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Seawater RO treatment of RO concentrate to extreme silica concentrations

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ABSTRACT

Severe restrictions exist in the disposal of the concentrate from the 15 mgd (2370 m^3/h) reverse osmosis (RO) plant in El Paso, Texas (i.e., 15 mgd blended to 27.5 mgd). The current permit for the disposal by deep well injection limits the total dissolved solids in the brine to 10,000 mg/l. This limits water recovery in the plant and drives up the cost of sending a large volume of the concentrate a long distance for discharge. We have continued to work on developing a concentrate treatment process aimed at zero liquid discharge or a greatly reduced concentrate volume suitable for evaporation ponds. This is an interim report documenting an exciting demonstration of the feasibility of using a seawater RO system and synergistic antiscalant and low pH inhibition of reactive silica polymerization to concentrate the primary brackish water RO concentrate to total silica concentrations exceeding 1000 mg/l. This approach makes possible the use of tandem brackish RO followed immediately by a seawater RO (SWRO) to achieve an overall water recovery of greater than 96%, limited only by the highest pump pressures to overcome the resulting osmotic pressures. Pilot plant data using a single SWRO membrane and 700–740 psi feed pressure concentrating the brackish RO concentrate in a batch recirculation mode is presented. Recoveries of water in the 84–96% range were performed repeatedly with no apparent fouling of the membrane and no precipitation in the super-concentrate. The flux reduction curves in each case are consistent with gradual reduction of net driving pump pressure due to the rise in osmotic pressure that needs to be overcome. The reactive and total silica concentration profiles provide insight on the effects on membrane operation during buildup of reactive silica concentration with or without the increasing amounts of colloidal polymeric hydrated silica expected from the spontaneous polymerization of the reactive silicic acid monomer.

Keywords: RO Concentrate; High silica; Seawater RO; Tandem RO; Zero liquid discharge; Concentrate disposal; Evaporation pond; Deep-well injection

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1. Introduction

The location of a 15 mgd (2370 m^3/h) capacity RO plant in a land-locked highly populated region makes the design of an acceptable concentrate disposal process a challenging task. Variable salinity in well waters reaching above 1500 mg/l and a cap of 10,000 mg/l allowed for deep-well injection of the concentrate restricts the degree of salinity concentration, hence limiting the maximum water recovery rate of the plant. Need for water conservation and the high cost of pumping the concentrate waste to a distant injection well provide strong incentives for developing an alternate, and more economic method of treating the RO reject [1].

We have reported on the pilot-scale demonstration of an overall recovery of 97% of water by operating the primary

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RO at 85–90% recovery, followed by lime-softening of the concentrate then a second RO in tandem for another high recovery [1]. The recovery-limiting foulant in the primary RO was shown to be silica, and lime-softening greatly reduced the silica concentration.

Spontaneous polymerization of silicic acid in water, generally referred to as molybdate-reactive silica, form larger and larger polymeric non-reactive silica species in water in colloidal forms [2–8]. Silica fouling is a major challenge to the operation and maintenance of brackish water ROs [9,10]. Laboratory studies discerned parameters that affect the severity of silica fouling [5,6,8,11,12]. Antiscalants and antifoulants are introduced aimed at inhibiting the rate of polymerization of reactive silica or at the dispersion of colloidal silica [10,13,14].

The objective of this research was to reduce concentrate volume using acidification to reduce silica polymerization rate as an alternative to the lime-softening approach reported earlier. In the laboratory, it can be shown that silicic acid polymerization is severely retarded by acidic pHs [15] as suggested in the literature [4,7], and that pH control can be synergistic with antiscalant action [15]. In this paper, we report our initial successes using this approach by which total silica concentrations exceeding 1000 mg/l using a seawater RO (SWRO) in tandem with the primary brackish water RO. The injection of acid into the SWRO feed along with an antiscalant achieved an overall recovery of 96% as a continuous process using a tandem RO. In the El Paso water, the limiting factor for higher recovery is projected to be the anticipated 1000 psi osmotic pressure that occurs at a concentrate total dissolved solids (TDS) of about 9% by weight at about 98% recovery.

The efficiency of a tandem RO process that can concentrate the total TDS in brackish waters to the maximum 1000 psi of osmotic pressure in the concentrate is highly desirable. Continuous operation without stoppage to treat the intermediate concentrate of the primary RO eliminates the time given to super-saturated brine to deposit foulants. Rapid concentration of dissolved salts improves the conditions in which the fractionation of the less soluble multivalent salts of calcium, magnesium, barium and strontium can be optimized, leaving the more soluble monovalent sodium and potassium behind for further concentration and recovery.

We report the initial successes in demonstrating that a continuous tandem RO process can be designed to reach an overall water recovery of 96% (or higher with a higher pressure pump), total silica concentration exceeding 1000 mg/l and TDS at least double the seawater range. The demonstration scale system is currently being modified for longer periods of continuous operation, and minimized antiscalant and acid dosages. Data on the fractionation of salts from the super-concentrate will be reported elsewhere.

2. El Paso RO plant concentrate

The Kay Bailey Hutchison (KBH) Desalination plant takes well water from the Hueco Bolson aquifer and filters it through a sand strainer and 5 micron cartridge filter before the RO plant. An antiscalant (Pretreat Plus-Y2K) with silica polymerization inhibitor activity is injected at a 4 ppm dosage. Five membrane banks with the capacity of producing 3 mgd (474 m^3/h) each of permeate give a total capacity of 15 mgd (2370 m^3/h) of permeate and 3 mgd (474 m^3/h) of concentrate at a recovery rate of 82%. The typical composition of the blended well water entering the plant and the concentrate are given in Table 1. The concentrate is pumped more than 20 miles across

Table 1
Typical composition of blended well water entering the plant and composition of plant reject water at 82% RO recovery

Analytes	Blended well water (5-day average, 8/2007)	RO plant reject water (2-mon average, 1–2/2008)
Calcium (mg/l)	107.5	540.7
Magnesium (mg/l)	32.5	142.2
Sodium (mg/l)	585.2	2520.5
Potassium (mg/l)	16.4	69.5
Barium (mg/l)	0.080	---
Strontium (mg/l)	2.81	---
Iron (mg/l)	0.068	0.096
Manganese (mg/l)	0.031	---
Bicarbonate (mg/l)	82.4	402.2
Sulfate (mg/l)	148.3	1104.3
Chloride (mg/l)	832.4	4665.2
Total dissolved solids (mg/l)	2222	10150.0
pH	7.8	8.0

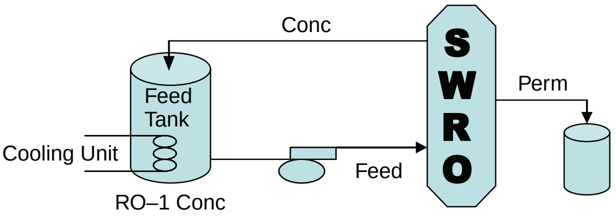

Fig. 1. Seawater RO pilot system schematic.

the desert to three deep well injection sites, where it is then distributed downward into a fractured rock formation of low quality water more than 3,500 feet (1070 m) below the surface. The discharge permit currently limits the maximum TDS of the concentrate to 10,000 mg/l, a very difficult and expensive situation for the plant. During the piloting period, the primary RO recovery of 86–90% was attained [1].

3. Pilot plant with tandem seawater RO

For the tandem SWRO pilot plant, the main plant RO concentrate at 82% recovery was received in a 30 gal (114 l) holding tank. It was acidified with sulfuric acid to pH 3–5 in the tank along with the addition of a second antiscalant (Pretreat Plus-0400) for controlling extremely high sulfate scaling potentials. Thus treated, a single SWRO element (Crane EPRO 150 model) with a 1000 psi high pressure pump set up in a recirculation mode (see Fig. 1) was used to concentrate the primary RO concentrate in a batch operation mode.

Following are representative data from five runs performed under different conditions on different days. In each case, the concentration process was continued to near the limit of the maximum net-driving pressure that could be developed by the high pressure feedwater pump. The super-concentrates remained clear, and the membrane did not appear to foul. Initial fluxes remained the same at the start of each run with just a simple rinse out with permeate water.

3.1. Run 1: (February 22, 2008 in duplicate)

3.1.1. Procedure

Started with 15 gal of plant RO concentrate, to which 0.3 ml of Pretreat Plus-0400 antiscalant was added, and concentrated sulfuric acid was added to lower the pH to 3.7–4.0. The concentrate was further concentrated with about 93% recovery of permeate (14 gal) using a 700 psi pump pressure over about 42 min. The permeate flowrate vs concentrate conductivity over time are plotted in Graph Run 1 (see Fig. 2).

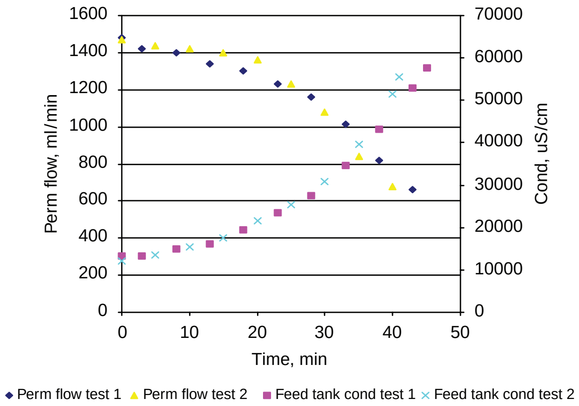

Fig. 2. Graph from Run 1.

3.1.2. Observations

No turbidity or precipitation was visible in the resulting super-concentrate. The absence of fouling of the membrane was indicated by two facts. One, the fall-off of the permeate flowrate was smooth coinciding with the gradual increase in the osmotic pressure exerted by the concentrate against the 700 psi pressure of the concentrating pump. Secondly, to refresh membrane for another run, brief flushing with the collected permeate fully restored the initial membrane flux. The conductivity of the collected permeate after stirring to mix were 203 and 263 μS/cm for the replicate runs. The corresponding super-concentrate conductivities were 56,200 and 60,800 respectively, representing average salt passage of about 0.4%.

3.2. Run 2: (February 26, 2008)

3.2.1. Procedure

Repeating the same conditions of Run 1 above, the run time was extended to 73 min. Starting volume of the plant RO concentrate was 20 gal. The permeate flowrate and concentrate conductivity over time are plotted in Graph Run 2 (see Fig. 3).

3.2.2. Observations

Again the super-concentrate showed no visible turbidity or precipitation. A total of 19.35 gal of permeate produced from 20 gal of plant RO (primary RO) concentrate represents 96.8 % recovery in the secondary seawater RO. The final mixed permeate had a conductivity of 450 μS/cm, and the concentrate 71,900 μS/cm. The average salt passage in this run is 0.6%.This super-concentrate sample was sent for a laboratory study on fractionation of dissolved salts to be reported elsewhere.

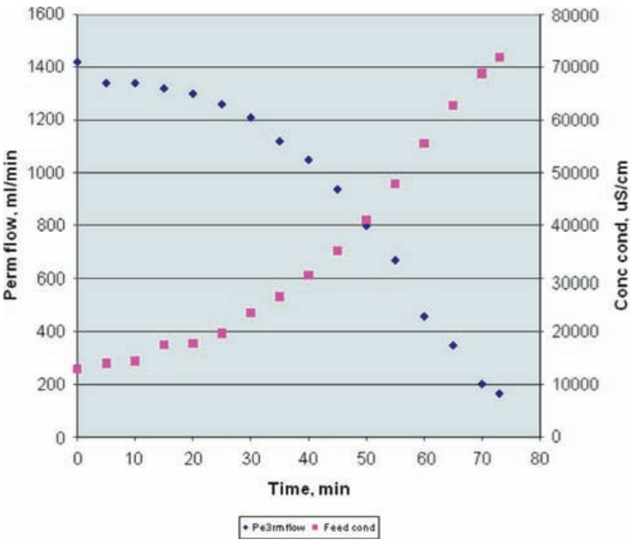

Fig. 3. Graph from Run 2.

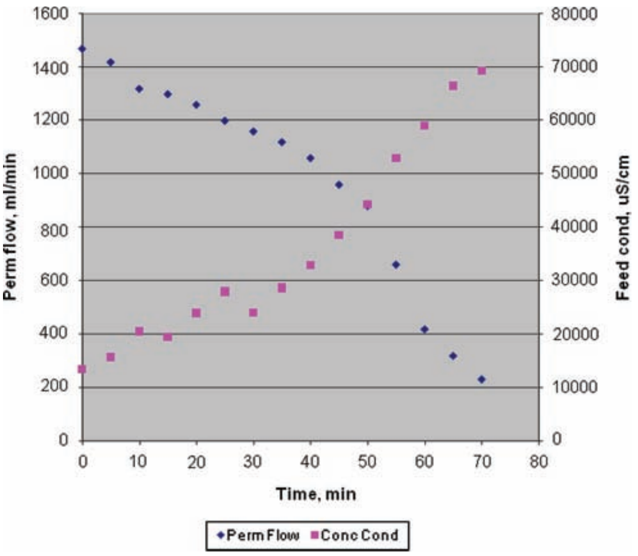

Fig. 4. Graph from Run 3.

3.3. Run 3: (March 20, 2008)

3.3.1. Procedure

The run started with 10 gal of plant RO concentrate, and 1.0 ml of Pretreat Plus-0400, followed by two 5-gal increments of plant RO concentrate at 10 min and 25 min time points, each time adjusting to pH 3.7–4.2 with concentrated sulfuric acid. The permeate flowrate at 700 psi and concentrate conductivity over 70 min are plotted in Graph Run 3 (see Fig. 4).

3.3.2. Observations

Again the super-concentrate showed no visible turbidity or precipitation, and the membrane showed no evidence of fouling by silica. A simple flushing of the system with RO permeate water cleaned the membrane which retained the original productivity (840 ml/min at 300 psi). From the initial 20 gal of plant RO concentrate, the final mixed permeate volume was 18.05 gal (500 µS/cm) and the final concentrate volume was 1.34 gal (71,500 µS/cm). This represents an apparent recovery of 93% and average salt rejection of 99.3%. Reactive silica (by Hach molybdate assay) in the super-concentrate was measured in triplicate as 870, 790 and 810 mg/l.

3.4. Run 4: (March 31, 2008)

3.4.1. Procedure

The run started with 10 gal of plant RO concentrate, and 1 ml of Pretreat Plus-0400, followed by three 5 gal increments of plant RO concentrate at 7, 17 and 27 min time points, each time adjusting to pH 3.1–3.3 range with concentrated sulfuric acid. The permeate flowrate at 700 psi and concentrate conductivity over 102 min showed similar gradual fall off of permeate flowrate of 1350 ml/min to 80 ml/min, while the concentrate conductivity increased from 13,810 to 82,600 µS/cm.

3.4.2. Observations

Again the super-concentrate showed no visible turbidity or precipitation, and the membrane showed no evidence of fouling by silica. A simple flushing of the system with RO permeate water cleaned the membrane which retained the original productivity (840 ml/min at 300 psi). From the initial 25 gal of plant RO concentrate, the final mixed permeate volume was 23.52 gal and final concentrate volume was 1.27 gal (82,600 µS/cm). This represents an apparent recovery of 95%. Reactive silica profile (by Hach molybdate assay) in the concentrate was measured as 110 and 115 mg/l at start, 340 and 390 mg/l at 52 min, and 880 and 980 mg/l at 92 min.

3.5. Run 5: (April 9, 2008)

3.5.1. Procedure

The run started with 30 gal of plant RO concentrate, and 0.3 ml of Pretreat Plus-0400, adjusting to pH 3.65 with concentrated sulfuric acid. The permeate flowrate at 700 psi (accidentally increasing to 740 psi after 70 min), and concentrate conductivity over 120 min showed similar gradual fall off of permeate flowrate of 1360 ml/min to 68 ml/min, while the concentrate conductivity increased from 15,740 to 86,100 µS/cm. The permeate flowrate and concentrate conductivity over 120 min are plotted in Graph Run 5. (see Fig. 5)

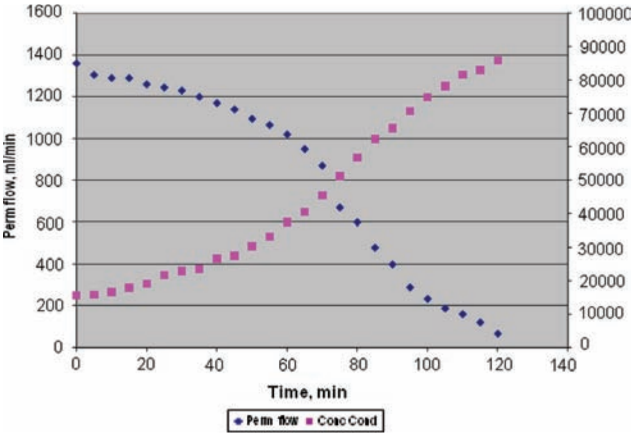

Fig. 5. Graph from Run 5.

3.5.2. Observations

The super-concentrate showed no visible turbidity or precipitation, and the membrane showed no evidence of fouling by silica. A simple flushing of the system with RO permeate water cleaned the membrane which retained the original productivity (840 ml/min at 300 psi). From the initial 25 gal of plant RO concentrate, the final mixed permeate volume was 27.43 gal and final concentrate volume was 2.38 gal (86,100 µS/cm). This represents an apparent recovery of 92%. Reactive silica profile (by Hach molybdate assay) in the concentrate was measured as 110 mg/l at start, 260, 255 and 285 mg/l at 55 min, and 700, 780 and 780 mg/l at 105 min. The TDS in the super-concentrate was determined by drying in the oven. The results were: 73,880, 73,175 and 72,475 = 73,183 mg/l average.

4. Silica concentration profile in the process

During the design phase of the current RO plant, we have shown in the pilot studies that silica was the limiting foulant for water recovery between 85–90% [1]. Now, using the effect of acidification of the primary RO concentrate in synergy with the antiscalant to inhibit the polymerization of reactive silica which triggers fouling, we are seeing for the first time in RO process design that chemical control can circumvent the fouling effects of high silica concentrations in brackish water. It is of interest to clearly document the concentration profiles of reactive and total silica [6] whose effects on RO membranes apparently have been completely controlled. A composite picture of the silica profile in this process is given in Table 2 and shown in Fig. 6.

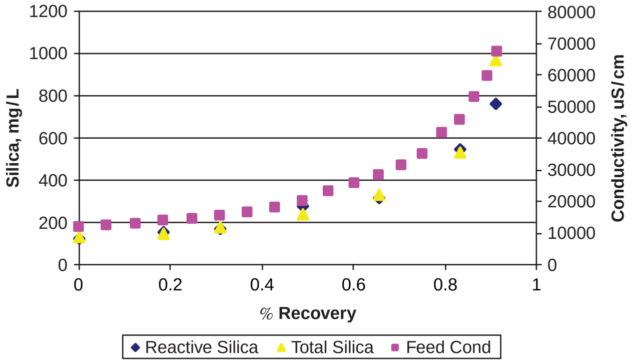

Fig. 6. Conductivity, Reactive Silica, and Total Silica of Reject vs Recovery.

Shown in Table 2 is the conductivity of the feed water along with the reactive silica and total silica concentrations at various point in a batch run conducted on 6 March 2008. The total silica concentration was calculated from silicon concentrations measured using inductively coupled plasma spectroscopy (ICP) without pre-digestion with acid. The data show that reactive silica and total silica concentrations are almost exactly the same for all recoveries except the last one at 91.3%. The difference could be due to polymerization of the silica. Polymerized silica is non-reactive towards molybdate colorimetric reagent, and would not show up in the reactive silica measurement. The data points that showed reactive silica exceeding the measured value of total silica on the same samples can be attributed to precision of the two analytical methods. The fact that spontaneous polymerization of reactive silica is expected to continue

Table 2
Feed conductivity and silica versus percent recovery

Percent recovery, %	Feed conductivity, µS/cm	Reactive silica, mg/l	Total silica, mg/l
0	11,690	123	130
18.6	13,760	153	149
31.0	15,340	172	179
48.8	19,780	280	235
65.6	28,300	318	328
83.2	45,700	545	528
91.3	67,400	765	965

in the delayed time periods before samples are analyzed by colorimetric assays contributes to lower precisions in reactive silica values.

5. Discussion of the results

For the El Paso KBH Desalination RO plant, this is an exciting first step towards the development of a process to greatly reduce the volume of RO reject that has to be disposed, and by an alternate method without using deep well injection. Very beneficial is the visualization of the use of sequential ROs in tandem to concentrate all brackish well waters continuously to the maximum limits of 1000 to 1200 psi seawater RO, at nearly 100% water recovery rates where the resulting osmotic pressure in the concentrate cannot be overcome. These results show in principle that a non-stop tandem RO process with near complete water recovery is possible. The super-concentrate resulting from such a process would still be brines that contain less than 10% by weight of dissolved salts. Such salt concentrations will facilitate the fractionation of less soluble calcium and magnesium salts from the more soluble sodium and potassium salts of some commercial value. The costs of zero-liquid-discharge from large inland municipal waterworks can be made affordable, and the control of salinity influx from the use of river waters such as exists in the arid southwestern US dealt with.

6. Conclusions

Synergistic effects of antiscalants and acids allows for non-stop recovery of pure water from brackish sources using a SWRO system following a primary RO. We expect such a tandem RO system to be capable of recovering pure water to the limits of osmotic pressures resulting from the use of 1000–1200 psi feedwater pumps driving against it.

Following this demonstration in principle, we are proceeding to minimize chemical dosages on pilot scale and perform cost analyses before proceeding to scale-up with a demonstration SWRO system. Fractionation of salts from the super-concentrate, and thermal reduction of volumes with equipment or drying ponds are to be explored.

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