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Reverse Osmosis Chemistry — Basics, Barriers and Breakthroughs

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Abstract

While reverse osmosis (RO) for desalination of brackish water, seawater and wastewater is a most economical and powerful method, its sensitivity to fouling points to the importance of understanding the water chemistry involved and methods of fouling control and system maintenance. As a chemical developer of antiscalants, antifoulants, and operation and maintenance chemicals needed for RO systems, we present here a basic understanding of RO chemistry, the challenges of scaling and colloidal fouling that limits % recovery of permeate and some breakthroughs we have attained.

Keywords: Reverse osmosis chemistry, scaling, colloidal fouling, antiscalant, antifoulant, tandem RO system

1. Introduction

The rapidly increasing introduction of reverse osmosis (RO) membrane plants around the world for treatment of water challenges the process of training professionals and technicians needed to design, operate and maintain such systems. The systems vary in size from 100 million gallons per day (15,800 m3/hour) municipal systems for municipal wastewater, brackish water and seawater desalination, down to 10 gallons per minute (38 liters per minute) used in kidney dialysis clinics. The sensitivities of RO membranes toward fouling and challenges in sustaining operation highlight the need for understanding the chemistry that impacts on the design, performance and maintenance of RO systems. In this chapter, the basics, barriers and breakthroughs in RO chemistry are briefly reviewed.

2. The water cycle

Water covers three quarters of the surface of our blue planet. It is the most powerful and essential solvent for life as we know it. The Water Cycle as depicted in Figure 1 is instructive for tracing the chemistry that occurs in water as it circulates in our environment and that which impacts the reverse osmosis process in water treatment.

Water evaporates from the oceans and from land as pure water vapor, then condenses in cooler atmosphere as clouds of minute droplets before falling as rain or snow. Streams form rivers and lakes before returning to the oceans, both above and below the surface of land. Of note is the portion of water that seeps deep underground and forms aquifers, from which we retrieve brackish well water. Summarized in Table 1 are the distinct stages of the water cycle in which we can discern unique chemistries that occur that will have impact on the RO system.
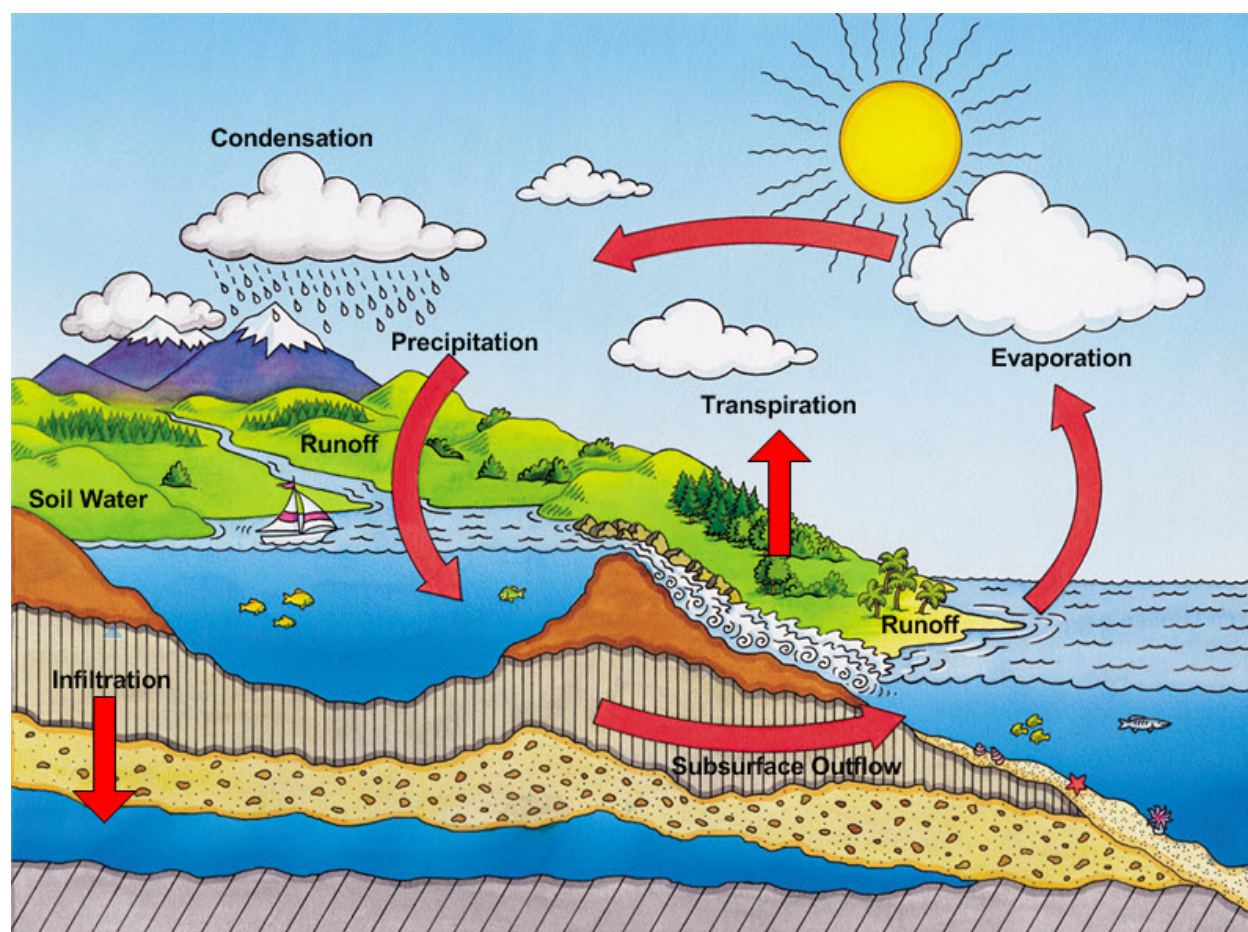

Figure 1. The Water Cycle.

2.1. Rain

As rain falls through air, dissolution of oxygen and nitric oxides will lead to oxidation-reduction reactions in the ground, and more significantly will lead to formation of carbon

Source of Feedwaters and Significant Chemistry that Impact RO

Source Waters	Significant Chemistry
1. Rain	- Oxidation reduction (eg. O_2+NO_x), acid base (eg. CO_2+H_2O)
2. Springs	- Dissolution, acid base (acid rain+carbonate rocks)
3. Ponds, Lakes	- Complex interactions of living and nonliving matter
4. Wells, Aquifers	- Dissolution-precipitaion (eg. $CaCO_3$, $CaSO_4$, $SrSO_4$, $BaSO_4$, silicates, iron and aluminum salts, sulfides), relatively low in organic matter
5. Rivers, municipal and industrial wastewater	- Complexation interations, precipitation
6. Ocean (99.4% of earth's water including 2% as ice)	- Biotic life, complexation interations, precipitation

Table 1. Sources of feed water and significant chemistry that impact RO

dioxide (subsequently forming carbonic acid) and sulfur dioxide (subsequently forming sulfurous acid), leaching lime stones and other alkaline rocks in the ground.

2.2. Springs

As soon as rain touches the ground, available water-soluble salts dissolve. As a general rule, it is good to remember that all salts of sodium and potassium paired with mono or divalent anions are soluble, and all salts of chlorides and nitrates paired with mono or divalent cations are soluble in water. Calcium, strontium and barium carbonates and sulfates have low solubility. Water dissolves the soluble sodium, potassium salts and chlorides and nitrates of calcium, strontium and barium from minerals, and solvates and separates them as a mixture of freely mixing cations and anions. This allows ion paring of the less soluble divalent salts like the carbonates and sulfates of calcium, strontium and barium to reach or exceed their solubilities in water, forming sediments.

2.3. Ponds and lakes

Accumulation of nutrients in ponds and lakes brings together complex interactions of living (bacteria, algae, diverse organisms) and non-living matter- organic (carbon-based) and inorganic (noncarbon-based) matter.

2.4. Wells and aquifers

Water that seeps deep into the ground, lacking air and light has relatively low organic activities and content. Chemistry is more limited to dissolution of rocks, which consist of largely silica

and silicate compounds of minerals. Hydrolysis of these rocks mobilizes the various ions we find in natural waters. Paring together of insoluble salts such as described in 2.2 above form deposits of pure compounds such as calcium carbonate (lime stone), calcium sulfate (gypsum), etc.

2.5. Rivers and municipal and industrial wastewater

Rivers are highly contaminated with natural plant and animal debris, along with municipal and industrial discharges. In addition, finely dispersed inorganic particles of eroded rocks and soil form complex sediments, silting up the rivers and causing rivers to meander.

2.6. Oceans

Oceans contain 99.4% of the water on earth, including 2% present as ice. Chemistries in seawater as far as it impacts seawater ROs is predominantly colloidal organic particles excreted by the abundance of algae and planktons in the sunlit upper regions of the sea. It has been observed, that in the deep ocean, coagulated organic mass fall like snow-flakes. Seawater RO with high salinity from sodium chloride and soluble salts in the feedwater seldom scales at 50% recovery. Extensive removal of colloidal organic matter is needed to avoid fouling, while avoiding carryover of coagulants used in pretreatment.

3. Deployment of RO system

Typical RO processes are depicted in Figure 2. Pretreatment of raw water before the RO has been described extensively in open access literature [1,2], and by searching the subject "RO pretreatment" with www.googlescholar.com. The basic recommended requirements for RO feedwater quality is turbidity of less than 1 NTU, and Silt Density Index of less than 3. Examples of the use of RO permeate is for drinking, boiler feedwater, cleaning processes in microelectronic manufacturing and in pharmaceutical industry. The brine (concentrated reject) has been used in cooling towers, evaporators or simply discharged.

When pretreated water sufficiently devoid of suspended particles is fed into the RO system through a cartridge guard filter, recoveries of 50–90% are typically attained (see Figure 3). Corresponding to these recoveries, the impurities in the RO feedwater are concentrated by a factor of 2–10 fold. Physical separation of any solids from the concentrated streams that clog the fine passages of the membrane elements constitute system fouling, lowering the productivity of the system, and requiring cleaning to restore performance. Clean-in-place equipment in each RO plant provides the ability to clean the system by recirculating appropriate cleaning solutions through the membrane elements. To avoid channeling of cleaning solutions during cleaning by excessive foulants, the system performance must be carefully monitored by trending normalized permeate flow rate, differential pressure and salt passage [3,4]. Effective cleaning is needed when performance by these parameters drop by 10–15% to fully restore performance. The need to replace hundreds or thousands of membrane elements would be extremely expensive. This is the reason that RO is commonly recognized as a very sensitive

Reverse Osmosis in Water Treatment Scheme

Raw Water

Clarification
Chlorination - Dechlorination
Acidification - Degasification (H_2S, CO_2)
Iron / manganese removal
Carbon Bed (organics)
Micro and Ultrafiltration (particulates)

Reverse Osmosis

Permeate
(with or without DI polishing)
Blend for Drinking
Boiler
Clean Processes
Pharmaceuticals

Brine
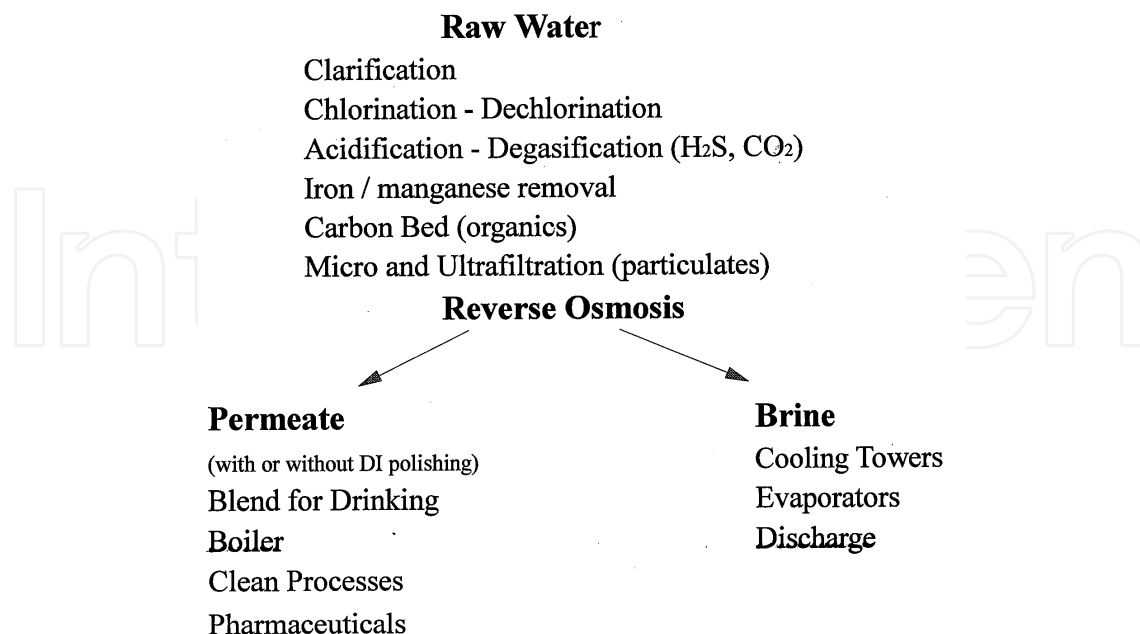Cooling Towers
Evaporators
Discharge

Figure 2. Reverse osmosis in water treatment scheme

unit operation. The tendencies to foul represent barriers to efficient operation and reliability of RO systems.
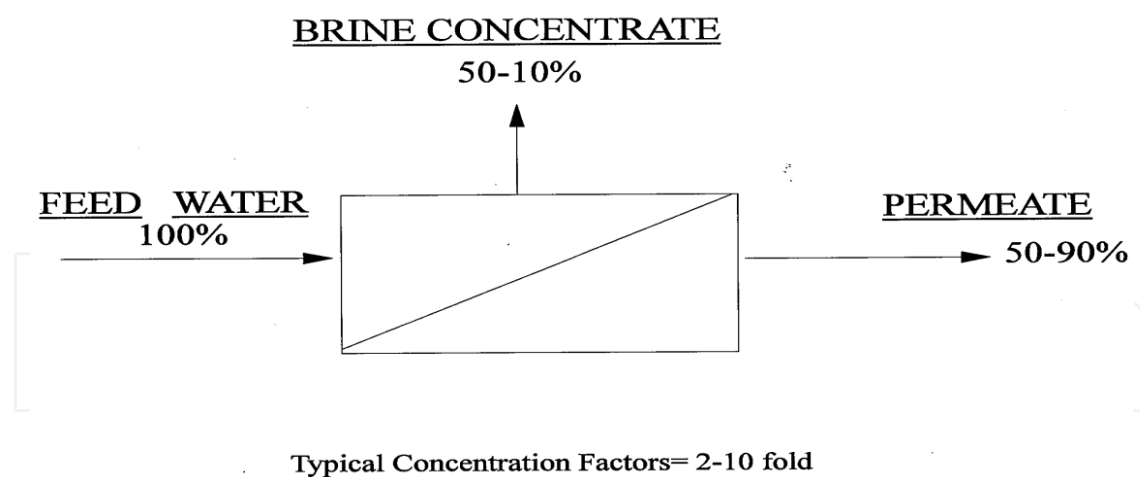
BRINE CONCENTRATE
50-10%

FEED WATER
100%

PERMEATE
50-90%

Typical Concentration Factors= 2-10 fold

Figure 3. Concentration factor in reverse smosis system

4. Barriers presented by membrane fouling

Membrane fouling mechanisms can be classified into three categories: crystallization of insoluble salts commonly termed scaling, coagulation of colloidal particles and polymers

known as colloidal fouling and microbial growth forming biofilm. We will examine each category in greater detail.

4.1. Scaling

Salts consist of pairs of positively charged cations and negatively charged anions forming neutral molecules. Sodium chloride (NaCl) is an example. Salt molecules of the same composition pack in regular repeated patterns in three-dimensional forms to form crystals of different shapes. Sodium chloride crystals are cubic when viewed under the microscope, or grown, as some hobbyists do, as large single cubic crystals. When crystalline salts dissolve in water, the ions dissociate into freely mobile cations (e.g., Na^+) and anions (e.g., Cl^-) each weakly bonded and stabilized (solvated) by water molecules (H_2O). Likewise, potassium nitrate (KNO_3) ionizes in water to form K^+ and NO_3^- ions each solvated by water molecules.

It is useful to remember that monovalent (singly charged) ions are easier for water to ionize (pull apart and solvate) than divalent (doubly charged) ions. Thus, it can be stated that in common water treatment, all salts of sodium, potassium, chloride, bicarbonate and nitrate are relatively soluble, and those of calcium, strontium, barium, carbonate and sulfate are much less soluble when paired. In the laboratory, it can be simply demonstrated that when perfectly clear water solutions of calcium chloride and sodium sulfate are mixed, crystals of calcium sulfate (gypsum, see Figure 4) will form. Such a demonstration illustrates two phenomena, firstly, ions freely mix in water solution, and secondly, that the doubly charged ions (Ca^{+2}) and (SO_4^{-2}) pair up to be less soluble in water. For this reason, most commonly observed scaling in brackish water RO systems are $CaCO_3$, $CaSO_4$, $SrSO_4$ and $BaSO_4$. In seawater, due to the high concentration of sodium chloride and a variety of competing ions, the same pairing of divalent ions to initiate regular stacking of crystal forms is greatly suppressed. Seawater ROs do not normally scale at 50% recovery. We will consider below the concentration of total dissolved solids in RO concentrate as one of the many critical parameters that affect scaling potentials. Other important parameters are degrees of supersaturation, presence of seed crystals, nature of the solutes, interfering impurities, pH and temperature.

4.1.1. Supersaturation

Different salts have different solubilities in water. When their natural solubilities are exceeded, given time, they will crystallize forming scales. When ionized by water and freely mixing in solution with ions from other salts, an important law determining the limits of solubility is a term called Solubility Product Constant. This law states that each combination of cations and anions in solution reaches a saturation value when the product of the concentration of the cation and the anion, whether they are the same concentration or not, cannot exceed a certain constant value. For instance, Table 2 shows the solubility product constants of four types of scales in terms of solubility products as mg/L concentrations.

Although when crystallized, $CaSO_4$ is a 1:1 pairing of Ca^{+2} and SO_4^{-2} ions, in solution for the calculation of solubility product constant, their concentrations do not have to be equal. Thus 100 mg/L Ca x 963 mg/L SO_4 = 96,300, so is 10 mg/L Ca x 9630 mg/L SO_4 = 96,300. Both solutions
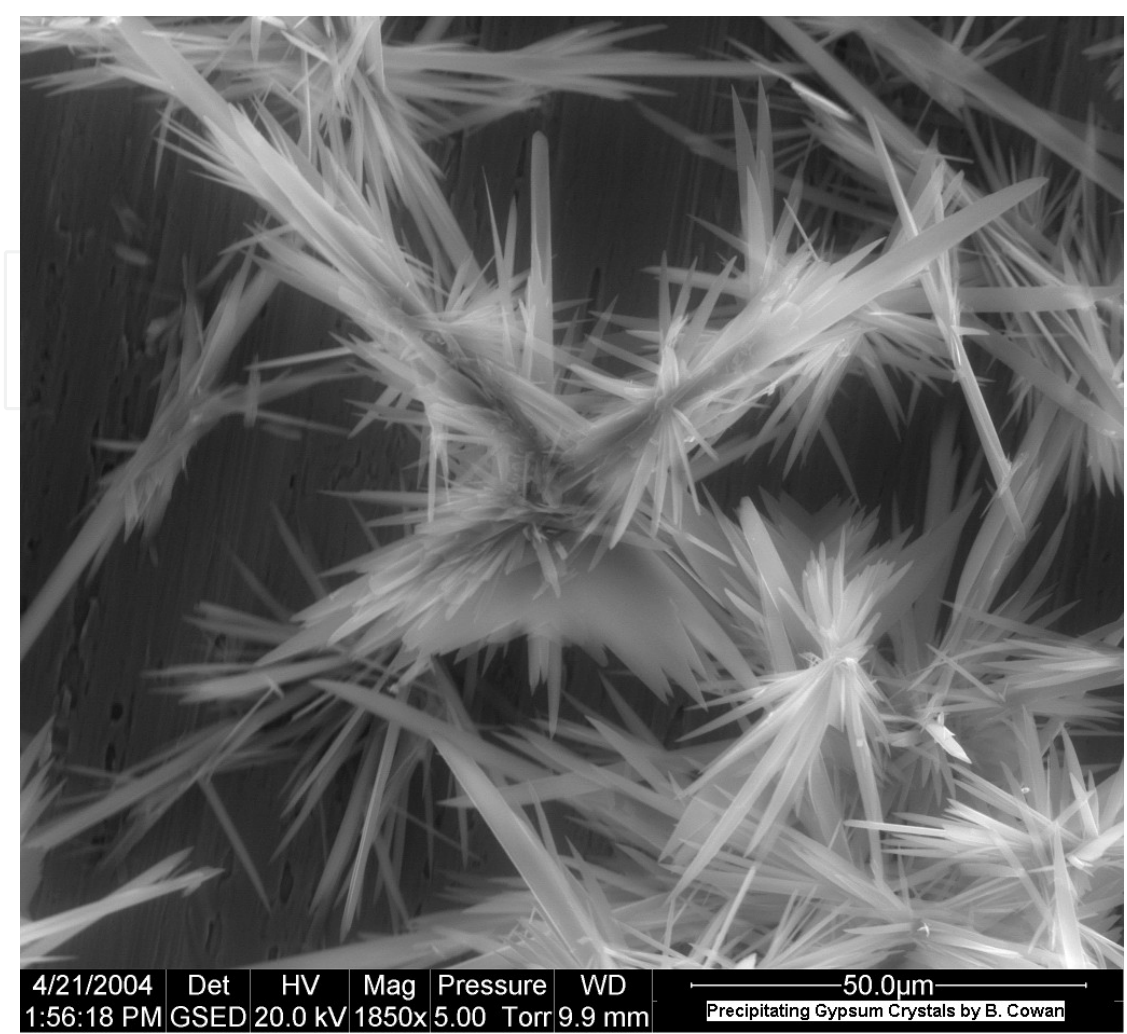
Figure 4. Gypsum seed crystals

have reached solubility product constant limit. In the case of CaF2, three ions are involved per molecule, thus 1 mg/L Ca^{+2} x 27 mg/L F$^-$ x 27 mg/L F$^-$ = 723 solubility limit. Barium sulfate is theoretically so insoluble that 1 mg/L Ba x 1.64 mg/L SO4 = 2.64 limit.

Salt	Mg/L Solubility Product
CaSO4	96,300
SrSO4	5,300
BaSO4	2.64
CaF2*	723

*The fluoride concentration is squared when calculating the solubility product. (taken from Stumm and Morgan, 1981)

Table 2. Solubility product of low solubility salts (concentrations expressed in mg/L as ions)

4.1.2. Seed crystals

Scaling begins with the formation of seed crystals, which provides the molecular scaffold to which additional molecules attach themselves to form unique three-dimensional structures. Figure 4 shows the needle-like crystals of gypsum ($CaSO_4.2H_2O$). Shown in Figure 4 are crystals in the tens of microns size range. This is intended to show the peculiar shapes of these crystals. Seed crystals that we refer to are much smaller than these, as configuration of small number of molecules. In solutions of low supersaturation devoid of seed crystals that are allowed to stand without agitation, it is possible to obtain large single crystals as the water is allowed to evaporate slowly. Conversely, in the crystallization processes for the production of crystalline products, addition of crushed crystals as seeds will accelerate the completion of crystallization. Repeated dissolution and crystallization of both inorganic and organic compounds is a powerful method for the preparation of high purity compounds.

4.1.3. Nature of solutes

Most commonly encountered scales in RO systems are calcium carbonate, calcium sulfate, strontium sulfate, barium sulfate, calcium fluoride, silica and silicates. True salts (pairs of ionizable cations and anions in water) crystallize in distinct shapes with gritty textures, whereas silica and silicates are not true salts, and appear in amorphous forms. They are dehydration polymers of silicic acid [Si(OH)4] with hydroxide forms of metals, most commonly those of aluminum, iron, magnesium and calcium [5,6], and they appear on membranes as a thin film of colorless or slightly yellow gel.

4.1.4. Interfering impurities – Antiscalant actions

The water solution matrix from which scales form has a decided effect on the solubility and the rates of crystallization of different scales. Freely moving cations and anions have to pair themselves before stacking on crystalline lattices in predetermined geometries. When the concentration of total dissolved solids (TDS) increases, the ease by which the pairing of the ions of the insoluble compound is reduced. In addition, different ions of similar charges, sizes and shapes can occupy unintended atomic positions on the surface of a growing crystal, covering up a growing surface stopping crystal growth, or in cases of partial inhibition, causing the resulting crystal to be deformed, a phenomenon called crystal modification. Effective antiscalants generally contain anions with multiple negative charges that have high affinities for the growing surfaces of seed crystals, preventing scaling and stabilizing the supersaturated condition. This mechanism of antiscalant action is referred in the literature as "threshold inhibition". The efficiency of this inhibition mechanism allows for the economic use of low dosages (< 10 mg/L) of continuously injected antiscalants into the RO feedwater.

4.1.5. Solution pH

The main effect of pH on scaling is the reversible formation of carbonate ions from bicarbonate. Calcium carbonate scaling occurs at higher pH due to the presence of higher concentrations of carbonate ions. The effect of pH can be seen in the reversible formation of CO_2 gas or

carbonate ions in natural water. Acid addition drives the equilibrium to the left (toward CO_2 formation). Caustic addition drives the equilibrium to the right (toward carbonate ion formation as shown below). A third and important phenomenon should be noted. Since CO_2 gas is easily degassed from water, its loss amounts to losing acidity, thereby increasing the alkalinity of the system, causing an increase in the carbonate ion concentration. This degassing of CO_2 in the presence of sufficient concentration of calcium can cause calcium carbonate scaling.

$$CO_2 + H_2O \rightarrow H_2CO_3$$
$$H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O$$
$$HCO_3^- + OH^- \rightarrow CO_3^{-2} + H2O$$
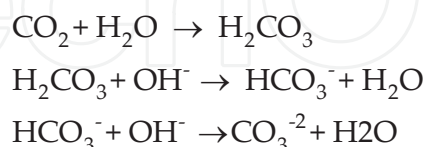
Natural waters are buffered by bicarbonate ions at pH 5.35–7.35. The pKa of the conversion of carbonic acid to bicarbonate, when titrated with alkalinity, is 6.35. At this pH, the concentration of carbonic acid equals that of bicarbonate ions. At pH=7.35, one log value above the pKa value, the ratio of molar concentration of HCO_3^-/H_2CO_3 = 10, rising to a ratio of 100 at pH=8.35. The pKa for the conversion of bicarbonate to carbonate is 10.33. When raising the pH of RO feedwater with caustic injection to help ionize the weak boric acid and silicic acid for rejection by membranes in the region of pH= 11, the use of antiscalant to control calcium carbonate scaling is needed due to increased carbonate ion concentration.

4.1.6. Temperature

Generally, higher temperatures increase the solubility of salts. In situations where higher temperatures cause degassing of acids like CO_2 and H_2S or bases like NH_3, membrane scaling chemistry may be affected.

4.2. Colloidal fouling

When fouled membrane elements are opened during autopsies for examination, more frequently than not, the foulants appear to be amorphous pastes or gels, with no crystalline shapes under the microscope. This is the result of colloidal fouling.

Colloidal particles by definition are pre-existing particles in water that are smaller than 0.1 micron in size. They are not visible to the naked eyes. They escape filtrations in RO pretreatment processes, and do not register in turbidity and Silt Density Index measurements. The latter records plugging rates while passing sample water through 0.4 micron filters. In municipal wastewater treatment processes, colloidal fouling of RO is commonly seen following microfiltration and ultrafiltration pretreatment, because fractions of smaller colloidal particles escape filtration.

An educational demonstration of colloidal particles in water can be easily done. Put perfectly clear distilled water and water from the tap in two separate clear glass beakers. Turn off all lights in the room. Shine a beam of laser light from a laser pointer through the beakers. The

beaker with tap water will show a line through the water, traced by colloidal particles. The beaker with distilled water will show no line through the water.

What characterizes the behaviors of colloidal particles is that they have huge surface areas per unit weight. Consider taking a brick of hard cheese, and cutting it in two. The cut exposes a new surface area. Cut each part into two again, gaining new surface areas. Imagine repeating this innumerable times. The particles each get smaller until they are too small to see, while the total surface area grows exponentially. Surface characteristics of colloidal particles become dominant factors in their inter-particle interactions, in which they can approach each other in very close distances. Controlled production of colloidal particles of uniform structures and coating them on prepared surfaces now constitute our newly named field, nanotechnology.

Naturally formed nano particles in water are impossible to speciate and quantitate. As foulants in RO systems, we can only hope to deal with them empirically with continuously injected antifoulants as anti-coagulants, dispersants and antideposition agents. It is assumed that by modifying the surface properties of the colloidal particles and the membrane surface, colloidal fouling can be and has been controlled in an increasing number of cases [7,8].

We consider below some main factors that affect the rates of coagulation and deposition of colloidal particles in RO systems.

4.2.1. Surface interactions

Hydrophilic, hydrophobic, ionic attraction/repulsion, hydrogen-bonding and van der Waals forces are terms that characterize complex surface interactions between particles, keeping them separated or causing them to coalesce. These forces typically increase by factors inversely proportional to the square of distances that separate them. Thus the close distances that these minute particles can approach each other greatly magnify their interactions.

4.2.2. Charge neutralization

Acidity or alkalinity (pH) changes in water can alter ionizable groups on the surfaces of particles to become more or less charged. Natural organic particles are predominantly characterized by surface ionization of carboxylic acids (pKa 4–5), ammonium groups (pKa 9) and phenols (pKa 10). Inorganic particle surface charges such as calcium carbonate, calcium phosphate, ferric and aluminum hydroxides are sensitive to changes in the pH 5–7 range. Particles in natural water at neutral pH generally carry net negative charges on their surfaces. In this state of mutual repulsion, they are stably suspended. When highly positively charged coagulants like aluminum and ferric salts, or cationic polymers are added to neutralize the surface charges, the colloidal dispersion become destabilized. Particles coagulate and flocculate, facilitating removal by filtration.

A good demonstration of charge neutralization causing coagulation is the curdling of milk by adding vinegar or lemon juice. Milk is a highly concentrated stable suspension of colloidal protein, fat and calcium phosphate, all of which are nutrients needed by the baby. When the negatively charged surfaces of the dispersed particles are protonated (H^+ added) by the added acid, the stable suspension collapses and curdles.

4.2.3. Concentration

While large sticky particles that pre-existed in the RO feedwater are retained by the first membrane element of an RO system, colloidal fouling and scaling occurs first in the last element, spreading forward, as the loss of membrane productivity also moves forward in the system. Colloidal fouling can be correlated to two factors: increased concentrations of the foulants as well as the rapid rise of concentration of total dissolved solids (TDS). The latter will be considered next as a very important factor.

4.2.4. TDS/ionic strength

The total dissolved solids (TDS) in the RO concentrate express the concentration by weight of all the dissolved salts. Collectively as a solution, the ionic strength takes into consideration the stronger effects of di and trivalent ions compared to the monovalent ions. Ionic strength greatly affects the stability of equilibrated colloidal dispersions.

As a model for understanding the colloidal fouling in RO systems, one can look at the formation of deltas at the mouth of large river systems. The Mississippi, Nile, Ganges and Yangtze rivers all have prominent delta regions. Deposits in the delta result from coagulation of colloidal particles, both organic and inorganic, when the low salinity river water suddenly meets with the high ionic strength seawater. This is equivalent to the rapid concentration of RO feedwater to high salinity in a few seconds during passage through the RO system. Coagulation of colloidal particles begins in the second and third stages of the RO system, and continues in the concentrate discharge system. It takes only a thin layer of coagulated colloidal matter to cause noticeable declines in membrane flux initially, before registering as increasing differential pressures through the membrane elements.

4.2.5. Organic coating

Colloidal particles can adsorb surface-modifying natural contaminants, or deliberately added coagulants or antifoulants that will affect their precipitation or dispersion, respectively. In pretreatment with low-pressure microfiltration and ultrafiltration membranes, coagulants can be used advantageously to form cake-layers to protect pores from plugging. Antifoulants can be found to control cake-layer fouling on RO membranes.

4.2.6. Flocculants

Large molecular weight polymers of natural or synthetic origin can gather colloidal particles, flocculating them into filterable masses, or causing membrane fouling.

4.2.7. Particle size distribution

Waters feeding RO systems contain a wide range of particle sizes. Currently, colloidal particle distributions cannot be measured by the most sensitive, commercial instruments usable in the field. Lacking instruments for process control, colloidal fouling by foulants derived from RO pretreatments is an ongoing challenge. Colloidal fouling is routinely seen in RO feedwater

with <1 NTU turbidity, and Silt Density Index of <2, which is an index derived from plugging rate of 0.45 micron filter, and even after microfiltration and ultrafiltration pretreatment [7,8].

4.3. Microbial fouling

Membrane fouling by colloids that originate from microbes in natural and wastewater invariably occurs. Dead or alive, microbes – viruses, sperm/eggs, bacteria, algae, fungi, diatoms, flagellates, amoebas, ciliates, planktons, worms, crustaceans, etc are physical particles ranging in size from 0.05 microns into the visible range. For purposes of procreation, colonization or defense, they also excrete huge volumes of biopolymers – mostly polysaccharides – into the aqueous environment. Polysaccharides are high molecular weight polymers composed of, almost exclusively, abundant carbon, hydrogen and oxygen elements from the environment, biologically synthesized by plant and animals in the water and on land. As a mechanism of membrane fouling, all this can be included in the category of colloidal fouling. However, in RO systems, microbial fouling is unique in that bacteria can grow explosively, and the biofilms they generate on the wetted surfaces of the equipment become operational and create maintenance challenges. We will touch on three aspects of microbial fouling.

4.3.1. Exponential growth

Operation of RO systems is most affected by bacteria. In natural bodies of water, bacteria exist in planktonic (moving) state or in sessile (anchored) state. It is estimated that 99% of all bacteria are anchored to surfaces and protected in a covering of polysaccharides that they create known as biofilm [9].

Bacteria that enter the RO system with the feedwater are mainly in the planktonic state. In relatively stagnant regions, and especially during system shutdowns without preservatives, they are encouraged to anchor to some surface and proliferate. When conditions are favorable, *Escherichia coli* (E. coli), a very common bacterium will undergo cell division once every twenty minutes. This means during an 8 hour shift in an RO plant, one bacterium at the start can potentially become 16,777,216 bacteria (2^{24}) at the end of one shift! Bacteria and microorganisms basically fix nutrients from the air (CO_2, O_2, N_2, H_2O) and water (sugars, amino acids, fats, nitrate, phosphate, calcium, potassium, sodium, trace minerals, water, digestible biomass, etc) to form a new biomass that physically separates from the water phase and becomes mechanical obstructions in the operation of the RO system. Even minute traces of biomass in high purity product water are objectionable to applications in microelectronics, pharmaceutical, and power production plants.

4.3.2. Biofilm and slime

In the literature, polysaccharides excreted by bacteria and planktons are referred to as exopolymers, transparent exopolymers (TEP), extracellular polymeric substances (EPS) or exopolysaccharide matrix. They form intricately defined habitat structures we call biofilm [9, 10]. Biofilms can literally be called bacterial cities, with high rises, subterranean compartments, roadways, and tunnels, occupied by communities of single or multiple species. Bacteria

respond to sensor molecules from the environment and neighbors. Some species of bacteria common in water treatment are strong producers of slime, such as *Pseudomonas aeruginosa*, *Aerobacter cloasae*, Enterobacteriaceae, iron bacteria (Gallionella) and sulfate-reducing bacteria (Desulfovibrio). Besides coating membrane surfaces with biofilm that reduces membrane permeability, free-floating slime from them block water flow-channels in the RO membrane elements, increasing differential pressures.

4.3.3. Colloidal particles and biopolymers in feedwater

Raw water from rivers, lakes, shallow wells and the sea contains an abundance of organic and inorganic colloidal particles that escape filtrations in RO pretreatment steps. Colloidal fouling of ROs are often seen even when the RO feedwater has a turbidity of <1 NTU, and Silt Density Index of <4 [7,8]. Exopolymers in seawater, especially during periods of high activities in the sea of picophytoplanktons present major challenges for designing pretreatment systems for seawater ROs (SWROs) [11,12].

4.4. Disposal of RO concentrate

For RO plant far from the sea, disposal of RO concentrates is a costly barrier to overcome [13, 14]. Conventional concentrate disposal methods involve discharge to surface water bodies or to a municipal sewer system. Deepwell injections require great depths and distances to avoid contamination of aquifers. Evaporation ponds are not practical for large plants with available land, evaporation rate and environment to permit treatment of million gallons a day discharge. All these discharge methods are increasingly being regulated and taxed for concerns with environmental impacts. Zero liquid discharge for maximum water recovery and having to only handle solid mineral recovery or waste has become an active field of research and development [15].

5. Breakthroughs on overcoming scaling and fouling barriers

Due to the limitation of time and knowledge, breakthroughs we discuss here will be limited to largely our own published data.

5.1. Advances with antiscalants and antifoulant development

A wide variety of antiscalants are now available for controlling all scaling seen in RO systems using the threshold mechanism for controlling seed crystals as described in 4.1.4 above. Full control is accomplished with continuous injection of an appropriate antiscalant at less than 10 mg/L dosage. The antiscalant and the dosage are selected based on the feedwater analysis, to control all scaling potentials for the specific water quality. For off-the-shelf small to medium-sized RO systems, or where water quality analysis is incomplete or not available, effective general-purpose antiscalants at a safe dosage can be prescribed, which will perform satisfactorily in almost every case. By carefully monitoring with input of daily sets of operating data

into personal computer programs that can generate trend-charts of normalized permeate flow rate, differential pressure and salt passage, RO system performance can be kept within 10–15% of the performance at startup [4]. With appropriate maintenance cleaning method, and timely adjustments in the choice of antiscalant and dosage if scaling appears, cleaning frequency can be kept to a minimum, and membrane service life can be extended to > 15 years.

The barrier of colloidal fouling and microbial fouling is the frontier for research and development today. We learn from every RO plant problem solved, and pilot plant study completed. The impossibility of speciating and quantitating colloidal particles within the cost constraints today blocks the first step necessary to proceed with developing control methods. Short of doing projections of colloidal fouling based on water analyses, we have made progress with addressing colloidal fouling in individual RO systems after assuring that scaling is fully controlled. A series of antifoulant chemicals have found success in empirically showing efficacy in controlling fouling by colloidal sulfur, silica, calcium phosphate, oil and grease, humic matter and exopolymers [7,8 and unpublished data]. Progress on controlling microbial fouling resulted from focus on not killing planktonic bacteria, but focusing on stripping biofilms with multistep cleaning methods.

Many fouling problems we encountered in RO plants were resolved by the elimination of some pretreatment steps, which actually contributed to colloidal fouling, and significantly to the cost of pretreatment and maintenance. Since colloidal contaminants in raw waters are impossible to remove completely, and since we do not care what goes into the RO system, as long as they pass through the system, helping them to get through the system without sticking is the guiding light for the development of continuously injected antiscalants and antifoulants. With the dual approach of simplifying existing pretreatment and maximizing the effectiveness of antiscalants and antifoulants, much value has been delivered to existing RO plants and to owners of future plants. Improvements made in RO processes and current capabilities of our antiscalants and antifoulants are summarized in Table 3, and briefly discussed below.

1. **Calcium Carbonate**: Many plants operate on using both acid and antiscalants to control calcium carbonate scaling. To overcome pH buffering capacities of natural waters, large amounts of concentrated sulfuric acid, and even hydrochloric acid are used to lower the Langelier Saturation Index of the RO concentrate. Since the new antiscalants alone can control Langelier Saturation Index of 3.3, and Stiff Davis Stability Index of >4.5 for high concentrations of total dissolved solids, we have found that acid injection simply for controlling calcium carbonate scaling can be universally eliminated.

2. **Iron and Manganese**: Soluble reduced iron and manganese in well waters quickly precipitate when exposed to oxygen in the air to form insoluble oxy-hydroxides. Traditional pretreatment involves accelerated oxidation followed by multimedia filtration or oxidation and simultaneous filtration with Greensand coated with black manganese dioxide. Manganese dioxide is consumed as oxidizing agent, and has to be periodically regenerated with chlorine or potassium permanganate. Such pretreatment method we have found to shed colloidal iron and manganese particles into the RO membranes, fouling them as well as catalyzing oxidative damages on the membranes when exposed

RO Foulant	Traditional Pretreatment	Current Capability
1. Calcium Carbonate	Acidification to lower LSI,	Antiscalant alone:
	then with antiscalant to	LSI=3.2;S&DSI=>4.5
	maximum LSI=2.5	
2. Iron, manganese	Oxidation/filtration: Greensand,	Antiscalant alone:
	manganese dioxide, catalytic ox.	Fe and Mn at > 8ppm
3. Silica: Reactive	Lime, Ion-Exchange (OH)	Antiscalant: >320ppm
Nonreactive	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	UF, MF, coagulation/	Antifoulant alone
Matter and Sulfur	clarification/ MMF.	
	slow sand and carbon filter	

slow sand and carbon filter

Table 3. Summary of improvements in pretreatment and current capabilities

to traces of oxidants carried over into the system. Using appropriate antiscalants alone, iron and manganese can be kept soluble in the RO feedwater, and safely pass through the system with the concentrate. Systems with > 8 mg/L of iron in feedwater containing the antiscalant alone, can be fed directly to the RO system through a cartridge filter without fouling events.

3.   **Silica – Reactive and Non-reactive**: Reactive silica measured by colorimetric assay using ammonium molybdate reagent is essentially silicic acid monomer [Si(OH)$_4$]. It spontaneously polymerizes by dehydration reaction to higher and higher molecular weights to form nonreactive silica, and together with hydroxides of iron, aluminum, magnesium etc, to form silicates during concentration in the RO system [5,6]. Traditional pretreatment to reduce silica concentrations involves lime softening or ion-exchange with quaternary ammonium resins in the hydroxide form to adsorb the weak silicic acid (pKa = 9.9, 11.8, 12, 12). Alternatively, appropriate antiscalants can inhibit the rate of polymerization to the extent that up to 320 mg/L of reactive silica can be tolerated in the RO concentrate without deposition of some polymeric hydrated silica and silicate gels. Feedwaters also contain nonreactive silica and silicates in the soluble colloidal forms. Silica in the non-reactive (towards molybdate reagent in colorimetric assay) form can be quantitated with emission spectroscopy as total silica, then subtracting the reactive component measured separately with colorimetric assay. Nonreactive silica and silicates of sufficient chain size,

shape and composition can stick and coat the surfaces of RO membrane causing severe drop in productivity. This type of colloidal fouling has to be controlled with antifoulant injection.

4. **Calcium, Strontium and Barium Sulfate**: Traditionally, reductions of concentrations of calcium, strontium and barium are accomplished by softening with lime or with ion-exchange resins. More efficiently, these sulfate scales can be controlled to high levels shown in the Table 2, expressed as multiples of saturation at Solubility Product Constants shown in Table 2.

5. **Calcium Fluoride**: It commonly appears in well waters as a milky suspension. It can be removed from RO feedwaters by softening with lime or ion-exchange resins, and by filtration of the larger preexisting particles. Colloidal particles of CaF_2 can be controlled with an antifoulant. Antiscalants can control very high scaling potentials of this salt.

6. **Colloidal Organic Matter and Sulfur**: Removal of preexisting particles involves coagulation/filtration with multimedia filters, slowsand filters, activated carbon towers and more recently, microfiltration and ultrafiltration, with or without assistance of coagulant addition. For clarified water feeding RO systems, we can, or try to, control colloidal fouling with antifoulants.

5.2. Tandem RO process- (Maximum water recovery at 1,000 psi pressure)

The physical limitation of operational pressure of RO systems is about 1,000 psi (68 atmospheres), since in maximizing water recovery, the total dissolved solids concentration in the RO concentrate is also maximized. The natural osmotic pressure created between the RO concentrate and the permeate across the membrane is in opposition to the mechanical pressure applied. Assuming osmotic pressure increases by a factor of 0.0115 psi/ppm of TDS [16], then we would run out of net driving pressure of a 1000 psi pump at a TDS value of about 87,000 ppm of TDS, about twice the salinity of seawater.

Maximized water recoveries in large municipal RO plants are in the region of 70–87% [17]. Addressing the barrier of concentrate disposal (4.4), and the need for minimization of concentrate volume, we demonstrated the possibilities of using a low pressure RO in tandem with a high pressure RO in continuous operation, to reach overall recoveries of brackish water in the region of 90–97% [18; 19; 20; 21; 22]. Beyond the limits of the RO system, thermal evaporation of the RO concentrates would be necessary for water recovery, solids recovery, or for use in cooling towers before final evaporation.

6. Conclusions

This brief overview of basics, barriers and breakthroughs in RO chemistry serves as an introduction for nonchemists in the practice of RO application in desalination.

For those pursuing process development, colloidal fouling of RO systems presents continued challenges, especially with the rising demands to treat municipal and industrial wastewaters

before discharge. The need in oil and gas exploration in preparing injection water and reusing produced water has become obvious. Expert attention to pilot studies becomes difficult due to the varieties of wastewater qualities and rapid changes and turn-over of raw water qualities and projects.

For large stable plants, continuous improvements are in progress with the following objectives:

a.   Increasing overall water recoveries with tandem RO process.

b.   Continuous RO system operation with no down time for cleaning.

c.   Reliable control of microbial growth.

d.   Long membrane service life of >15 years.

e.   Zero liquid discharge of waste.

f.   Economic recovery of minerals from water (water mining).

g.   Training of ever increasing number of people needed to design, build, operate and maintain RO plants.

We write this chapter hoping very much that it will be found useful for training.

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