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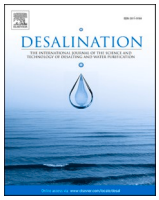

Effect of sodium chloride on yield, purity, morphology and polymorphs of calcium or magnesium carbonate sequentially precipitated from brine solution

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HIGHLIGHTS

- Study shows the effect of 0.0 M to 2.0 M NaCl on precipitation calcium or magnesium carbonates from oilfield brine.
- The concentration of 1 M NaCl offered maximum yield and purity of the precipitates.
- 0–0.5 M NaCl favored more precipitation of aragonite and calcite whereas 1–2 M NaCl favored aragonite, vaterite, and calcite.
- 0.0 M to 2.0 M NaCl did not change the polymorph of magnesium carbonate only it affected its morphology.
- The findings show that $CaCO_3$ or $MgCO_3{\cdot}3H_2O$ can be produced from oilfield brine for various industrial applications.

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ABSTRACT

Oilfield brine disposal in marine environments is undesirable due to concentrated salts of calcium, magnesium, sodium, and others which endanger aquatic organisms. Thus, it is paramount to precipitate the dissolved ions into stable carbonates for industrial applications. However, the effect of NaCl in the brine solution on the quantity and quality of precipitated carbonates is not yet reported. In this study, microwave plasma atomic emission spectrometer (MIP AES), x-ray diffraction (XRD), and scanning electron microscopy (SEM) were employed to investigate the effect of 0–2 M NaCl on the yield, purity, polymorph, and morphology of calcium and magnesium carbonates. The yields of 96.2% to 98.9% and 53.7% to 69.6% and the purity of 90.9% to 92.7% and 96% to 99.5% $CaCO_3$ and $MgCO_3{\cdot}3H_2O$ were obtained, respectively. Moreover, the maximum yield and purity of carbonates were obtained from a brine solution of 1 M NaCl. The concentration of 0–0.5 M NaCl favored more the formation of aragonite whiskers and rhombohedral calcite whereas the concentration of 1–2 M NaCl favored more the formation of aragonite whiskers, lamella vaterite,and rhombohedral calcite. Nevertheless, only nesquehonite ($MgCO_3{\cdot}3H_2O$) precipitated regardless of brine concentration. The crystal surface and length of the precipitated nesquehonite from 1 to 2 M NaCl brine were affected.

1. Introduction

Water flooding and other oil enhancement methods are frequently used to enhance the recovery of crude oil from aged oil wells. American Petroleum Institute (API) estimated that nine barrels of water can be produced for each barrel of oil during crude oil production [1]. Depending on the nature of geological formations, the oilfield brine and produced water come out of the reservoir with dissolved ions such as Na^+, Ca^{2+}, and Mg^{2+} [2–6]. It is common practice to dispose of oilfield brine (produced water) into water bodies. However, this approach is not safe for plants and animals' lives [1,5]. When brine is disposed of in water bodies, it can change the salinity and pH of water, causing the death of aquatic organisms [1,7]. For that reason, many environmental regulatory bodies for example, Environmental Protection Agency (EPA) have set regulations that require the oil brine solutions or produced water to be treated before disposal into water bodies [1,8].

Precipitation as an alternative method for brine treatment has attracted many researchers nowadays due to its low cost while solving

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Table 1
Concentrations of major cations in produced water from oilfields per world.

Range of concentrations in different oil fields			References
Ca^{2+} (Mg/L)	Mg^{2-} (mg/L)	Na^{+} (mg/L)	
13–29,222	8–600	132–97,000	[21]
4–78,000	2–7000	850–20,000	[22]
13–74,000	8–6000	132–150,000	[23]
416–26,000	1294–8400	10,760–120,000	[24]
13–30,800	<8–10,000	50–29,700	[25]
0–74,000	0–6000	0–150,000	[26]

Table 2
Composition of synthetic brine solution used in study.

Experiment	$CaCl_2$		$MgCl_26H_2O$		NaCl
	$CaCl_2$ [M]	Ca^{2+} (mg/L)	$MgCl_2 \cdot 6H_2O$ [M]	Mg^{2+} (mg/L)	NaCl [M]
1	0.5	20,000	0.4	10,000	0.0
2	0.5	20,000	0.4	10,000	0.5
3	0.5	20,000	0.4	10,000	1.0
4	0.5	20,000	0.4	10,000	1.5
5	0.5	20,000	0.4	10,000	2.0

Table 3
Precipitating reagents tested in preliminary precipitation of carbonates.

Experiment	Precipitating reagents	Weight (g)	Concentration [M]
1	$NaHCO_3$	10.5	0.5
2	$NaHCO_3$	16.8	0.8
3	$NaHCO_3/Na_2CO_3$	12.6/5.3	0.6/0.2
4	$NaHCO_3$	21.0	1.0
5	$NaHCO_3/Na_2CO_3$	21.0/5.3	1.0/0.2
6	Na_2CO_3	26.5	1.0

environmental challenges [9]. Through the precipitation method, high-purity mineral carbonates can be produced for industrial applications. Calcium carbonate, for example, is used in papers, cosmetics, toiletries, food, pharmaceuticals, plastics, paints, inks, sealants, and adhesives [10]. On the other hand, hydrated magnesium carbonate compounds like nesquehonite ($MgCO_3 \cdot 3H_2O$) can be used in the production of construction materials such as thermally insulating boards, blocks, and panels [11]. Thus, it is important to recover these mineral carbonates from oilfield brine solution or produced water.

Different types of polymorphs of carbonates can be precipitated depending on the conditions used. For examples, magnesium carbonates can exist as magnesite ($MgCO_3$), nesquehonite ($MgCO_3 \cdot 3H_2O$), dypingite ($Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$), hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$), Lansfordite ($MgCO_3 \cdot 5H_2O$) and Artinite ($MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$) [12,13]. On the other side, calcium carbonate can exist as calcite, vaterite, aragonite, and hydrated compounds like ikaite ($CaCO_3 \cdot 6H_2O$) and monohydrated calcium carbonate ($CaCO_3 \cdot H_2O$) [14–16]. Different past research focused on the precipitation of calcium or magnesium-based carbonates from various sources. The combination of Na_2CO_3 solutions in equilibrium with a CO_2 atmosphere and $MgCl_2$ solutions resulted in precipitation of $MgCO_3 \cdot 3H2O$ at 25 °C and $PCO_2 = 1$ bar, hydromagnesite ($(Mg_5CO_3)_4$ $Mg(OH)_2 \cdot 4H_2O$) at 120 °C and $PCO_2 = 100$ bar, and magnesite $MgCO_3$ at 120 °C and $PCO_2 = 100$ bar [12]. $MgCO_3 \cdot 3H_2O$ was prepared by using brine rich in Mg from the desalination plant, CO_2, and NaOH at 20 °C to 25 °C and atmospheric pressure [11]. Nevertheless, >95 % of calcium was converted into $CaCO_3$ by reacting phosphogypsum with NH_3 and CO_2 at ambient conditions [17]. Costa and Teir (2016) [18] prepared $CaCO_3$ by reacting steelmaking slag as a raw material with $NHCl_4$ and CO_2. Other research shows that >99.4 % pure $CaCO_3$ can be produced by reacting CO_2, cement kiln dust, and seawater [19]. $CaCO_3$ and $MgCO_3 \cdot 3H_2O$ were prepared from seawater by reacting CO_2, MgO, and NaOH at 80 °C [20]. Based on our knowledge and level of literature survey, the effect of NaCl on the yield, purity, polymorphs, and morphology of the precipitated carbonates is not yet known. Therefore, we conducted an experimental study to investigate the effect of varying the concentration of NaCl on the yield, purity, polymorphs, and morphology of calcium and magnesium carbonates obtained by sequential precipitation.

Table 6
Initial and final pH during sequential precipitation of carbonates.

Experiment	NaCl [M]	First precipitation step		Second precipitation step	
		Initial pH	Final pH	Initial pH	Final pH
1	0.0	8.93	4.01	3.99	9.72
2	0.5	8.72	3.93	3.96	9.61
3	1.0	8.51	3.87	3.92	9.53
4	1.5	8.32	3.68	3.83	9.45
5	2.0	8.21	3.56	3.71	9.32

Table 4
Preliminary findings of $CaCO_3$ based precipitates at 25 °C and 50 °C.

Experiment	Precipitating reagents	Concentration [M]	Precipitation temperature (25 °C)		Precipitation temperature (50 °C)	
			%Yield	%Purity	%Yield	%Purity
1	$NaHCO_3$	0.5	55.4	82.8	82.4	86.6
2	$NaHCO_3$	0.8	57.1	84.0	78.0	87.7
3	$NaHCO_3/Na_2CO_3$	0.6/0.2	72.9	84.7	85.6	89.4
4	$NaHCO_3$	1.0	85.6	85.9	85.6	88.7
5	$NaHCO_3/Na_2CO_3$	1.0/0.2	95.6	88.7	96.2	91.0
6	Na_2CO_3	1.0	93.5	83.3	94.8	90.0

Table 5
Preliminary findings of $MgCO_3 \cdot 3H_2O$ based precipitates at 25 °C and 50 °C.

Experiment	Precipitating reagents	Concentration [M]	Precipitation temperature (25 °C)		Precipitation temperature (50 °C)	
			%Yield	%Purity	%Yield	%Purity
1	$NaHCO_3$	0.5	34.4	59.8	50.1	82.9
2	$NaHCO_3$	0.8	84.4	61.4	51.5	77.4
3	$NaHCO_3/Na_2CO_3$	0.6/0.2	52.9	65.6	52.0	85.7
4	$NaHCO_3$	1.0	77.0	78.3	52.9	93.1
5	$NaHCO_3/Na_2CO_3$	1.0/0.2	34.4	88.9	54.1	95.5
6	Na_2CO_3	1.0	32.2	86.8	53.5	95.8

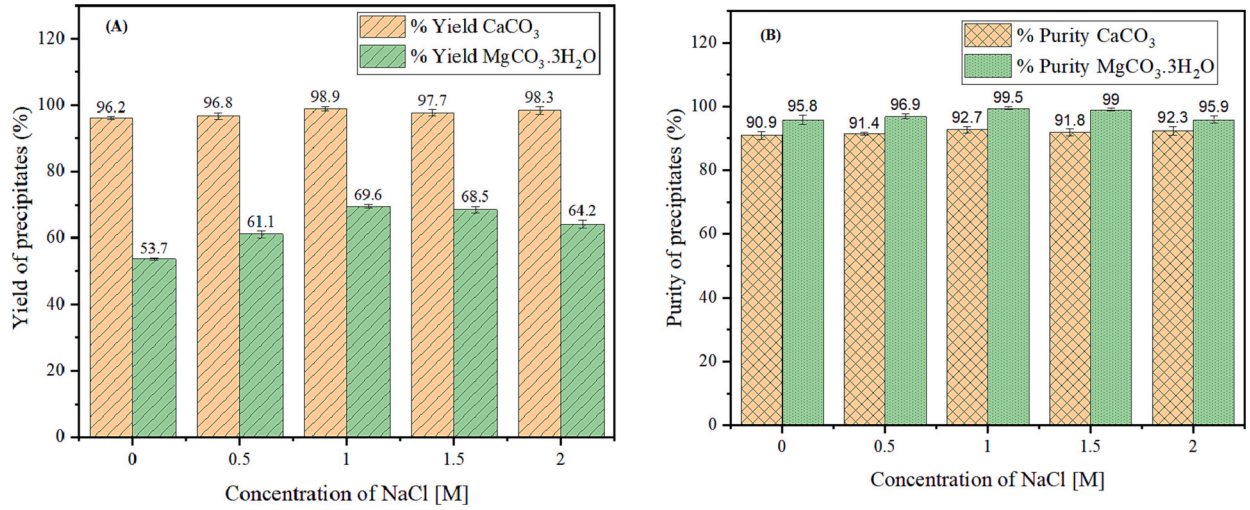

Fig. 1. (A and B): The precipitates yield (%) (A) and purity (%) (B) Against concentration of NaCl in the brine solutions.

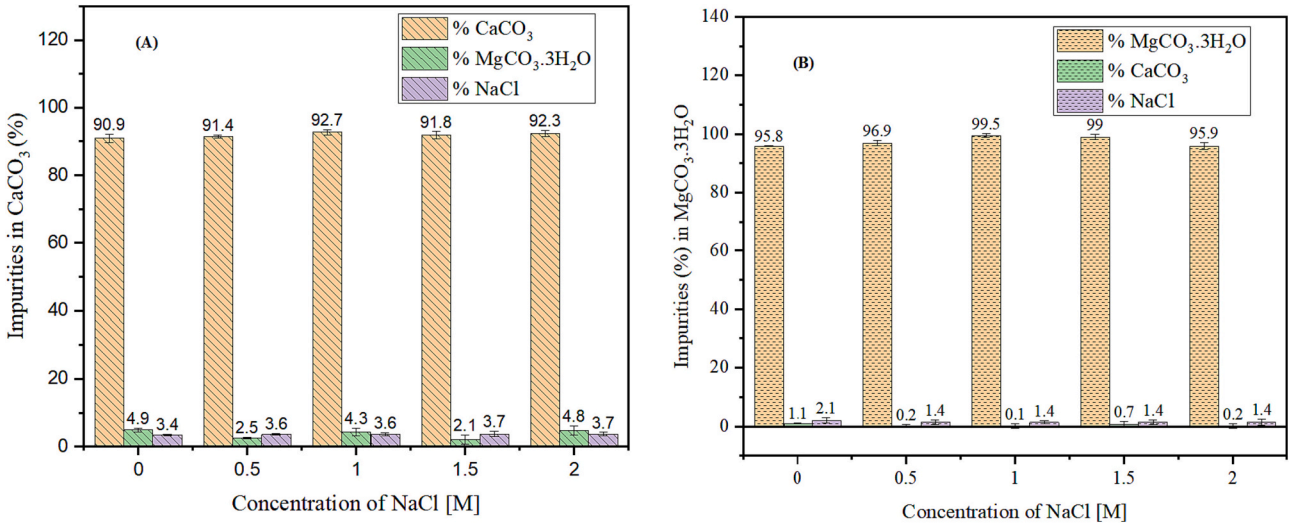

Fig. 2. (A and B): The precipitates impurities (%) in $CaCO_3$ (A) and $MgCO_3{\cdot}3H_2O$ (B) against concentration of NaCl in the brine solutions.

2. Material and Methods

2.1. Chemicals used

This study involved the use of $NaHCO_3$, Na_2CO_3, $CaCl_2$, $MgCl_2{\cdot}6H_2O$, HNO_3, and distilled water and deionized water. All chemicals were used as purchased at analytical grade (≥99% purity) and no further purification treatments were required.

2.2. Experimental design

2.2.1. Preparation of synthetic brine

Table 1 shows the composition of produced water from oilfields. The data were collected from various published reviews and research papers. Based on the level of concentrations in various oilfield-produced water, sodium, calcium, and magnesium are the most ions with high concentrations. Therefore, the design of the experiment under this study aimed to investigate the effects of NaCl on the precipitation of calcium and magnesium carbonates from oilfield-produced water. A total of five synthetic brine solutions were prepared by adding various amounts of (0–2.0 M) NaCl in the mixture of 20,000 Mg/L Ca^{2+} and 10,000 Mg/L Mg^{2+} (Table 2). The control setup was prepared without adding NaCl. The composition of studied synthetic brine solutions was within the common range of the concentrations of calcium and magnesium ions in oilfield-produced water as reported in different literature (Table 1). Thus, the concentration of calcium ions in the synthetic brine solutions was high compared to that of magnesium ions.

2.2.2. Preparation and optimization of precipitating reagents

To obtain optimum yield and purity of precipitates, it was deemed necessary to perform a preliminary set of experiments to select the proper precipitating reagents [27]. The series of precipitating reagents were prepared from $NaHCO_3$ and Na_2CO_3 at different concentrations (Table 3). The choice of the reagents comes from the fact that different researchers used the reagents in the precipitation of calcium or magnesium carbonates with promising results [28]. In this study, the precipitating reagents were prepared at different concentrations ranging from 0.5 M to 1.0 M to obtain the optimum reagent concentration. The prepared reagents were tested by sequential precipitating the brine solution to obtain $CaCO_3$ and $MgCO_3{\cdot}3H_2O$ at 25 °C and 50 °C. The brine solutions used in preliminary experiments were composed of only 20,000 Mg/L and 10,000 Mg/L Mg^{2-} and Ca^{2+}, respectively. Preliminary findings indicated that the concentration of 1.0/0.2 M $NaHCO_3/Na_2CO_3$ and 1.0 M Na_2CO_3 were optimum to achieve the

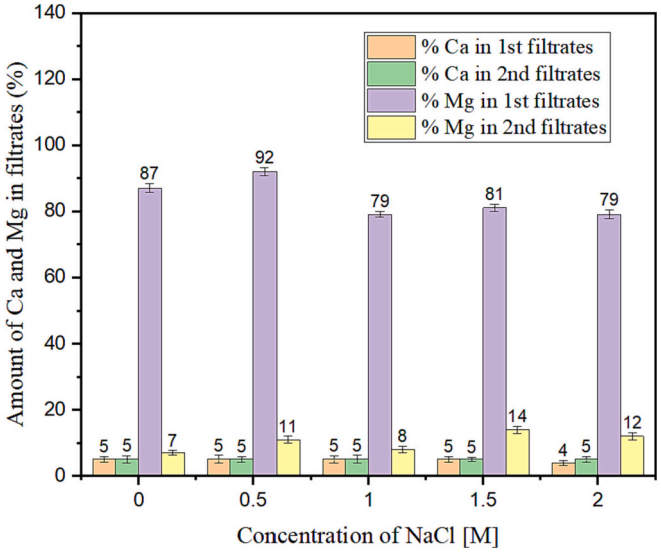

Fig. 3. Amount of Ca^{2+} and Mg^{2+} remained in the first filtrates after removal of $CaCO_3$ precipitates and in second filtrates after removal of $MgCO_3{\cdot}3H_2O$ precipitates.

highest yield and purity of the precipitates from the brine solutions (Tables 4 and 5). It is suggested that the high pH of the brine solution favors more precipitation of the carbonates [27]. Thus, the observed high yield and purity of precipitates could be associated with high pH levels of 8.93 and 9.72 for 1.0/0.2 M $NaHCO_3/Na_2CO_3$ and 1.0 M Na_2CO_3, respectively. Additionally, the yield and purity of the precipitates increased at elevated temperatures (50 °C) due to a high reaction rate at the highertemperature. Therefore, the optimized reagent concentrations of 1.0/0.2 M $NaHCO_3/Na_2CO_3$ and 1.0 M Na_2CO_3 from preliminary investigations were used in this study to investigate the precipitation of $CaCO_3$ and $MgCO_3{\cdot}3H_2O$ at 50 °C, respectively.

2.2.3. Sequential precipitation of carbonates

The precipitation processes were conducted according to Wang et al., 2008 [28] and Zhao et al., 2018 [20] with some modifications. The sequential precipitation experiments were conducted in the simulated temperature environment of an oilfieldproduced water at 50 °C using a water bath. This means that oilfield-produced water flows back to the surface from the reservoir in hot conditions [29]. Therefore, the volume of 20 mL of synthetic brine solutions for each experiment was poured into a 250 mL conical flask and heated to 50 °C using a water bath. In the first precipitation step, an equal volume of 20 mL of 1 M $NaHCO_3$/0.2 M Na_2CO_3 was slowly added to the brine solution using a burette while the brine was continuously stirred at 350 RPM. The pH was recorded initially and at the end of the precipitation process using HANNA pH meter. The pH meter was calibrated using buffer solution at pH of 4.1, 7.0, and 9.2 to ensure correct readings. It was observed the pH of the solutions dropped continuously with the addition of 1 M $NaHCO_3$/0.2 M Na_2CO_3 up to the end of the precipitation process (Table 6). The decrease in pH as precipitation preceded could be caused by the formation of carbonic acid through the interaction of CO_2 and brine water [27].

The formed precipitates were filtered, washed three times using deionized water to remove the ions, and air-dried at room temperature for 24 h. The second precipitation step was conducted following the same procedures as in the first step. The only difference was the use of filtrates collected from the first step and 1 M Na_2CO_3. Therefore, the volumes of 20 mL of 1 M Na_2CO_3 were added slowly by using the burette into filtrates (liquids) collected after the first precipitation step. The mixtures were continuously stirred at 350 RPM. Notably, the pH of the solution for each experiment increased with the addition of 1 M Na_2CO_3 in the filtrate during the second precipitation stage.

2.3. Characterization of precipitates and filtrates

2.3.1. MIP AES analysis

The precipitates and filtrates were analyzed with an Agilent Technologies 4100 MIP-AES equipped with an Agilent Technologies 4107 nitrogen generator and a Hydrovane air compressor. Before sample analysis, the standard solutions were prepared as follows. The stock solutions (1000 mg/L) of calcium, magnesium, and sodium were prepared separately by dissolving $CaCl_2$, $MgCl_26H_2O$, and NaCl in distilled water. The multi-element intermediate solution containing 200 mg/L of Ca^{2+}, Mg^{2+}, and Na^+ was prepared by dilution of the stock solutions. The series of seven standard solutions containing 2 mg/L, 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L, 50 mg/L and 60 mg/L of Ca^{2+}, Mg^{2+} and Na^+ of Ca^{2+}, Mg^{2+} and Na^+ were prepared by further diluting intermediate solution.

Thereafter, the samples of precipitates and filtrates were prepared. The mass of 0.100 g of precipitates was digested using HNO_3 acid and diluted to 100 mL in volumetric flasks. The prepared solutions of precipitates and filtrates were separately filtered by using 0.22 μm micro filter to remove the particulates that could damage the MIP AES plasma torch. The precipitate solutions were further diluted by the factor of 10 and 5 for Ca^{2+} and Mg^{2+}, respectively whereas the filtrate solutions were more concentrated and were diluted by a factor of 500. The precipitates and filtrate were diluted to lower the concentration of ions to the range of the concentrations in standard solutions. Afterward, all prepared samples were analyzed by using MIP-AES. The MIP AES nebulizer pressure was optimized at 120 kPa. The precipitate-based solutions were analyzed at 317.933 nm, 383.933 nm, and 568.820 nm for Ca^{2+}, $Mg^{2+,}$ and Na^+, respectively. The filtrate samples were analyzed at 616.217 nm, 383.829 nm, and 589.592 nm for Ca^{2+}, $Mg^{2+,}$ and Na^+, respectively. The lines were selected to avoid interferences from other elements. All samples were analyzed in the triplicate and the results were recorded at average level.

2.3.2. XRD analysis

The samples of dry powder of the precipitates were analyzed using Pan analytical X-ray diffraction (XRD) equipped with a Cu Kα X-ray tube. Each sample was scanned by XRD operating at 45 kV and 40 mA at an angle 2θ ranging from 10° to 60° for 15 min and a scanning rate of 0.021/s. The diffraction pattern of each sample was collected for mineral phase identification. The mineral phases were identified by matching the collected XRD diffraction patterns with the ICDD database (PDF) which was accessed through XRD-X pert high score software.

2.3.3. SEM analysis

The morphology of the synthesized precipitate was analyzed using a JSM-6360LV scanning electron microscope. The finely powdered samples were mounted on 12.5 mm aluminum pin stubs containing adhesive materials. The stubs were inserted in Quorum Q150T ES gold palladium sputter coater instrument for 5 to 7 min to coat the sample with a 10 nm layer of gold and palladium. Afterward, a batch of 10 labeled stubs containing samples was inserted into an SEM sample holder for analysis. All images were scanned at 2 μm and collected for morphological identification.

2.4. Yield and purity determination

The percentage yield and purity of the precipitates were calculated (Eq. 1–3) based on MIP-AES results. The percentage yield of the mineral carbonates was calculated (Eq.1). The actual yield of the precipitates represents the actual weighed mass of obtained dry precipitated from precipitation experiments. The theoretical yield represents the yield obtained from theoretical calculations. The theoretical yields of $CaCO_3$ and $MgCO_3{\cdot}3H_2O$ were 1.008 g and 1.1353 g, respectively.

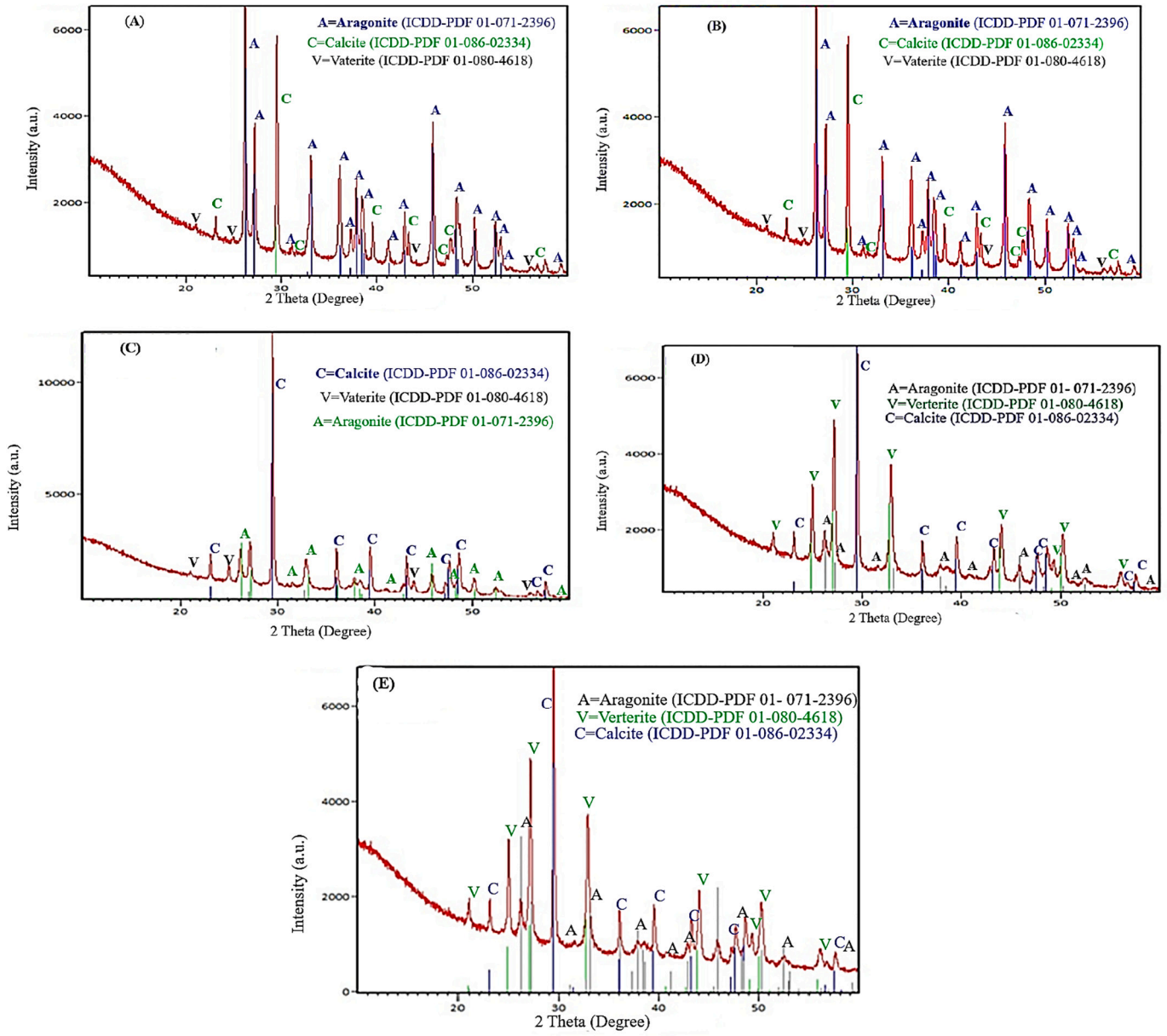

Fig. 4. (A-E): XRD diffraction patterns of $CaCO_3$ precipitates which were obtained from the brine solutions containing 0.0 M (A), 0.5 M (B), 1.0 M (C), 1.5 (D) and M 2.0 M (E) NaCl.

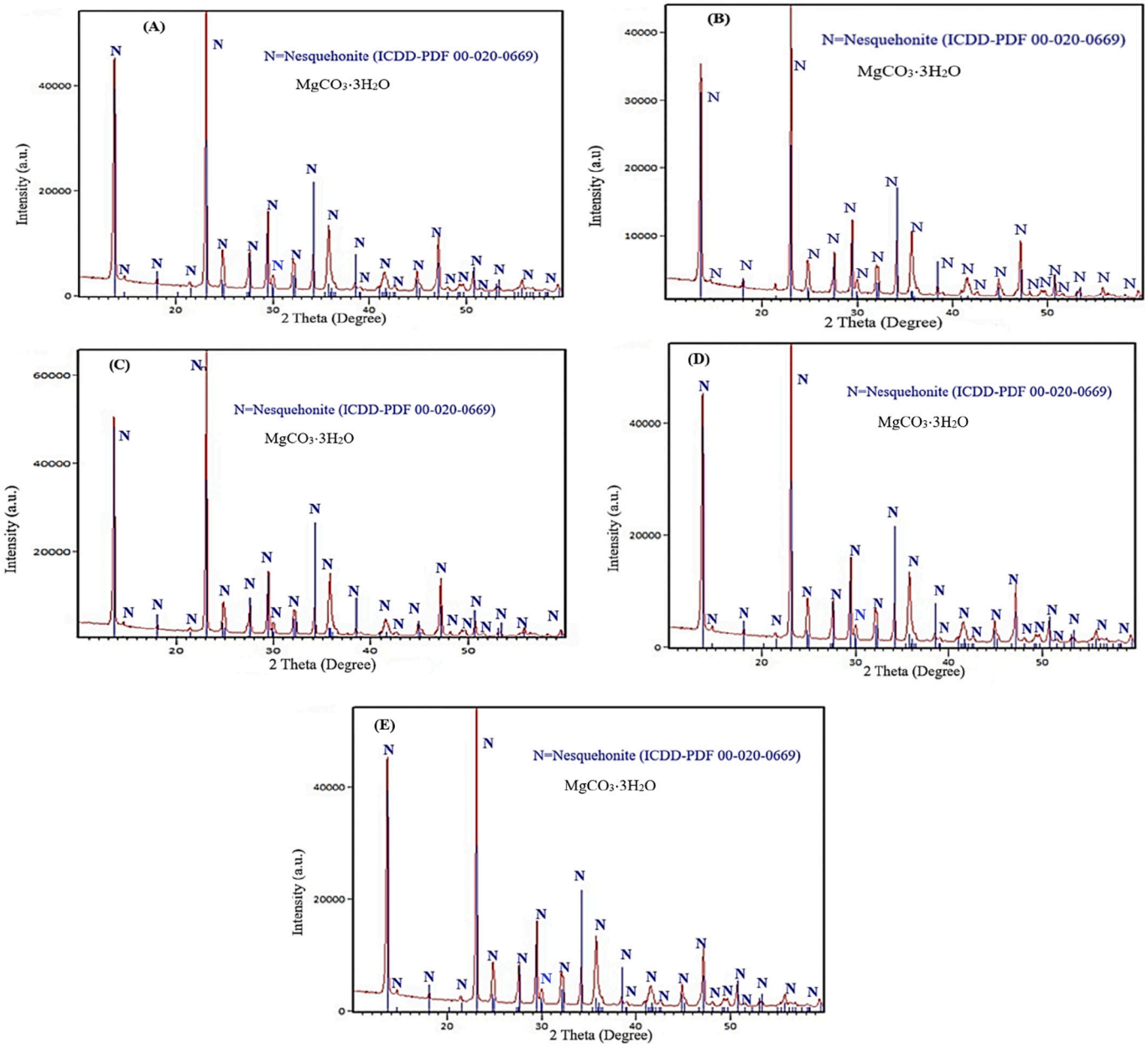

Fig. 5. (A-E): XRD diffraction patterns of $MgCO_3{\cdot}3H_2O$ which were obtained from the brine solutions containing 0.0 M (A), 0.5 M (B), 1.0 M (C), 1.5 (D) and M 2.0 M (E) NaCl.

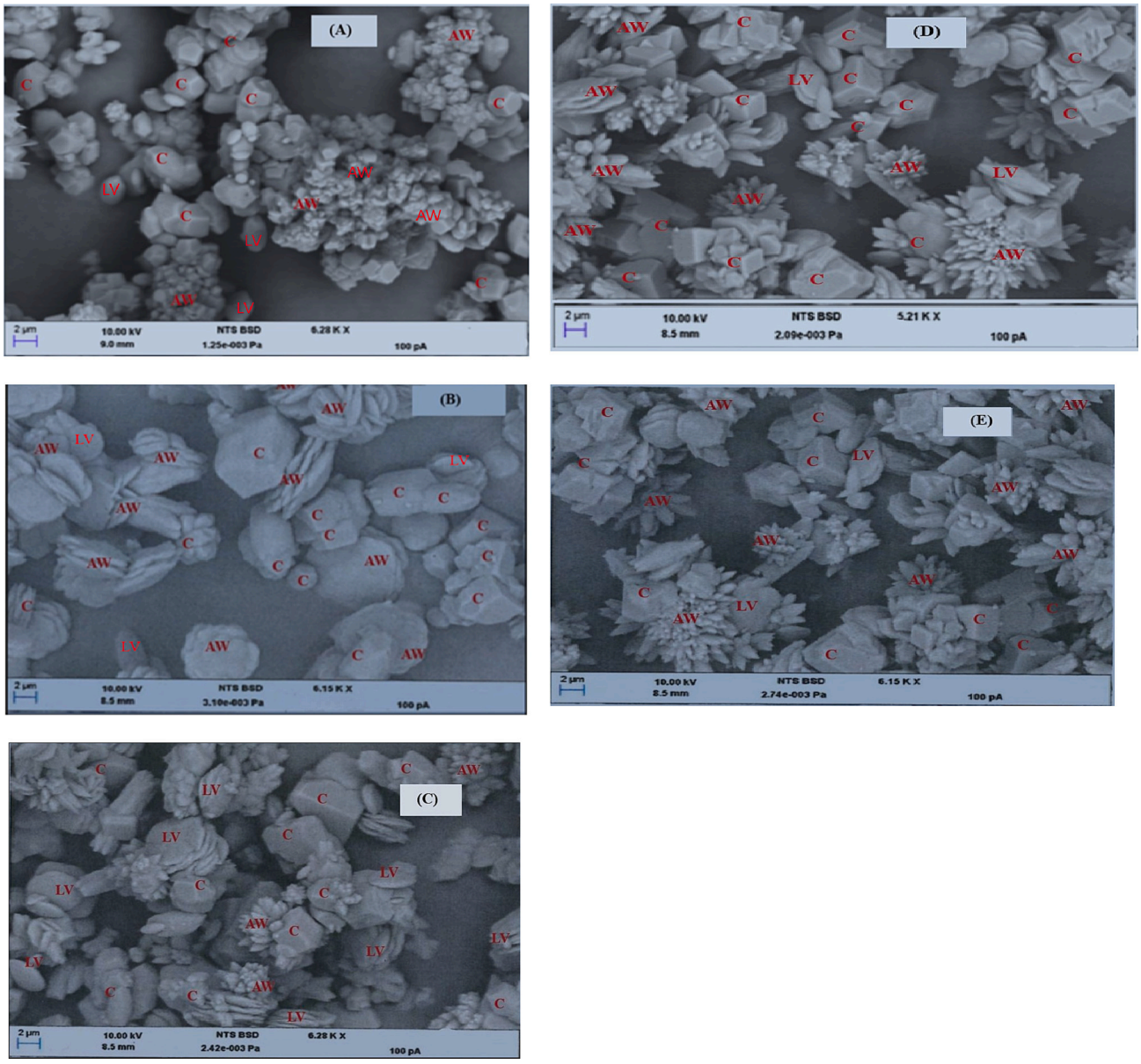

Fig. 6. (A-E): SEM images of $CaCO_3$ precipiates which were obtained from the brine solutions containing 0.0 M (A), 0.5 M (B), 1.0 M (C), 1.5 (D) and M 2.0 M (E) NaCl.
AW is Aragonite Whiskers
LV is Lamella Vaterite
C is Rhombohedral Calcite.

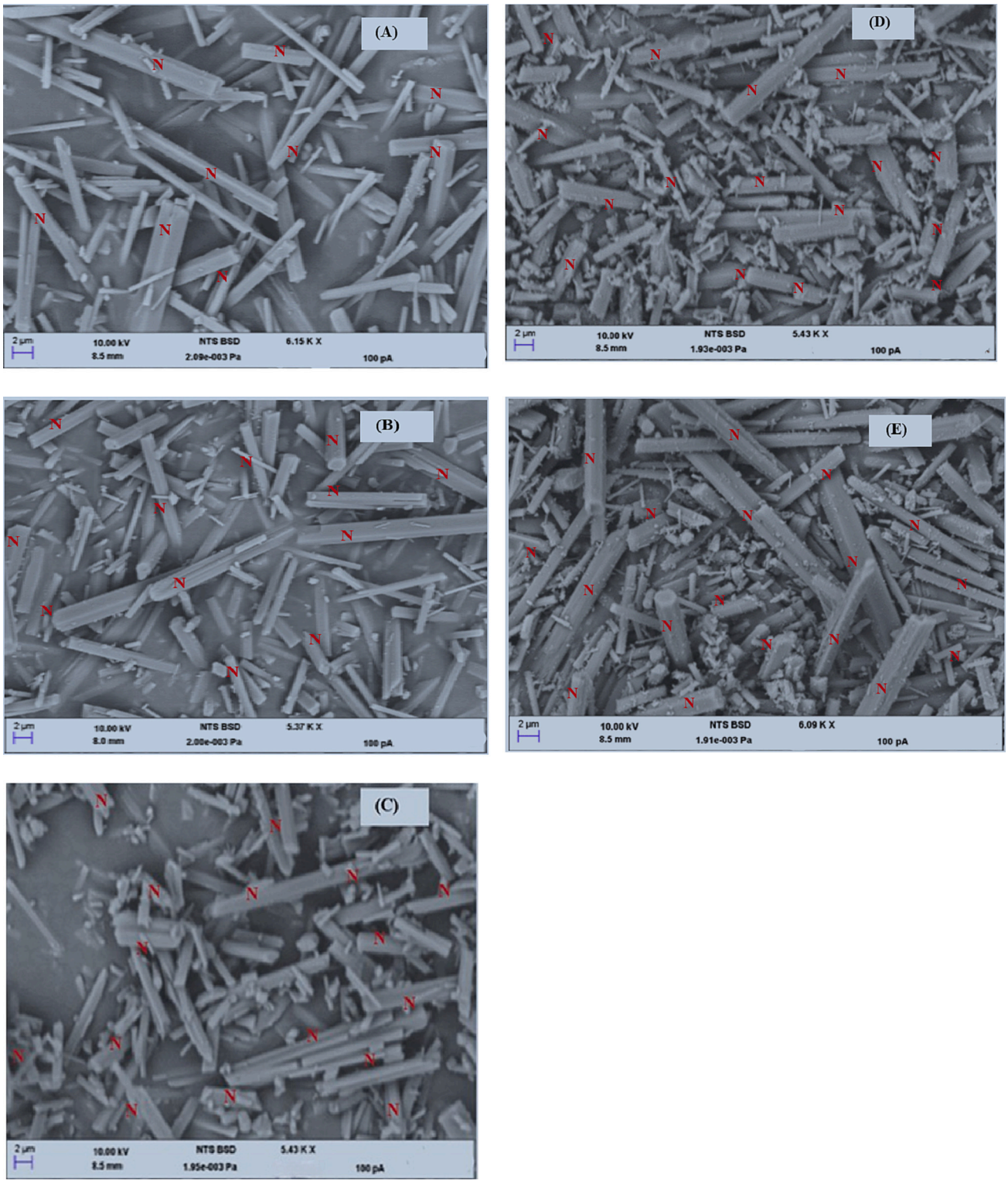

Fig. 7. (A-E): SEM images of $MgCO_3 \cdot 3H_2O$ precipiates which were obtained from the brine solutions containing 0.0 M (A), 0.5 M (B), 1.0 M (C), 1.5 (D) and M 2.0 M (E) NaCl.
N is Nesqeuhonite ($MgCO_3 \cdot 3H_2O$).

Table 7
XRD summary of identified polymorphs of carbonates.

Expt No.	NaCl [M] in the brine solutions	First precipitates ($CaCO_3$)	Second precipitates ($MgCO_3{\cdot}3H_2O$)
1	0.0	Calcite, vaterite, aragonite	Nesquehonite
2	0.5	Calcite, vaterite, aragonite	Nesquehonite
3	1.0	Calcite, vaterite and aragonite	Nesquehonite
4	1.5	Calcite, vaterite and aragonite	Nesquehonite
5	2.0	Calcite, vaterite and aragonite	Nesquehonite

$$\%\text{yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100 \quad (1)$$

To quantify the purity of the precipitates, the amount (mg/L) of metal in the solutions was first converted into the mass of metal by multiplying with the volume (L) of the solution. Thus, the mass of pure metal was obtained. Afterward, the mass of the pure metal (Ca or Mg) was converted into the mass targeted pure carbonates ($CaCO_3$ and $MgCO_3{\cdot}3H_2O$) according to eq. 2. The percentage purity of targeted pure carbonates ($CaCO_3$ and $MgCO_3{\cdot}3H_2O$) in the precipitates was calculated according to eq. 3.

$$\text{Mass of pure carbonates} = \frac{\text{Mass of metal (g)}}{\text{Molar mass of metal (g/mol)}} \times \text{Molar mass of carbonate (g/mol)} \quad (2)$$

$$\text{Purity of carbonates (\%)} = \frac{\text{Mass of pure carbonate (g)}}{\text{Mass of dry precipitate obtained from experiments (g)}} \times 100 \quad (3)$$

3. Results and Discussion

3.1. Effects on the yield and purity of carbonates

The results (Fig. 1) indicate the percentage yield and purity of the mineral carbonates obtained from brine solutions by sequential precipitation. The percentage yield of $CaCO_3$ ranged from 96.2% to 98.9% whereas its purity ranged from 90.9% to 92.7%. The percentage yield of $MgCO_3{\cdot}3H_2O$ ranged from 53.7% to 64.2% whereas its purity ranged from 95.8% to 99.5%. Furthermore, the yield of $CaCO_3$ is higher than the yield of $MgCO_3{\cdot}3H_2O$. This is due to ions that remained in the filtrates (Fig. 3) after the first precipitation and the removal of $CaCO_3$ from filtrates. The presence of ions in the filtrates might cause the $MgCO_3{\cdot}3H_2O$ precipitation inhibition resulting in an observed low percentage yield. The maximum yield and purity were obtained from 1 M NaCl brine solution. That's the maximum yield and purity of $CaCO_3$ were 98.9% and 92.7%, whereas for $MgCO_3{\cdot}3H_2O$ were 69.6% and 99.5%, respectively. The result of these findings is similar to the yield of $CaCO_3$ (>95 %) precipitated by mixing 200 mL phosphogypsum, 100 mL NH_3 and CO_2 (flow rate of 0.07 to 0.16) at 20 °C, 45 °C and 80 °C. The reactants concentrations were 2.7 to 4.0 mol/mol $NH_3/CaSO_4$ and 1.7 to 5.3 mol/mol $CO_2/CaSO_4$ whereas the pH ranged from 7.2 to 8.0 [17]. On the other side, the observed purity of $CaCO_3$ was lower compared to 99 -% purity of $CaCO_3$ from the reaction of 400 mL sea water and 100 mL of 10 mmol/L $NaCO_3$/ $NaHCO_3$ (1.8–8:1) in the temperature ranging from 30 °C to 70 °C and the pH ranging from 7.9 to 8.9 [30]. The slight difference in purity of $CaCO_3$ between these findings and others reported in the literature is due to different experimental conditions and reagents which were used. Fig. 2 shows the percentage of impurities that remained in the precipitates. There is no specific trend on the level of impurities in precipitates obtained from 0.0 to 2.0 M NaCl brine solutions. The precipitates of $CaCO_3$ contained 3.4% to 3.7% NaCl and 2.1% to 4.9% $MgCO_3{\cdot}3H_2O$ (Fig. 2 A). The precipitates of $MgCO_3{\cdot}3H_2O$ had a small amount of impurities <2% NaCl and 1% $CaCO_3$ (Fig. 2 B). Thus, the precipitated $MgCO_3{\cdot}3H_2O$ was more pure compared to the precipitated $CaCO_3$.

3.2. Effect on the polymorphs of carbonates

3.2.1. XRD results for $CaCO_3$ based precipitates

The XRD diffractograms are shown in Fig. 4 A-E. Three polymorphs i. e. vaterite (ICDD-PDF 01-080-4618), calcite (ICDD-PDF 01-086-02334), and aragonite (ICDD-PDF 01-071-2396) were identified by matching the patterns with the library database. The observed diffraction angle 2θ of each identified polymorph is similar to those reported in the literature by Chen and Xiang (2009) [14], Dickinson and McGrath (2001) [16], and Adavi and Dehkordi (2021) [31]. The effect of NaCl on the polymorphs of carbonates is observed. At a low concentration of NaCl (0–0.5 M), the peak intensities of vaterite were lower compared to calcite and aragonite (Fig. 4 A and B). It indicates that vaterite was less favored to precipitate from brine solutions compared to calcite and aragonite. However, as the concentration of NaCl increased from 1 to 2 M, the vaterite peak intensities increased. It indicates that vaterite was more favored formed from the brine solutions as the concentration of NaCl was increased. This observation is in agreement with the earliest researcher who concluded that vaterite was easily formed from calcium bicarbonate solutions with an increase of NaCl concentration in the solution at elevated temperatures [32]. Additionally, the formation of calcite or vaterite could be influenced by the high pH and Ca^{2+}/CO_3^{2-} of the brine solutions. Oral et al., 2018 [33], conducted a study by precipitating $CaCO_3$ from 4 mL calcium acetate and $NaHCO_3$ at Ca^{2+}/CO_3^{2-} of 5:1, 2:1, 1:2, and 1:3 at pH of 8.0, 10.0, 11.0, 12.0, 13 and temperature of 23 °C in the presence of 20 mL ethylene glycol. They concluded that at high pH and Ca^{2+}/CO_3^{2-}, vaterite transformed into calcite [33]. Therefore, in comparison to the current study, it can be suggested that vaterite precipitated more in the brine solutions with a slightly low pH of 8.51 to 8.21 caused by an increased concentration of NaCl in the brine solution (Table 6). This is supported by the identified varterite polymorph in the XRD patterns in Fig. 4 C to D. Nevertheless the findings (Fig. 4 A-E) show that no diffraction peaks correspond to impurities (NaCl and $MgCO_3{\cdot}3H_2O$) which could be due to low amounts of impurities (Fig. 2) in the precipitates which could not be detected by XRD.

3.2.2. XRD results for $MgCO_3{\cdot}3H_2O$ based precipitates

The XRD patterns of magnesium carbonate-based precipitates obtained from filtrate experiments are shown in Figs. 5 (A-E). According to the comparison made between diffractograms and the library database (00–020-0669 ICDD-PDF reference code), results showed that only nesquehonite ($MgCO_3{\cdot}3H_2O$) precipitated. Previous findings also reported the formation of similar rod-like nesquehonite at a pH of 9.5 and temperature of 338 K [34]. The presence of various amounts of NaCl in the brine solutions did not change the morphology of nesquehonite. This

result is in agreement with the observed high purity of the precipitates (Fig. 1) and no peak of impurities was identified in the XRD diffractograms. Thus, the precipitate contained a trace amount of impurities (Fig. 2) which could not be detected in XRD analysis. The summary of the carbonate polymorphs identified from XRD diffractograms is indicated in Table 7.

3.3. Effect on the morphology of carbonates

3.3.1. SEM results for $CaCO_3$ based precipitates

SEM images of analyzed calcium carbonate precipitates are shown in Fig. 6 (A-E). A total of three morphologies of carbonates i.e. lamella vaterite, aragonite whiskers, and rhombohedron calcite were identified [33,35,36]. The image (Fig. 6 A and B) is dominated by rhombohedron calcite and aragonite whiskers. This result is consistent with XRD results showing that the formation of lamella vaterite was less favored in the brine solution containing 0–0.5 M NaCl. At elevated concentrations of 1–2 M NaCl (Fig. 6C-E) lamella vaterite, aragonite whiskers, and rhombohedron calcite were formed which means that an increase in salt concentration in the brine solution facilitated the formation of three morphologies of the precipitates. It is also observed that rhombohedron calcite contains distorted edges and surfaces. This indicates that Mg^{2+} ions in the solution interacted with crystal surfaces during precipitation causing the edges and surface modification [37,38]. Furthermore, the images (Fig. 6C-E) show that aragonite whiskers grow on the surface of calcite. It can be suggested that calcite precipitated first giving the nucleation site for aragonite precipitation.

3.3.2. SEM results for $MgCO_3{\cdot}3H_2O$ based precipitates

Fig. 7(A-E) shows SEM images of magnesium carbonate precipitates. The elongated rod-like structure was observed in the images (Fig. 7 A-E). The formation of a rod-like structure indicates the presence of nesqeuhonite ($MgCO_3{\cdot}3H_2O$) in the precipitates [11,24,25]. Based on a visual comparison of the SEM images, images (Fig. 7 A-B) show clear, smooth, and elongated crystals than images (Fig. 7 C-E). It shows that the increase in concentration of NaCl (1 M to 2 M) in brine solutions had an influence on the smoothness and length of the crystals but did not change the morphology of $MgCO_3{\cdot}3H_2O$ to other shapes.

4. Conclusion

This study was conducted to investigate the effect of 0–2 M NaCl in brine solution on the sequential precipitation of calcium and magnesium carbonates. The yield of 96.2% to 98.9% $CaCO_3$ and 53.7% to 69.6% $MgCO_3{\cdot}3H_2O$ with the purity of 90.9% to 92.7% $CaCO_3$ and 96.0% to 99.5% $MgCO_3{\cdot}3H_2O$ were obtained. The salt concentration of 1 M NaCl in the brine solution offered the maximum yield and purity of 98.9% and 92.7% $CaCO_3$ and 69.6% and 99.5% $MgCO_3{\cdot}3H_2O$, respectively. Polymorphic and morphological studies revealed that 0–0.5 M NaCl solutions influence more the formation of only two polymorphs of $CaCO_3$ with various morphologies (aragonite whiskers and rhombohedral calcite). The concentration of 1–2 M NaCl in the brine solutions favors more the formation of three polymorphs of different morphologies (aragonite whiskers, lamella vaterite, and rhombohedral calcite). The variation in NaCl concentration in brine solutions does not affect the polymorph and morphology of magnesium carbonate. Regardless of brine concentration, only elongated road-like structure nesquehonite ($MgCO_3{\cdot}3H_2O$) was obtained. Furthermore, the increase in salt concentration of the brine solution affects the smoothness and length of the $MgCO_3{\cdot}3H_2O$ crystal.

CRediT authorship contribution statement

Naswibu A. Kasimu: Writing – review & editing, Writing – original draft, Validation, Software, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Jun Gu:** Writing – review & editing, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors do not have permission to share data.

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