

DETERMINING THE OPTIMAL ZLD METHOD FOR Ca AND SiO₂ REMOVAL FROM RO SYSTEMS EFFLUENT^{*}

M. NOSHADI^{**} AND M. KAZEMIZADEH

Dept. of Water Eng., Shiraz University, Shiraz, I. R. of Iran
Email: noshadi@shirazu.ac.ir

Abstract– In RO (Reverse Osmosis), water on the feed side of the membrane becomes increasingly concentrated and supersaturated, with respect to sparingly soluble salts such as calcium carbonate (CaCO₃), calcium sulfate (CaSO₄), barium sulfate (BaSO₄), and silica (SiO₂). Therefore, recovery in RO systems is limited by the precipitation potential of sparingly soluble salts. Therefore, reuse of RO effluent could be limited by the precipitation potentials of these salts. Thus we were looking for procedures to prevent precipitation of soluble salts on the membrane surface in secondary RO. The objective of this research was to investigate methods to achieve maximum efficiency for precipitation of soluble salts in RO effluent by ZLD process as intermediate treatment step. This research was conducted on samples collected and tested from RO system effluent in Tange Alhad, Hajiabad, Zarin Dasht, Darab city, Fars province, Iran. In bench-scale for Ca removal, chemical precipitation with sodium hydroxide and fluidized bed crystallization and for silica removal adsorption with alum and sodium aluminate was used. The optimum ZLD processes for Ca and silica removal was fluidized bed crystallization with 100 mg/L of sodium aluminate and 100 mg/L NaOH. In this ZLD method, silica and calcium concentrations reduced by 90 and 55 percent, respectively.

Keywords– Fluidized bed crystallization, alum, calcium, sodium aluminate, silica

1. INTRODUCTION

Need for urban water supply in many parts of the world has become a crisis. The need for affordable inland desalination is critical in many regions of the world where communities strive to meet rapidly growing water demands with limited freshwater supplies [1].

There are many difficulties in supplying fresh water in the southern and southeast regions of Iran. Limitations and requirements to management available fresh water resources cause utilization of uncommon resources such as salty and brine water. Among various desalination technologies, reverse osmosis (RO) has wide acceptance [2]. However, like most desalination technologies, treatment of brackish water by RO results in two streams: a usable desalinated water stream and a highly saline concentrate stream that contains the dissolved substances removed from the desalinated water. This concentrate stream must be managed, and its disposal is becoming increasingly difficult, particularly for the inland regions. The currently available options for concentrate management are direct discharge to surface water, deep well injection, discharge to a publicly owned treatment works, evaporation pond, zero liquid discharge (ZLD).

The need to protect surface and groundwater resources in many cases may preclude concentrate disposal by the first three methods. A suitable alternative is zero liquid discharge (ZLD). In ZLD, concentrate water is treated to produce desalinated water and essentially dry salts. Consequently, there is

^{*}Received by the editors November 4, 2013; Accepted June 28, 2015.

^{**}Corresponding author

no discharge of liquid waste from the process [3]. There are a variety of process options that can be considered for the intermediate concentrate step including adsorption processes, chemical precipitation, and ion exchange, or even combinations of these processes [4]. In RO, water on the feed side of the membrane becomes increasingly concentrated and supersaturated, with respect to sparingly soluble salts such as calcium carbonate (CaCO_3), calcium sulfate (CaSO_4), barium sulfate (BaSO_4), and silica (SiO_2) [5, 6, 7]. If the feed solution becomes sufficiently supersaturated, these salts precipitate and form deposits on the membrane surface. Deposition of these inorganic precipitates on the membrane surface, scaling, reduces the permeability of the membrane [8, 9]. Therefore, recovery in RO systems is limited by the precipitation potential of sparingly soluble salts [10].

Limited researches have been conducted about RO effluent concentrate for reuse of it in secondary RO. Bond and Veerapaneni (2007) conducted many experiments on five brackish water sources in five states of the United States of America. These water sources were selected to cover a broad range of brackish water such as surface water, ground water and RO effluent. Bench-scale testing was conducted at each of the five states to evaluate and compare treatment options for the intermediate concentrate step. At the end of bench-scale testing, fluidized bed crystallization with sodium aluminate was selected for evaluation at pilot-scale [3].

Ning and Troyer (2009) showed that 70-90% of water could be recovered by insoluble salts precipitation and coagulation of colloidal particles. If there is an intermediate treatment step that can limit suspended particles, secondary RO recovery is about 97-99%. Precipitation salts from primary RO are mainly bivalence cations (Ca, Mg, Ba, Sr), coagulated silica and colloidal particles, but remaining salts from secondary RO are mainly soluble cations (Na, K). Therefore, secondary RO is separator bivalence cations from mono valence cations that each fraction has commercial usage [11]. Sheikholeslami and Tan (1999) evaluated the effects of water hardness and Ca:Mg ratios on silica precipitation. The results showed that the silica polymerization rate increased with increasing total hardness [7]. Ning et al. (2006) designed a process for increasing water recovery of RO in El Paso city of Texas in the Southwest of United States. They showed that high recovery was limited by silica and barium sulfate in pilot-scale [12].

Sheikholeslami (2004) evaluated the effect of Na_2SO_4 , MgCl_2 or NaCl on calcium carbonate precipitation in seawater. There was significant difference in calcium carbonate precipitation at the same TDS by adding them. Calcium carbonate precipitation decreased with increasing TDS for each of the three samples. MgCl_2 had the greatest effect followed by Na_2SO_4 then NaCl [8].

The main objective of this research is determination of optimum method of ZLD to maximize the efficiency of the precipitation process and minimize the volume of solid material for preparing concentrated water of RO system for desalination in the secondary RO system. The precipitation of calcium carbonate (CaCO_3) and silica (SiO_2) are important in this research. But barium concentration in water was negligible. The precipitation of CaCO_3 is important because it is the key component of the process selected for precipitation. Silica and barium are important because they are critical to RO system performance.

2. METHODS AND MATERIALS

In this research concentrated water generated by RO system in Zarindasht of Darab city, Fars province, Iran was investigated. The RO system was operated 4 hours per day with 65% recovery and a flux $15 \text{ m}^3/\text{d}$. Samples were collected in 10-L plastic containers. Water quality data from RO effluent are shown in Table 1. These data were used to perform a preliminary process analysis to establish treatment goals for removal of critical elements. According to Table 1 salts that produce hardness in effluent were $\text{Ca}(\text{HCO}_3)_2$, CaSO_4 and MgSO_4 . Silica and calcium were critical in effluent and concentration of barium was

negligible. Bench-scale testing was conducted to evaluate and compare different alternatives for precipitation and removal of these critical elements. At the end of bench-scale testing, the best process for removal of critical elements was selected. In bench scale chemical precipitation with sodium hydroxide or lime and fluidized bed crystallization were used for Ca removal and adsorption with alum and sodium aluminate was utilized for silica removal. Of course, some experiments were conducted as combination of different processes.

a) Calcium removal

In laboratory several techniques have been used for calcium removal such as chemical precipitation with sodium hydroxide or lime and fluidized bed crystallization by calcium carbonate seed.

1. Chemical precipitation with sodium hydroxide (NaOH) or lime (Ca(OH)₂): Use of lime and sodium hydroxide is the general technique for hardness reduction. In this experiment 1 liter of RO effluent was mixed with different doses, 100, 300, 500, 700 and 900 mg/L of NaOH or lime in various mixing conditions (mixing conditions are given in Tables 4 and 5). Samples were filtered by 0.45 micron filter after mixing and the remaining amount of calcium and silica in each sample was measured with Laviband and Titration methods, respectively (Table 1).

2. Fluidized bed crystallization (FBC): This experiment was conducted in two steps: In the first step, to evaluate the effect of CaCO₃ seed on Ca and silica removal, 1 liter of concentrated water was mixed with CaCO₃ seed without adding NaOH or Ca(OH)₂ and adjusting pH. The amounts of 95, 185, 370, 740 and 1480 g/L of CaCO₃ seed in 2, 4, 6, 8, 12 and 14 minutes contact time were tested and evaluated.

In the second step, for evaluation of contact time and pH effects on Ca removal, 740 g/L CaCO₃ with various doses of 100, 300, 500, 700, 900 mg/L of NaOH were simultaneously mixed for 2 and 6 minutes, so pH changed from 10.48 to 12.47.

Table 1. Quality parameters of RO effluent

Testing Apparatus	MU* ±Amount	Unit	Parameter
Spectrophotometer	3.54 ± 0.067	mg/L F ⁻	F ⁻
Titration	706.32	mg/L Cl ⁻	Cl ⁻
Spectrophotometer	1201.1	mg/L SO ₄ ²⁻	SO ₄ ²⁻
Titration	0	mg/L CO ₃ ²⁻	CO ₃ ²⁻
Calculation	760.91	mg/L HCO ₃ ⁻	HCO ₃ ⁻
Spectrophotometer	47.76 ± 0.03	mg/L NO ₃ ⁻	NO ₃ ⁻
Spectrophotometer	0.031 ± 0.001	mg/L PO ₄ ³⁻	PO ₄ ³⁻
Titration	136.69 ± 0.89	mg/L Ca ²⁺	Ca ²⁺
Calculation	172.04	mg/L Mg ²⁺	Mg ²⁺
Flamephotometer	712 ± 3.02	mg/L Na ⁺	Na ⁺
Flamephotometer	18 ± 0.15	mg/L K ⁺	K ⁺
Conductometer	4966	µmho/cm	EC
pH meter	8.84	–	pH
Titration	1331.99	mg/L (CaCO ₃)	Total Hardness
Titration	624.875	mg/L (CaCO ₃)	Ca Hardness
Laviband	29.68	mg/L SiO ₂	SiO ₂
Titration	623.7	mg/L (CaCO ₃)	Total Alkalinity
Titration	623.7	mg/L (CaCO ₃)	Methyle Orange Alkalinity
Titration	0	mg/L (CaCO ₃)	Phenol Phethalein Ikalinity
Gravimetry	3484.9	mg/L	TDS
Atomic	0.07234 ± 0.00245	mg/L Ba ²⁺	Ba ²⁺
Polarography	0.472926 ± 0.017321	mg/L Fe ²⁺	Fe ²⁺
Polarography	0.099577 ± 0.012091	mg/L Al	Al
Polarography	0.0121064 ± 0.012091	mg/L Mn	Mn

*Confidence Range

b) Silica removal

Three precipitation techniques, precipitation with NaOH and alum, fluidized bed crystallization with alum and fluidized bed crystallization with sodium aluminate were used to enhance removal of both silica and Ca.

1. Precipitation with alum and NaOH: In this test, various doses of alum (50 -500 mg/L) and an NaOH dose of 100 mg/L were added to a series of jars (rapid mixing 90 rpm for 10s and slow mixing in 30 rpm for 3 min) and mixed for 3 minutes. Then samples were filtered with 0.45 micron filter and silica and Ca were measured.

2. Fluidized bed crystallization with alum and NaOH addition: In this test, various doses of alum and NaOH with 740 g/L CaCO_3 seed were added to 1 liter of RO effluent simultaneously and mixed for 2 minutes. Then samples were filtered with 0.45 micron filter and silica and Ca were measured.

3. Fluidized bed crystallization with NaOH and addition Sodium aluminate: This test was carried out similar to the last experiment but sodium aluminate was used instead of alum.

3. DISCUSSION

a) Chemical Precipitation of Ca and silica with NaOH or $\text{Ca}(\text{OH})_2$

Two processes used for Ca and silica removal were chemical precipitation (with NaOH or lime) and fluidized bed crystallization with CaCO_3 seed. Results for precipitation experiments with NaOH and lime are shown in Figs. 1 and 2 and a summary of results is given in Tables 2 and 3. This series of experiments were carried out for each chemical material (NaOH and lime) in different mixing speed (Tables 4 and 5) with attention to the point that silica and Ca are the critical elements that should be removed. Rapid and slow mixing were 90 rpm for 10 s and 30 rpm for 3 min for NaOH, and 90 rpm for 10 s and 30 rpm at 15 min for lime.

Using lime a sharp decrease in silica concentration occurred in $\text{pH} > 10$ because of magnesium precipitation (Fig. 1 and Table 2). In each experiment calcium has been effectively removed with NaOH addition (Fig. 2). With increasing pH above 10, addition of lime caused increased calcium concentration (Table 3).

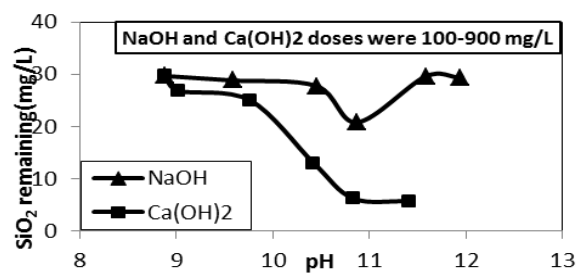


Fig. 1. Effect of pH changes on the remaining silica

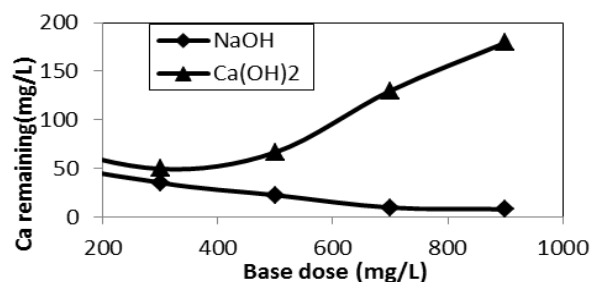


Fig. 2. Remaining calcium concentration changes in relation to NaOH and lime consumption

Table 2. Results of precipitation with NaOH (mixing condition: 90 rpm for 10s and 30 rpm for 3min)

NaOH dose (mg/L)	NaOH dose (mg/L CaCO ₃)	pH	Ca remaining (mg/L)	SiO ₂ remaining(mg/L)
0*	0	8.88	136.69	29.68
100	125	9.58	62.72	28.83
300	375	10.45	35.38	27.76
500	625	10.87	22.51	20.83
700	875	11.58	9.65	29.61
900	1125	11.90	8.04	29.30

*Blank sample (effluent of RO system without adding any chemical)

Table 3. Results of precipitation with Ca(OH)₂ (mixing condition: 90 rpm for 10s and 30 rpm for 15min)

Ca(OH) ₂ dose (mg/L)	Ca(OH) ₂ dose (mg/L CaCO ₃)	pH	Ca remaining (mg/L)	SiO ₂ remaining(mg/L)
0*	0	8.84	136.69	29.68
100	135.13	9.02	78.93	26.84
300	405.40	9.76	49.52	25.04
500	675.67	10.42	66.54	13.04
700	945.94	10.83	130	6.28
900	1216.22	11.41	179.53	5.74

*Blank sample (effluent of RO system without adding any chemical)

Table 4. Mean Ca and silica remaining in various mixing conditions with 100 mg/L of NaOH

Ca (mg/L)	SiO ₂ (mg/L)	Mixing conditions
56.53b	28.80a	100rpm•15s, 40rpm•5min
60.73ab	29.42b	100rpm•10s, 40rpm•3min
61.46a	29.00ab	90rpm•10s, 30rpm•3min

Mean values that have the same letter do not have significant difference at 95% level of probability

Table 5. Mean Ca and silica remaining in various mixing conditions with 100 mg/L of Ca(OH)₂

Ca (mg/L)	SiO ₂ (mg/L)	Mixing conditions
68.74b	26.60a	100rpm•15s, 40rpm•20min
81.53a	27.41b	100rpm•10s, 40rpm•15min
78.77ab	26.70ab	90rpm•10s, 30rpm•15min

Mean values that have the same letter do not have significant difference at 95% level of probability

By adding lime, shortage of Calcium for reaction was provided. Therefore, CaCO₃ returns to solution and Ca concentration increases (Fig. 3). Calcium concentration was reduced about 64 percent (from 136.69 mg/L to 49.52 mg/L) and 74 percent (from 136.69 mg/L to 35.38 mg/L) by using 300 mg/L lime with 15 min contact time and 300 mg/L NaOH with 3 min contact time, respectively (Table 2). Calcium removal in NaOH doses of 100, 300, 500, 700 and 900 mg/L was 54.11, 74.12, 83.53, 92.94 and 94.12%, respectively. Also, Ca removal rate was extensive using lime until dose of 300 mg/L. In lime doses of 100 and 300 mg/L, Ca removal was 42.26 and 63.77%, respectively (Fig. 2 and Table 3). The rate of Ca removal was high in NaOH doses of 0-300 mg/L and was low in doses of 300-900 mg/L (Fig. 2 and Table 2).

With application of more than 500 mg/L of NaOH and Ca(OH)₂, silica concentration was increased and decreased, respectively (Tables 2 and 3). In pH 10.4 and 10.8 decreasing rate of silica concentration was highest (Table 3). Using lime in pH<9.76, silica removal was negligible (Tables 3) and effect of mixing speeds was not significant. Therefore, usage of conventional softening for silica removal requires high pH because of the main mechanism for silica removal is adsorption to magnesium hydroxide

precipitation. In pH between 8.84-9.76 calcium carbonate could not remove silica effectively. In pH between 9.76-10.8 magnesium hydroxide (Mg(OH)₂) precipitated and simultaneously silica removal increased. According to Fig. 4 in pH=11.7 magnesium concentration was very low, so precipitated magnesium hydroxide also was negligible and no silica reduction was observed. In pH about 10 to 10.5 magnesium precipitates as magnesium hydroxide that has positive charge and calcium precipitates as calcium carbonate that has negative charge. Silica exists with high negative charge as colloidal particles. Therefore, magnesium and calcium simultaneously precipitate and silica adsorbed to magnesium hydroxide precipitation (Figs. 4 and 5).

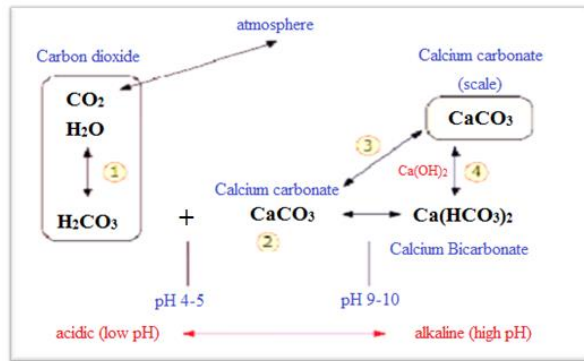


Fig. 3. Equilibrium reaction of calcium carbonate precipitation

As previously mentioned, using more than 500 mg/L of NaOH and Ca(OH)₂ (pH above 10.87) silica concentration was increased. In contrast to using lime, silica concentration in pH between 9.76-10.8 was decreased, because in equal doses of NaOH and lime, high pH was observed with NaOH due to sodium carbonate (Fig. 1).

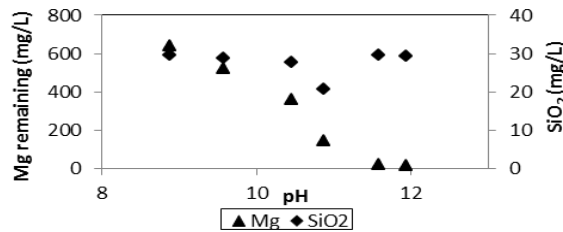


Fig. 4. Effect pH on silica and magnesium removal in chemical precipitation with NaOH

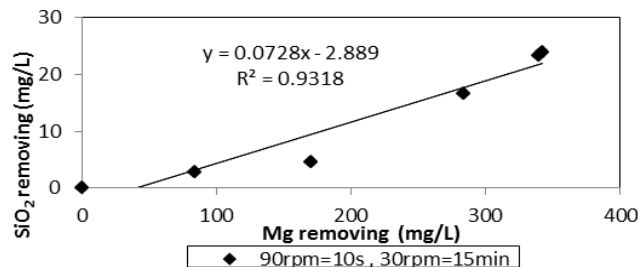


Fig. 5. The relationship between the removal of silica and magnesium in chemical precipitation with Ca(OH)₂

b) Fluidized bed crystallization

As previously mentioned, this experiment was conducted in two steps: at first, effect of various doses of CaCO₃ without adding NaOH for evaluation of CaCO₃ seed effects on Ca removal without pH adjustment was investigated and used contact times ranged between 2 to 24 minutes. Maximum removal of Ca occurred at contact time 2 minutes and 740 g/L of CaCO₃ seed (Fig. 6). Test results demonstrated fluidized bed crystallization does not improve treatment efficiency with contact time more than 2 minutes.

Thus 2 minutes contact time is used for the next fluidized bed crystallization experiments. Slight increase in calcium removal with increasing of CaCO₃ doses indicated that removal was not proportional to seed mass. The minimal differences in Ca removal at various seed doses suggest that crystal growth was more responsive from super saturation rather than seed surface area. In presence of CaCO₃ crystals and contact time of 2 minutes, without adding any chemical, Ca removal was approximately 25%. While experiments conducted by Bond and Veerapaneni (2007) showed approximately 50 percent of Ca removal.

The effects of contact time and pH on calcium and silica removal were evaluated in the second part. In these experiments, a 740 g/L CaCO₃ dose was selected simultaneously with various doses of either NaOH or Ca(OH)₂ to change the pH from 8.01 to 13.45, and the jars were mixed for either 2 or 6 minutes. Results of remaining Ca are shown in Fig. 7. There are only slight differences in remaining calcium in pH range 8.0-10.5 if NaOH or Ca(OH)₂ are used with contact time 2 minutes and NaOH with contact time 6 minutes. Therefore, calcium removal was not improved by increasing contact times from 2 to 6 minutes. Of course, at pH>10.5 by adding lime, Ca concentration was increased. In experiment with NaOH, calcium concentration was decreased sharply in pH 8 to 10.5. Calcium removal was 90% at pH 10.5 and increasing pH did not change Ca concentration. With increasing pH to 12.47, Ca removal was 98.5%, which showed little decrease (8.5%) occurred in Ca removal from 10.48 to 12.47 (table 6). The results in Tables 6 and 7 showed that Ca removal was lower when lime was used instead of NaOH in fluidized bed crystallization at pH 8-10.5.

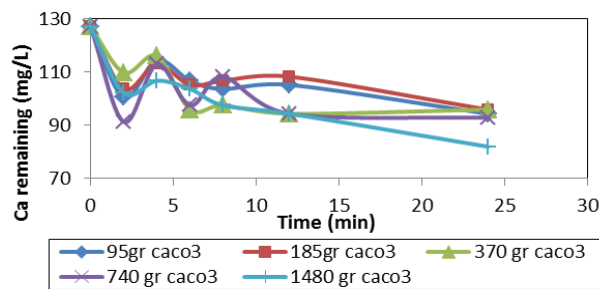


Fig. 6. The effect of different amounts of fluidized bed crystallization on the calcium removal at different mixing times

Table 6. Results of fluidized bed crystallization experiment with different doses of NaOH in 2 minutes contact time

NaOH dose (mg/L)	pH	Ca remaining (mg/L)	SiO ₂ remaining (mg/L)
0	8.01	100.60	29.59
100	10.48	9.29	28.60
300	12.14	4.64	27.31
500	12.19	3.09	20.45
700	12.29	1.55	28.78
900	12.47	1.55	29.65

Table 7. Results of fluidized bed crystallization experiment with different doses of Ca(OH)₂ in 2 minutes contact time

Ca(OH) ₂ dose (mg/L)	pH	Ca remaining (mg/L)	SiO ₂ remaining (mg/L)
0	8.01	100.60	29.43
100	9.54	38.69	27.54
300	10.68	111.43	26.35
500	11.74	225.96	13.88
700	12.30	366.80	6.76
900	13.45	550.97	5.36

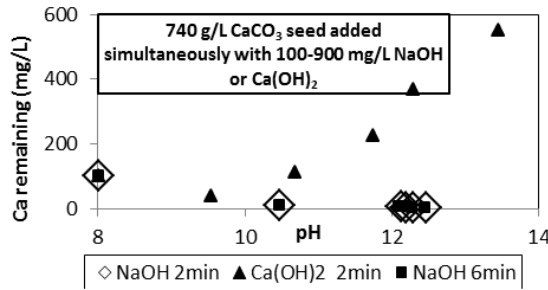


Fig. 7. Effects of pH on calcium removal in the fluidized bed crystallization test at different contact times

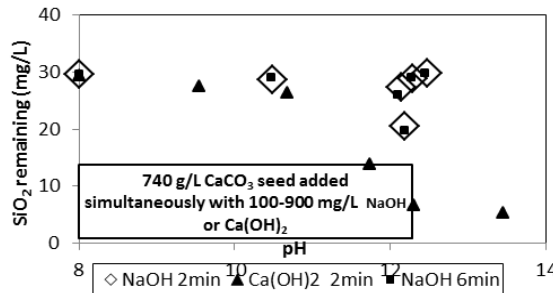


Fig. 8. Effects of pH on silica removal in the fluidized bed crystallization test at different contact times

c) Precipitation with alum and NaOH

Results of this experiment are given in Table 8 and Figs. 9 and 10. At first, Ca concentration rapidly decreased in 50 mg/L alum and in more than 50 mg/L alum, Ca concentration was increased because of CO₂ gas formation and increased of hardness due to using alum. This gas interferes with coagulation process and causes floating of precipitate, so to prevent gas formation and better performance of coagulation process, control of pH is necessary. For effective alum performance and pH adjustment, adding amount of alkalinity material and alum should be adequate. At first, with alum addition, silica concentration also decreased sharply, but in more than 300 mg/L of alum, silica concentration was increased (due to pH reduction).

Table 8. The results of chemical precipitation with 100 mg/L of NaOH and different doses of alum (90 rpm for 10 s and 30 rpm for 3 minutes)

Alum dose (mg/L)	pH	Ca remaining (mg/L)	SiO ₂ remaining (mg/L)
0	9.58	122.27	28.83
50	8.97	63.25	19.36
100	8.88	77.38	14.94
200	8.82	112.98	9.54
300	8.45	126.91	9.26
500	7.78	128.46	15.80

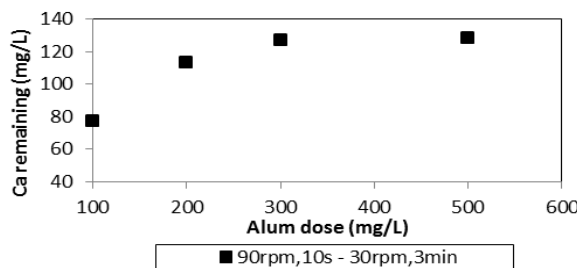


Fig. 9. Changes in calcium concentrations in relation to alum and NaOH concentration

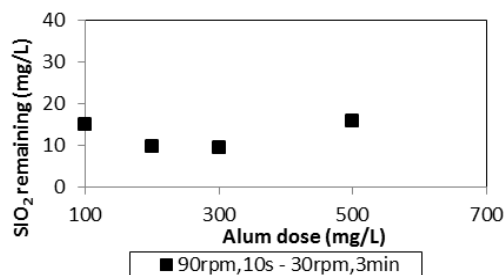


Fig. 10. Changes in silica concentrations in relation to alum and NaOH concentration

d) Fluidized bed crystallizer with NaOH and alum addition

In this experiment alum, CaCO₃ seeds and NaOH were added simultaneously and were mixed for 2 minutes. Doses of NaOH and alum and also results of remaining Ca and silica are shown in Table 9. NaOH and alum doses were between 100-900 mg/L and 100- 800 mg/L, respectively. Remaining silica concentration in solution was between 8.34-22.44 mg/L. Silica removal is affected by alum and pH. Furthermore, alum and pH are not independent variables because alum consumes alkalinity and pH will be decreased.

One method for capturing the effects of both variables simultaneously is to calculate the molar ratio of silica removal per dose of aluminum as a function of pH. Reduction of magnesium hydroxide precipitation due to increases of pH, result in silica concentration increase but additional use of alum reduces pH (Table 9) and results in silica concentration increase. Therefore, in this experiment adequate combination of chemical doses for alum and NaOH should be used, so pH was effective in silica and Ca removal. Silica removal efficiencies in fluidized bed crystallization with and without addition of alum are compared in Figs. 11 and 12. According to these figures at similar pH and NaOH dose, use of alum caused more than 30% removal of initial silica concentration.

Table 9. Results of fluidized bed crystallization with NaOH and alum addition

NaOH dose (mg/L)	Alum dose (mg/L)	pH	Ca remaining (mg/L)	SiO ₂ remaining (mg/L)
100	100	9.42	18.57	22.44
100	200	9.21	23.21	11.76
100	400	8.48	63.45	9.75
100	600	8.12	112.98	13.46
100	800	8.02	164.05	13.56
300	100	11.57	4.64	21.53
300	200	11.10	6.19	9.98
300	400	9.36	23.21	8.34
300	600	8.12	114.53	12.78
300	800	7.37	17.02	12.83
500	100	12.01	1.55	13.65
500	200	11.94	1.55	10.89
500	400	11.69	4.64	9.64
500	600	11.20	7.74	12.34
500	800	9.82	9.29	12.23
700	100	12.25	1.55	19.75
700	200	12.02	3.09	15.32
700	400	10.97	7.74	13.64
700	600	9.78	9.29	14.87
700	800	8.97	10.83	14.96
900	100	12.45	6.19	18.98
900	200	12.37	3.09	14.75
900	400	12.02	1.55	12.78
900	600	11.30	3.09	13.28
900	800	9.91	9.29	13.76

e) Fluidized bed crystallization with sodium aluminate addition

A series of experiments were conducted to evaluate the efficiency of various combinations of NaOH and Na₂Al₂O₄ doses. The matrix of NaOH and Na₂Al₂O₄ doses and the water quality results for this experiment are listed in Table 10. The RO concentrate effluent contained 136.69 mg/L calcium and 29.68 mg/L silica (Table 1). Results of silica removal are shown in Figs. 13 and 14. With increasing NaOH, Ca always decreases but silica until 300 mg/L of NaOH decreases and adding high NaOH causes silica to increase (Table 10). The use of sodium aluminate lead to increased pH, so remaining Ca and silica decreased.

In Fig. 14 silica removal with equal doses of NaOH in fluidized bed crystallization with and without sodium aluminate were compared. At equal pH and NaOH, silica concentration in the tests with sodium aluminate was 45% less than without sodium aluminate. Therefore, using sodium aluminate caused more than 45% removal of initial silica with NaOH doses between 100- 300 mg/L. Therefore, with consumed sodium aluminate and increased pH silica removal rate was increased.

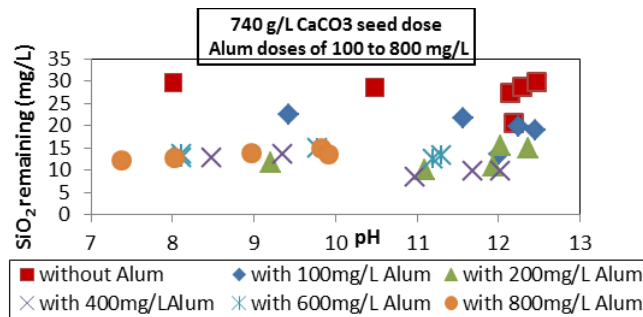


Fig. 11. Silica concentration in fluidized bed crystallization tests with and without alum at different pH

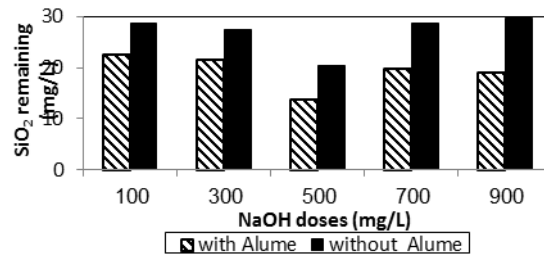


Fig. 12. Silica concentrations in fluidized bed crystallization test with alum (100mg/L) and without alum at different doses of NaOH

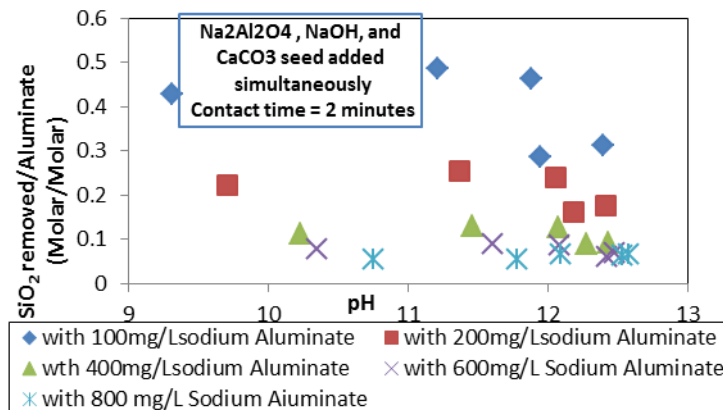


Fig. 13. Silica removal efficiency by adding sodium aluminate at different pH

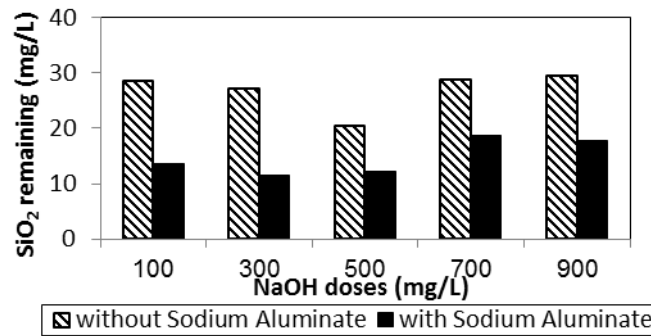


Fig. 14. Comparison of silica removal at the equal doses of NaOH in fluidized bed crystallization with 100mg/L aluminate and without aluminate

Table 10. Results of fluidized bed crystallization with sodium aluminate and NaOH addition

NaOHdose (mg/L)	Na ₂ Al ₂ O ₄ dose (mg/L)	pH	Ca remaining (mg/L)	SiO ₂ remaining (mg/L)
100	100	9.31	13.93	13.56
100	200	9.70	10.83	13.02
100	400	10.23	6.19	12.65
100	600	10.35	1.55	11.97
100	800	10.75	1.55	11.06
300	100	11.21	3.09	11.45
300	200	11.37	3.09	10.67
300	400	11.46	3.09	10.25
300	600	11.61	1.55	9.87
300	800	11.78	1.55	9.63
500	100	11.88	1.55	12.26
500	200	12.06	1.55	11.76
500	400	12.07	3.09	10.75
500	600	12.08	4.64	10.08
500	800	12.09	6.19	9.87
700	100	11.95	3.09	18.76
700	200	12.18	1.55	17.43
700	400	12.28	3.09	16.19
700	600	12.42	4.64	15.74
700	800	12.58	4.64	13.62
900	100	12.40	3.09	17.76
900	200	12.41	1.55	16.39
900	400	12.43	4.64	15.74
900	600	12.48	4.64	14.16
900	800	12.53	6.19	12.93

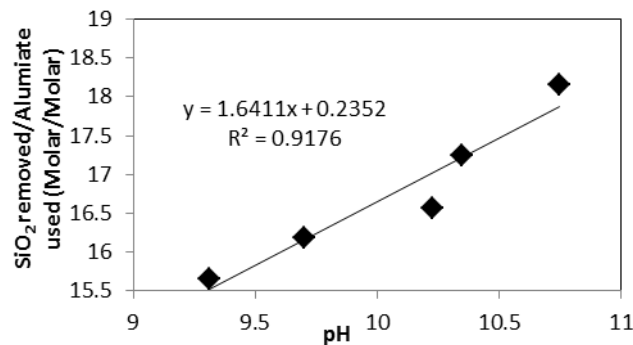


Fig. 15. Silica removal efficiency in fluidized bed crystallization test in different pH

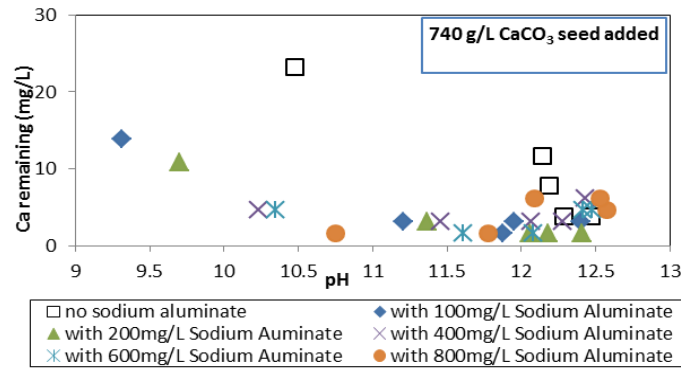


Fig. 16. Results of calcium removal in fluidized bed crystallization test by adding sodium aluminate

4. CONCLUSION AND RESULTS

In this research, fluidized bed crystallization with 100 mg/L sodium aluminate and 100 mg/L NaOH was the optimum ZLD process because of further removal of Ca and silica with consume low chemical compounds consumption. Based on this experiment, silica and calcium removal rate were about 55 and 90 percent, respectively. The main reasons for selecting fluidized bed crystallization for the intermediate concentrate treatment step were as follows:

- Precipitation of a salt in the solution required supersaturation state of that solution in presence of solid and crystalline particles of the same salt. The results of the fluidized bed crystallization and chemical precipitation tests conducted in this research showed that calcium was removed with lower chemical doses in the presence of CaCO_3 seed.
- The solids volume generated by fluidized bed crystallization is easily separated by gravity (to 99 percent solids by weight).
- With most probability the solids volume generated in fluidized bed crystallization can be used by other industries.
- Fluidized bed crystallization requires a short contact time. Therefore, this process requires small equipment and less cost.

In these experiments calcium with fluidized bed crystallization was removed effectively in a pH 8-9 but this range of pH was ineffective for silica removal. Thus in fluidized bed crystallization sodium aluminate is used to raise pH above 10 for silica removal.

The addition of alum or sodium aluminate for silica removal will be more logical and cheaper than raising the pH above 10 with either the fluidized bed crystallization or chemical precipitation process. Raising the pH of concentrate above 10 requires large base doses. Furthermore, raising the pH causes more solids precipitation to be produced, and the management of these solids must be considered. Raising pH above 10 would also require greater acid doses to reduce pH ahead of the secondary RO.

Of the two aluminum salts that were used in these experiments, fluidized bed crystallization by sodium aluminate rather than alum was selected because it adds alkalinity while alum consumes alkalinity. The tests results showed that both alum and sodium aluminate effectively removed silica in the pH 8-9.5, where fluidized bed crystallization was effective for calcium removal. A greater NaOH dose, however, is required to maintain this pH range when alum is used rather than sodium aluminate.

The tests results also showed that silica removal with an aluminum salt when applied with fluidized bed crystallization is the best alternative.

REFERENCES

1. Gardner-Outlaw, T. & Engelman, R. (1997). *Sustaining water, Easing scarcity: A second update*. Washington D.C.: Population International. pp. 1-20.
2. Sandia National Laboratories and U.S. Bureau of Reclamation. (2003). *Desalination and water purification technology roadmap*. Denver, Colo.: Water and treatment engineering and research group.
3. Bond, R. & Veerapaneni, S. (2007). Zero liquid discharge for inland desalination. *Awwa Research Foundation*, U.S.A, pp. 1-233.
4. Stumm, W. & Morgan, J. J. (1996). *Aquatic chemistry. In chemistry equilibria and rates in natural waters*. New York: John Wiley and Sons. pp. 1-1022.
5. Jones, F., Olivera, A., Parkinson, G. M., Rohl, A. L., Stanley, A. & Upson, T. (2004). The effect of calcium ions on the precipitation of barium sulphate 1: calcium ions in the absence of organic additives. *Journal of Crystal Growth*, Vol. 262, pp. 572–580.
6. Sheikholeslami, R. (2004). Assessment of the scaling potential for sparingly soluble salts in RO and NF units. *Desalination*, Vol. 167, pp. 247–256.
7. Sheikholeslami, R. & Tan, S. (1999). Effects of water quality on silica fouling of desalination plants. *Desalination*, Vol. 126, pp. 267–280.
8. Semiat, R., Sutzkover, I. & Hasson, D. (2003). Scaling of RO membranes from silica supersaturated solutions. *Desalination*, Vol. 157, pp. 169–191.
9. Sheikholeslami, R. & Ong, H. W. K. (2003). Kinetics and thermodynamics of calcium carbonate and calcium sulfate at salinities Up to 1.5 M. *Desalination*, Vol. 157, pp. 217–234.
10. Sudmalis, M. & Sheikholeslami, R. (2000). Coprecipitation of CaCO₃ and CaSO₄. *The Canadian Journal of Chemical Engineering*, Vol. 78, pp. 21–31.
11. Ning, R. Y. & Troyer, T. L. (2009). Tandem reverse osmosis process for zero-liquid discharge. *Desalination*, Vol. 237, pp. 238–242.
12. Ning, R. Y., Tarquin, A., Trzcinski, M. C. & Patwardhan, G. (2006). Recovery optimization of RO concentrate from desert wells. *Desalination*, Vol. 20, pp. 315–322.