

Minimizing Liquid Waste Discharge from Municipal Reverse Osmosis Plants

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ABSTRACT

High recovery of water with RO membranes is by far the most efficient method of processing waste and brackish water. If emerging successes in the intermediate precipitative treatment of the limiting foulants can become widely successful, a tandem second RO step of similar recovery rates will already reach an overall water recovery of 97-99%. The remaining 1-3% of the original water volume can be addressed with evaporative concentrators. Here we present the well water analyses of three municipal systems within 25 miles radius of Riverside, CA. In each case, due to the 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 a secondary RO.

KEYWORDS: Tandem reverse osmosis; concentrate reduction; zero liquid discharge; brackish ground water; foulant analyses.

INTRODUCTION

Major sources of wastewater generated on land can benefit from, and often are needy of processes for the complete recovery of water, and having only solid by-product 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 (Ahmed, 2003; Mackey et al, 2005; Mickley, 2006a and b).

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 micrometer down to molecular sizes of about 1 nanometer constitute the class of colloidal particles, with huge surface areas per unit mass and complex coagulative and aggregation properties.

Since reverse osmosis 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 (Ning et al, 2005). Powerful antiscalants are used to control inorganic scaling or fouling (Ning, 2003). 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 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 favours 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 m³/hr) of RO concentrate by remote deepwell injection. By a tandem RO process (Primary RO → Concentrate Foulant Reduction Treatment → Secondary RO for treated Concentrate from Primary RO) on the pilot scale, we have reached an overall water recovery of 97% (Ning et al, 2006).

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.

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 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 instability under the conditions of maximized recoveries.

Table 1: Typical RO Feedwater Analyses and Current % Water Recovery.

	Plant A	Plant B	Plant C
Capacity (permeate flow)	9 mgd (1422 m ³ /hr)	6 mgd (948 m ³ /hr)	2.5 mgd(395)
Recovery	86-87 %	80%	70%
Reject Discharged (approx.)	1.47 mgd	1.50 mgd	1.07 mgd
Feedwater Analyses:			
Calcium	190 mg/l	169 mg/l	330 mg/l
Magnesium	33	64	110
Sodium	120	157	300
Potassium	12	4	9
Barium	0.11	0.05	0.15
Strontium	-	-	1.6
Iron	0.10	0.13	0.36
Aluminum	-	-	-
Manganese	0.02	-	0.30
Bicarbonate	198	319	800
Sulfate	443	297	608
Chloride	170	197	605
Fluoride	0.5	-	-
Nitrate	81	80	12
Phosphate	-	<0.1	-
Carbonate	-	-	-
Silica	31	45	68
Total Dissolved Solids	1278	1210	2490
pH	7.2	7.8	6.0 (H ₂ SO ₄)

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.

Table 2: Summary of Fouling Pattern, Foulant Analyses and Cleaning Studies.

	Plant A	Plant B	Plant C
1. Location of initial fouling	-2 nd Stage	-Entry of 1st Stage	-2 nd Stage
2. Symptom	-flux reduction and flux reduction	-high diff. Pressure	-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	<u>1.4</u>
Chromium		1.3	<u>100.0 %</u>
Titanium		1.2	
Chlorine		<u>0.3</u>	
	<u>101.5 %</u>	<u>99.4 %</u>	
7. Foulant Identity:	-Silica gel and colloidal silicates	-Colloidal silicates, silica gel; silt; bacterial slime	-iron-rich clay; bacterial slime

Summary data in Table 2 provide the basis for our conclusions that water recoveries and maximum reduction of concentrate waste in Plant A is limited by fouling by silica gel and colloidal silicates; in Plant B by silica gel, colloidal silicates, silt, clay and bacterial slime; in Plant C by iron rich bacterial slime, apparently resulting from the coagulation of ferric oxyhydroxides with microbial debris. The locations of initial fouling were determined by trend charts of normalized permeate flow and differential pressures of each stage. The types of foulants identified here are quite common among hundreds of RO membrane autopsies we have performed.

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 (Ning, 2002) and sub-surface colloids involved

(Kanti and Khilar, 2006; Ranville et al, 2005; McCarthy and McKay, 2004; McCarthy and Zachara, 1989). By definition, colloidal particles fall in the range of 0.1 micron (100 nanometers) to 1 nanometer in size. These particles are invisible to naked eyes, do not register in turbidity or Silt Density Index measurements, and have tremendous surface areas per unit weight. Most microfiltration, ultrafiltration and RO membrane foulings encountered today are 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 (Ning et al, 2005; Ning, 2003).

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 (Rakovan et al, 1999; Guyodo et al, 2003) and strongly attracted to negatively charged RO membranes (Shroll and Straatsma, 2003). 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, presence of colloidal foulants in the primary RO reject is not expected to be a problem for precipitative treatments prior to feeding a tandom 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 (Ning et al, 2006) and organic colloids and remove them from the primary RO reject.

CONCLUSIONS

Tandom 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 tandom 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 (Ning et al, 2006) and will not hinder recoveries in the secondary RO.

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