate. The capabilities of certain antiscalants in controlling the most common scales are listed in Table 1. Such antiscalants can be used to effectively replace traditional pretreatment methods of removing the offending foulants from the raw water stream [4-7, 21].

2.2. Secondly, there is colloidal fouling

The foulants appear typically as colorless to yellow or brown soft amorphous layer during autopsy when membranes are cut and unrolled for visual examination [10]. Raw waters contain heavy loads of particles ranging from the visible kind to the smallest of the invisible. Colloidal particles can be considered here as less than 1.0 micron in size. Below 1 micron, they are invisible to the naked eye, nearly undetected by turbidity and Silt Density Index (SDI) measurements. The 0.45 micron filters used in SDI measurement do not retain colloidal particles. In fact even microfiltration and ultrafiltration pretreatment in RO systems still pass colloidal particles that result in severe colloidal fouling of the RO membranes [14,18,19]. Elemental composition analyses of washed and dried colloidal foulants for elemental carbon, hydrogen and nitrogen generally show predominance of complex microbial matter from natural sources. Inorganic components clearly discernable are clays (aluminum

silicate), silt (ferric-aluminium-magnesium silicates), silica (polymer represented by composition of SiO₂), and ferric and aluminum oxyhydroxides when such are used as coagulants for water clarification upstream [10, and unpublished data].

RO Foulant	Traditional Pretreatment	Current Capability
1. Calcium Carbonate	Acidification to lower LSI, then with antiscalant to maximum LSI=2.5	Antiscalant alone: LSI=3.3; S&DSI=" /4.5
2. Iron, manganese	Oxidation/filtration: Greensand, manganese dioxide, catalytic oxid'n	Antiscalant alone: Fe and Mn at " /8ppm
3. Silica: Reactive	Lime, Ion-Exchange (OH)	Antiscalant: " /280ppm
Non-reactive	None	Antifoulant: variable
4. Calcium Sulfate	Lime, Ion-Exchange	Antiscalant: " /400x sat'n
5. Strontium Sulfate	Ion-Exchange	Antiscalant: " /43x sat'n
6. Barium Sulfate	Ion-Exchange	Antiscalant: " /51x sat'n
7. Calcium Fluoride	Lime, Ion-Exchange	Antiscalant: " /16,000x sat'n
8. Colloidal Organic Matter and Sulfur	UF, MF, coagulation/clarification/MMF, slow sand and carbon filter	Antifoulant alone

Table 1. RO System Design Advances Made Possible by New Antiscalant and Antifoulant Chemicals.

Colloidal matter pre-existing in feedwater can aggregate and adhere to the membrane and brine flow channels due to increased concentration, salinity, compaction, flocculation, surface interactions and other physical and chemical factors [11, 17-19]. The colloids can become organic or inorganic or composite flocs. Dissolved ionic ferric, aluminum and calcium hydroxides and silicic acid grow to increasing particle sizes by polymerization [3,17,18]. Cross-linking, and complexation of organic and inorganic polymers become gels and amorphous foulants commonly seen on membranes [10,11]. Biotic debris such as polysaccharides and dead cellular matter contribute largely to this type of foulants. Through solving numerous fouling problems in existing RO plants, it has become obvious that excessive and inappropriate application of pretreatment chemicals aggravate the tendency of natural colloids present in RO feedwaters to coagulate and become foulants. Anticoagulants and anti-deposition agents recently developed show promise in inhibiting this fouling process [14]. The term antifoulants then can be a term applied specifically in this particulate fouling context.

2.3. Thirdly

Biofouling is a prominent source of fouling. True of all water treatment or distribution systems, is the growth and anchoring of microorganisms. Moderate temperatures and minimal nutrient levels in RO raw waters can support at times explosive growths of microorganisms. Bacteria capable of cell division every 20 minutes can grow from a normal count per unit vol-

ume of water to millions in the period of an 8 hours 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. This threat is compounded by the great difficulty of treating and completely removing biofilm from the membrane surface. Associated with biofouling of proliferating nature, is the large presence of non-proliferating organic materials secreted or deposited in natural waters. Microbes and planktons secrete into their water environment large amounts of exocellular polysaccharides in the sunlit surface waters on land and at sea, then remain in the waters as cellular debris. For RO systems maintenance, biofouling then has the two separate component of biofilm proliferation and the colloidal organic fouling by mobile colloidal particles.

2.4. An over-riding effect

Involving coagulation and deposition of colloidal particles in the RO system parallels the delta effects of large river systems. Finer and finer particles in river water that survive physical deposition during the river's meandering course reaches the sea. When the low salinity (low Total Dissolved Solids-TDS) river water meets the high TDS seawater, colloidal particles coagulate and precipitate to form the river delta. This is a model of what happens in the last stages of the RO membrane system where concentrations of colloidal particles and TDS rise rapidly, and colloidal fouling takes place.

3. Antifoulant Chemical 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. Strategies aimed at controlling each type of fouling is summarized here.

3.1. For scale control

The development and application of antiscalants is well known and reviewed in the field of boiling water and cooling water chemistry, and applied to boilers, evaporators, cooling towers and cooling systems. Anionic polymers, polyphosphates and organo-phosphorous compounds, sometimes referred to as threshold inhibitors and dispersants, are used in sub-stoichiometric amounts, usually in the range of 1-5 mg/liter concentrations in RO systems. 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 super-saturation 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 temperature is constant. For this reason, higher levels of super-saturation 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. Assumptions of RO fouling limits vary considerably among practitioners.

3.2. For controlling colloidal fouling

The task is much more challenging due to the variety of types of potential foulants and the complexity of their interactions [3,4,8-11,13,14, 17-19], 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 as well as in the treatment of process waters [14]. Drawing on the basic science of colloids, and testing of model foulants suggested by RO foulant analysis data [10,14,19], progress is made steadily with the development of antifoulants.

3.3. Concerning prevention and management of bio-fouling

In water treatment systems, the literature is extensive. Much of the art and science found useful, 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, polyamide or cellulose acetate barrier membrane. Of prime concern is that accumulation and exponential growth of the microorganisms 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 used of preservatives during downtime [15] are important to this end. Normalized permeate flow and differential pressure in the system [20] are sensitive indicators of bio-fouling.

4. Membrane Cleaning

Practical procedure for maintenance cleaning is limited to the re-circulation of cleaning solutions through the membrane elements. By a patented method [16] of membrane reconditioning, spiral wound elements with the hard casing removed, are routinely used in selecting effective cleaners for cleaning by re-circulation. This allows for visual inspection of membrane surface after each cleaning test. It is apparent that except for easily soluble foulants like calcium carbonate, calcium phosphate or ferric and aluminum hydroxide, and less easily dissolved foulants like silica, silicates, calcium sulfate and strontium sulfate, nearly all other RO foulants are only slightly dissolved in even the best matched cleaning solutions with extensive soaking. Removal requires high tangential flow velocities to facilitate detachment of foulants from the surfaces of the membrane and the brine-side spacer screen. Cleaning is usually partially effective, especially where flow channels are clogged, and large patches within the elements are inaccessible to the re-circulating cleaning solution. For this reason, the need for cleaning should be minimized or completely eliminated by the new antiscalants and antifoulants now available, and adequate pretreatment and pilot testing of cleaning process developed during pilot testing stage. When cleaning is necessary during operation, it should be performed at the earliest stages of fouling.

It is generally agreed among membrane manufacturers and practitioners that RO systems should be cleaned before the following performance changes are reached:

1. Loss of 10 to 15% in normalized permeate flowrate.
2. Increase of 10 to 15% in differential pressure.
3. Decrease of 1 to 2% in salt rejection.

If a cleaning procedure fails to fully restore the system performance to the reference RO system startup values, it is certain that continued use of the same cleaning procedure will lead to accelerating decline in system performance and increasing cleaning frequency. For this reason, it is important to address two issues at this point: a) find an improved cleaning procedure, b) investigate possible improvement of pretreatment to avoid membrane fouling. Continue cleaning and process improvement efforts until stability of the RO performance is attained. Even with well piloted and designed RO plants, and smooth operations initially, source water qualities invariably change over time. Equipment and personnel changes also impact performance, requiring constant vigil and preparedness for continuous improvement of the plant.

4.1. Choosing Cleaners

Major membrane manufacturers generally define five types of foulants for which various generic chemicals are recommended for blending at the site where cleaning solutions are prepared. The five types of foulants are: 1) Acid-soluble Foulants, 2) Bio-film/Bacterial Slime/Biological Matter, 3) Carbon-containing Oils/Organic Matter, 4) Dual Organic and Inorganic Coagulated Colloids, and 5) Silica and Silicates. Proprietary booster cleaners are commercially available to fortify the effectiveness of these generic cleaners that are formulated at the site. For convenience and technical support, a large variety of proprietary RO membrane cleaners are available from chemical suppliers that specialize in RO operations. Such proprietary cleaners and cleaning support are available when generic cleaners do not perform adequately.

4.2. Cleaning Strategies

Experience has shown that within the same class of foulants, responses to the same cleaning solution can vary considerably. Elemental analyses of foulants and cleaning studies have shown that more than one type of foulant can be present on the membrane at the same time, requiring sequential cleaning with different cleaners. Sometimes even the order of cleaners used would make a significant difference. All this is to say that the choice of cleaners and the cleaning procedure to be used is an empirical science. For a given set of conditions in a plant, cleaning efficiencies are improved by trials over time. The progress of improvement can be greatly accelerated by conducting off-line cleaning studies on test skids for single fouled elements taken from the plant.

When a better cleaning method is needed in the plant, the following are the alternative strategies:

Strategy 1: The plant has a history of using generic cleaning chemicals, and modest improvement in effectiveness is needed, consider purchase of proprietary booster cleaners.

Strategy 2: A significant cleaning improvement is needed, look for proprietary cleaner supplier with associated cleaning expertise. Option 1: With prior knowledge of the characteristics of the foulant on hand, with consultation with the supplier, select a combination of cleaners for trial in the plant. Option 2: Send one to three fouled elements to specialist for cleaning study, foulant analysis and review of plant performance history and pretreatment process. Document the findings along with pilot cleaning results using a recommended improved cleaning procedure. Simultaneously address recovery of the plant and avoidance of repeated fouling. Option 3: Send all fouled elements for off-site cleaning by specialist.

Strategy 3: All cleaning efforts by re-circulation of cleaning solutions have failed, consider non-routine methods like using proprietary membrane conditioning liquids or membrane reconstruction process by which membrane bundle is unrolled, cleaned leaf by leaf, then restored with a new hard-casing.

4.3. On-line Cleaning Procedure

Basically there are six (6) steps in the cleaning of membrane elements in place in RO systems:

1. Mix Cleaning Solution.
2. Low Flow Pumping. Pump preheated cleaning solution to the vessels at conditions of low flow rate (about half of that shown in Table 2) and low pressure to displace the process water. With the RO concentrate throttling valve completely open to minimize pressure during cleaning, use only enough pressure to compensate for the pressure drop from feed to concentrate. The pressure should be low enough that essentially no permeate is produced. A low pressure minimizes re-deposition of dirt on the membrane. Dump the concentrate, as necessary, to prevent the dilution of the cleaning solution.
3. Re-circulate. After the process water is displaced, cleaning solution will be present in the concentrate stream. Re-circulate the concentrate to the cleaning solution tank and allow the temperature to stabilize.
4. Soak. Turn the pump off and allow the elements to soak. Sometimes a soaking period of about 1 hour is sufficient. For difficult to clean foulants, an extended overnight soaking period of 10-15 hours is beneficial. To maintain a high temperature during an extended soaking period, use a slow re-circulation rate (about 10% of that shown in Table 2).
5. High Flow Pumping. Feed the cleaning solution at the rates shown in Table 2 for 30-60 minutes. The high cross-flow rate flushes out the foulants removed from the membrane surface by the cleaning, with minimal or no permeation through the membrane to avoid compacting the foulant. If the elements are heavily fouled (which should not be a normal

occurrence), a flow rate which is 50% higher than shown in Table 1 may aid cleaning. At higher flow rates excessive pressure drop may be a problem. The maximum recommended pressure drop is 20 psi per element or 60 psi per multi-element vessel, whichever value is more limiting.

Note: In this cleaning mode, foulants are generally partially dissolved in the cleaner and partially dislodged physically from the membrane and flow channels without dissolving. An in-line filter removes the re-circulated particles, and should be monitored for cartridge replacement.

6. Flush Out. Pre-filtered raw water can be used for flushing out the cleaning solution, unless there will be corrosion problems such as with seawater corroding stainless steel piping. To prevent precipitation, the minimum flush temperature is 20 deg. C.

Additional Notes: The pH should be monitored during acid cleaning. The acid is consumed when it dissolves alkaline scales. If the pH increases more than 0.5 pH units, add more acid.

Feed Pressure*	Element Diameter	Feed Flow Rate
(psig)	(inches)	Per Vessel (GPM)
20 - 60	2.5	3 - 5
20 - 60	4	8 - 10
20 - 60	6	16 - 20
20 - 60	8	30 - 40

* Dependent on the number of elements in the pressure vessel

Table 2. Recommended High Re-circulation Flow Rates During Cleaning.

Multi Stage Systems

For tapered multi-staged systems the flushing and soaking steps can be performed simultaneously in the entire array. The high flow-rate re-circulation step however should be carried out separately for each stage, so that the flow-rate is not too low in the first stage and too high in the last. This can be accomplished either by using one cleaning pump and operating one stage at a time, or using a separate cleaning pump for each stage.

4.4. Control and Improvement of Cleaning Process

To assure complete recovery of membrane performance by cleaning, the system performance should be adequately controlled by trending of normalized flux, differential pressure and salt rejection [20] to 1) trigger a cleaning when any monitored parameters change from normal baseline by 10-15%, 2) record the trended parameters before and after each cleaning, 3) initiate improvement actions for better cleaning if membrane performance does

not fully recover. A change in responsiveness to previously effective cleaning process signals a change in fouling pattern that requires immediate attention. If partial cleanings are allowed to continue, the system performance will decline at increasing rate, and will become increasingly difficult to recover.

In-place cleaning processes are improved primarily by the choice of cleaning chemicals and the order of the application sequence. Depending on the composition of the complex foulants, when two or more cleaners are found necessary, often the order in which they are used is important. Also critical, but to lesser extents are the variables of time, temperature, and cross-flow rate.

Through thorough review of the water and pretreatment chemistry, analyses of the foulant composition and source, and customized selection of antiscalants, dispersants and high performance cleaners, both fouling avoidance and reliable plant performance can be attained. Practical experiences show that plant performances invariably change over years of service due to imposed changes in source water, equipment, regulatory and human factors. Attentive operation and maintenance assures early detection of developing problem, and timely adjustments.

5. Conclusion

High rejection of dissolved salts and suspended colloidal particles in RO feedwater cause scaling and colloidal fouling of membranes. Understanding the chemistry of membrane fouling and methods of control, coupled with keen monitoring during O&M, are necessary for the assurance of RO process stability. Ever increasing need for maximum water extraction, while reducing the volume of concentrate requiring disposal pose challenges to chemical understanding and control by O&M personnel. Information provided in this chapter provide key words and concepts for the readers to glean from the expansive literature.

For readers who assume responsibilities of existing RO plants, problems may have arisen due to inadequate pretreatment design, or due to changed sources of raw water. A companion chapter on pretreatment for reverse osmosis systems is available on line in an open-access book on Desalination [22].

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