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Effect of chemical and physical factors on the crystallization of calcium sulfate in seawater reverse osmosis brine

Youngkwon Choi[a], Gayathri Naidu[a], Sanghyun Jeong[b], Sangho Lee[c], Saravanamuthu Vigneswaran[a],*

[a] Faculty of Engineering, University of Technology Sydney (UTS), P.O Box 123, Broadway, NSW 2007, Australia
[b] Graduate School of Water Resources, Sungkyunkwan University (SKKU), 2066, Seobu-ro, Jangan-gu, Suwon-si, Gyeonggi-do 16419, Republic of Korea
[c] School of Civil and Environmental Engineering, Kookmin University, Seoul 136-702, Republic of Korea

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ABSTRACT

A major challenge of seawater reverse osmosis (SWRO) desalination process corresponds to the management of concentrated brine waste because discharging the brine back into the sea influences the marine ecosystem and incurs additional costs to plants. A membrane distillation crystallizer (MDC) can further produce clean water and simultaneously recover valuable resources from the concentrated brine; this is more environmentally and economically optimal. SWRO brine contains salts, which contribute to scaling development during the MDC operation. Hence, the main goals of this study was to observe the crystallization tendency of calcium sulfate ($CaSO_4$) under high salinity and, to examine other inorganic and organic compounds and operational conditions that affect the $CaSO_4$ crystallization. The crystallization tendency of $CaSO_4$ in SWRO brine was examined with respect to different temperatures; changes in pH values; and in the presence of co-existing ions, chemical agents, and organic matters as well as physical factors. The results showed that the size and quantity of crystals formed increased at higher temperatures. Furthermore, an increase in the pH values increased the crystal size. At higher pH, the complexion of NaCl along with $CaSO_4$ was created. Moreover, stirring enhanced $CaSO_4$ crystal formation due to the kinetic mechanism.

1. Introduction

The demand for desalination technology based on seawater reverse osmosis (SWRO) process is continuously increasing with the global lack of potable water [1,2]. However, SWRO generates a high amount of concentrated brine containing high salt concentration that causes serious environmental issues [3]. The treatment or disposal methods of SWRO brine are highly dependent on the location of the SWRO plant. For example, an inland SWRO plant requires brine disposal methods such as an evaporation pond and deep well injection. When SWRO brine is directly discharged into seawater, additional facilities are required to transport it, thereby incurring additional operational costs. Furthermore, the direct discharge of SWRO brine to sea influences the marine eco-system due to the high concentration of salt and chemicals in the SWRO brine [4]. Extant studies reported on the contamination of soil, ground water, and the marine eco-system by brine [4,5]. Several researchers tested alternative methods for brine treatment and used methods mainly based on membrane technologies, such as forward osmosis (FO), pressure retarded osmosis (PRO), and membrane distillation (MD), to recover valuable resources or energy from the brine while producing water, and subsequently resulting in the reduction of environmentally negative effect of brine on the ecosystem [6–13].

The MD process is a promising technology for treating high salinity solution such as SWRO brine [12–14]. This is because MD is a mechanically and thermally driven desalination process that is operated by the vapor pressure difference between hot feed solution and cool permeate solution flowing across a micro-porous hydrophobic membrane. Thus, the effect of solution concentration on permeate flux is less than that of the other desalination processes [3,15]. Additionally, MD possesses several advantages including high rejection of non-volatile components, lower operational pressure when compared to that of reverse osmosis (RO), and lower operating temperature and smaller footprints when compared to those of conventional distillation processes [16–18]. Recently, a novel combined process, namely MD with a crystallizer (MDC), is highlighted with an increase in the interest to recover valuable resources from seawater [3,19–23].

Specifically, SWRO brine contains a higher concentration of

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* Corresponding author.
E-mail address: Saravanamuth.Vigneswaran@uts.edu.au (S. Vigneswaran).

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valuable resources when compared to feed water (seawater). During the crystallization process, salts in the SWRO brine can be separated and used as a valuable resource. However, although these salts may be used as valuable resources, they may display a negative influence at high concentrations and especially when they are treated by using conventional treatment methods [24]. The application of MD enables in achieving a highly concentrated brine, and thereby generating a supersaturation state for crystallization [25]. Theoretically, MD concentrates the feed solution to create a super-saturated solution to form crystals [22]. Meanwhile, the crystallization part of MDC mitigates the scaling phenomenon on membrane surface because salts are continuously removed as solid crystals in the crystallizer [19,26].

Despite the high potential of the MDC, fouling and scaling phenomena are inevitable. These phenomena are more evident with the SWRO brine treatment when compared to the desalination process [19,27]. The SWRO brine contains calcium (Ca^{2+}) based crystalline matters with a high concentration; calcium sulfate ($CaSO_4$) and calcium carbonate ($CaCO_3$) that possess low solubility [28]. Thus, Ca^{2+} based crystalline matters first precipitate in the form of crystals prior to reaching a super-saturation state of the target material. Hence, the surface and pores of the MD membrane can be covered by these sparingly soluble salts [29]. Previous studies investigated the scaling of $CaSO_4$ and $CaCO_3$ in the MD process [13,30]. He et al. (2009) examined the effect of temperature and feed flow velocity on crystallization tendency in a direct contact membrane distillation (DCMD) process. Curcio et al. (2009) investigated the interaction between $CaCO_3$ crystallization and biofouling in a high salinity solution. However, there is a lack of fundamental studies on the salts crystallization tendency due to various factors because most studies on Ca^{2+} scaling and fouling phenomenon focus on the membrane surface. It is important to understand Ca^{2+} crystallization tendency in terms of the influence of chemicals and physical factors.

The characteristics of SWRO brine depend on feed water quality, the recovery ratio of the SWRO process, the pre-treatment methods of feed water, and the chemical cleaning methods of the membrane [1,31–33]. The SWRO brine contains various ions and chemical components that are used in the pre-treatment processes and during membrane chemical washing in the RO process. Additionally, the concentration of these ions in the brine is double or higher than that in feed water [33]. The ionic interaction among the ions leads to the crystallization propensity of $CaSO_4$ in the SWRO brine. Therefore, it is important to understand the influence of all ions on the crystallization tendency of $CaSO_4$ for the stable operation of the MDC process. This also obtains reliable information on the ionic interaction for $CaSO_4$ crystallization because it can act as a major foulant in the MD part of MDC process, thereby resulting in the degradation of process performance [34]. Moreover, physical factors, such as agitation (in feed tank) and stirring speed, can affect crystallization during the MDC process [35].

Thus, the present study investigates the crystallization tendency of $CaSO_4$ in the SWRO brine for different conditions: temperatures (50–80 °C) and pH values (5–9). The study also examined the effect of (1) chemical factors (temperature, pH, NaCl concentration, and chemical agents); (2) organic matters (alginate (AA), humic acid (HA), and bovine serum albumin (BSA)); and (3) physical factors (agitation) on the $CaSO_4$ crystallization. The crystal growth was evaluated in terms of the crystal size distribution (CSD) and calcium ion (Ca^{2+}) removal efficiency (variation in the Ca^{2+} concentration before and after the crystallization).

2. Materials and methods

2.1. Preparation of feed solution

In order to observe $CaSO_4$ crystallization phenomenon in high salinity solution, a synthetic feed solution containing high concentrations of calcium (Ca^{2+}) and sulfate (SO_4^{2-}) ions as approximately twice as seawater (to represent 50% recovered real SWRO brine) was prepared [36]. The stock solutions of sodium chloride (NaCl), sodium sulfate (Na_2SO_4), and calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$) were prepared and used as a feed solution, and its composition is specified in Table 1.

Table 1
Composition of the synthetic feed solution for the $CaSO_4$ crystallization experiment.

Ions	Concentration (mg/L)
Calcium (Ca^{2+})	1620
Sodium (Na^{+})	51,460
Chloride (Cl^{-})	73,770
Sulfate (SO_4^{2-})	11,520

2.2. Batch crystallization experiment

In order to examine the tendency of $CaSO_4$ crystallization in the concentrated brine, batch experiments were conducted under same standard conditions with the exception of a single parameter that was changed to examine the effect of the specific parameter on crystal formation. The feed corresponds to a mixed solution of NaCl, Na_2SO_4, and $CaCl_2 \cdot 2H_2O$. Given all the ions that are present, Ca^{2+} and SO_4^{2-} are combined by an ionic electric bond force and precipitation in the form of $CaSO_4$ crystals (Fig. 1). The crystallization phenomenon is influenced by chemical and physical factors. Hence, all experimental sets were initially conducted at a standard condition (heating temperature: 60 °C, pH 7, and stirring speeds: 200 and 50 rpm). The high speed (200 rpm) was to homogeneous the solution and lower speed of 50 rpm was to generate a crystallization. The temperature, pH value, and stirring speed conditions were altered to examine the effect of them individually on crystallization. In order to examine the effect of temperature on $CaSO_4$ crystallization, feed solutions were heated in a water bath set at the following temperatures: 50 °C, 60 °C, and 80 °C.

Essentially, a heating temperature of 60 °C was used and first tested with synthetic feed solution as shown in Table 1. A 500 mL feed solution was prepared in a beaker with pH adjusted by using 0.1 M HCl and 0.1 M NaOH. In order to examine the effect of temperature on $CaSO_4$ crystallization, feed solutions were heated in a water bath set at the following temperatures: 50 °C, 60 °C, and 80 °C. Subsequently, feed solutions were mixed in a jar-tester at a high speed (200 rpm) for 2 min for complete mixing and then allowed to stand for 24 h at a room temperature with a stirring at low speed (50 rpm) for continuous mixing while facilitating crystallization. After 24 h, the crystals were separated from the solution by using a glass microfiber filter (Whatman, Grade GF/C, pore: 1.2 μm).

2.3. Chemicals and solutions

2.3.1. $CaSO_4$ with other ions

The effect of other ions on $CaSO_4$ crystallization was investigated with sodium chloride (NaCl), bicarbonate (HCO_3^{-}) (by using sodium bicarbonate ($NaHCO_3$)), magnesium (Mg^{2+}) (by using magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$)), and potassium (K^{+}) (by using potassium chloride (KCl)).

2.3.2. Chemical washing agent

The effect of alkaline reagents of ethylene diamine tetraacetic acid (EDTA) was used as a chemical washing agent in the membrane of a SWRO desalination plant to remove fouling on the membrane surface [37,38].

2.3.3. Coagulant

Coagulation decreases biological materials in the feed water of the