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Crystallization of salts from super-concentrate produced by tandem RO process

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ABSTRACT

We continue to address the challenge of improving concentrate disposal for the large 15 mgd (2370 m^3/h) inland reverse osmosis (RO) plant in El Paso, Texas. For the first time on a pilot scale, the feasibility of using two RO systems in tandem and using appropriate antiscalants and pH control, continuous production of permeate to limiting osmotic pressure of about 1000 psi (69 Bars) is possible [1,2,12]. Recovery is simply limited by the highest pump pressure available to overcome the resulting osmotic pressure [2]. Tandem RO without interstage treatment is being demonstrated. We envision that such a continuously operated tandem RO process can recover all the water possible to be produced from brackish ground waters at the highest possible pump pressures. At the maximum system pressure of 1000 psi, the highest total dissolved solids attainable in the concentrate are about 8–9% by weight.

Anticipating the universal application of the continuous tandem RO process to generate super RO concentrates, an alternate path is now open for fractional crystallization of salts before thermal evaporation of water. Pursuing the development of an economical zero-liquid-discharge process applicable to inland municipal water treatment plants, we wish to explore the feasibility of fractionating the less soluble divalent calcium and magnesium salts from the monovalent sodium and potassium salts. In relatively large amounts, even in mixtures, these fractionated salts may have economic values such as in soil and dust control and for softening and deicing applications. Further more, 8–9% brine softened by the removal of multivalent salts and silica may have utility in cooling towers while being thermally concentrated for the ultimate recovery of the soluble sodium and potassium salts. In this paper, we present our initial investigation into a super-concentrate depleted of bicarbonates due to acidification needed for silica control.

The concentrate at maximum recovery with a secondary RO in tandem in the demonstration plant was treated for calcium sulfate, magnesium, iron and silica precipitation. This paper describes the laboratory conditions used and observations made on the use of lime in preparation for scale-up.

Keywords: Tandem RO; Super-concentrate; Crystallization; Calcium sulfate; Silica precipitation; Zero-liquid-discharge; Salt fractionation; Divalent salts; Monovalent salts

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1. Introduction

In recent studies [1–3,12], it appears that tandem RO can concentrate brackish water to the limit of about 1000 psi osmotic pressure continuously with just chemical control. An alternate path is opened for the generation of RO super-concentrates of about 8–9% by weight of dissolved salts that can be fractionated by selective crystallizations of the less soluble salts of multivalent cationic salts of Ca, Mg, Sr and Ba from the more soluble monovalent cationic salts of Na and K. Furthermore, softened concentrates can conceivably be used in corrosion-resistant cooling towers for the dual purpose of cooling with the high heat of evaporation of water while simultaneously increasing the concentrations of Na and K salts for crystallization and final distillation of water for an overall zero liquid discharge (ZLD) process. We wish to focus on developing methods of selective crystallization of salts from super-concentrates resulting from tandem-RO process, using a concentrate derived from a demonstration plant in El Paso, Texas.

The 15 mgd (2370 m^3/h) municipal reverse osmosis (RO) plant in El Paso, Texas represents several of the many challenges encountered in the disposal of RO concentrate in an inland location. Current permit for the disposal by deep well injection limits the total dissolved solids (TDS) in the brine to 10,000 mg/L. When TDS of blended well waters rise above 2000 mg/L, water recovery is curtailed. When blending down the TDS of the concentrate with fresh well water becomes necessary, it drives up the cost of sending a large volume of the concentrate to a long distance for discharge.

An effort has been on the way to develop an alternate method of concentrate discharge, with a solar drying pond, or even a zero liquid disharge process with thermal distillation. We have reported [1] on the pilot-scale demonstration of an overall recovery of 97% of water by operating the primary RO at 85–90% recovery, followed by lime-softening of the concentrate then a second RO in tandem for another high recovery. The recovery-limiting foulant in the primary RO was shown to be silica, and lime-softening greatly reduced silica concentration. To avoid the problems associated with primary RO concentrate treatment for the reduction of silica by lime softening and fouling of the secondary RO due to colloidal particles generated by the precipitative treatment, we succeeded in controlling silica polymerization by acidification of the primary RO concentrate received from the main plant. This eliminates the lime softening step between the primary and the secondary RO. We then showed the feasibility of a continuous permeate production using a secondary RO with seawater RO element in tandem with the plant RO, to an overall recovery of greater than 96%, limited only by the secondary RO feed pump pressure to overcome the osmotic back pressure [2]. The feedwater to the secondary RO with seawater RO element is the concentrate from the main brackish water RO plant collected in batches.

To further reduce the volume of the 8–9% by weight RO super-concentrate, we see the possibility of precipitating the insoluble salts of calcium and magnesium and other multivalent metals along with polymerized silica and silicates. This will leave a softened brine with less scaling potential in thermal evaporation of water. The ultimate fractionation of useful calcium and magnesium salts for soil and dust control and the soluble sodium and potassium salts with commercial value in sequential steps of a process is a worthwhile objective.

In this paper, we describe the laboratory conditions and observations made in the precipitation of insoluble salts, silica and silicates, in preparation for scale-up.

2. Precipitation of insoluble salts

Well waters in contact with minerals over a long time are usually saturated with respect to minerals of low solubility they are in contact with. Such low solubility minerals encountered in reverse osmosis chemistry are predominantly carbonates, oxyhydroxides and silicates of calcium, magnesium, barium, strontium, iron, aluminum and manganese, and sulfates of calcium, barium and strontium. The RO concentrates are invariably super-concentrated with respect to one or more of the mentioned salts, and are kept in solution by inhibition by other ions or by scale inhibitors. A broad statement can be made that all salts of sodium and potassium are soluble as well as chlorides and nitrates of multivalent ions. Crystallization of these soluble salts requires very high concentrations.

Reduction of multivalent ion concentrations in drinking water by the addition of lime followed by filtration constitutes the lime softening process used by some municipalities. Precipitation of highly insoluble fluorides, phosphates and heavy metals are industrial methods of removing trace contaminants [4]. Softening by precipitation of highly concentrated Colorado River water has been studied in the laboratory [5,6]. Since the Colorado River water has sufficient hardness and bicarbonate alkalinity, sodium hydroxide was used as in situ lime to cause precipitation of calcium carbonate and the removal of antiscalant from the solution. The feasibility of feeding the lime-softened primary RO concentrates to a secondary RO for another high recovery of water have been shown on laboratory scale, reaching overall recoveries by two ROs in tandem of 95–97% [1,5,6]. In the three studies cited, precipitative softening allowed for the operation of a secondary RO which in each case water recovery was still limited by scaling. In the current study, by a combination of antiscalants and pH control, scaling has been fully controlled, allowing the secondary seawater RO to reach the maximum osmotic back-pressure. The recovery in the secondary RO is limited only by the pressure available from the high pressure pump.

The purpose of the precipitation of insoluble salts from the super-concentrate from the secondary RO is to test the feasibility of [1] softening the brine to facilitate thermal evaporation of water, and [2] fractionating salts for possible economic utility.

3. Precipitative treatment and observations

One [1] gallon sample of super-concentrate from the secondary seawater RO was prepared and sent on February 26, 2008 from the El Paso Water Utility pilot plant with the following process description to laboratory in San Diego for precipitative studies. The antiscalant used in the primary plant RO is Pretreat Plus-Y2K and in the secondary RO is Pretreat Plus-0400.

EPWU RO → Concentrate → Acidification+antiscalant
→ SWRO → Super-concentrate

(PTP-Y2k , 3.75ppm) ($\mathrm{H2SO_4}$ to pH = 3–3.5; PTP-0400
Conc. 4 ppm) Overall recov. = 96% 82% recovery
80% recovery

Sample has remained clear with no visible precipitate after 2 weeks of shipping by courier and standing. The following measurements were taken:

Turbidity (Hach) = 5 NTU
Conductivity (Myron Meter, 1:100 dilution) = 100,000 microS/cm
pH = 4.5.

Antiscalents are threshold inhibitors that bind to seed crystals thus keeping super-saturated salts from crystallizing. To test the deactivation of the antiscalants, both of which are highly active towards calcium carbonate scaling, we tested the removal of antiscalants from solution by contact with solid calcium carbonate. Addition of $CaCO_3$ powder and filtration through a bed of $CaCO_3$ did not induce crystallization of scales after 3 days.

Using our optimized condition with $Ca(OH)_2$ powder [1], the following experiment was conducted: To 1.00 L of the super-concentrate in a graduated beaker equipped with magnetic stirrer, 3.3 g of $Ca(OH)_2$ powder (USP grade from EM Chemicals) was added in portions while monitoring the pH with a pH meter and stirring, to reach pH 11.0 from the initial pH = 4.5. After 5 min at pH = 11.0, stirring was stopped to let the white precipitates settle. The following are the settling rates and pH change:

Time	Settled volume	pH
Start	0 mL	11.0
15 min	210 mL	10.9
30 min	350 mL	10.9
60 min	460 mL	10.9
90 min	580 mL	10.9
2.5 days	690 mL	10.9

After 1 h while the solids were settling, the clear supernatant began to be filtered through a 1.2 µm fiber glass filter (4.7 cm dia.) into a filter flask equipped with vacuum from a water aspirator. Filtrate measuring 250 mL was sent for analyses by a certified laboratory along with the untreated super-concentrate for comparison (results in Table 1). An additional 400 mL of the filtrate was retained.

After further settling over the weekend (2.5 days), the settled solid was washed with RO permeate water three times by decantation, then collected in the 1.2 µm 4.7 cm diameter fiber glass filter. The solid cake was washed with RO permeate water and sucked dry to a consistency of cream cheese. It was transferred to a glass dish and dried overnight in an oven at 105°C. The dried white solid weighed 9.4 g. The elemental composition was obtained by SEM-EDX. The results are given in Table 2.

Total dissolved solids in the liquids-treated and untreated super-concentrate, from the drying of 10.0 mL aliquots of the samples were collected, and their weights in duplicate are recorded in Table 3.

4. Results

The elemental composition of the precipitated solids from the super-concentrate is consistent with mostly $CaSO_4$, with some MgO, $CaCO_3$ and iron-magnesium silicate. Despite the complexity of the mixture and the fact that hydrated silica and silicates can be gelatinous, the insoluble solids precipitated quickly, completely and settled easily. This suggests that the separation of solids from the liquid will not be a problem for scale-up. Reactive silica in the concentrate is rapidly reduced in the concentrate by 97% shows that polymerization [7] at pH 11 in the presence of magnesium and iron is rapid. Reactive silica spontaneously polymerizes with itself and with magnesium and iron hydroxides to form silica and silicate polymers respectively [7].

The clarity of the untreated super-concentrate over several weeks and the estimated osmotic pressure of 738

Table 1
Water analysis of super-concentrate before and after treatment with lime.

Analyte	Untreated super-concentrate		Treated super-concentrate		Method
	mg/L	mmoles	mg/L	mmoles	
Bicarbonate	2.00	0.033	<1.00	–	SM2320B
Carbonate	<1.0	–	110	1.83	SM2320B
Hydroxide	<1.0	–	416	24.5	SM2320B
Chloride	30,900	870	31,000	873	EPA300.0
Fluoride	11.6	0.61	0.30	0.02	EPA300.0
Silica (reactive)	120	2.00 (SiO_2)	4.00	0.07	SM4500SiD
Total Dissolved Solid	64,000	–	55,400	–	SM2540C
Sulfate	8,450	87.9	3,500	36.4	EPA300.0
Barium	0.64		0.57		SM3120B
Calcium	3,070	76.6	750	18.7	SM3120B
Magnesium	535	22.0	0.89	0.04	SM3120B
Silica (Total)	165	2.75 (SiO_2)	2.01	0.03	SM3120B
Strontium	64.6	0.74	40.4	0.46	SM3120B

Table 2
Elemental composition of solids precipitated by lime from super-concentrate (Scanning electron microscope-energy dispersive X-ray analysis).

C = 18.1%
O = 47.6
Na = <0.2
Mg = 6.2
Al = <0.1
Si = 3.3
P = <0.3
S = 9.9
Ca = 13.8
Fe = 0.5
K = <0.2
100%

psi shows that higher recovery can be obtained with the SWRO if a higher pressure pump is available. Further, the antiscalants and pH in SWRO has controlled all scaling and silica fouling.

Lime softening at pH=11.0 with quick lime nearly completely removed silica and magnesium along with considerable calcium sulfate. Calcium at 750 mg/L compared with the initial 3070 mg/L (76% reduction) remains as the major multivalent cation left in the treated brine, while magnesium at 0.89 mg/L reduced from 535 mg/L is essentially completely removed.

The salt residues from the gravimetric determination of total dissolved solids of the untreated and treated super-concentrate were collected for examination and estimation of osmotic pressures by assuming 0.0115 psi/mg/L [11]. Both salt residues are colorless, free-flowing and not hygroscopic on storage for several months. The estimated osmotic pressures for the untreated and treated super-concentrates of 738 psi and 661 psi respectively show that with a higher pressure SWRO system capable of attaining 80,000 mg/L TDS in the concentrate significantly more water can be recovered.

5. Discussions

Crystallization of calcium sulfate from aqueous solutions has been studied for many years [8–10]. Pure

Table 3
Dried dissolved solids from treated and untreated super-concentrate liquids
Procedure: Clear liquid samples (10.0 mL) in duplicate were evaporated to dryness at 180°C in tared porcelain dishes to give the following:

	Untreated super-concentrate	Treated super-concentrate
	1. 0.0 mL → 0.644 g	10.0 mL → 0.554 g
	2. 10.0 mL → 0.640 g	10.0 mL → 0.597 g
Average TDS :	64,200 mg/L	57,500 mg/L
Osmotic pressures (0.0115psi/mg/L) =	738 psi	661 psi

calcium sulfate with a theoretical molar solubility product constant of 7.10×10^{-5} is relatively soluble among the insoluble salts compared to calcium carbonate of 4.96×10^{-9}. The approximately 68×10^{-5} molar ion product of calcium and sulfate left in the treated super-concentrate is consistent with the solubilization effect of other dissolved salts. Since the feedwater to the secondary RO has been acidified to pH 3.0–3.5, and carbon dioxide gas has spontaneously degassed, the super-concentrate itself contains little bicarbonate ions. The resulting carbonate alkalinity in the treated brine likely came from the reagent lime.

To minimize sulfate scaling potential in subsequent thermal evaporation of water, additional treatment will be considered for further reduction of calcium, barium and strontium ion concentrations. Also planned during process scale-up, is the optimization of the antiscalant and sulfuric acid dosages, and continuous operation of a seawater RO with maximum feed-pressures.

This paper has focused on the technical aspects of the process, and directions that need exploration. Eventually, cost-effectiveness of various process alternatives need to be assessed.

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