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Pretreatment for Reverse Osmosis Systems

Robert Y. Ning

*King Lee Technologies, San Diego, California
United States of America*

1. Introduction

Reverse osmosis (RO) membranes are very sensitive to fouling by seawater or brackish water on which desalination is conducted. In this chapter, the nature of foulants, the mechanism of fouling and the methods of monitoring and diagnosis of RO fouling are discussed. Based on this, methods of pretreatments are presented, and recommended specifications for the pretreatment of RO feedwater are described.

2. Fouling of RO membranes

2.1 Commonly observed foulants on reverse osmosis (RO) membranes

(Ning and Shen, 1998; Ning, 2004) can be divided into hard scales and soft amorphous complexes. The most common scales from brackish waters, seldom seen on seawater membranes, are calcium carbonate, calcium sulfate, strontium sulfate, barium sulfate, calcium fluoride and calcium phosphate. Amorphous gels are composed of natural exocellular polysaccharides from microorganisms, hydrated silica, ferric and aluminum hydroxides, colloidal iron and manganese compounds and pretreatment polymers. Fine silt, clay and media from filters such as activated carbon and manganese greensand that escape guard filters also deposit on membranes.

2.2 Mechanisms of fouling

Scales result from super-saturation of the RO brine with respect to salts of low solubility as those mentioned above. RO systems are typically operated with recoveries in the range of 50-90%. This means feed waters entering the RO are concentrated 2-10 fold. Under suitable conditions of concentrations of total dissolved solids, intrinsic crystallization rates of specific compounds and presence of seed crystals, scales can form, build up and move forward from the back-end of the RO system where concentrations are the highest towards the front where the concentrations are lower. With the advent of effective modern antiscalants (Ning, 2003 and Ning et al. 2009) scaling today is a much smaller problem than colloidal fouling by coagulation of particles invisible to the naked eyes. Natural waters are full of suspended particles that are extremely small (<0.1 micron, defined as colloidal). At such sizes, surface to mass ratio are so much larger than visible particles that large surface to surface interactions cause them to self-assemble in discernable patterns (termed Nanotechnology when synthetic and controlled) or coagulate. The coming together of particles and sticking

to membrane surfaces results in what we observe in membrane autopsies as amorphous gels. Such foulants are complex mixtures and are difficult, sometimes impossible to clean. Larger, visible particles if not removed from RO feed water will naturally plug the feed flow channels in the membrane elements. To prevent such fouling, RO feed water needs to have turbidities of less than 1 NTU, and Silt Density Index (SDI), a flowrate over time through a 0.45 micron filter, of less than 4.0. Turbidity and SDI do not detect colloidal fouling potentials.

To control scaling, antiscalants are used to bind to nascent seed crystals preventing them from growing into scales and safely discharged with the reject water. For this reason it is commonly called threshold inhibition mechanism. Antifoulants for controlling colloidal fouling works on the principle of keeping the colloidal particles from coagulating or even dispersing the coagulate once formed on the membrane (Ning et al. 2005; Ning and Troyer, 2007; Ning, 2009). Colloidal iron and manganese compounds, due to their positively charged characteristics are particularly sticky on the negatively charged membranes (Ning, 2009). Special mention should be made on the mechanism of fouling by colloidal silica and silicates due to the spontaneous polymerization of monomeric silicic acid in all natural waters (Ning, 2002; Ning, 2010). Silicic acid [$\text{Si}(\text{OH})_4$] is the reactive silica species commonly measured by the molybdate colorimetric assay. It spontaneously polymerizes by elimination of water during RO concentration, generating in the RO concentrate a reaction mixture of oligomeric silica and silicates. The representation of silica in the ultimate dehydrated state is SiO_2 (eg. sand, quartz). When hydroxides of iron, aluminum, magnesium and calcium are involved in copolymerization with silicic acid, complex silicate oligomers are formed in the RO concentrate, some of which may be large enough and sticky enough to end up on the membrane.

2.3 Monitoring and diagnosis of fouling

Due to the myriad possibilities of irreversible fouling of RO membranes, careful monitoring of the RO performance is necessary for operation and maintenance and solution of fouling problems as soon as they appear. Monitoring is accomplished ideally with normalized values of permeate flowrate, differential pressure and salt passage plotted as trend charts (Ning, 2004; Troyer et al., 2006). For two stage RO systems, it is best to install an inter-stage pressure gauge so that differential pressures for the first and the second stages can be monitored separately.

To diagnose fouling, scaling occurs in and grows from the back end forward, and shows prominent increases in differential pressure. Colloidal fouling begins with severe normalized permeate flowrate, long before significant differential pressures appear. Fouling by visible particles is more severe in the lead elements, often limited to the element in the first position, and accompanied by rapid fouling of the 1 to 20 micron cartridge guard filters.

3. Seawater pretreatment

3.1 Intake systems

Seawater can be drawn into the plant from open sea, or through beach well or seabed. Popular these days is to co-locate the seawater RO next to an existing power plant that discharges seawater used in cooling residual heat. Intake system design has considerable impact on the feed water quality, hence the entire pretreatment design. Open intake suffers from fluctuating, often high turbidities and colloidal contaminants such as algal matter,

transparent exopolymer particles (about 0.4-200 microns), colloidal extracellular polymeric substances (<0.4 microns), humic substances, oils, clay and other organic and inorganic matter from surf action and nearby discharges from shore. Beach well and under-seabed intakes act as filters to reduce suspended particles as well as colloidal dispersions to some extent. Depending on the sites, beach wells can introduce foulants more commonly seen on land. The advantage of using power plant cooling seawater is the reduced cost of building a new intake and discharge structure, while using warm water that increases membrane flux and reduces pump power consumption..

3.2 Recommended RO feedwater quality

The quality of seawater is defined by turbidity, Silt Density Index, Total Organic Carbon, Critical Flux (the maximum membrane flux above which colloidal fouling will occur for a particular pretreated water), Red Tide algal bloom events, colloidal destabilization caused by blending with river discharge or chemical dosing such as with chlorine. While these parameter provide useful data for designing and operating pretreatment unit operations, no model currently exists that can predict with certainty, the maximum RO fouling rate of a pretreated RO seawater. For this reason, careful monitoring is essential for the operation and maintenance of the system.

3.3 Shock vs continuous chlorination

Chlorination (sodium hypochlorite or chlorine dioxide) is needed to minimize the population of growing sea organisms such as algae, mussels, clams and microorganisms that inhabit the surfaces of pipes and tanks in the intake system. Long term experiences in many seawater RO plants have shown that shock chlorination is better than continuous chlorination. Continuous chlorination chemically reacts with and adds its weight to planktonic (moving) colloidal organic matter and causes destabilization and more coagulation of the natural colloidal polymers. It is possible also that continuous chlorination only irritates the larger anchored sea organisms in the intake system rather than killing them, allowing them to multiply and continue to shed foulants.. Biofilms and microbial control in plant equipment contacting water remains a major challenge to RO pretreatment.

3.4 Clarification

Coagulants are added to seawater before sand or multi-media filters to enhance removal of suspended particles. Dissolve air floatation by deliberate introduction of a dispersion of air bubbles while extending contact time with coagulants improves the removal of algae and natural organic materials (NOM) sometimes called transparent exopolymeric particles (TEP), or extracellular polymeric substances (EPS). These coagulated sticky transparent gels are composed of primarily complex polysaccharides.

3.5 Microfiltration/ultrafiltration

Membranes having tortuous pores, with diameters in the approximate range of 0.05 to 1.5 microns (MF) and smaller pores in the range of 0.002 to 0.10 microns (UF) are used as alternatives to traditional clarification with media filters. Timed backwashing cycles are necessary to recover trans-membrane pressures, along with periodic chemical cleanings to recover productivity. MF and UF membranes, usually called low-pressure membranes in contrast to RO membranes suffer from fouling by cake-layers of foulants as well as

plugging of pores. Pores on the membranes once plugged are difficult if impossible to recover. For this reason, low flux and judicious use of coagulants to form cake-layers of protective foulants are strategies to extend service lives of the membranes.

3.6 Antiscalant

Due to the high dissolved total solid concentrations of seawater, and the resulting increased solubilities of scales, along with low water recoveries of about 50% to minimize energy consumption, the need for antiscalants in seawater ROs are minimal. Almost all fouling seen are due to colloidal organic matter on which antiscalants exert little effect. Carryovers of iron and aluminum coagulants, or colloidal inorganic particles picked up from beach wells however can be controlled by appropriate antiscalants.

3.7 Antifoulant

The application of antifoulants as anti-coagulants and dispersants of colloidal matter in seawater (Ning, 2003; Ning et al, 2005) show promise, but not yet adopted on large scale.

4. Brackish water pretreatment

4.1 Well vs surface water

Due to long equilibration times and adsorption and filtration actions of soils in the aquifer, well waters have low turbidities and Silt Density Indices compared with surface waters from rivers, lakes and ponds. Surface waters in contrast have high turbidities and SDI, and natural organic matter derived from abundance of biotic life. Reactive silica can be very high from wells, especially in the volcanic regions of the world, but low in surface waters. Silica and silicates in surface waters tend to be in colloidal non-reactive forms. Ferrous ions associated with iron-reducing bacteria survive air oxidation in the anaerobic environments of wells, so does sulfide ions associated with sulfate-reducing bacteria in some wells. Upon emerging to the atmosphere on the surface, ferrous ions oxidize to the red ferric hydroxide species in surface water and sulfide waters form colloidal sulfur and hydrogen sulfide gas.

4.2 Clarification

Deep-well waters can typically be pumped directly to the RO system through cartridge guard filter after dosing with antiscalant (Ning, 2003). Surface waters need clarification to turbidity of <1 NTU and SDI of <3-4. Coagulant, sand or multimedia filters are used. Filtration through activated carbon should be avoided if possible due to propensity for microbial growth. MF and UF are sometimes used, especially for brackish municipal wastewater. This expensive pretreatment is primarily for the purpose of gaining virus removal credits as process steps for certifiable process designs for treating municipal wastewater.

4.3 Chlorination

Surface waters and shallow well waters are sometimes chlorinated followed by dechlorination with bisulfite, metabisulfite or activated carbon before entering RO. In successful resolution of membrane biofouling problems, we have found that this pretreatment is not necessary. Short contact time of low dosages of chlorine affect planktonic bacteria to a degree but is ineffective in controlling biofilms. Membrane damage from iron-catalyzed oxidation by residual chlorine or even chloramines can be rapid and

severe. Activated carbon filters always grow bacteria and shed microbial slime, and are difficult to maintain. Effective control of biofilm on RO membrane is best performed during periodic maintenance cleaning and sanitization of the system.

4.4 Antiscalant

Antiscalants as threshold inhibitors in pretreatment greatly simplifies the design of RO pretreatment process (Ning, 2003). Scaling, dissolved iron, aluminum and manganese, and silica polymerization chemistry are almost always controlled in the typical range of 75-85% RO water recovery. For extreme recoveries of 90-98% of brackish water, antiscalants play essential roles. In inland regions where RO concentrates are expensive or impossible to dispose of, ROs are being tested to the limiting opposing osmotic pressure of 1000 psi (68 atmospheres) to reduce the volume of RO concentrate requiring disposal (Ning et al, 2010).

4.5 Antifoulant

Antifoulants acting as anti-coagulants for colloidal foulants and dispersants for colloidal coagulates are specifically developed for colloidal sulfur, silica and microbial slime in brackish water (Ning et al, 2005). Simultaneous use of an antiscalant along with an antifoulant has long been used in medium-sized RO systems. Application in major municipal RO plant is thus far rare due to the high cost of required dosages that are larger than those of antiscalants.

5. Summary comments

5.1 Limits to scaling and fouling projections

Although proprietary software programs that predict scaling potentials are available from membrane and RO chemical suppliers, no standard formulae exist today on predicting scaling potentials for RO. Textbook Solubility Product Constant values are adopted, but proprietary formulae used are varied and unpublished. It must be understood that solubility products are reported for single pure substances at equilibrium in distilled water, and very difficult to measure experimentally with any precision. Further, the confounding factors when applied to RO concentrates are disequilibrium conditions, variable interferences from other ions on crystallization rates, intrinsic crystallization rates, total dissolved salt concentrations, effects of seeding by particles and surfaces, just to mention a few. Although it is necessary to use arbitrary calculations of scaling potentials to determine antiscalant dosages needed, large body of field data correlating RO performance with water chemistry, antiscalant selection and antiscalant dosages provide some confidence in the selection of antiscalants and dosages. Likewise, the complexity of the surface properties and variety of uncharacterizable colloidal particles in raw water precludes possibility of projecting fouling potential and interactions with antifoulants. Antifoulants and dosages are developed entirely empirically.

5.2 Importance of trend-charting

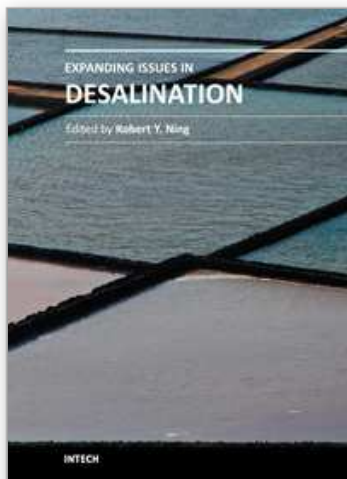
Due to the sensitivity of RO systems to fouling, good pretreatments need to be coupled to continuous monitoring to avoid irreversible fouling. It is the general practice that whenever productivity, differential pressure and salt passage change by 10-15%, cleaning is called for. The longer the system is left uncleaned, the less recoverable the lost performance is. Since system feed pressure and water temperature can change day-to-day that affects the three

parameters mentioned, normalization to the same temperature and feed-pressure is necessary to compare performance data from day to day and from year to year. This is accomplished by using software for normalization and trend-charting (Troyer et al, 2006).

Beyond pretreatment process upsets, since feedwater quality and operating conditions can change from time to time, trend-charting is also necessary to detect ineffectiveness and insufficiencies of maintenance cleaning procedures. When this occurs, optimized cleaning methods need to be validated on-line with trend charts. Likewise, optimization of pretreatment steps are accomplished with trend charts of normalized data.

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For this book, the term “desalination” is used in the broadest sense of the removal of dissolved, suspended, visible and invisible impurities in seawater, brackish water and wastewater, to make them drinkable, or pure enough for industrial applications like in the processes for the production of steam, power, pharmaceuticals and microelectronics, or simply for discharge back into the environment. This book is a companion volume to “Desalination, Trends and Technologies”, INTECH, 2011, expanding on the extension of seawater desalination to brackish and wastewater desalination applications, and associated technical issues. For students and workers in the field of desalination, this book provides a summary of key concepts and keywords with which detailed information may be gathered through internet search engines. Papers and reviews collected in this volume covers the spectrum of topics on the desalination of water, too broad to delve into in depth. The literature citations in these papers serve to fill in gaps in the coverage of this book. Contributions to the knowledge-base of desalination is expected to continue to grow exponentially in the coming years.

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InTech Europe

University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

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