



Tandom reverse osmosis process for zero-liquid discharge

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Abstract

Major sources of wastewater generated on land can benefit from, and often are in need of, processes for the complete recovery of water, having only solid by-products or waste for disposal. This applies to municipal and industrial wastewater and brackish water reverse osmosis (RO) plants and agricultural irrigation. High recovery of water with RO membranes is by far the most efficient method of processing waste and brackish water. Recoveries ranging from 70 to 90% are possible, limited by precipitation of insoluble salts and coagulation of colloidal particles. If emerging intermediate precipitative treatments of the limiting foulants can become widely successful, a tandom second RO step of similar recovery rates will reach an overall water recovery of 97–99%. The remaining 1–3% of the original water volume can be addressed with evaporative concentrators. Based on our initial successes, we clearly see this tandom RO process to be of universal utility. Precipitated salts from the treatment of the primary RO concentrate are mainly divalent cations (Ca, Mg, Sr, Ba) with coagulated silica and colloidal matter. Solutes that survive the secondary RO are mainly soluble monovalent cations (Na, K). The overall tandom RO process thus constitutes a way to fractionate divalent cation salts from the monovalent cation salts. Both salt fractions may find commercial use and not be entirely wasted. We currently are actively assisting municipal RO plants in California in maximizing the percent recovery in the primary ROs, and for the moment, minimizing the volumes of raw water needed and volumes of concentrate that have to be discharged. To illustrate the necessity of dealing with the unique water chemistry of each RO plant, we present the well water analyses of three municipal systems within a 25-mile radius of Riverside, CA. In each case, due to the high cost of discharging concentrate into a brine line to the sea, close to limiting primary RO recoveries have been reached. The results of autopsies and foulant analyses performed on membranes from these three plants identify the foulants that need to be precipitatively removed before treatment with secondary RO. Further work is being considered along these lines.

Keywords: Tandom reverse osmosis; Concentrate reduction; Zero-liquid discharge; Brackish ground water; Foulant analyses

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1. Introduction

Major sources of wastewater generated on land can benefit from, and often are in need of, processes for the complete recovery of water, with only solid by-products or waste for disposal. Zero-liquid discharge of concentrates from municipal and industrial wastewater and brackish water reverse osmosis (RO) plants and treatment of agricultural irrigation run-off is considered highly desirable [1–4].

High recovery of water with RO membranes is by far the most efficient method of processing waste and brackish water. Water is the most powerful solvent on earth, and serves as the medium for biological life. Whether water is purified for the first time from natural sources or for reuse from human activities, a myriad of organic and inorganic solutes and suspended particles, including microorganisms, need to be removed. The suspended particles may be visible or invisible to the naked eye. Invisible particles smaller than 0.1 μm down to molecular sizes of about 1 nm constitute the class of colloidal particles, with huge surface areas per unit mass and complex coagulative and aggregation properties.

Since RO membranes can reject nearly all solutes and colloids with reasonably low net driving pressures, it is an ideal method for purifying water and wastewater. At high recoveries of 70–90% however, the contaminants are concentrated by factors of 3–10 times, causing membrane fouling due to coagulation of colloids from sharp rise in salinity of the brine and crystallization of salts with low solubility from the super-saturated brine.

Anticoagulants and dispersants are now available to control colloidal fouling [5]. Powerful antiscalants are used to control inorganic scaling or fouling [6]. With these agents, the recoveries in the primary ROs can be maximized. For brackish well waters, limits of recoveries usually are reached between 80–92%. For a zero-liquid discharge process, it is critical that the primary RO

recovery be at the absolute maximum. This will facilitate the precipitative step to knock down the limiting foulant, and to raise the total dissolved solids (TDS) in the water, which favors the recovery in the secondary RO. The higher the TDS (approaching that of seawater), the less tendency there is for scaling.

Our current work in the area of developing zero-liquid discharge processes is to work with inland municipal RO systems where reducing the volume of concentrate discharge is of significant value. In El Paso, Texas, we are involved in developing an alternative for disposing 3 mgd (474 m^3/h) of RO concentrate by remote deepwell injection. By a tandem RO process on the pilot scale, we have reached an overall water recovery of 97% [7].

In this paper, we describe the water and foulant chemistry of three municipal RO plants where we are currently helping to maximize water recovery as a first step in potentially developing a zero liquid discharge process.

2. Maximizing primary RO recovery

In water-starved rapidly developing area around Riverside, CA, three large desalters within 25 miles of Riverside have very different chemistry (Table 1) that limit RO water recovery. A large operating cost of these plants is the charge levied on using a common brine line for concentrate disposal to the sea. Reducing the volume of concentrate discharged by increasing RO recoveries is greatly desired. We also view these situations as opportunities to develop a zero-liquid discharge process.

Over several years of operation, RO recoveries were increased as much as possible by optimizations with a small pilot system running in parallel in the plant, and allowing a low frequency of maintenance cleaning. Fluctuations of feedwater qualities from multiple wells contributed largely to observed and tolerated degrees of process

Table 1
Typical RO feedwater analyses and current percent water recovery

	Plant A	Plant B	Plant C
Capacity (permeate flow), mgd	9 (1422 m ³ /h)	6 (948 m ³ /h)	2.5 (395 m ³ /h)
Recovery, %	86–87	80	70
Reject discharged (approximate), mgd	1.47	1.5	1.07
Feedwater analyses:			
Calcium, mg/l	190	169	330
Magnesium, mg/l	33	64	110
Sodium, mg/l	120	157	300
Potassium, mg/l	12	4	9
Barium, mg/l	0.11	0.05	0.15
Strontium, mg/l	—	—	1.6
Iron, mg/l	0.10	0.13	0.36
Aluminum, mg/l	—	—	—
Manganese, mg/l	0.02	—	0.30
Bicarbonate, mg/l	198	319	800
Sulfate, mg/l	443	297	608
Chloride, mg/l	170	197	605
Fluoride, mg/l	0.5	—	—
Nitrate, mg/l	81	80	12
Phosphate, mg/l	—	<0.1	—
Carbonate, mg/l	—	—	—
Silica, mg/l	31	45	68
Total dissolved solids, mg/l	1278	1210	2490
pH	7.2	7.8	6.0 (H ₂ SO ₄)

instability under the conditions of maximized recoveries.

3. Limiting fouling mechanisms

As part of the efforts in maximizing water recoveries, hence maximized concentration factors of the RO reject stream, we performed autopsies, foulant analyses and cleaning studies on fouled membranes from each plant. Summary results are presented below in Table 2.

It is interesting to note that the fouling mechanisms found in each case are different, even though the plants are located quite close to each other. The aquifers they draw from might be expected to be similar, but apparently appear to be not quite so due to the complexity of reactive

silica polymerization (8) and sub-surface colloids involved [9–12]. By definition, colloidal particles fall in the range of 0.1 micron (100 nm) to 1 μm in size. These particles are invisible to the naked eye, do not register in turbidity or silt density index measurements, and have tremendous surface areas per unit weight. Most microfiltration, ultrafiltration and RO membrane fouling encountered today is due to colloids. Recovery-limiting foulants in these cases are colloidal silica/silicates, with or without involvement in coagulation with bacterial slime. The colloidal fouling potentials of waters in RO systems are impossible to predict with any accuracy, even though some successes have been reached in controlling them chemically with anti-coagulants and dispersants [5,6].

Table 2
Summary of fouling pattern, foulant analyses and cleaning studies

	Plant A	Plant B	Plant C
1. Location of initial fouling	2nd stage	Entry of 1st stage	2nd stage
2. Symptom	Flux reduction	High diff. pressure and flux reduction	Flux decline
3. Appearance of foulant	Thin layer of colorless gel	Brown clots and colorless gel	Red–brown powder
4. Effective cleaners	Silica; organics	Silica; organics	None
5. Cleaning periodicity	About 12 months	About 12 months	Frequent
6. Foulant composition (washed and dried):			
Absolute % by wt:			
Carbon	4.12	20.48	7.66
Hydrogen	1.68	3.10	1.52
Nitrogen	0.39	1.66	0.53
Ash	82.06	62.23	75.14
SEM–EDX (relative % of ash atomic wt. Mg and higher):			
Silicon	91.4	41.0	34.5
Aluminum	4.4	16.0	14.8
Calcium	2.4	9.8	4.9
Magnesium	1.8	2.9	2.3
Iron	1.5	10.0	38.0
Silver		4.9	—
Potassium		4.5	2.6
Sulfur		4.0	—
Phosphorous		2.1	1.4
Sodium		1.4	1.4
Chromium		1.3	
Titanium		1.2	
Chlorine		0.3	
	101.5	99.4	100.0
7. Foulant identity	Silica gel and colloidal silicates	Colloidal silicates, silica gel; silt; clay; bacterial slime	Iron-rich bacterial slime

4. Discussion

Although surface waters like the sea, rivers and lakes are better known to cause colloidal fouling, in this paper we present three RO systems on deep-well waters that suffer colloidal fouling when water recovery is maximized. The iron-rich colloidal particles seen in Plant 3 is particularly troublesome due to the absence of good cleaning methods to recover membrane flux. It is suspected that these are goethite (ferric

oxyhydroxide)-like colloidal particles with positive surface charges (13,14) and strongly attracted to negatively charged RO membranes (15). Consideration is currently given to speciate forms of iron found in these wells, and to pilot pretreatment methods that might remove non-ionic iron in well waters.

In the context of zero liquid discharge, the presence of colloidal foulants in the primary RO reject is not expected to be a problem for preci-

pitative treatments prior to feeding a tandem secondary RO for a repeated high recovery rate of water. Inorganic colloids are formed as intermediates during the precipitation of calcium and magnesium salts. They will adsorb and coagulate with the silica, silicate [7] and organic colloids and remove them from the primary RO reject.

5. Conclusions

Tandem RO process for maximum water recovery is highly promising as a universally applicable process. Detailed process conditions need to be optimized on a site-by-site basis. Maximum recovery in the primary RO is important for the overall success of the tandem RO process. Colloidal fouling is the limiting factor for primary RO recovery even with deep well waters in the three cases studied.

We expect that the colloidal fouling that limits the recoveries in the primary RO steps can be removed by precipitative treatments [7] and will not hinder recoveries in the secondary RO.

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