Antiscalants for near complete recovery of water with tandem RO process

Robert Y. Ning*, Thomas L. Troyer, Roger S. Tominello

King Lee Technologies, 8949 Kenamar Drive, Bldg. 107, San Diego, CA 92121, USA
Tel. +1 (858)693-4062; Fax. +1 (858)693-4917; email: rning@kingleetech.com

ABSTRACT

Near complete recovery of water from desalination of brackish and wastewater on land using a reverse osmosis (RO) system followed in tandem by a seawater RO system is highly desirable. Such a tandem RO process is being demonstrated for overall recovery of water in the range of 96%–98%, and fractionation of dissolved salts aimed at zero liquid discharge for municipal water plants. Serious issues of RO concentrate disposal, scaling of waste disposal lines, and salinity contamination of aquifers and soils are being addressed with such an approach.

A wide range of differentiated antiscalant formulations is applied towards the task of maximizing water recovery of current municipal RO plants for maximized productivity and minimized concentrate disposal costs. Primary RO concentrates resulting from maximized recoveries are realized in the 70%–90% range. The concentrates from the primary ROs are being tested at pilot demonstration scales with seawater ROs for the highest possible recoveries of water limited by the high-pressure pumps to drive against the osmotic pressures of the resultant brine.

We are providing a summary report on the limits of controls of our antiscalants for brackish water, the overall tandem RO recoveries attained in the initial pilot demonstration plants, and laboratory data pointing to our expectation that the tandem RO process is a universally usable process to generate super-concentrates from which the principal dissolved divalent salts of Ca^{+2} and Mg^{+2} can be separated from the mono-valent Na^+ and K^+ salts with commercial utility. Such zero liquid discharge processes will represent the ultimate environmentally friendly water treatment for large municipal plants.

Keywords: Reverse osmosis; Tandem RO process; Zero liquid discharge; Concentrate minimization; Recovery maximization; Antiscalants; Antifoulants; Control limits; Salt fractionation; Brackish water RO; Seawater RO; Inland desalters

1. Introduction

Maximum water recovery and restricted concentrate disposal are two major issues faced by inland reverse osmosis plants. Advances in antiscalant and antifoulant development and application [1–3] has allowed maximum recoveries in major municipal brackish water RO plants in the range of 70%–90% [4, 5]. The high expenses of discharging the RO concentrates into the Santa Anna River Intercepter line in Southern California, or deep-well injection 22 km from the plant in El Paso, Texas [6] provides a strong motivation for developing alternate disposal methods for the concentrate aiming at zero-liquid discharge. High pH softening of the concentrate from the primary RO allows for a further high recovery in a secondary RO. This use of an RO one after another that we term tandem RO has been demonstrated to attain an overall water recovery of 95%–98% in pilot scale tests [4, 7, 8].

Critical to the success of such a tandem RO process is the control of scaling and colloidal fouling by antiscalants and antifoulants [2], and their removal in the intermediate precipitative treatment. Our continued success in on-going trials with the tandem RO process points to the universal applicability and the simplicity of such a process as a key to zero liquid discharge. In this paper, we project such a vision, and take a step in reviewing the key role played by the antiscalant and antifoulants. These chemicals at low dosages will extend the concept of tandem RO beyond brackish well waters to surface and wastewaters.

In discussing the control limits of antiscalants and antifoulants, we find it necessary to discuss the problem of saturation product values as applied to RO, crystallization rates in the nonequilibrium state during passage of brine through the ROs, and the difficulty in projecting scaling and fouling potentials. Such difficulties in accurate projections makes us very dependent on correlations with field data. The simplicity we find of not needing traditional pretreatments to control RO fouling is a huge benefit in the context of tandem RO process.

2. Antiscalant and antifoulants

Antiscalants acts as threshold inhibitors of growth of crystals (scales) from supersaturated brine. In minute concentrations, they complex with the surfaces of seed crystals preventing them to grow in the super-saturated brine. Some antiscalants also inhibit the precipitation of inorganic gels such as hydroxide/oxides of aluminum, iron, manganese and other heavy metals and silica and silicates. Certain antiscalants also inhibit the polymerization of reactive silica that result in membrane fouling by polymeric hydrated silica and silicates [3].

Antifoulants is a term that has been used for pretreatment chemicals that prevent fouling of RO membranes in general. In the context of our paper and our work, we choose to reserve this name for anticoagulant and dispersant chemicals that control colloidal fouling. Colloids are different from dissolved salts that crystallize or precipitate from solution. They are preexisting particles that range in particle sizes of between 0.1 to 0.005 microns, invisible to naked eyes but having properties of particles. These particles can pass 0.45 micron filters used in the measurement of Silt Density Index thus not detected in that measurement, and can pass microfiltration and ultrafiltration membranes. Due to the extremely large surface areas relative to its mass, when destabilized from its equilibrium state in water, colloids can coagulate and flocculate in infinite complexities of composition. In the RO when concentrations and salinity suddenly increases, affinity of destabilized colloids towards the membrane surface is increased leading to accelerated membrane fouling. Antifoulants inhibit coagulation of colloids, disperses associated particles and reduces their affinity for the membrane surfaces.

3. Saturation values of scales

To define saturation values in the context of this paper, it is necessary to state that in contrast to the applications to cooling systems and boiler waters, the saturation thresholds of sparingly soluble salts in the RO process is very different [9]. Water being concentrated during passage through the brine channels of membrane elements is in disequilibrium, and will not reach equilibrium state until long after discharge.

In the disequilibrium state, factors regulating the rate of crystallization of low solubility salts from the supersaturated brine includes concentration of ions, presence of seed crystals, intrinsic crystallization rates of each salt, common ion effects, ionic strength, temperature among other factors. No reliable, commonly accepted models for calculating scaling potentials in RO systems exist. Langelier Saturation Index (LSI) and the Stiff and Davis Stability Index modification of LSI for high salinity water

Table 1
Control limits of antiscalant and antifoulant relative to traditional ro pretreatment.

RO foulant	Traditional pretreatment	Current capability
1. Calcium carbonate	Acidification to lower LSI, then with antiscalant to maximum LSI = 2.5	Antiscalant alone: LSI=3.2;S&DSI=>4.5
2. Iron, manganese	Oxidation/filtration: Greensand, catalytic ox.	Antiscalant alone: Fe and Mn at > 8ppm
3. Silica: reactive non-reactive	Lime, ion-exchange (OH) None	Antiscalant: >280ppm 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.	Antifoulant alone

are used as approximations of calcium carbonate scaling potential in RO systems. No such conventional model exist for all the other scales and gels seen in RO systems such as calcium, strontium and barium sulfate, calcium fluoride and phosphate, iron and manganese oxide/hydroxides, aluminum hydroxide, silica and silicates. In the absence of convention, proprietary formulae are used in the various computer software from membrane and chemical suppliers with resultant variations in the projection of fouling potential for each of the scales commonly experienced in RO systems. As imperfect as such projections might be, quantitative values are needed to calculate antiscalant dosages needed to control scaling, and for the documentation in databases for correlation with actual data obtained from model test systems performed in the laboratory and data from the field. To communicate current control capabilities however, we use in Table 1 the conventional LSI and S&DSI for calcium carbonate scaling, and Solubility Product Constants for the saturation values of calcium, strontium and barium sulfate, and calcium fluoride. The nature of solubility product constants as saturation values of these salts however needs to be qualified and defined.

4. Solubility product constant

For sparingly soluble salts with solubilities of less than 0.1 mole per liter, it is an experimental fact that the product of the total molar concentrations of the ions is a constant at constant temperature. The solubility product is the ultimate value which is attained by the product of the ionic concentrations when equilibrium has been established between the solid phase of a difficultly soluble salt and the solution in low salinity waters. As salinity of the water increases, the ionic concentration, and therefore the ionic strength of the solution increases. This will, in general, lower the activity coefficients of both ions, and consequently the ionic concentrations (and therefore the solubility) must increase in order to maintain the solubility product constant. This effect, which is most marked when salts present in solution does not possess an ion in common with the sparingly soluble salt [10]. This is the reason seawater has much lower scaling potential than similar concentrations of sparingly soluble salts in low salinity well waters.

Available compilations of solubility products illustrate that measurements are not trivial, and values given by different authors for the same solubility products often differ markedly. Differences of a few orders of magnitude are not uncommon [12]. For uniformity with other workers, we use the solubility product values for the sulfate scales and calcium fluoride shown in Table 2.

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

Salt	Mg/L Solubility Product
$CaSO_4$	96,300
$SrSO_4$	5300
$BaSO_4$	2.64
CaF_2*	723

*The fluoride concentration is squared when calculating the solubility product. (Taken from reference 11; originally from Stumm and Morgan, 1981)

5. Application of antiscalant to brackish water tandem RO process

The availability thus far of ten differentiated antiscalants and four antifoulants, a broad range of scaling and fouling potentials of RO feedwaters are controlled. To maximize the recoveries of water in the primary ROs in municipal waterworks, we offer software and support in trending normalized permeate flow, differential pressure and salt passage in each major RO plant [5]. Systematic analyses of recovery-limiting foulants coupled with cleaning method developments, maximum water recoveries in the 70%–90% range are attained with minimum acceptable frequencies of cleaning even when feedwater qualities unavoidably varied. By this approach, many municipal primary RO systems in the Southwestern US have been optimized. Concentrates from these RO plants are being investigated for treatments that would allow passage through a tandem RO for another high water recovery.

The feasibility of precipitative treatments of primary RO concentrates to brine qualities suitable for feeding to a tandem RO system is being actively pursued [4, 7, 8, 13, 14]. A continuous tandem RO process without interruption of a precipitative treatment of the primary RO concentrate has been demonstrated and is being reported. Since calcium and magnesium and other multivalent cationic salts can be fractionated from the very soluble monovalent sodium and potassium salts [4, 7, 8, 13, 14], mining useful minerals from the super-concentrates from tandem RO becomes worthwhile objectives we are currently pursuing.

6. Conclusion

It appears now tandem RO process for overall water recoveries of 96%–98% for brackish water is universally practicable, limited only by the approximately 1,000 psi available in the RO system to drive against the eventual osmotic pressure generated by the super-concentrate. The limiting total dissolved solids with 1,000 psi osmotic

pressure is about 87,000 mg/L, a little more than twice that of seawater.

To attain zero liquid discharge, thermal evaporation or distillation of the water from the super-concentrate from the tandem RO process would be necessary. Preliminary studies of the feasibility of fractionating dissolved salts from the super-concentrate are in progress. Mining useful minerals from the super-concentrates generated would make the tandem RO a truly green and valuable process.

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