Mechanism studies of a CO_2 participant softening pretreatment process for seawater desalination

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HIGHLIGHTS

- The mechanism of CO2 decalcification using NaOH as alkali source was studied.
- Mg(OH)2 and Ca(OH)2 firstly formed, and then dissolved but CaCO3 crystallized.
- The material conversion was analyzed with the ion concentration variation.
- The new enlightenment of magnesium hydrate as the new alkali source.

ARTICLE INFO

ABSTRACT

To explore the mechanism of the CO_2 participant softening pretreatment process, a series of experiments and analyses have been conducted to study the process of decalcification with NaOH as alkali source and CO_2 as precipitator, which includes the material conversion of precipitate, Ca^{2+}, Mg^{2+}, CO_3^{2-}, HCO_3^-, and OH^- ion concentrations and pH in solutions. It is found that the decalcification pretreatment process is a complex reaction involving first formation of $Mg(OH)_2$ and $Ca(OH)_2$ before CO_2 is injected, and then $CaCO_3$ is nucleated and crystallized, following the dissolving of $Mg(OH)_2$ and $Ca(OH)_2$ with the continuous influx of CO_2. $MgCO_3 \cdot 3H_2O$ is not formed until all the $Ca(OH)_2$ gradually transformed to $CaCO_3$, and it begins to dissolve as there is only $CaCO_3$ left in the precipitates. Then the added amount of NaOH is changed to study the precipitate before CO_2 is injected, and material transformation of deposit with bubbling CO_2 is investigated. This further study provides a favorable evidence for a new enlightenment, that is, magnesium hydrate may work as the new alkali source for CO_2 participant softening pretreatment technology, which has more economical value than sodium hydroxide.

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1. Introduction

Desalination plants have undergone considerable expansion during the past decade as the need for drinking water increases with population growth [1,2]. Although technological advances have resulted in the development of new and highly efficient desalination processes, little improvements have been reported in the management and handling of the decalcification pretreatment to avoid the calcium scaling in the desalination process, which caused the increase of cost for periodic cleaning, the extension of production cycle, the deterioration of the basic equipment functions, a negative effect on heat and mass transfer, the reduction of the yield, and such drawbacks [3–5].

Al-Rawajfeh et al. [6] presented a model for the development of scale formation in once-through (OT) and brine-recycle (BR) multi-stage

flash (MSF) evaporator, showing fouling factor increases with increasing the temperature. Therefore, the removal of calcium and magnesium ions will allow the operation of thermal desalination units at higher temperatures, thus leading to increased performance ratio, lower volumes of brine reject and energy consumption [7], reduced need of anti-scalants, and ultimately, lower desalinated water costs.

For membrane processes, the removal of Ca and Mg will significantly reduce the risks of inorganic fouling, thus leading to reduced need of anti-scalants and consequently resulting in reduced membrane replacement, operation, and maintenance costs. For example, many researchers have reported the positive effect of using UF membranes as a pretreatment for RO desalination [8–11]. However, Li et al. [12] proposed that the fouling of UF membranes is a challenge for the widespread application of UF in seawater desalination as well. He put forward an improved seawater UF fouling control by demineralized water backwashing, yet the calcium ions in UF permeate probably deteriorate the fouling control efficiency by maintaining a Ca-bridging effect between the membranes and natural organic matter.

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Precipitation softening through the use of a variety of chemicals, such as lime, sodium bicarbonate, sodium carbonate, and sodium hydroxide, whether individually or in combination, has been utilized for the removal of calcium and magnesium ions from various water and seawater [13–16]. Ayoub et al. [16] evaluated the use of precipitation softening techniques as a pretreatment step for seawater desalination and propose that precipitation softening of seawater has received limited attention in the literature where the process was investigated as a pretreatment step, either on a stand-alone basis or in combination with other processes.

In previous work [17], we have realized the importance of decalcification pretreatment for seawater desalination and proposed a different approach for seawater decalcification pretreatment using carbon dioxide as precipitator. Seawater decalcification pretreatment was successfully realized using CO_2 as precipitator and NaOH as alkali source, demonstrating that decalcification pretreatment by CO_2 injection has the potential of eliminating the major fouling and scaling caused by calcium in seawater desalination plants. $CaCO_3$ was controlled to precipitate using the carbon dioxide as precipitant by alkalization to remove calcium ions and then avoid the fouling during desalination, for the dissolution ability of CO_2 in seawater increased with the increase of pH values. Then the feed seawater for the following desalination requires no chemical adjustment for no other additional ions are added in expect for sodium ions substitution of calcium ions. Meanwhile, CO_2 is mineralized by reacting with natural mineral in seawater, reducing the emissions of greenhouse gas. Moreover, CO_2 and natural mineral in seawater, referring mainly to calcium ions, can be transformed into valuable calcium carbonate.

In order to explore the mechanism and the optimum process conditions for realizing industrialization, a series of experiments and analyses have been conducted in this paper to study the process of pretreatment. The aim of this work was to study the pretreatment process at a lab scale with an emphasis on the changes in the relative composition of sediment material as a function of operating time.

2. Experimental procedure

2.1. Experimental unit

The pretreatment process was studied carefully by monitoring five measured parameters simultaneously, that included: pH, calcium concentration $[Ca^{2+}]$, magnesium concentration $[Mg^{2+}]$, and CO_3^{2-},

HCO_3^-, and OH^- ion concentrations. The experimental unit used is represented in Fig. 1.

A CO_2 steel cylinder (1) equipped with decompressor (2) and rotameter (3 and 4) was used to control the flowrate of CO_2, and CO_2 was well dispersed by a gas sparger (8) in a three flask (7) of a capacity of 500 mL, which was used to maintain the solution at constant temperature by a thermostatic bath (10) with a magnetic stirring (11) to keep the solution homogeneous. The solution pH was measured using ZD-2 automatic potentiometric pH meter (12). Burettes were used to determine $[Ca^{2+}]$, $[Mg^{2+}]$ and alkalinity.

2.2. Experimental process

Solutions were prepared using calcium chloride ($CaCl_2$) and magnesium chloride ($MgCl_2$) dissolved in deionized water without CO_2. Ionic concentration was referred to the $[Ca^{2+}]$ and $[Mg^{2+}]$ in artificial seawater, as listed in Table 1. Experiments were conducted by firstly introducing a weighed amount of sodium hydroxide into 250 mL prepared solution, which would react with each other and be stirred sufficiently. The suspension was injected CO_2 at a controlled flowrate for a certain period of time. The input gas was fully in contact with the solution by dispersing with the use of a gas sparger. After a certain time, the solutions were immediately filtered through MiUipore @ 0.45 μm filters. Samples were collected at 0–10 min at a time interval of 1 min, and 10–20 min at a time interval of 2 min on a batch mode. Calcium and magnesium ions were measured by EDTA complexicretric titration method, carbonate, bicarbonate and hydroxyl ions by acid–base titration method with standardized 0.025 M HCl and phenolphthalein and methyl orange as indicators respectively.

Sediment characterization was performed by XRD and SEM. X-ray diffraction analysis (XRD) was used to characterize the precipitation on a D8 Focus diffractometer (Bruker, Germany) using monochromatic radiation (40 kV and 40 mA) in the range of 2θ from 10.0° to 80.0°, at a step size of 0.05° with a counting time of 5 s for each step. Scanning electron microscope (FEI NanoSEM 450) analysis were used to identify the morphology of the precipitates and to confirm the electro microscopic results.

3. Results and discussion

In this study, certain amount of sodium hydroxide was added one-time but CO_2 was continuously injected at fixed flowrate, a series of
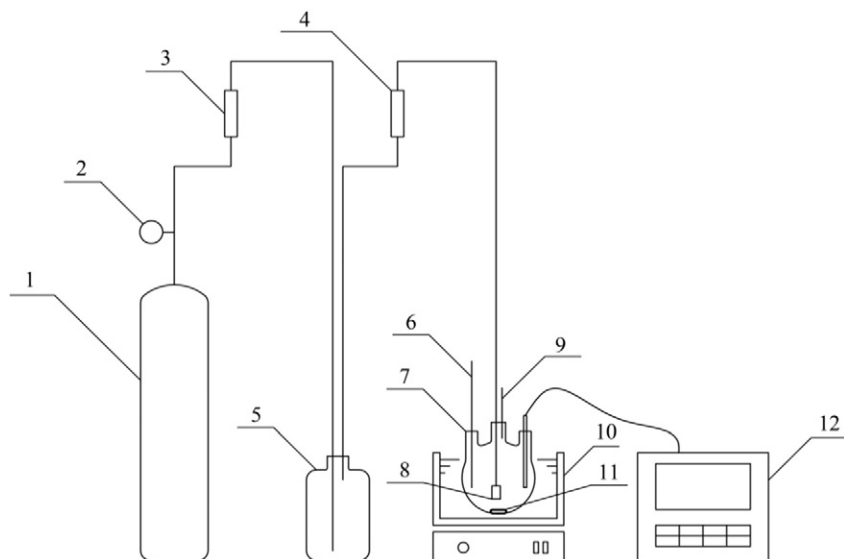

Fig. 1. Experimental unit, (1) CO_2 steel cylinder, (2) decompressor, (3) rotameter, (4) rotameter, (5) surge flask, (6) thermometer, (7) thermostatic cell, (8) gas sparger, (9) gas outlet, (10) thermostatic bath, (11) magnetic stirring, (12) pH meter.