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Effects of temperature on precipitation kinetics and microstructure of calcium carbonate in the presence of magnesium and sulphate ions

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ABSTRACT

In the present work, the effects of the temperature on the kinetics and microstructure of $CaCO_3$, precipitated in the presence of magnesium and sulphate ions, were studied using degassing dissolved CO_2 method. The precipitates were identified by X-ray diffraction, atomic absorption spectroscopy and scanning electron microscopy. It was shown that at fixed temperature and ionic strength, the presence of sulphate and magnesium ions increased the induction time, decreased the crystal growth rate and reduced the amount of the $CaCO_3$ precipitates obtained. Magnesium induced the formation of aragonite form rather than the calcite and vaterite form. The increase of temperature in presence of magnesium and sulphate ions lead to a change on the effect of magnesium on kinetics of $CaCO_3$ precipitation and caused the Mg^{2+} ions incorporation in the $CaCO_3$ lattice. The increase of temperature favoured the aragonite phase in magnesium solutions and both aragonite and vaterite in presence of sulphate ions.

Keywords: Calcium carbonate; Magnesium; Sulphate; Temperature; CO_2 degassing

1. Introduction

Scale deposits on different equipment such as pipes, taps and heat exchangers, in contact with hard or hot water, create numerous technical and economic problems in desalination and water exploitation units by blocking the water flow in pipes or limiting the heat transfer. In most cases, the major constituent of scale is the calcium carbonate ($CaCO_3$). It has three anhydrous polymorphs which are, in order of increasing solubility, calcite (rhombohedra), aragonite (orthorhombic) and vaterite (hexagonal). The calcium carbonate polymorph and precipitation rate depends on several parameters; i.e. water composition, temperature and supersaturation [1–5]. At ambient temperature, calcite is the most predominant phase. At temperatures higher than 50°C, calcium carbonate scale precipitates as needles-like aragonite crystals [6–9].The presence of mineral species can have a major influence on the calcium carbonate crystal-growth process [10,11]. This is the case of SO_4^{2-} and Mg^{2+} ions which are present at significant concentration in natural waters. Sulphate ions are known that they inhibit vaterite transformation and enhance the calcite formation for low concentrations [12–14]. The presence of high

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sulphate concentration increased the nucleation time, favoured the aragonite formation and decreased precipitation rate of calcite formation [15].

Mg^{2+} ions are well known to influence the scaling phenomenon. In the presence of significant amounts of Mg^{2+}, calcium carbonate exclusively precipitates as aragonite while calcite and vaterite can also be formed when no Mg^{2+} ions are present [16]. Other studies show that Mg^{2+} ions can inhibit the nucleation and/or the crystalline growth rate of calcite. Tlili et al. [2] showed that when the Mg^{2+}/Ca^{2+} ratio passes from 0 to 4, with a concentration of Ca^{2+} of 4×10^{-3} mol. L^{-1}, the scaling time increases from about 50–400 min. The most common explanation for this reduction was the possible preferential adsorption of strongly hydrated magnesium ions onto the growing calcite surface, or by enhancement of the calcite solubility caused by the incorporation of magnesium into the calcite structure [17–19].

Many studies have been carried out to investigate the effect of magnesium on the $CaCO_3$ precipitation and its incorporation into the calcite crystal lattice. However, to our knowledge, only a few were interested in the incorporation of magnesium ions into the aragonite crystal lattice. In our previous work [9], the effect of magnesium and sulphate ions on the kinetics precipitation and morphology of aragonite was studied in standard seawater solution at fixed temperature of 60° C. It was shown that the magnesium ions were inserted in the aragonite crystal structure by substituting calcium ions. This substitution depends on the Mg^{2+}, Ca^{2+} and SO_4^{2-} ions concentrations. The introducing of foreign ions into the solution is not the only parameter which modifies the precipitation kinetics and the morphology of $CaCO_3$, the temperature variation could also affect these parameters. However, it appears to be a lack of reliable kinetics data to estimate calcium carbonate scaling rates when Mg^{2+} or SO_4^{2-} ions are present in the solution, particularly for freshwater and at high temperature. The aim of the present work is to study the effects of the temperature on the kinetics precipitation and microstructure of calcium carbonate precipitated in presence of Mg^{2+} and SO_4^{2-} ions by using degassing dissolved CO_2 method. The results obtained allowed to understand the scaling phenomenon observed, particularly, in heated water desalination units and pipes.

2. Experimental procedure

Along this study, calcium carbonate precipitation was provoked by degassing dissolved CO_2 method [20] which was previously described [21,22].The reference solution was prepared by mixing 1 L of solution containing 1.008 g of $NaHCO_3$ and 500 mL of solution containing 0.88 g of $CaCl_2.2H_2O$. The mixture was placed in a cylindrical glass cell, with a capacity of 2 L, immersed in a thermostat until the desired temperature was obtained. The initial pH solution was adjusted to 7 by bubbling pure CO_2. In order to initiate the precipitation of calcium carbonate, the calco-carbonic equilibrium was displaced by degassing the dissolved carbonic gas by air bubbling. $CaCO_3$ precipitated according to the following reaction:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3(s) + CO_2 \uparrow + H_2O \qquad (1)$$

The atmospheric air used in the present work ($P_{CO_2} = 3 \times 10^{-4}$ atm.) was dispersed uniformly in the solution by a perforated spiral glass tube [20,22]. This diffuser was located at the bottom of the cell. The air flow rate was fixed at 10 L min^{-1}. The time of degasification varied between 90 and 150 min. The initial concentrations of Ca^{2+} and HCO_3^- ions were kept constant at 4×10^{-3} M and 8×10^{-3} M, respectively. The effects of temperature in presence of SO_4^{2-} and Mg^{2+} ions were investigated by using Na_2SO_4 and $MgCl_2.6H_2O$ salts. The different working temperatures were 30, 40, 50 and 60°C. A different amount of $MgCl_2.6H_2O$ salt was added to give a molar magnesium/calcium ratio, R = [Mg]/[Ca] of 1, 2 and 5. The Na_2SO_4 salt was added to obtain a solution with sulphate concentration that corresponds to 2×10^{-3} mol/L. All solutions were prepared in deionized water. The NaCl salt was used to keep the ionic strength of solution fixed at 0.08 mol/L in all experiments. During the precipitation test, the pH of solution was continuously measured by Hanna pH-metre. Samples of 1 mL were withdrawn from the solution and analysed for the determination of HCO_3^- ions concentration by acid–base titration with the sulphuric acid as the titrant and the bromocresol green as an indicator. The concentration of HCO_3^- ions was considered equal to total alkali concentration (TAC).

According to the definition of TAC:

$$TAC = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] \qquad (2)$$

In the usual conditions, ($6 < pH < 8.5$), $[CO_3^{2-}]$ and $[OH^-]$ are small and in a first approximation, $TAC \approx [HCO_3^-]$.

At $t = t_{nucl}$ the supersaturation coefficients were determined as following:

$$\Omega = \frac{a_{Ca^{2+}} . a_{CO_3^{2-}}}{K_s} \qquad (3)$$

Where K_s is the equilibrium solubility product for given calcium carbonate polymorph, more generally for calcite, which is the most stable form.

The solids formed during the precipitation test were filtered through a 0.45 µm filter. The collected precipitates were dried at room temperature (25 ± 1 °C), then analysed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD was carried out at room temperature with a Philips X′ PERT PRO diffractometer in step scanning mode using Cu_Kα radiation. The XRD patterns were recorded in the scanning range $2\theta = 15–60°$. A small angular step of $2\theta = 0.017°$ and a fixed counting time of 4 s were used. The determination of magnesium concentration was carried out by using the atomic adsorption spectroscopy method.

3. Results and discussion

3.1. Effect of the temperature on $CaCO_3$ precipitation kinetics in the presence of sulphate ions

Fig. 1 presents the typical variations of the pH and the HCO_3^- concentration vs. time. The nucleation time, t_{nucl}, was determined from a discernible change in the slope of the pH vs. time experimental curve and from the drop of HCO_3^- concentration in the precipitation curve using the method of Dedieu et al. [20]. The t_{nucl} values are deduced from the two curves which are in good agreement. The crystalline growth rate (V_c) was determined from the slope of the linear part of the precipitation curve. The precipitation ratio $\tau_{p\ (\%)}$, was determined from the following equation:

$$\tau_p = \frac{TAC_0 - TAC_t}{TAC_0} \times 100 \tag{4}$$

where TAC_0 is the TAC at $t = 0$ min and TAC_t is the TAC at the end of precipitation test.

The results obtained are summarized in Table 1. In all experiments, the ionic strength was kept constant at 0.08 M and temperature range was from 30 to 60 °C. This table shows clearly that the temperature tend to reduce nucleation time, increases crystalline growth rate and precipitation rate. In fact, without Na_2SO_4, t_{nucl} decreased from 19 min at 30 °C to 3 min at 60 °C and V_c became more significant. Indeed, V_c passed from 0.16 mol L^{-1} min^{-1} to 1.1 mol L^{-1} min^{-1} at $T = 30$ and 60 °C, respectively. Moreover, the temperature influenced the precipitation ratio which increased from 44 to 85% when the temperature passed from 30 to 60 °C. The effect of temperature can be related to supersaturation [14]. In fact, Table 1 shows that the supersaturation was dependent of an increase of temperature. When the temperature increases, the CO_2 tend to expel and the supersaturation tend to increase due to the retrograde solubility of $CaCO_3$ with respect to temperature.

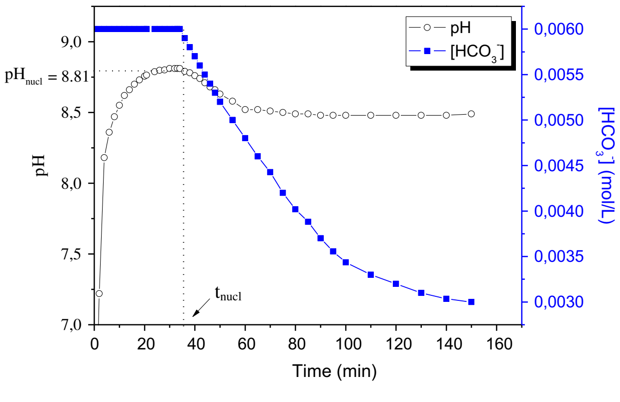

Fig. 1. Variation of pH and $[HCO_3^-]$ *vs.* time during a precipitation test by the CO_2 degassing method.

In the presence of 2×10^{-2} M of sulphate, the effect of the temperature on the kinetics of precipitation of $CaCO_3$ became less pronounced comparable to that without sulphate. Indeed, in the presence of sulphate, the induction time becomes the twice compared to that without sulphate for all range of temperature. This result might be due to the fact that the sulphate ions have an inhibitor effect [12,23,24]. For a fixed temperature, the presence of sulphate ions increased the induction time and decreased both the initial crystalline growth rate and the precipitation ratio of $CaCO_3$.

3.2. Effect of temperature on $CaCO_3$ precipitation kinetics in the presence of magnesium ions

The effect of magnesium ions on the calcium carbonate precipitation was studied at different temperatures in the range of 30–60 °C and with different magnesium/calcium molar ratios ($R = 2$ and 5). Examples of the TAC evolution vs. time with different experimental conditions are given in Fig. 2. For all experiments, the TAC remained relatively constant up to the induction time; then, it decreased significantly due to $CaCO_3$ precipitation before remaining constant. Results of nucleation time, crystalline growth rate, supersaturation and precipitation rate are summarized in Table 2.

At fixed temperature, the increase of Mg^{2+} concentration increased significantly t_{nucl}, and decreased both V_c and τ_p. For example, at 40 °C, t_{nucl} passed from 7 to 30 min, V_c passed from 0.57 to 0.49 M.min^{-1} and τ_p decreased from 81 to 56 % when R passed from 0 to 5, respectively. Comparable results were obtained at 60 °C. Indeed, t_{nucl} increased and it passed from 2 to 6 min for $R = 0$ and $R = 5$, respectively. The crystalline growth rate decreased with the molar ratio R. Thus,

Table 1
The effect of Na_2SO_4 on the crystalline growth rate (V_c), supersaturation (X), the nucleation times (t_{nucl}), and the precipitation ratio (τ_p) for the same ionic strength (0.08 mol/L) and at different operating temperatures

Without Na_2SO_4					With Na_2SO_4			
T (℃)	t_{nucl} (min)	Ω	V_c ($\mathrm{M.min^{-1}}$)	τ_p (%)	t_{nucl} (min)	Ω	V_c ($\mathrm{M\,min^{-1}}$)	τ_p (%)
30	19	47.16	0.16	44	42	62.17	0.18	35
40	8	49.23	0.47	73	17	71.15	0.26	56
50	5	51.68	0.75	81	9	62.14	0.35	71
60	3	56.14	1.1	85	6	77.49	0.73	76

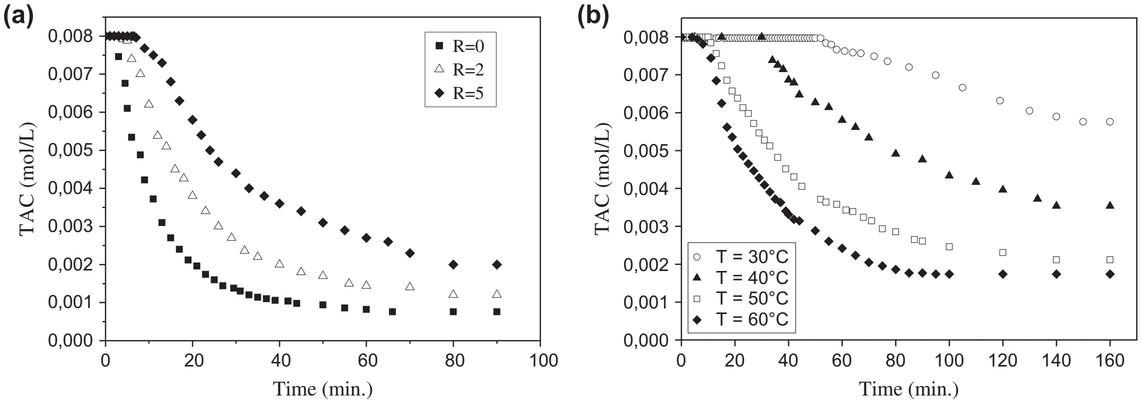

Fig. 2. Experimental TAC variation vs. time, during the solution degassing for (a) various Mg/Ca molar ratios (R) at 60℃ and for (b) various temperatures for $R = 5$.

V_c passed from 2.6 $\mathrm{M.min^{-1}}$ in a pure calco-carbonic solution ($R = 0$) to 0.84 $\mathrm{M.min^{-1}}$ for $R = 5$. An increase of Mg^{2+} concentration causes a significant retardation of $CaCO_3$ nucleation. Consequently, higher supersaturation thresholds for $CaCO_3$ polymorphs are reached at high Mg^{2+} concentration (Table 2). This suggests that Mg^{2+} ions have a strongest inhibiting effect on the $CaCO_3$ precipitation. These results are in line with research conducted by other researchers [4,25–27], where induction time was improved significantly due to the presence of Mg^{2+}. In principle, the retardation of $CaCO_3$ nucleation by Mg^{2+} can be caused by: (i) $MgCO_3$ aquo-complex formation, which reduces free CO_3^{2-} ions, (ii) covering active surface sites of $CaCO_3$ nuclei and crystals with Mg^{2+} [28] and (iii) incorporation of Mg^{2+} in $CaCO_3$, which induces changes in calcite solubility [29].

The effect of the temperature on the $CaCO_3$ precipitation kinetics in the presence of $MgCl_2$ salts was studied. The results are summarized in Table 2. The increase of the temperature decreased significantly t_{nucl} and increased both V_c and τ_p. In fact, t_{nucl} became eight times lower at 60℃ than at 30℃. V_c passed from 0.11 to 0.81 $\mathrm{M.min^{-1}}$ and τ_p passed from 28 to 75 % when the temperature increased from 30 to 60℃, respectively. This effect is due to $CaCO_3$ retrograde solubility. In the presence of Mg^{2+} ions, the temperature favoured the precipitation of $CaCO_3$. This effect was less significant in the presence of $MgCl_2$ than that in the absence of $MgCl_2$. The elevated temperature weakens the impact of Mg^{2+} on the retardation of $CaCO_3$ formation.

Table 2
The experimental t_{nucl}, Ω, V_c and τ_p obtained at different temperatures for various [Mg]/[Ca] molar ratios and different ionic strength (I S)

T (℃)	R	I S (M)	t_{nucl} (min)	Ω	V_c ($\mathrm{M\,min^{-1}}$)	τ_p (%)
30	5	0.08	52	45.04	0.11	28
40	0	0.02	7	41.93	0.57	81
	2	0.04	6	27.89	0.51	67
	5	0.08	30	53.97	0.49	56
50	5	0.08	10	51.55	0.52	74
60	0	0.02	2	31.16	2.6	90
	2	0.04	3	35.9	1.3	85
	5	0.08	6	56.14	0.81	75

3.3. Precipitates microstructures

The XRD patterns of the precipitates obtained at various temperatures in the presence and absence of Na_2SO_4 are presented in Fig. 3. At 30˚C, the three variety of $CaCO_3$ (aragonite, calcite and vaterite) coexisted. When the temperature increased, the intensities of vaterite and calcite reflections decreased and aragonite became the major phase. Therefore, the temperature promotes the aragonite phase. Working at 60˚C, the calcite reflections is scarcely visible; however, those of vaterite persisted. Accordingly, the increase of the temperature in the presence of sulphate promotes the aragonite variety and slightly affects the vaterite phase.

The XRD patterns of the precipitated obtained at 40 and 60˚C for various [Mg]/[Ca] molar ratio *R* are shown in Fig. 4(a) and (b). As can be observed, in

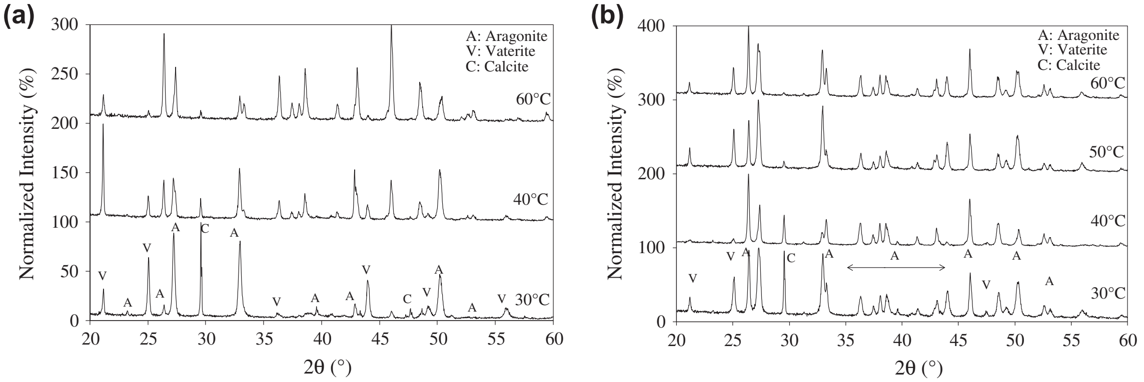

Fig. 3. Superposition of XRD patterns (a) without Na_2SO_4 and (b) with Na_2SO_4 ($R = 5$), obtained at different temperatures.

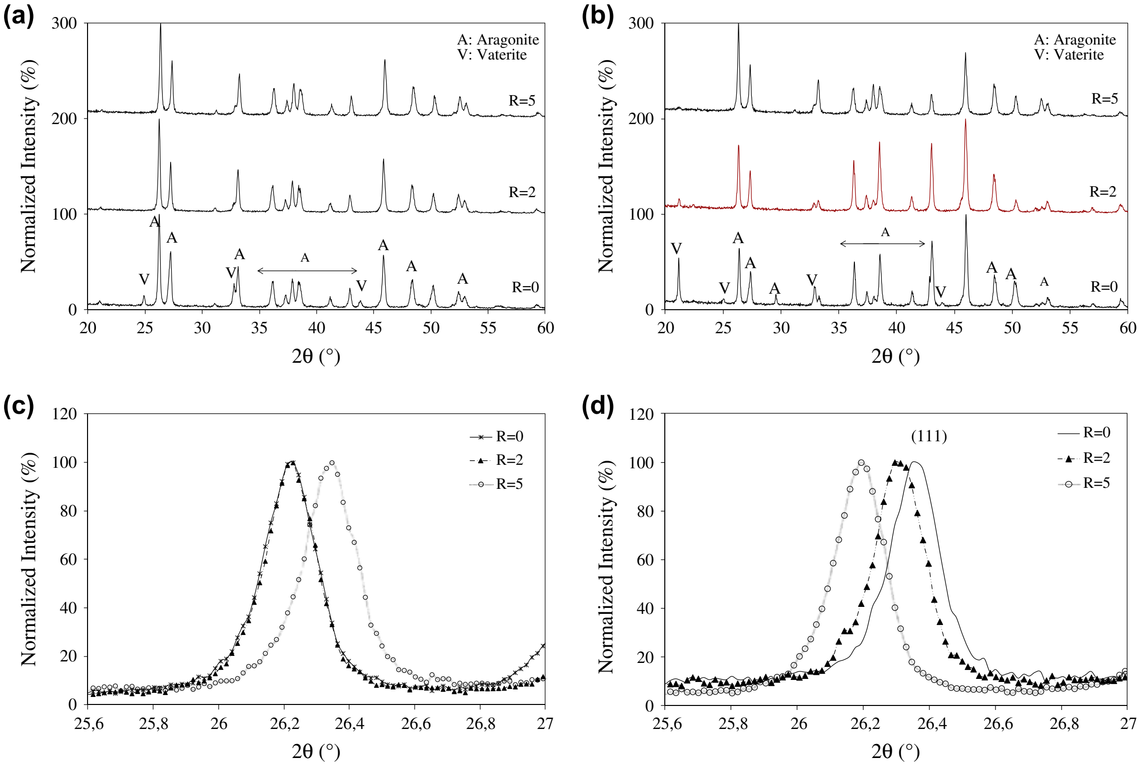

Fig. 4. Superposition of XRD patterns at (a) 40˚C and (b) 60˚C and there correspondent 111 XRD reflection profiles of the aragonite at (c) 40˚C and (d) 60˚C for various magnesium/calcium molar ratios.

absence of magnesium ($R = 0$), the aragonite and vaterite coexisted. However, in presence of magnesium, for $R \geqslant 2$, the reflections corresponding to vaterite were not observed and the precipitate was exclusively consisted of aragonite. Calcite is generally formed at low [Mg]/[Ca] ratios; the limit of the [Mg]/[Ca] ratio for calcite formation depends on the temperature. Our results strongly suggest that magnesium promote the formation of aragonite. These results are in agreement with observations of Ahn et al. [30], who postulated that magnesium concentration controls aragonite formation, with a minimum Mg^{2+} concentration being required to suppress calcite formation.

The profile of the aragonite reflection located at d spacing of 3.384 Å ($2\theta = 26.2$ °) is given in Fig. 4(c) and (d). A significant reflection shifted to higher 2θ angles was observed at 40℃ when R increased (Fig. 4(c)), whereas a significant shift towards lower angles was observed at 60℃ (Fig. 4(d)). The reflection shift towards higher 2θ angles at 40℃ is due to slight distortions in compression of the crystal lattice. This is due to the substitution of the calcium ions by the magnesium ions. Since the atomic ion radius of Mg^{2+} (1.598 Å) is smaller than that of Ca^{2+} (1.974 Å), the aragonite lattice parameter decreased. The reflection shift to the lower 2θ angles at 60℃ could be explained by the incorporation of the magnesium ions in the aragonite crystal lattice which causes distortions in tension of the aragonite lattice and consequently the lattice parameter increased.

Fig. 5(a) shows the XRD patterns of the precipitates obtained at different temperature in the presence of $MgCl_2$ salt (2×10^{-2} M). The XRD analyses show that only aragonite is formed despite a low temperature. This result confirms the effect of temperature on promoting aragonite formation in the presence of magnesium ions [31]. Contrarily to Wang et al. [32], which showed that at lower temperatures, such as ambient, vaterite formation is possible; however, its conversion to calcite is rapid.

The superposition of the 111 reflection profiles of the aragonite (Fig. 5(b)) located at d spacing of 3.384 Å ($2\theta = 26.2$°) showed a reflection shift towards lower 2θ angles indicating that the temperature leads to the incorporation of the Mg^{2+} ions in the aragonite lattice. In order to confirm the presence of magnesium in the aragonite crystal lattice, the precipitates were analysed by atomic absorption spectroscopy (AAS) and the magnesium content in the precipitates was determined. Fig. 6 shows the evolution of the Mg^{2+} mass fraction (%) in the aragonite crystal lattice with the Mg^{2+} concentrations in the solution (mg/L) at 40 and 60℃. When the Mg^{2+} concentration in the solution increased, the Mg^{2+} mass fraction in the aragonite

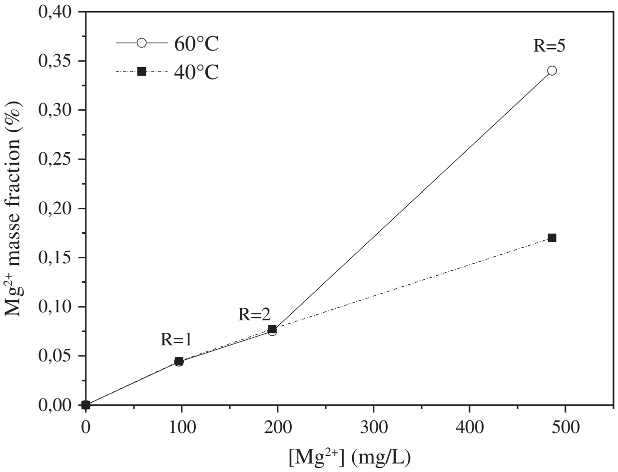

Fig. 6. Evolution of the Mg^{2+} mass fraction (%) in the aragonite with the Mg^{2+} concentrations in the solution (mg/L) at 40 and 60℃.

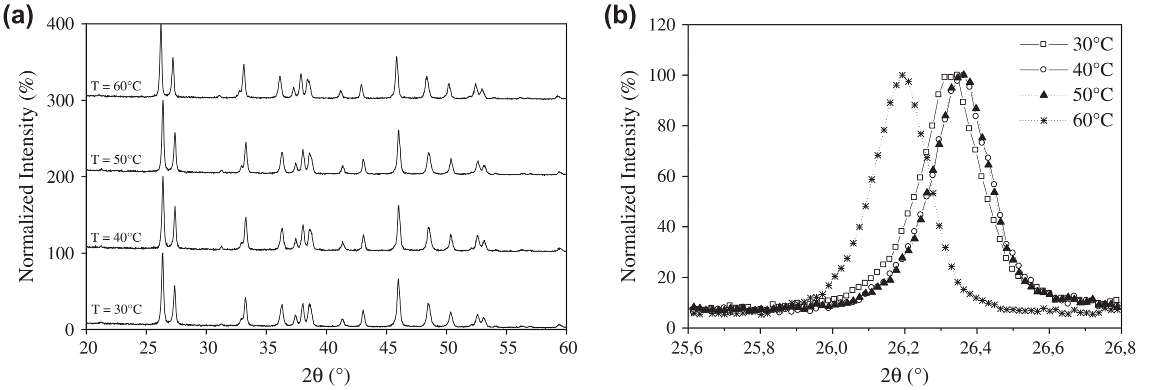

Fig. 5. (a) Superposition of XRD patterns and (b) the 111 XRD peak profiles of the aragonite obtained at different temperatures in the presence of magnesium ($R = 5$).

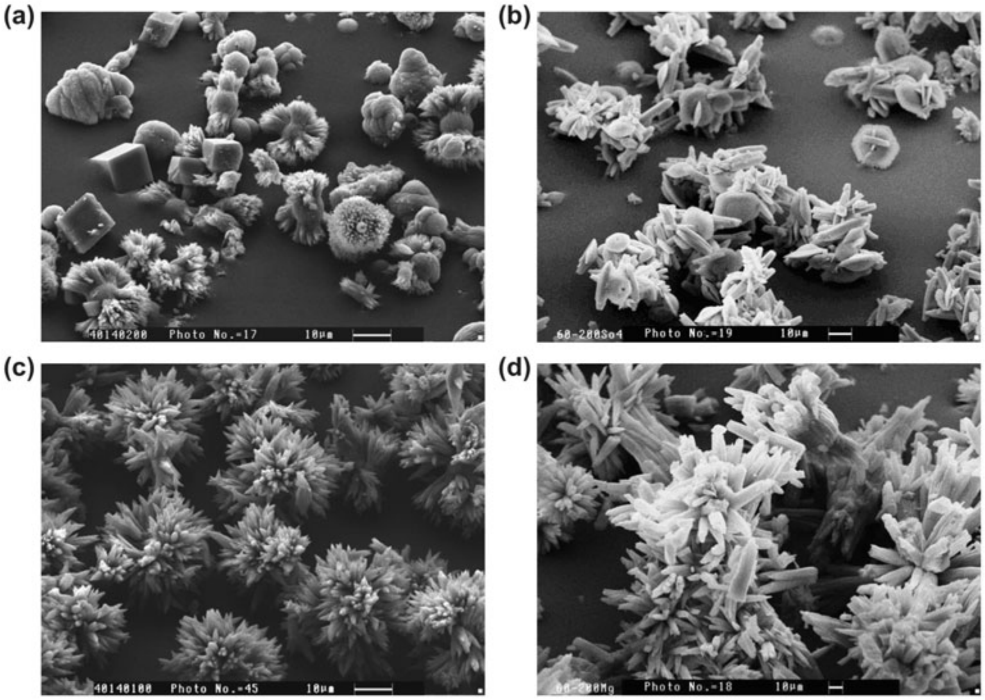

Fig. 7. SEM micrographs of the calcium carbonate crystals obtained at different temperatures in the presence of Na_2SO_4 at (a) 30°C and at (b) 60°C and in the presence of $MgCl_2$ at (c) 30°C and at (d) 60°C.

precipitates increased. At 60°C, it passed from 0.04 to 0.34% when the Mg^{2+} concentration in the solution passed from 97.2 mg.L^{-1} ($R = 1$) to 486 mg.L^{-1} ($R = 5$). The values of the Mg^{2+} mass fraction for both temperatures were comparable up $[Mg^{2+}]$ = 194.4 mg/L ($R = 2$). However for $R = 5$, the Mg^{2+} mass fraction obtained at 60°C was significantly greater than that obtained at 40°C. This is in agreement with the XRD results.

The morphology of the crystals formed during the precipitation experiments, investigated by SEM, is showed in Fig. 7. At 30°C, in the presence of Na_2SO_4 salt, the microscopic observation (Fig. 7(a)) revealed the coexistence of the three varieties of $CaCO_3$: the vaterite crystals with a characteristic lentil, the calcite with its characteristic rhombohedral shape and the aragonite present in branched-like shape. With increasing the temperature (Fig. 7(b)), the three varieties were present with the predominance of aragonite. It is noteworthy that aragonite is the most abundant polymorph at elevated temperatures [33]. SEM investigations on crystals confirmed the previous XRD results. Indeed, on SEM images, it can be seen that at low temperature of 30°C, the presence of Mg^{2+} ions promoted the crystallization in the bulk solution of secondary aragonite, issued from the transformation of vaterite nuclei (Fig. 7(c)). However, at high temperature of 60°C, Mg^{2+} ions favoured the primary aragonite (Fig. 7(d)). Temperature and the ratios of foreign cations to Ca (magnesium and sulphate) control not only the type of polymorph but also the morphology of the precipitate [34]. In fact, aragonite made at high temperature has larger particles sizes.

4. Conclusion

The effects of the temperature on the kinetics and microstructure of $CaCO_3$, in the presence of magnesium and sulphate ions, were studied using degassing dissolved CO_2 method. The precipitates were identified by XRD, AAS and SEM. The principal results show that the Mg^{2+} or SO_4^{2-} ions have an inhibiting effect on the precipitation of $CaCO_3$ which depends on the temperature. The temperature increase enhanced the rate of calcium carbonate precipitation, favoured the formation of aragonite and increased significantly the amount of $CaCO_3$ precipitated. Magnesium incorporation within the aragonite lattice is possible only at high temperature.

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