

Selective removal of calcium ions from seawater or desalination brine using a modified sodium carbonate method

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ABSTRACT

Brine drained from desalination plants or obtained from underground is a valuable source of minerals. However, the presence of calcium ions in the brine makes its direct application uneconomical. Sodium carbonate can be used to selectively remove calcium ions from brine but is associated with drawbacks, including low calcium removal efficiency, slow settling of the precipitate, significant magnesium loss, and high reagent cost. In this study, the influence of the operating conditions on calcium removal was systematically evaluated. The experimental results revealed that temperature was the most important factor affecting calcium removal efficiency and calcium/magnesium selectivity. The optimum operating conditions were determined to include a reaction temperature of 85°C, an equimolar dosage of sodium carbonate, and a brine salinity of >56 g kg⁻¹. These conditions afforded a calcium removal efficiency of up to 85.4% with a magnesium loss of <6.7%. A pilot plant with a capacity of 120 m³ d⁻¹, based on static mixing/reaction and membrane distillation, was operated continuously for the decalcification and concentration of brine obtained from a desalination plant. The integration of the developed decalcification method, a brine-concentrating technology and separation technology such as nanofiltration would provide an alternative technique for exploiting brine.

Keywords: Calcium removal; Sodium carbonate; Brine; Calcium/magnesium selectivity

1. Introduction

As freshwater scarcity is becoming an increasingly serious concern worldwide, greater attention is being paid to the production of drinking water by seawater desalination. At present, the three main commercially available desalination technologies for large-scale applications are multi-stage flash distillation (MSF), multiple-effect distillation (MED), and reverse osmosis (RO). However, these desalination technologies typically afford a water recovery ratio of only 40%–55%, which is mainly attributable to scaling problems caused by calcium ions (Ca²⁺) [1]. The scale deposits, which consist

of insoluble calcium salts such as calcium sulfate (CaSO₄) and calcium carbonate (CaCO₃), can decrease the flow rate of the feed water through the pipes, reduce the heat transfer efficiency of heat exchangers, and diminish the productivity of membrane and thermal processes [2,3]. Owing to the low water recovery of current desalination technologies, a tremendous amount of desalination brine is produced as a by-product. In most cases, this brine is directly discharged into the sea. However, it is anticipated that the discharge of brine can harm aquatic ecosystems [4]. Furthermore, similar to brine from saline lakes or underground, this brine is also a potential source of water and salts that are wasted by

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discharging it into the sea. Consequently, numerous countries are considering more stringent regulations to control the discharge of seawater desalination brine.

Solar evaporation ponds, which are commonly regarded as the most cost-effective method to treat brine and produce salts or chemicals for the marine industry, are the main treatment method in many countries. However, owing to the amount of land required to treat huge volumes of brine, solar evaporation ponds are unable to meet the requirements of the rapidly developing seawater desalination and marine industries. This is especially true in China, where the land used for solar evaporation ponds is gradually being transformed into commercial land, which means that its availability for treating brine and producing raw salts is correspondingly decreasing. In 2018, the total production of raw salt, caustic soda, and soda ash in China was 58.6, 34.2, and 26.2 million tons, respectively [5,6]. Approximately 6 million tons of raw salt must be imported annually to support caustic soda and soda ash production and other aspects of the marine industry [5]. Consequently, it is crucial to develop improved strategies for recovering water and salts from seawater desalination brine.

Besides further concentration to recover water and salts, there is another potential application for brine drained from desalination plants, saline lake brine, and underground brine, namely, as a source of both sodium chloride and water for caustic soda and soda ash plants. However, the presence of sulfate, calcium, and magnesium ions in the brine prevents the direct application of seawater desalination brine for such purposes, as these ions are considered impurities in the caustic soda and soda ash industry and must be removed from the feed. As a result, the cost of purification by adding chemicals far exceeds the value of the water and sodium chloride in the brine. Nanofiltration (NF) is typically used to retain the sulfate, magnesium, and calcium ions from underground brine and desalination brine, and the resulting permeate can be directly used as the water source for caustic soda and soda ash plants. However, the rejection rate of calcium ions by NF membranes is generally low, the recovery ratio of the permeate is limited by scaling problems due to calcium sulfate, and the NF process cannot be used for the treatment of brine with a high calcium sulfate saturation index.

To recover water and salts from seawater desalination brine via evaporation or NF, the scaling problems due to calcium ions must first be addressed. Methods commonly used to prevent scaling include acidification of the water, the addition of chemical inhibitors, and so on. However, the high salinity and hardness of the brine reduce the effectiveness of these methods [1]. Another approach is to treat the brine using anti-fouling systems. For instance, He et al. and Song et al. employed a porous fluorosiloxane-coated hollow-fiber-based cross-flow membrane module for the concentration of brine via direct-contact membrane distillation (MD) [7–9]. Scaling salt precipitates did not form scale in the membrane module. Although this technique is useful, pretreatment of the brine was also necessary as scaling problems can also occur in pipelines, heat exchangers, and other devices. A combination of crystallization and MED, mechanical vapor recompression (MVR), or MD could also be used to further concentrate seawater desalination brine

[10,11]. In these processes, the brine is concentrated in the concentrator and calcium carbonate and calcium sulfate are continuously removed as solid crystals in the crystallizer [10]. Despite their high potential for industrial applications, these processes require bulky crystallization equipment and are associated with a high risk of scaling in the concentrator.

An alternative approach is the selective removal of calcium ions from the brine, which permits the further concentration of the brine to increase the water recovery ratio and allows more convenient downstream utilization of the mineral resources in the brine owing to its higher salinity [12,13]. In seawater, natural underground brine, and brine discharged from seawater desalination plants, the molar ratio of calcium ions to magnesium ions is approximately 1:4.1. As magnesium ions can interfere with the commonly used decalcification methods, it is necessary to find the optimum balance between achieving high levels of calcium removal and minimizing magnesium removal, to reduce the overall cost of the calcium removal pretreatment and retain magnesium in the brine as a useful resource. Typical methods include chemical precipitation, exchange resins, solvent extraction, and membrane techniques such as NF [2,3,14]. Ion-exchange methods are suitable for application to various wastewaters containing low calcium concentrations. However, the high salinity of seawater not only lowers the exchange kinetics for calcium removal but also decreases the regeneration efficiency, therefore making the process uneconomical [14]. Novel softening methods for calcium removal have also been reported, such as precipitation to reduce seawater hardness using carbon dioxide at a high pH [15], electrochemical precipitation [16], microbiological carbonate precipitation [17], and enhancement of calcium carbonate crystallization by the hyperkinetic vortex crystallization process [18]. However, these processes have not been implemented on an industrial scale owing to their operational complexity and high cost. A simpler and more practical routine treatment procedure is traditional precipitation softening via the addition of lime, sodium hydroxide, or sodium carbonate [19], which converts calcium ions to insoluble or slightly soluble calcium salts and delivers high softening performance.

In contrast to the addition of lime or sodium hydroxide, which achieves calcium removal by significantly increasing the pH of the seawater, the pH of the feed water changes only slightly upon the addition of sodium carbonate [20]. Because magnesium ions only precipitate significantly as magnesium hydroxide above a pH value of 10.5, the use of sodium carbonate for calcium removal can mitigate the loss of magnesium from the seawater [19–22]. However, the buffering capacity of seawater and the influence of salt species increase the solubility of calcium carbonate and prolong the time required for settling of the calcium carbonate crystals (to approximately 1.5–4.0 h), resulting in a low removal efficiency under typical reaction conditions [19]. Therefore, an excess of sodium carbonate is generally needed to attain good calcium removal performance, thus increasing the cost of softening and resulting in a highly alkaline effluent. Jia et al. [13] reported that even when sodium carbonate was added in 30% excess, under the experimental conditions of room temperature and a reaction time of over 4 h, the calcium removal efficiency from the brine was only approximately 60% and the magnesium loss rate was about 9%.

An alternative method for accelerating the softening process is to increase the reaction temperature. Casas et al. [22] reported that increasing the reaction temperature to 60°C improved the calcium removal efficiency from brine to as high as 94%–96% after a reaction time of 30 min. However, these experiments also involved an excess of sodium carbonate and the conditions using stoichiometric quantities of sodium carbonate were not stated clearly. To achieve the maximum removal efficiency, an excess of sodium carbonate ranging from 0.35 to 14 g L⁻¹ was required. As a result, the loss of magnesium exceeded 60%. Therefore, it is crucial to carefully control the reaction conditions to achieve the effective removal of calcium ions with the minimum amount of sodium carbonate.

In this study, calcium ions were selectively removed from brine via the addition of sodium carbonate. The influence of the operational parameters, including the sodium carbonate dosage, stirring rate, reaction temperature, reaction time, and brine concentration, on the calcium removal efficiency using sodium carbonate, was evaluated in a batch-wise manner. Moreover, the loss of magnesium ions and the variation of the pH of the brine during the softening process were also examined. Based on the results of the batch-scale study, a 120 m³ d⁻¹ pilot test was conducted using a static mixer/reactor for the decalcification of brine obtained from a desalination plant. The selectively decalcified brine was directly used as the feedstock for a multiple-effect membrane distillation (MEMD) desalination process. This integration of decalcification and MEMD processes demonstrates that the effective combination of the developed selective decalcification method and a thermally driven brine-concentrating technology such as MED, MD, or MVR could represent an alternative strategy for the full exploitation of the mineral resources present in brine.

2. Precipitation mechanisms

The crystallization of calcium carbonate from the solution phase involves three distinct steps: supersaturation, nucleation, and crystal growth. The scaling process can be divided into bulk precipitation and surface deposition. The mechanism of calcium carbonate precipitation from aqueous solution at high supersaturation involves amorphous calcium carbonate formation followed by transformation to a metastable polymorph and calcite through a recrystallization process. The complexity of calcium carbonate precipitation is mainly caused by the combined effects of several mass transfers, chemical reaction, and flow processes. The magnesium ions present in seawater act as scale inhibitors, severely increasing the induction time and significantly reducing the growth rate of calcium carbonate crystals [23,24]. The inhibition of calcium carbonate growth by magnesium ions is mainly due to the incorporation of the magnesium ions into the calcite seed surface, which affects the morphology of the crystal and therefore its growth [25]. Compton and Brown proposed models of reaction/molecule integration to explain the inhibition of calcite growth by magnesium ions [26]. As depicted in Fig. 1, some of the magnesium ions adsorb on the calcium carbonate crystal surface, then the adsorbed inhibitors (i.e., magnesium ions) hinder the adsorption of calcium or carbonate ions and hence decrease the rate of

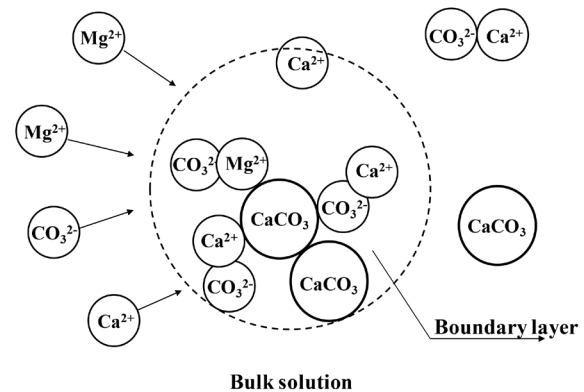


Fig. 1. Model of the adsorption processes occurring on the calcium carbonate crystal surface.

crystal growth. Also, magnesium ions adsorb at lattice sites and prevent the transfer of calcium carbonate units from the adsorbed state on the crystal lattice. As the solubility product of magnesium carbonate (3.0×10^{-5} , 25°C) is greater than that of calcium carbonate (3.80×10^{-9} , 25°C), calcium ions compete with magnesium ions reacting into the stable calcium carbonate precipitates with the precipitation-dissolution equilibrium of magnesium carbonate. The amount of magnesium incorporated into the crystal surface is proportional to the reduction in the growth rate of calcium carbonate. Therefore, increasing the precipitation rate of calcium carbonate by increasing the temperature and saturation level can effectively reduce the loss of magnesium ions [26]. The main variables that influence calcium carbonate precipitation from seawater include the calcium carbonate saturation level, pH, ionic strength, reaction temperature, and magnesium ion concentration. In a vessel containing a stirrer or during industrial crystallization, the main nucleation mechanism is secondary nucleation. The rate of crystal growth is proportional to the rate of crystal nucleus generation [27]. Zhang et al. [28] proposed a kinetic model for predicting the calcium carbonate scaling rate, in which the rate equation and rate constant of calcium carbonate formation can be expressed as follows:

$$R_L = K_p (S^{0.5} - 1)^2 \quad (1)$$

$$\log K_p = \frac{0.126(IS)0.5 - 240}{(T + 273) - 0.34pH + 0.444} \quad (2)$$

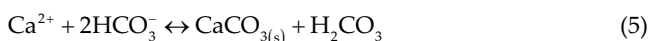
where R_L and K_p are the crystal surface linear growth rate and rate constant (m s⁻¹), respectively, IS is the ionic strength (mol kg⁻¹), T is the temperature of the feedwater (°C), and S is the saturation index, which is the driving force for precipitation and is defined as [29]:

$$S_{CaCO_3} = \frac{(\gamma_{Ca^{2+}} [Ca^{2+}])(\gamma_{CO_3^{2-}} [CO_3^{2-}])}{K_s} \quad (3)$$

where $[Ca^{2+}]$ and $[CO_3^{2-}]$ are the molar concentrations of calcium ions and carbonate ions, respectively, K_s is the apparent

solubility product of calcium carbonate [16], and $\gamma_{\text{Ca}^{2+}}$ and $\gamma_{\text{CO}_3^{2-}}$ are the ionic activity coefficients of calcium ions and carbonate ions, respectively.

The precipitation of calcium carbonate involves the following reactions:



3. Experimental

3.1. Feed preparation

The raw seawater used in this study was obtained from the Bohai Bay area, China. The raw seawater was first pretreated by ultrafiltration to remove insoluble particulates, alga, and other microorganisms. Table 1 summarizes the chemical

Table 1
Chemical composition and physical properties of the raw seawater and brine used in this study^a

Parameter	Seawater	Brine
Ca ²⁺ , mg L ⁻¹	413.6	695.2
Mg ²⁺ , mg L ⁻¹	1,034.6	2,110.4
Na ⁺ , mg L ⁻¹	10,124.6	17,207.8
K ⁺ , mg L ⁻¹	421.2	709.1
Cl ⁻ , mg L ⁻¹	18,126.3	31,223.7
SO ₄ ²⁻ , mg L ⁻¹	2,836.8	4,714.9
Br ⁻ , mg L ⁻¹	59.5	99.2
HCO ₃ ⁻ , mg L ⁻¹	146.1	245.2
Salinity, g kg ⁻¹	33	56
Density, g mL ⁻¹	1.0223	1.0371
pH	8.2	8.2
Total hardness ^b (mg L ⁻¹)	5,293	10,529

^aAll of the properties of the raw seawater and brine was measured at 25°C.

^bTotal hardness according to CaCO₃ terms.

Table 2
Concentrations of calcium and magnesium ions in the brine samples of various salinities^a

Salinity (g kg ⁻¹)	Ca ²⁺ (mg L ⁻¹)	Mg ²⁺ (mg L ⁻¹)	Salinity (g kg ⁻¹)	Ca ²⁺ (mg L ⁻¹)	Mg ²⁺ (mg L ⁻¹)
43	542.9	1,433.1	90	1,133.2	2,980.3
56	706.6	1,862.5	102	1,284.7	3,378.8
66	839.3	2,215.8	110	1,401.3	3,687.4
81	1,021.6	2,686.8	125	1,580.7	4,173.0

^aAll of the properties of the brine was measured at 25°C.

composition and physical properties of the raw seawater and brine. The seawater was concentrated (approximately 2–4-fold) by hollow fiber air gap membrane distillation-based MEMD process as described in a previous study [30]. The pH values of the seawater concentrates (referred to as brine) were maintained at 8.2 despite the change in concentration via the addition of hydrochloric acid. The concentrations of calcium and magnesium ions in the brine samples of various salinities were measured as listed in Table 2.

3.2. Chemicals and materials

All of the chemical reagents used in this study were of analytical grade. A 2 mol L⁻¹ aqueous solution of sodium carbonate was used as the calcium removal reagent. Deionized water was used to prepare all aqueous solutions of chemical reagents and standards and to dilute samples where necessary. All of the glassware was cleaned thoroughly to eliminate potential interference by residual reagents.

3.3. Analytical methods

All of the seawater samples of various concentrations, before and after softening using sodium carbonate, were analyzed for salinity, pH, and calcium and magnesium ion concentrations. The salinity of the samples was measured using a salinometer (BEC-950, Bellid, China). The pH of the samples was measured using a pH meter (SG78-FK-CN, Mettler Toledo, Switzerland) at room temperature (25°C). Calcium and magnesium ions were measured using the ethylene diamine tetraacetic acid titrimetric method (ISO 6059:1984) [31].

The removal efficiency of calcium and magnesium ions was calculated as follows:

$$R = \frac{C_i - C_f}{C_i} \times 100\% \quad (8)$$

where C_i is the initial molar concentration of the ion j and C_f is the final molar concentration of the ion j after the softening treatment.

The selectivity for the removal of calcium ions over magnesium ions $\beta_{\text{Ca}^{2+}/\text{Mg}^{2+}}$ was calculated as follows:

$$\beta_{\text{Ca}^{2+}/\text{Mg}^{2+}} = \frac{(C_{\text{Ca}^{2+},i} - C_{\text{Ca}^{2+},f}) / (C_{\text{Mg}^{2+},i} - C_{\text{Mg}^{2+},f})}{C_{\text{Ca}^{2+},f} / C_{\text{Mg}^{2+},f}} = \frac{R_{\text{Ca}^{2+}} / (1 - R_{\text{Ca}^{2+}})}{R_{\text{Mg}^{2+}} / (1 - R_{\text{Mg}^{2+}})} \quad (9)$$

where $C_{Ca^{2+},i}$ and $C_{Mg^{2+},i}$ are the initial molar concentrations of calcium and magnesium ions, respectively, $C_{Ca^{2+},f}$ and $C_{Mg^{2+},f}$ are the final molar concentrations of calcium and magnesium ions, respectively, $R_{Ca^{2+}}$ and $R_{Mg^{2+}}$ are the removal efficiencies of calcium and magnesium ions, respectively.

3.4. Calcium ion removal

3.4.1. Batch tests

The process of removing calcium ions using 2 mol L⁻¹ sodium carbonate was first performed on a laboratory scale. Fig. 2 shows a schematic diagram of the experimental setup. The brine sample (200 mL) was transferred into a 500 mL three-necked round-bottom flask. The dosing of the 2 mol L⁻¹ aqueous solution of sodium carbonate was based on the calcium ion concentration in the brine. The sodium carbonate solution was injected into the flask using a 5 mL syringe once the temperature of the brine in the flask had stabilized at the preset temperature for >5 min. During the process of heating and calcium ion removal, the solution was stirred continuously using a magnetic stirrer. The reaction time was recorded from the addition of sodium carbonate. Once the precipitation reaction was complete, the softened sample was filtered through filter paper (0.25 μm) to remove the precipitated calcium carbonate. The filtrate was analyzed for the concentrations of calcium and magnesium ions. The pH was also measured both before the addition of sodium carbonate and after precipitation. All of the experiments were repeated at least twice under the same operational conditions, and the experimental data reported are the average values.

3.4.2. Continuous test

To evaluate the long-term performance of the selective decalcification process and the possibility of its integration with a thermally driven concentrating process such as MED or MEMD, a pilot plant with a capacity of 120 m³ d⁻¹ was constructed and operated continuously for six months. Brine

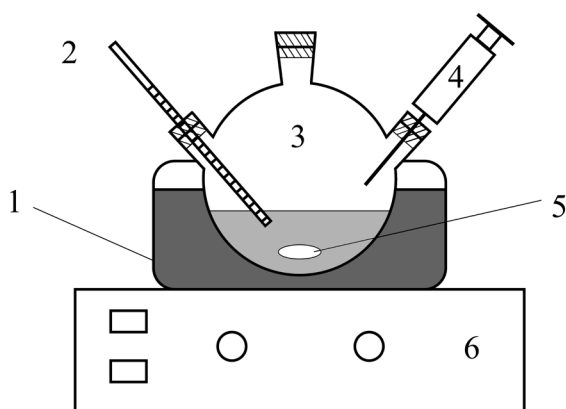


Fig. 2. Schematic diagram of the experimental setup for calcium ion removal (1, oil bath; 2, thermometer; 3, three-necked round-bottom flask; 4, syringe; 5, magnetic stirrer bar; 6, magnetic stirrer).

with a salinity of approximately 56 g kg⁻¹ was drained from a MED-based desalination plant in Tianjin, China, and used as the feed stream. Fig. 3 shows a flow chart for the continuous test system. The system mainly consists of two parts: a decalcification unit and a concentration unit. Static mixers were used as the decalcification unit rather than the traditional stirred reactor owing to their superior mixing and dispersion performance, smaller volume, and easier coupling with other equipment; the streams can be mixed thoroughly in a static mixer within only a few minutes or even a few seconds. MEMD modules supplied by PureSea Spring Membrane Technology Co. Ltd., (Tianjin, China) were used as the concentration unit, and the characteristics of these modules are listed in Table 3. The cold feed water was pumped into the lumen side of the dense-wall hollow fibers of the MEMD modules, in which the feed water was preheated to approximately 80°C (the principle of the MEMD system was the same as that described in previous studies [30,32,33]). After leaving the MEMD modules, the feed water was heated to 85°C using an external heat exchanger and then pumped into the static mixers. The reaction time in the static mixers was approximately 3 min, while the reaction temperature was maintained at 85°C and the 2 mol L⁻¹ sodium carbonate dosage was kept at the stoichiometric value. After microfiltration and pH adjustment to 7–8 using hydrochloric acid, the hot decalcified feed water reflowed into the lumen side of the porous hollow fibers in the same MEMD modules. This integrated process afforded precipitated calcium carbonate, freshwater, and concentrated brine.

4. Results and discussion

4.1. Effect of reaction temperature on calcium removal efficiency

Experiments were conducted to investigate the variation of the calcium removal efficiency at reaction temperatures ranging from 25°C to 95°C. In these experiments, the sodium carbonate dosage was fixed at the stoichiometric value

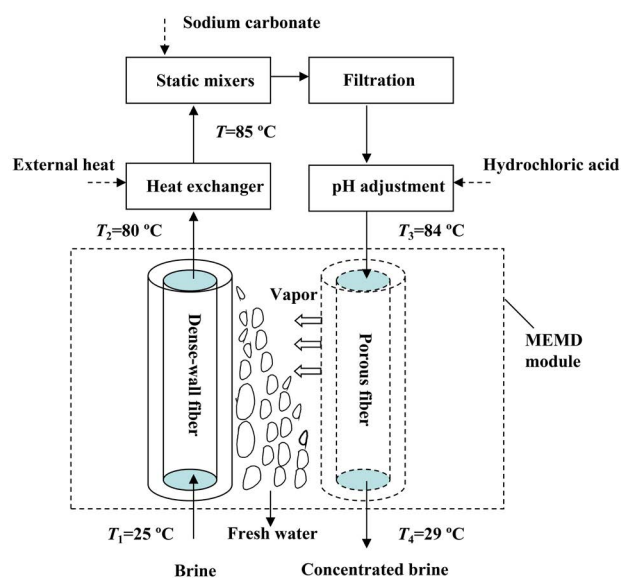


Fig. 3. Flow chart for the continuous pilot system.

Table 3
Characteristics of the MEMD module

Parameters	Values	
Porous fiber	ID/OD(mm)	0.44/0.75
	Average pore size (μm)	0.20
	Porosity (%)	68
Dense-wall fiber	ID/OD (mm)	0.40/0.50
Number of porous fibers		6,000
Ratio of the number of porous fibers and dense-wall fibers		1:1.5
Effective membrane surface area (m^2)		9.95
Effective length of the porous fiber (m)		1.20
Packing density (%)		45.5

(i.e., the molar ratio of sodium carbonate to the initial amount of calcium ions in the brine was 1:1), the stirring rate was fixed at 200 rpm, and the reaction time was fixed at 40 min.

As shown in Fig. 4, the calcium removal efficiency increased sharply with increasing reaction temperature. A similar upward trend was observed for the three brine samples with different salinities. The main reason for this trend is that the solubility of calcium carbonate decreases markedly with increasing temperature [20]. Also, increasing the temperature also increases the degree of supersaturation and the rate constant for crystal growth, leading to a higher growth rate and greater calcium carbonate crystallization [28]. Furthermore, increasing the temperature favors the precipitation reaction [30]. At the same time, the desorption rate of carbon dioxide from seawater increases with increasing temperature, resulting in an increase in pH, which can contribute to the increasing calcium carbonate precipitation rate [20,34]. Fig. 4 also shows that the increasing trend in calcium removal efficiency gradually reduced with increasing reaction temperature. In particular, the calcium removal efficiency increased only slightly in the temperature range of 85°C–95°C, because the carbon dioxide desorption and calcium carbonate solubility do not substantially change

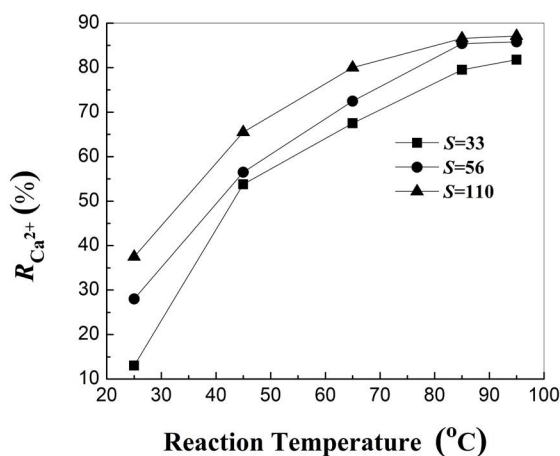


Fig. 4. Effect of reaction temperature on calcium removal efficiency for brine samples with various salinities (sodium carbonate dosage, equimolar; reaction time, 40 min; stirring rate, 200 rpm).

with increasing temperature at temperatures exceeding 85°C [35,36].

4.2. Effect of stirring rate on calcium removal efficiency

Experiments were conducted to evaluate the influence of the stirring rate on the calcium removal efficiency for brine samples with various salinities. The sodium carbonate dosage was fixed at the stoichiometric value, the reaction time was fixed at 40 min, and the reaction temperature was either 85°C or 25°C. As shown in Fig. 5, the calcium removal efficiency initially increased sharply upon increasing the stirring rate from 100 to 200 rpm. At stirring rates above 200 rpm, the calcium removal efficiency remained essentially unchanged with increasing stirring rate, indicating that the system was completely mixed at a stirring rate of 200 rpm. In particular, the calcium removal efficiency clearly increased with the increasing stirring rate at the reaction temperature of 85°C, because faster stirring enhanced the mass and heat transfer during the crystallization and the interface kinetics, which are the rate-determining factors of crystal growth [37]. It has also been reported that the nucleation incubation time decreases sharply when stirring is applied [38].

Fig. 5 also shows that the calcium removal efficiency increased considerably with increasing salinity and reaction temperature. In particular, the reaction temperature plays a key role in the precipitation of calcium carbonate [39], as described in detail in Section 4.1. To achieve the optimum calcium removal efficiency, the stirring rate was set to 200 rpm in the following experiments.

4.3. Effect of reaction time on calcium removal efficiency

The influence of the reaction time on the calcium removal efficiency was investigated for reaction times ranging from 10 to 60 min and four brine samples with different salinities. The sodium carbonate dosage was fixed at the stoichiometric value of 1:1, the reaction temperature was fixed at 85°C, and the stirring rate was set to 200 rpm.

As shown in Fig. 6, the calcium removal efficiency initially increased upon increasing the reaction time from 10 to 40 min, indicating that the nucleation and precipitation of calcium carbonate occurred during this period. This increasing trend was particularly noticeable for the brine samples with low salinities of 33 and 43 g kg^{-1} . Nevertheless, the calcium removal efficiency also increased slightly with increasing reaction time for the brine samples with high salinities of 56 and 110 g kg^{-1} . After 40 min, the calcium removal efficiency was essentially stable with increasing reaction time, reaching 84%–88% depending on the salinity. These results indicate that the precipitation process had almost reached completion after 40 min. Therefore, to reduce the energy consumption and reactor size, a reaction time of 40 min was selected for the subsequent experiments, as this afforded sufficiently high calcium removal efficiency.

4.4. Effect of salinity on calcium and magnesium removal efficiency

Fig. 7 shows the variation of the removal efficiency of calcium and magnesium ions for brine samples with salinities

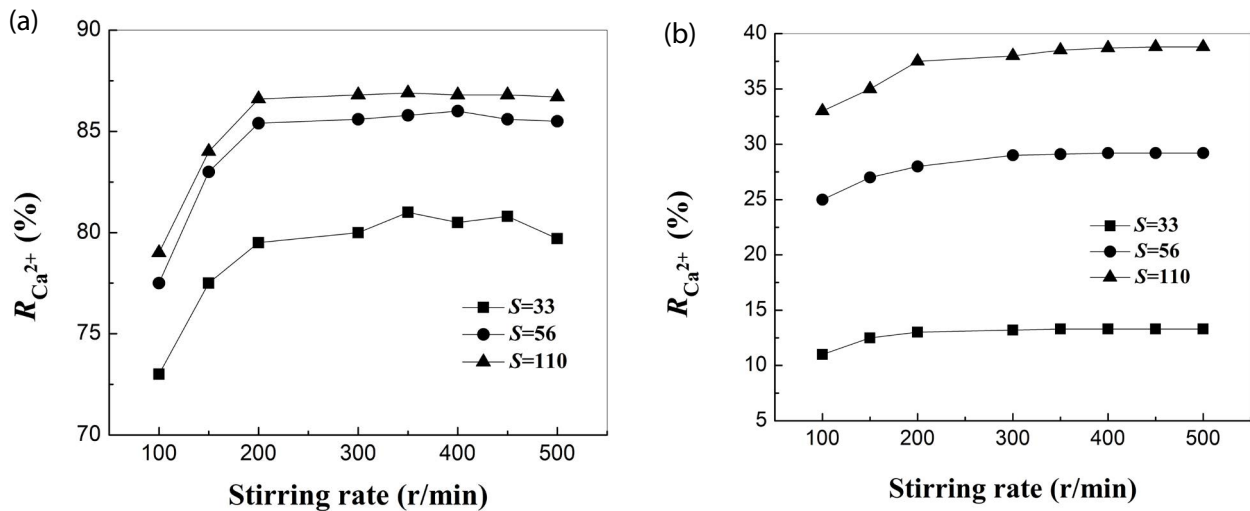


Fig. 5. Effect of stirring rate on calcium removal efficiency for brine samples with various salinities at reaction temperatures of (a) 85°C and (b) 25°C (sodium carbonate dosage, equimolar; reaction time, 40 min).

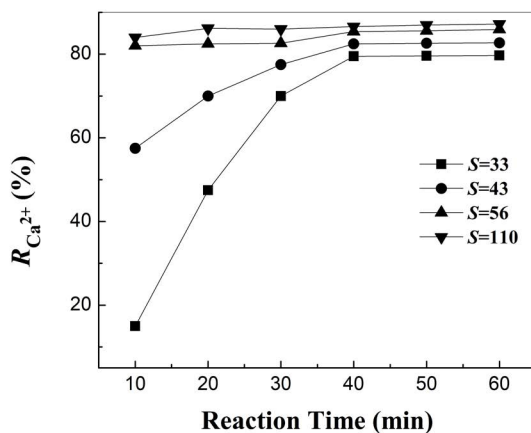


Fig. 6. Effect of reaction time on calcium removal efficiency for brine samples with various salinities (sodium carbonate dosage, equimolar; reaction temperature, 85°C; stirring rate, 200 rpm).

ranging from 33 to 125 g kg⁻¹. The sodium carbonate dosage was fixed at the stoichiometric value, the stirring rate was set at 200 rpm, the reaction time was 40 min, and the temperature was 25°C or 85°C.

As shown in Fig. 7a, the calcium removal efficiency initially increased with increasing salinity in the range of 33–56 g kg⁻¹. This increasing trend of calcium removal efficiency was more apparent at the temperature of 25°C, for which the calcium removal efficiency increased by almost three-fold as the salinity was increased from 33 to 66 g kg⁻¹. This could mainly be ascribed to the increased nucleation rate due to the higher initial calcium carbonate saturation level [35,40]. As the calcium ion concentration in the brine increased with increasing salinity, the saturation level of calcium carbonate, which is the main driving force for calcium carbonate precipitation, correspondingly increased. As shown in Fig. 7b, the magnesium removal efficiency decreased with increasing salinity in the range of 33–56 g kg⁻¹. At salinities exceeding 66 g kg⁻¹, the removal

efficiencies of both calcium and magnesium ions were essentially stable with increasing salinity. This can be attributed to the interaction between the positive and negative effects of increasing salinity. Although the saturation level of calcium carbonate initially increased with increasing salinity, in the range of 66–125 g kg⁻¹ the saturation level of calcium carbonate remained essentially stable owing to the low ionic activity of calcium ions and increasing calcium carbonate solubility [20]. As shown in Fig. 7c, the value of $\beta_{Ca^{2+}/Mg^{2+}}$ increased with increasing salinity in the range of 33–66 g kg⁻¹ and became stable thereafter. The experimental results also revealed that $\beta_{Ca^{2+}/Mg^{2+}}$ increased considerably with increasing reaction temperature. For the brine sample with a salinity of 56 g kg⁻¹, $\beta_{Ca^{2+}/Mg^{2+}}$ increased from 4 to 83 when the reaction temperature was increased from 25°C to 85°C. Therefore, a higher reaction temperature led to higher calcium removal efficiency and lower magnesium removal efficiency. The influence of the reaction temperature on the calcium removal efficiency was discussed in Section 4.1. The observed influence of the reaction temperature on magnesium removal efficiency is in good agreement with the results of Stefánsson et al. [41], who reported that the formation constants of the $MgHCO_3^+(aq)$ and $MgCO_3(aq)$ ion pairs increase significantly with increasing temperature, leading to a higher solubility of magnesium carbonate.

4.5. Effect of sodium carbonate dosage on calcium removal efficiency

The influence of the sodium carbonate dosage on the calcium removal efficiency was investigated for molar ratios of sodium carbonate to the initial amount of calcium ions in the brine ranging from 0.8 to 1.2 equivalents. The reaction temperature was fixed at 85°C, the reaction time was 40 min, and the stirring rate was 200 rpm. As shown in Fig. 8, the calcium removal efficiency increased with increasing sodium carbonate dosage. In particular, for the brine sample with a salinity of 110 g kg⁻¹, the calcium removal efficiency increased from 74.12% to 90.80% as the molar ratio of sodium carbonate

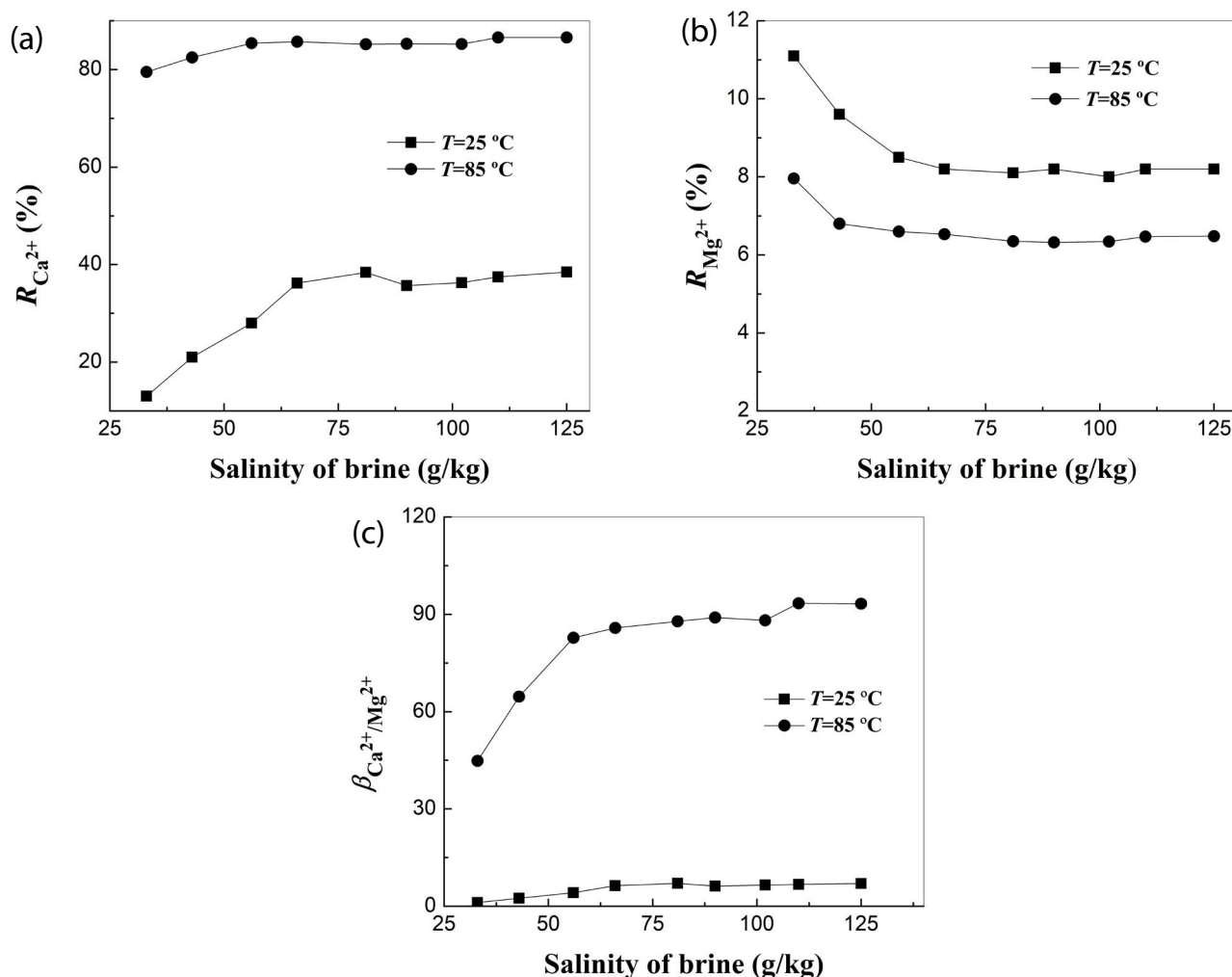


Fig. 7. Effects of salinity on the removal efficiency of (a) calcium ions and (b) magnesium ions and (c) selectivity for the removal of calcium ions over magnesium ions (sodium carbonate dosage, equimolar; reaction time, 40 min; stirring rate, 200 rpm; reaction temperature, 25°C or 85°C).

to calcium ions increased from 0.8 to 1.2. This trend was because the saturation level of calcium carbonate increased with increasing sodium carbonate dosage.

4.6. Variation of pH for the initial and decalcified brine samples

The brine samples used in this study were obtained by concentrating raw seawater via MEMD as described in Section 3.1. Before calcium ion removal, the pH values of the brine samples were adjusted to 8.2, which is a typical value for raw seawater. As shown in Fig. 9, the pH of the filtrate (the decalcified brine at the reaction endpoint) had significantly increased during the course of the precipitation reaction from the initial pH of 8.2 to a higher value owing to the addition of sodium carbonate, which is a weak base whose aqueous solution has a buffering pH value of ca. 11.5; however, the final pH of the decalcified brine decreased with increasing initial salinity. This decreasing trend was mainly ascribed to the fact that the amount of calcium carbonate precipitation increases with increasing salinity, as shown in Fig. 7a. The pH of the decalcified brine was

relatively low at the reaction temperature of 85°C compared with that at the reaction temperature of 25°C in the same range of salinity, because the higher reaction temperature promoted the hydrolysis of carbonate ions and the precipitation of calcium carbonate. When the reaction temperature was set to 85°C, the pH of the decalcified brine was approximately 8.5 for salinities above 66 g kg⁻¹, which is similar to the pH of the initial brine. These results demonstrate that the softening process based on sodium carbonate can deliver good performance for the selective removal of calcium ions without a substantial change in the pH; thus, it is convenient for minimizing the cost of acidification during subsequent pH adjustment, which is commonly used in the following concentration processes as a pretreatment to control salt precipitation and membrane scaling.

4.7. Effect of magnesium ions on calcium removal efficiency

The influence of magnesium ions on the calcium removal efficiency was investigated using aqueous solutions of calcium chloride/sodium chloride (i.e., without magnesium ions)

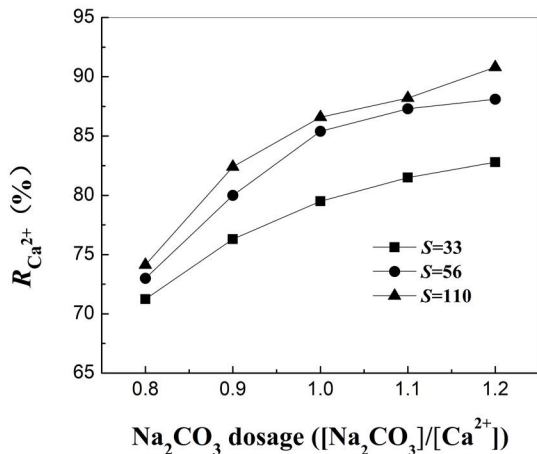


Fig. 8. Effect of sodium carbonate dosage on calcium removal efficiency for brine samples with various salinities (reaction temperature, 85°C; reaction time, 40 min; stirring rate, 200 rpm).

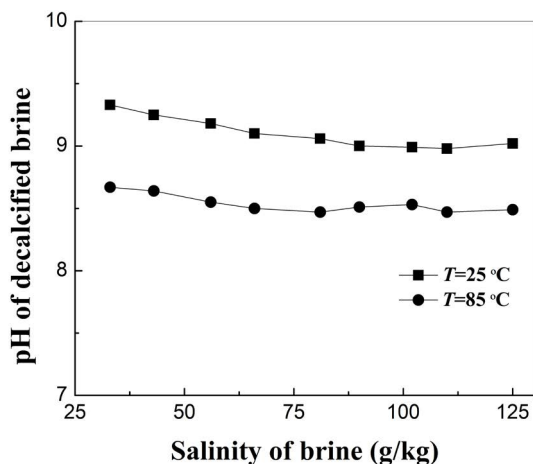


Fig. 9. Variation of the pH of the decalcified brine to the salinity of the initial brine (pH of the initial brine, 8.2; sodium carbonate dosage, equimolar; reaction time, 40 min; stirring rate, 200 rpm; reaction temperature, 25°C or 85°C).

and calcium chloride/magnesium chloride/sodium chloride. These aqueous solutions were prepared by dissolving appropriate amounts of the salts in water according to the molar ratio of calcium, magnesium, and sodium ions in raw seawater ($\text{Ca}^{2+}:\text{Mg}^{2+}:\text{Na}^+ = 1:4.1:42.7$). The calcium ion concentration in the aqueous solutions was varied from 410 to 1,600 mg L⁻¹, based on the range of calcium ion concentrations in the brine samples with salinities of 33–125 g kg⁻¹ (Table 2).

As shown in Fig. 10a, the calcium removal efficiency was greater than 96.2% at the reaction temperature of 25°C for the solutions lacking magnesium ions. In contrast, as shown in Fig. 10b, for the solutions containing magnesium ions the calcium removal efficiency, was less than 36% at the reaction temperature of 25°C, even at the high calcium ion concentration of 1,600 mg L⁻¹. This was ascribed to the inhibition of calcium carbonate crystallization by magnesium ions owing

to the formation of precipitates of magnesium carbonate and calcium magnesium carbonate upon the addition of sodium carbonate [42]. Numerous studies have demonstrated that magnesium ions exert a profound effect on scale formation and the growth rate of calcium carbonate [23,42,43]. For example, Chen et al. reported that the quantity of calcium carbonate precipitate decreased sharply with increasing magnesium ion concentration at a reaction time of 8 h [23]. Similarly, Dawe and Zhang [42] reported that the presence of magnesium ions at $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratios between 0.1 and 0.5 caused a 50% reduction in calcium carbonate growth. The current experimental results also demonstrate that the presence of magnesium ions severely interfered with calcium ion removal, reducing the calcium removal efficiency from 98.1% to 65.1% at 85°C and a calcium ion concentration of 410 mg L⁻¹, despite the high reaction temperature. However, increasing the reaction temperature substantially enhanced the calcium removal efficiency for the solutions containing magnesium ions.

Following the removal of calcium ions, the treated brine can be further concentrated via RO, MD, MED, or MVR processes to produce a stream of water and concentrate. The concentrate can be used to obtain salts and other chemicals. Alternatively, the decalcified brine and the concentrate can be further subjected to NF to retain the sulfate ions, magnesium ions, and remaining calcium ions, while the permeate can be directly used as the water source in caustic soda and soda ash plants. The permeate contains water and salts in moderate purity and concentration, which makes the replacement of water by the permeate beneficial to the caustic soda and soda ash industry.

4.8. Long-term operation of the pilot system

The long-term operational performance of the selective decalcification process was evaluated by plotting R (i.e., the calcium removal efficiency) vs. the operation time, as shown in Fig. 11. It can be observed that 83%–85% removal of calcium ions was achieved in the decalcification process during the six months of operation. Although the reaction time in the static mixers was only approximately 3 min, the calcium removal performance was superior to that of a traditional stirred reactor at a reaction time of 30 min (as shown in Fig. 6). This significantly decreased reaction time greatly reduced the bulk of the reactor. In addition to the high performance of the static mixers, these results also demonstrate the effectiveness and long-term operational stability of the selective decalcification process.

After decalcification, the feed water could be concentrated to at least 180 g kg⁻¹ using MEMD. During the six-month operational period of the continuous test, no fouling or scaling phenomena occurred in the MEMD modules. In contrast, non-decalcified brine could only be concentrated to 130 g kg⁻¹ before precipitation of calcium sulfate occurred [44].

In a conventional MEMD process, the maximum temperature of the feed water exerts a considerable influence on the performance (a detailed description of the operating principle of the MEMD process was provided in our previous papers [30,33]). In the pilot system, the heated feed-in temperature was 84°C (T_3 in Fig. 3). To perform the MEMD

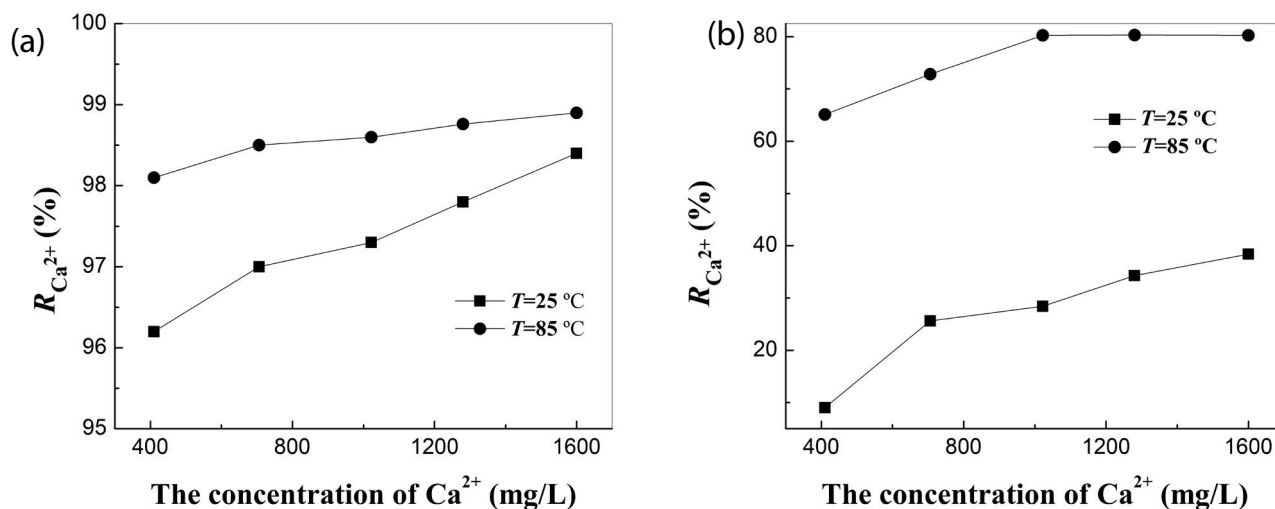


Fig. 10. Effect of the presence of magnesium ions on calcium removal efficiency for mixed aqueous solutions of (a) calcium chloride/sodium chloride and (b) calcium chloride/magnesium chloride/sodium chloride (sodium carbonate dosage, equimolar; reaction time, 40 min; stirring rate, 200 rpm; reaction temperature, 25°C or 85°C).

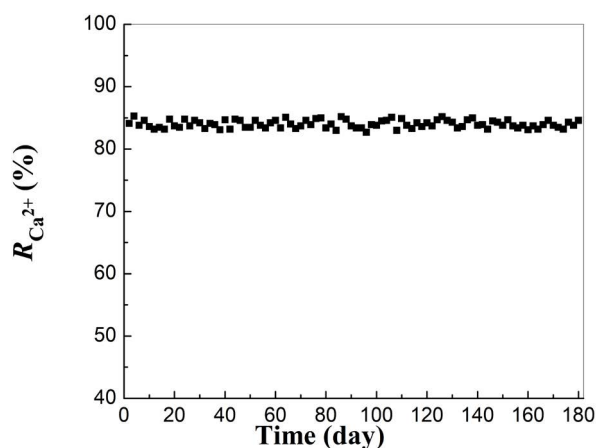


Fig. 11. Long-term operational stability test of calcium removal efficiency.

process, a small amount of external heat was required to further increase the temperature of the feed water from 80°C to 84°C. To account for the anticipated heat loss in the subsequent processes such as decalcification and filtration, the feed water was heated from 80°C to 85°C. Therefore, the additional heat consumed by the decalcification process was simply the amount needed to increase the feedwater temperature by approximately 1°C (thus the steam consumption was approximately 1.87 kg per ton of feed water). To realize the integrated system, additional pumps were needed for the decalcification and filtration steps, and the electricity consumption increased by approximately 0.3 kWh per ton of feed water. Therefore, the energy cost for the decalcification process in the pilot system was very low. Although sodium carbonate was needed for the pilot system, which increased the operating cost, this also permits the utilization of the mineral resources present in the concentrated brine. Additionally, high-purity calcium carbonate is produced as a by-product of

the decalcification process, which can be used as a reagent for the flue-gas desulfurization technologies used in coal-fired power plants. Furthermore, the concentrated brine with a salinity of 180 g kg⁻¹ or higher could be directly used to produce sodium chloride and other salts in plants instead of evaporation in solar evaporation ponds. Moreover, the sulfate ions still present in the brine could also be recovered in the form of magnesium sulfate rather than the less useful calcium sulfate.

4.9. Effective integration of the decalcification process and routine desalination processes

Besides MEMD, the selective decalcification process could be effectively combined with other routine concentration or separation processes. Decalcification at high temperatures is an efficient procedure for selectively removing calcium ions from seawater or brine. Following this process, the decalcified brine is at a high temperature, e.g., 85°C. Thus, it must be considered firstly how to heat the feed stream, that is, the seawater or brine, which is typically cold, and secondly how to use the hot brine for further desalination. Although high-temperature decalcified brine can be used directly as the feed water for MD processes, hot feed with a temperature of 85°C is not suitable for routine RO, NF, MSF, or MED processes. The practical operating temperature of RO membranes is typically limited to less than 40°C–45°C, while MED processes are usually operated at temperatures of less than 65°C [45,46]. Therefore, the procedure depicted in Fig. 12 is proposed to increase the feed temperature, decalcify the feed water, and decrease the temperature of the decalcified brine to near the original temperature of the cold feedwater. This scheme does not require a large heat input. For example, even though the decalcification is performed at 86°C, the external heat consumed is only the amount needed to increase the feedwater temperature from 80°C to 86°C, and increasing the temperature of the cold feedwater from 25°C to 80°C is achieved via a simple heat exchanger that

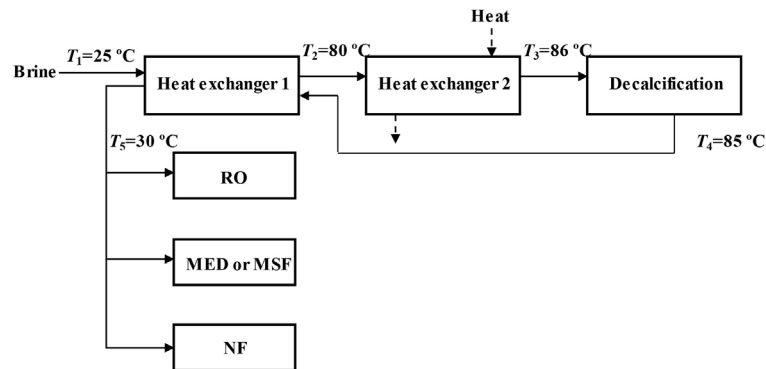


Fig. 12. Flow chart showing the proposed integration of the decalcification and desalination processes.

requires no external heat input. In this system, the steam consumption needed to heat the feed water from 80°C to 86°C is 11.2 kg per ton of feed water. As shown in Fig. 12, the hot decalcified brine is cooled down to 30°C alongside the preheating of the cold brine in the heat exchanger, which meets the feedwater temperature requirements of RO or NF processes.

It must be pointed out that the decalcified brine still cannot be directly used in caustic soda and soda ash plants. However, NF can be further applied to remove sulfate ions, magnesium ions, and residual calcium ions. The purified permeate can then be used directly with or without further concentration via RO treatment, to increase the water recovery ratio as well as produce a highly concentrated saline solution.

5. Conclusions

The selective removal of calcium ions from seawater or brine using sodium carbonate was systematically investigated to enhance calcium removal efficiency. The results revealed that the reaction temperature was an important factor that influenced the calcium removal efficiency and calcium ion/magnesium ion selectivity; the calcium removal efficiency and selectivity increased by up to approximately 6-fold and 44-fold, respectively, when the reaction temperature was increased from 25°C to 85°C . The calcium removal efficiency also increased with increasing sodium carbonate dosage. Also, the calcium removal efficiency increased with increasing stirring rate and brine salinity to a certain extent.

In the batch-scale experiments, the optimum calcium removal performance was achieved using a reaction temperature of 85°C , a reaction time of 40 min, a stirring rate of 200 rpm, and an equimolar sodium carbonate dosage relative to the initial calcium ion concentration. Under the optimized conditions, the calcium removal efficiency reached 85% at the cost of ca. 6.7% loss of magnesium ions, and the calcium ion/magnesium ion selectivity was up to 83 for a brine salinity of 56 g kg^{-1} . In the continuous test experiments, static mixers were used for the decalcification process, and the calcium removal efficiency reached 82%–85% after a reaction time of only 3 min. Owing to the high mixing and dispersion efficiency of the static mixers, the reactor volume was decreased considerably. These results demonstrate

that the use of sodium carbonate solution at high operating temperatures provides an effective means for selectively removing calcium ions from brine with a high magnesium-to-calcium ratio, and static mixers are suitable for its industrial application.

The developed decalcification process can be used as a pretreatment step to improve water recovery during desalination processes. For example, the hot decalcified brine could be used directly as the feed water for MD processes, especially via integration with MEMD, where only a very small amount of external heat is required for the high-temperature decalcification step. Alternatively, the hot decalcified brine could be cooled down to the appropriate temperature for routine desalination processes such as RO or NF by using a heat exchanger to preheat the initial cold brine.

The developed decalcification process can also improve the cost/benefit analysis for desalination processes by allowing utilization of the mineral resources present in concentrated seawater. For example, the sulfate ions present in the decalcified brine could be recovered in the form of magnesium sulfate rather than the less useful calcium sulfate by introducing subsequent concentration/crystallization steps. High-purity calcium carbonate, which is obtained as a by-product from the decalcification process in the shape of a fine powder, can be used in the flue-gas desulfurization technologies used in coal-fired power plants.

Following the removal of calcium ions, the treated brine can be further concentrated via RO, MD, MED, or MVR processes to produce a stream of water and concentrate. The concentrate can be used to obtain salts and other chemicals. Alternatively, the decalcified brine and the concentrate can be further subjected to NF to retain the sulfate ions, magnesium ions, and remaining calcium ions, while the permeate can be directly used as the water source in caustic soda and soda ash plants. The permeate contains water and salts in moderate purity and concentration, which makes the replacement of water by the permeate beneficial to the caustic soda and soda ash industry. Moreover, with the effective integration of the developed decalcification and NF processes, brine with high salinity and calcium sulfate saturation index can be used for the production of caustic soda and soda ash.

With the effective integration of the developed decalcification process and brine concentration/separation technologies, zero or near-zero liquid discharge of seawater desalination brine from plants could be achieved, thereby reducing or

even eliminating the adverse impact of desalination on aquatic ecosystems.

Acknowledgments

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