

## Recovery optimization of RO concentrate from desert wells

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### Abstract

Process design for a 15 mgd (2370 m<sup>3</sup>/h) reverse osmosis (RO) plant in El Paso, Texas, in the desert area of the US southwest presents many challenges. High recoveries in the pilot plant were limited by silica and barium sulfate scaling. Following testing at 85–90% recovery using a silica polymerization inhibitor and antiscalant, the disposal of a projected 2.1 mgd (332 m<sup>3</sup>/h) of an unstable supersaturated RO concentrate presents a significant problem. While deepwell and evaporative disposal alternatives are being considered, a pilot program towards a zero liquid discharge process to recover more water and perhaps useful by-products has progressed with very encouraging results. We report here our initial results, attaining a further recovery of 70% of water, and the production from a lime-softening step of sludge with high silica content, and promise as a useful road-base and embankment materials additive.

**Keywords:** Silica; Barium sulfate; Zero liquid discharge; Lime-softening; High recovery; Cement additive; Process design; Calcium fluoride; Calcium carbonate; Calcium sulfate

### 1. Introduction

El Paso, Texas, in the arid expanse of the US southwest expects soon to be the site of the world's largest inland desalination plant [1]. For the initial design of a 15 mgd (2370 m<sup>3</sup>/h) RO plant, even at the highest possible recovery of 86%, a waste stream of 2.1 mgd (332 m<sup>3</sup>/h) of an unstable supersaturated RO concentrate would

pose a major disposal challenge [2,3], by deepwell injection [4,5] or by evaporation ponds [6,7]. The ideal process of zero liquid discharge with feasibility of extracting useful minerals from desalination brines [8,9] however, offers intriguing potentials, not only for this project, but any insights generated would be of practical importance to the science of brine disposal. We undertook a feasibility study, using El Paso well water concentrated up to 10 times via 90%

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recovery in a primary RO unit. This report describes lab and pilot plant results of using a lime-softening unit to reduce the limiting foulants of silica and barium sulfate, then proceeding to further recovery of water with a secondary RO unit until fouling occurred at 70% recovery of the concentrate. This set of data will serve as possible scale-up information for the lime-softening system and secondary RO unit for reaching towards zero-liquid discharge. Meanwhile, the data allows for the consideration of a concentrate disposal method at a less expensive cost. Interestingly, the silica-rich lime sludge is found by a local cement manufacturer to be of possible interest as a road-base and embankment material additive.

## 2. Generation of the primary RO reject

The schematic diagram of the process flow in the pilot plant is given in Fig. 1. A typical feedwater analysis and RO reject composition projected for 85% recovery is given in Table 1. Using the best available antiscalant [10] with silica polymerization inhibitor (Pretreat Plus-Y2K at 4.0 ppm), the limit of recovery was found to be 86 to 90%. The limit was reached by occurrence of silica fouling. The use of a silica cleaner fully recovered the flux. The pilot primary RO skid built by Camp Dresser & McKee for El Paso Water Utilities has six pressure vessels in a 2:1 array with 4" Koch membrane elements and a maximum 25 gpm (5.6 m<sup>3</sup>/h) feedflow rate. At above 90% recovery, the low reject flowrate of <2 gpm became difficult to measure and maintain.

## 3. Laboratory tests in reducing silica and barium in concentrate

A concentrate generated by the primary RO pilot plant operated at 85% recovery was collected for laboratory experiments described

Table 1

Primary RO feedwater analysis and projected composition of reject at 85% recovery

Analyte	Feedwater	RO concentrate projected for 85% recovery
Calcium (mg/l)	74.6	497.3
Magnesium (mg/l)	25.0	166.7
Sodium (mg/l)	279	1860
Potassium (mg/l)	14.7	98.0
Barium (mg/l)	0.13	0.9
Strontium (mg/l)	2.38	15.9
Manganese (mg/l)	0.02	0.1
Bicarbonate (mg/l)	94.4	627
Sulfate (mg/l)	76	507
Chloride (mg/l)	517	3447
Fluoride (mg/l)	0.67	4.5
Nitrate (mg/l)	0.6	3.3
Silica (mg/l; reactive)	30	200
pH	8.0	8.8
TDS (mg/l)	1120	7465

below. Total silica and barium concentrations were analyzed by Inductively Coupled Plasma Method (Standard Methods 3120 B). Slurries were filtered by vacuum filtration through a 4.7 cm diameter glass microfiber filter pad (VWR, Cat. No. 28333-139).

### 3.1. Pulverized dolomite marble (calcium and magnesium carbonate)

Very fine calcium and magnesium carbonate powder is available in the form of dolomite marble (Dolocron 4013 from Specialty Minerals). Knowing that the antiscalant will adsorb on this material and be removed, we tested the efficiency of dolomite marble powder in catalyzing the polymerization of reactive silica [11] and crystallization of barium sulfate.

When the slurry of 200 ml of the concentrate and 1.00 g of the marble powder is stirred for up to 1 h then filtered through a 4.7 cm diameter

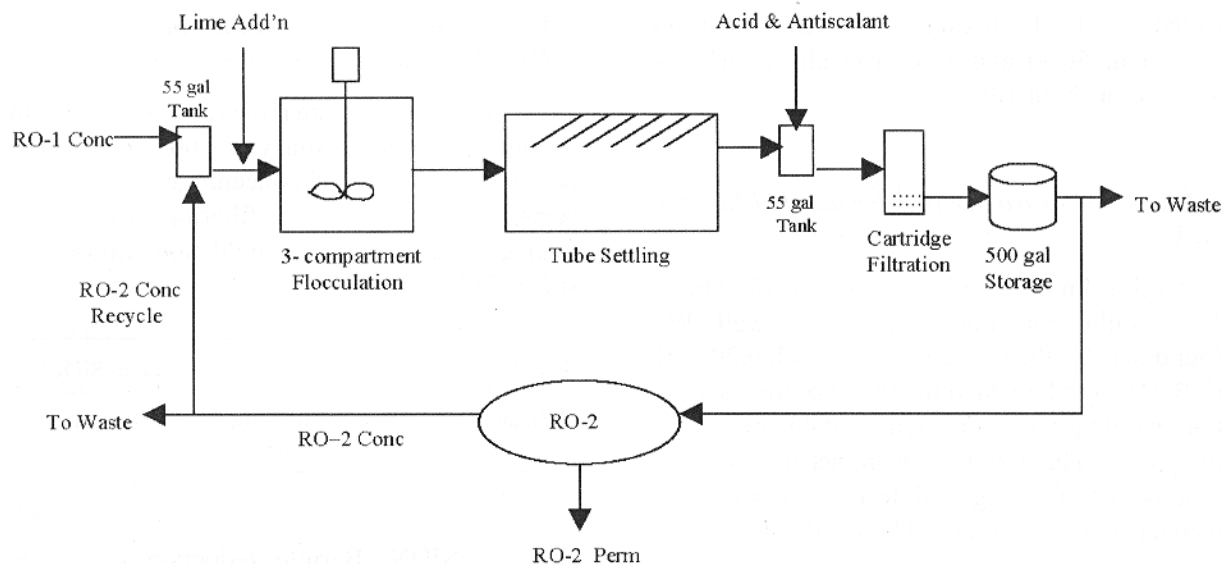


Fig. 1. Pilot plant process flow diagram.

glass microfiber filter, no reduction of barium or reactive silica was seen.

### 3.2. Magnesium hydroxide powder

Magnesium hydroxide being quite insoluble was tested as a solid-phase initiator for silica polymerization for the selective reduction of reactive silica. A slurry of 1.00 g of USP grade  $\text{Mg}(\text{OH})_2$  in 200 ml of the RO concentrate was stirred for 10 min and replicated slurry for 60 min, for 3 h and for 3 days in covered beakers. The pH of the slurries rose from 7.8 to 9.1 over 1 h, to 9.2 in 3 h, then 8.8 after 3 days. The slurries were filtered through 4.7 cm diameter glass microfiber filter. The clear filterates were analyzed by ICP for Ba and  $\text{SiO}_2$ . The results are shown below:

Sample	Ba	Total $\text{SiO}_2$
Untreated	0.90 mg/l	158 mg/l
10 min	0.54	153
60 min	0.34	133
3 h	0.32	119
3 days	0.30	78

**CONCLUSION:**  $\text{Mg}(\text{OH})_2$  powder is effective in reducing Ba concentration within 1 h by 64%, but is not sufficiently active towards  $\text{SiO}_2$  (16% reduction in 1 h).

### 3.3. Calcium hydroxide powder (at pH 10.2 dropping to 9.4 over 18 h)

Conventional lime softening process is conducted in the pH range of 10.3 to 10.6, at which pH calcium carbonate is precipitated, leaving magnesium in solution. We found that for the concentrate sample at hand, 0.10 g of  $\text{Ca}(\text{OH})_2$  USP grade powder added to 200 ml of the concentrate would give a slurry with an initial pH = 10.2, which then would drop to 9.9 in 3 h and to 9.4 in 18 h. Three slurries were set up for three time-points, filtering and testing in the same manner described above. The results are shown below:

Sample	Ba	Total $\text{SiO}_2$
Untreated	0.88 mg/l	143 mg/l
1 h	0.43	48
3 h	0.41	39
18 h	0.37	52

**CONCLUSION:** Maximum reduction of barium (by about 50%) and silica (by about 66%) is attained in about 1 h.

### 3.4. Calcium hydroxide powder (at pH 12.0 over 18 h)

Excess lime softening process at pH above 10.6 would precipitate  $\text{Mg}(\text{OH})_2$  as well. We found that for the concentrate at hand, 0.20 g of  $\text{Ca}(\text{OH})_2$  powder added to 200 ml of the concentrate would give a slurry with a stable pH= 12.0 over 18 h. Three slurries were set up for three time-points, filtering and testing in the same manner described above. The results are shown below:

Sample	Ba	Total $\text{SiO}_2$
Untreated	0.92 mg/l	155 mg/l
1 h	0.65	6
3 h	0.30	3
18 h	0.50	2

**CONCLUSION:** It is observed that the sludge from the pH 12.0 treatments settle much more readily than the sludge from the pH=10.2 treatments. This is perhaps due to the coagulative effect of the positively charged  $\text{Mg}(\text{OH})_2$  particles on the negatively charged  $\text{CaCO}_3$  and colloidal silica particles. The precipitation of  $\text{Mg}(\text{OH})_2$  from solution dramatically reduces silicic acid concentration by 96% rapidly, presumably through magnesium silicate polymerization. This is in sharp contrast to the addition of the highly insoluble  $\text{Mg}(\text{OH})_2$  powder to the RO concentrate in the first set of experiments above. Barium reduction of 30% in 1 h is the same as if a large excess of  $\text{Ca}(\text{OH})_2$  is added (see below). Further reduction of barium occurs over 3 h. The apparent redissolution of some barium hydroxide after 18 h needs confirmation.

### 3.5. Calcium hydroxide powder in large excess (pH= 12.5 over 60 min)

To test the maximum reductions possible with calcium hydroxide, a slurry of 1.00 g of  $\text{Ca}(\text{OH})_2$  powder in 200 ml of concentrate sample was stirred for 60 min before filtering in the same manner. The maximum reduction values are shown below:

Sample	Ba	Total $\text{SiO}_2$
Untreated	0.90 mg/l	158 mg/l
60 min	0.65	<1

**CONCLUSION:** Barium reduction is not as effective as it was at pH=10.2 because barium hydroxide ( $K_{sp} = 5 \times 10^{-3}$ ) is more soluble than barium carbonate ( $K_{sp} = 5.1 \times 10^{-9}$ ). Silica is completely removed with the involvement of  $\text{Mg}(\text{OH})_2$  precipitation.

### 3.6. Overall conclusions

1. Magnesium hydroxide precipitation by lime addition can completely extract silica from the process water.
2. Maximum reduction of silica, barium, calcium and magnesium hardness can be accomplished by treating the first pass RO concentrate with lime at pH of about 11.5 for 1 to 3 h.

## 4. Pilot lime treatment, sludge separation and effluent clarification

The concentrate from the primary RO operated at between 85–90% recovery is fed continuously to the lime treatment unit at a flowrate of 2–3 gpm (0.45–0.68  $\text{M}^3/\text{h}$ ). The lime unit consists of a three-compartment flocculator (stirring speeds of 225, 105, and 75 rpm, respectively), an inclined tube settling tank, and three cartridge filters.

Table 2  
Analysis of primary RO concentrate and lime reactor effluent

Analyte	90% primary RO recovery <sup>a</sup>		85% primary RO recovery <sup>b</sup>	
	Concentrate	Lime effluent	Concentrate	Lime effluent
Barium, soluble	0.87 mg/L	0.53 mg/L	—	—
Barium, total	0.94	0.52	—	—
Bromide	1.93	2.09	1.29 mg/L	2.08 mg/L
Calcium	772	901	582	1540
Chloride	4880	4880	3690	5430
Fluoride	4.12	1.01	3.34	1.01
Magnesium	206	<1.00	153	4.00
Nitrogen–nitrate	0.94	0.97	0.76	1.08
Nitrogen–nitrite	<0.25	<0.25	0.05	0.25
Phosphate, ortho	<0.25	<0.25	0.58	1.00
Potassium	119	120	84	124
Sodium	2680	2720	1990	3070
Sulfate	905	866	680	1870

<sup>a</sup>Analyzed August 12, 2004.

<sup>b</sup>Analyzed February 22, 2005.

Lime (chemical grade pulverized quicklime from Mississippi lime) is fed as an 8.5% slurry to maintain a reaction pH above 10.5. The theoretical residence time of water in the reactor is approximately 160 min (65 min in the flocculator and 95 min in the tube settler). The treated concentrate exits into a 55-gallon (208 liter) drum into which acid is added to maintain a pH of about 4, along with Pretreat Plus-Y2K antiscalant at a dosage of about 4 ppm to control calcium carbonate scaling. Sulfuric acid (96%) was initially used, but it was later replaced by hydrochloric acid (37%) because of calcium sulfate precipitation. The acidified lime reactor effluent is then filtered through a series of 50, 20 and 5 micron cartridge filters, and stored in a 500 gallon (1890 liter) storage tank from which the secondary RO unit is fed.

The analysis of primary RO concentrate at 90% and 85% recovery and the respective lime reactor effluent concentrations are given in Table 2. The analyses show reductions in barium

and fluoride concentrations. Silica concentrations were not measured in these samples, but other analyses showed normal concentrations to be above 155 mg/L in the RO concentrate and as low as 10 mg/L in the lime treatment effluent (depending on the lime concentration in the reactor) [12].

## 5. Secondary RO

Due to the low volumes of available lime-treated concentrate, the secondary RO unit consisted of a single 4"×40" thin-film composite polyamide element (Filmtec BW30-4040), operated by recycling secondary RO concentrate back to the influent of the lime reactor to increase recovery. The feed from the lime reactor effluent storage tank was filtered through a 5 micron cartridge filter on the secondary RO unit.

Due to the lack of automatic controls, the feed quality was difficult to control, and was often turbid when the acid feed rate (following lime

Table 3  
Analyses of secondary RO feed and permeate

Analyte	Secondary RO feedwater	Secondary RO permeate
Bromide	1.94 mg/L	0.40 mg/L
Fluoride	1.07	0.90
Nitrogen–nitrite	0.25	0.05
Nitrogen–nitrate	0.98	0.24
Phosphate, ortho	1.05	0.05
Chloride	4950	784
Sulfate	1990	124
Calcium	1040	78.2
Potassium	108	20.9
Magnesium	6.6	2.0
Sodium	2720	377

treatment) was too low. Despite this, 70% recovery was attained before the element became fouled. The analyses of the secondary RO feed and permeate are given in Table 3. The quality of the permeate has undoubtedly suffered from membrane scaling.

The membrane element was removed from the system and thoroughly examined and autopsied to sample the foulant from the membrane surface. The foulant was analyzed for elemental composition to document the limiting foulant at this stage of the process.

The casing of the element was carefully removed and the membrane leaves unrolled. The membrane surface was covered with a layer of yellowish white scales, thick enough to intrude into the feed spacer. A representative sample of the foulant was collected, washed several times with deionized water by decantation then dried at 120–130°C. The dried sample was analyzed quantitatively for absolute % by weight of carbon, hydrogen, nitrogen and ash, and by Scanning Electron Microscopy with Energy Dispersive X-Ray (SEM-EDX) for the relative % composition of all elements with atomic number of oxygen and higher.

Table 4  
Carbon, hydrogen, nitrogen and ash in secondary RO foulant

	Absolute % by weight
Carbon	0.24
Hydrogen	0.61
Nitrogen	0.00
Volatile (oxygen)	6.4
Ash	92.8
Total	100

Table 5  
Elemental composition of secondary RO foulant by SEM-EDX

	Relative % weight composition in ash
Calcium	45.9
Fluorine	25.6
Oxygen	22.0
Sulfur	6.6
Total	100.1

The C,H,N and ash results (Table 4) showed that the foulant is composed of 7% by weight of combustible and volatile material (organics and water of crystallization), and 93% by weight of inorganic ash. Of this ash, SEM-EDX results (Table 5) showed 45.9% calcium, 25.6% fluorine, 22.0% oxygen and 6.6% sulfur. Since the quantification of relative weight compositions of the light atomic numbered fluorine and oxygen by SEM-EDX has an uncertainty of  $\pm 25\%$ , we can calculate for the presence of the following scales, and their approximate relative composition by weight: 59%  $\text{CaF}_2$ , 11%  $\text{CaCO}_3$  and 8%  $\text{CaSO}_4$ . Due to the noted inaccuracy in the relative % by weight of fluorine and oxygen atoms, the calculated relative % composition of the three insoluble scales may be a bit off, but their presence in approximate proportions is certain.

It is very interesting to note that silica and barium sulfate that are the limiting foulants for

the primary RO is not found in this secondary RO foulant. They appear to be sufficiently reduced in lime treatment. Calcium fluoride, calcium carbonate and calcium sulfate particles clearly have their origin in lime treatment whether preexisting as colloidal particles in the pulverized quick lime slurry that was added, or was irreversibly formed during the heterogeneous phase of the dissolution of the lime slurry. These insoluble salts are expected to be in a state of fine dispersion entering the secondary RO unit.

## 6. Conclusions

We have presented here a pilot study aimed at a zero liquid discharge process for a large inland RO plant at El Paso, Texas. Concentrates from a primary RO operated at 85 to 90% recovery are treated by lime-softening to reduce the limiting foulants of silica and barium sulfate. Following laboratory experiments, a pilot lime-softening unit was operated, feeding the lime-treated concentrate into a secondary RO unit. A maximum recovery of 70% was reached in the secondary RO unit, accounting for an overall recovery of 97%. Interestingly, autopsy and foulant analysis performed on the fouled membrane element showed that the foulant was primarily calcium fluoride with smaller amounts of calcium carbonate and calcium sulfate. None of the original limiting foulants for the primary RO (silica and barium sulfate) is found in the foulant from the secondary RO unit, showing that the reduction of silica and barium by lime treatment has been successful.

The data reported here are useful to two objectives. An interim objective in the El Paso project is to design for the deep-well injection of the primary RO concentrate operated at 85% recovery. For this design, there is concern with the instability of the 85% concentrate towards precipitation of solids by itself or after mixing with the aquifer water that might scale the con-

centrate system and/or plug the wells. The data reported here helps guide the investigation of reducing super-saturation by a precipitative/clarification step before disposing the concentrate in the wells.

A second longer-term objective is to develop a near zero liquid discharge process that would have generic value for treating similar well waters. For this objective, larger demonstration concentrate treatment unit with better instrumentation is needed to generate larger feedflow and feed quality to the secondary RO unit.

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