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Sirine Ben Latifa, Hélène Cheap-Charpentier, Hubert Perrot, Yasser Ben Amor. Effects of Magnetic Field on Homogeneous and Heterogeneous Precipitation of Calcium Carbonate. *ChemElectroChem*, 2023, 10, pp.e202300105. 10.1002/celec.202300105 . hal-04160362

HAL Id: hal-04160362

<https://hal.sorbonne-universite.fr/hal-04160362v1>

Submitted on 12 Jul 2023

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Effects of Magnetic Field on Homogeneous and Heterogeneous Precipitation of Calcium Carbonate

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Abstract: In this study, fast controlled precipitation (FCP) and chronoamperometry (CA) methods were performed to evaluate the influence of the magnetic treatment at 0.70 T, upon the scale formation in synthetic solutions (hardness 25  F), exposed to a static magnetic field for different exposure times. According to FCP results, homogeneous CaCO₃ precipitation rates in treated solution were lower than those in the absence of the magnetic field. It has been found that the memory effect can last up to 24 h after the magnetic treatment even if it decreases over time. As purpose of comparison, CA method was applied to investigate the influence of the magnetic treatment on heterogeneous CaCO₃ precipitation. The magnetic field effect increased with the increasing exposure time. The obtained scale, characterized by scanning electronic microscopy and X-ray diffraction, was formed by a mixture of calcite and aragonite in the presence of magnetic field.

Introduction

Scale precipitation, principally formed by calcium carbonate (CaCO₃), often leads to numerous technical problems in industrial and domestic equipment, such as a partial or total obstruction of pipes, causing a decrease in flow rate, a reduction of heat transfer in heat exchangers, a seizure of valves and a clogging of filters.^[1,2] The economic losses associated with these technical problems can be significant. Calcium carbonate is the most common scale encountered in water systems. To control scale formation, two main preventing processes can be used in industrial plants: chemical and physical methods.^[3,4,5] One of the most efficient methods used to prevent scale formation is the addition of antiscalants in water also called scale inhibitors.^[6,7] Nowadays, as new international guidelines for industrial discharges are becoming more stringent in terms of ecology, the use of these antiscaling substances is more limited and physical

treatments such as magnetic field (MF) are becoming a well adapted and pertinent possibility. Physical water treatments were developed to substitute chemical water treatments which employ chemicals products, such as phosphonates that are harmful to the environment and human health.

The magnetic treatment of hard water is an interesting alternative to prevent scaling problem in domestic and industrial installations. Indeed, the magnetic field can reduce or prevent scale formation in several sectors of activity such as health, environment, industry and agriculture.^[8, 9, 10, 11] This method is particularly used for the treatment of drinking water as it does not change the water potability.^[12, 13] It seemed that a MF causes changes only in the distribution and polarization of the molecules but not in the constitution of water.^[14] It is known for decades as an effective technique both in preventing the scale formation and in detaching already formed scale in industrial water systems, that could be eliminated by water flow or filtration.^[15] The magnetic treatment can be applied either in static mode for a certain period of time or on flowing water with a given velocity.^[16, 17] Different parameters such as the temperature, the pH, the strength and the direction of the magnetic field can influence the inhibition efficiency of this treatment.^[18, 19] Positive results based on magnetic field, have been reported by various authors.^[15, 20, 21, 22, 23, 24] Zaidi et al. proved that magnetic treatment can promote the solid-liquid separation by improving the gathering of colloidal particles.^[25] However, some reports found in the literature present contradictory results. According to Alimi et al. it was found that magnetic treatment increases the total amount of precipitate and favours the homogeneous nucleation depending on pH or the flow rate values.^[26] Elaoud et al. showed the effect of magnetic treatment on water quality and on the yield of the melon culture which increased by 39 % compared to raw water.^[27] Some authors claim favorable effects of this technology on water such as the removal of scale deposits in water pipes. For example,

Chibowski et al. and Barrett and Parson have found that the application of a magnetic field on hard water decreases the amount of scale deposits on the walls.^[28, 29] They proposed that it is thanks to the Lorentz force exerted either between ions or uncharged particles. The magnetic treatment could modify the ionic double layer surrounding the colloidal particles and therefore, their zeta potential. By modifying the charge distribution, the interaction energy between the Ca^{2+} and CO_3^{2-} ions is modified and thus, could limit the formation of calcium carbonate particles. Some authors claim that the magnetic field tends to reduce the nucleation kinetics and accelerate the crystal growth.^[29, 30] Ferreux has concluded that the free enthalpy of calcium carbonate formation could be affected by the magnetic field.^[31] It is also reported that the magnetic field alter the morphology and the adhesion of calcium carbonate scale on a surface. The modified scale formation may be the result of the preferential formation of aragonite compared to calcite.^[32, 33, 34] The needles of aragonite crystals could be formed by the transformation of metastable vaterite with hexagonal structure.^[35] Changes in water that occur due to the magnetic field can include wettability, viscosity and surface tension reduction, refractive index, dielectric constant and conductivity increase.^[14, 36, 37] Hardness reduction of water to 51 %, vaporization rate increase and hydrogen bonds increase could also induce changes in water.^[38, 39, 40] Recently, the magnetic treatment was combined to chemicals used as antiscalant to enhance the inhibition efficiency against scale formation. Liu et al. have demonstrated an increase of the inhibition efficiency of 100 % when a magnetic field at 0.6 T was applied with a 0.5 mg LIA/SAS/SHP copolymer (pH=7.3, T= 40 °C).^[41]

In our study, the influence of the magnetic treatment on calcium carbonate (CaCO_3) formation was investigated by using fast controlled precipitation (FCP) method and chronoamperometry (CA).^[42, 43, 44] On the one hand, FCP method allows the homogeneous precipitation of CaCO_3 in solution before and after a magnetic treatment to be done. On the other hand, the CA was used to assess the effect of magnetic field on the formation of CaCO_3 on a metallic surface. In order to evaluate the scale inhibition, the time exposure, the resting time after an exposure and the solution temperature have been varied. In order to determine the influence of magnetic field on scale formation, the morphology of CaCO_3 crystal formed in solution and on the electrode surface was analyzed by scanning electronic microscopy (SEM). The proportion of vaterite, calcite and aragonite was investigated using X-ray diffraction (XRD).

Results and Discussion

Effect of magnetic treatment on the homogeneous CaCO_3 precipitation

Evolutions of the pH and resistivity

FCP method was used in order to evaluate the scaling power of the untreated and treated solution with a magnetic field at 0.7 T. The inhibition efficiency can be extracted and estimated through

these measurements. It was calculated from the resistivity measurements by the following relation (Eq. 1):

$$E_{\text{FCP}} = \frac{\int_0^t (\rho_{\text{NT}} - \rho_0) - \int_0^t (\rho_{\text{T}} - \rho_0)}{\int_0^t (\rho_{\text{NT}} - \rho_0)} \quad (1)$$

where ρ_0 is the initial resistivity, ρ_{NT} the resistivity of untreated water and ρ_{T} the resistivity of the treated water.

Figure 1 presents the evolutions of the pH and the resistivity values as a function of time of the tested solution after a magnetic treatment for different exposure times: 0 min, 15 min, 30 min, 1 h, 2 h and 18 h. The graphical exploitation of the FCP curves allows the determination of scaling parameters: 1) the precipitation time, t_p , which corresponds to the pH maximum value; 2) the precipitation rate, r_p , the slope of the linear part of the curve resistivity vs time, of CaCO_3 in solution and 3) the inhibition efficiency E_{FCP} (%) which was calculated from Eq. 1. These data are presented in Table 1.

According to the pH curves as a function of time, three steps can be distinguished (Fig. 1A).^[44, 45] Firstly, an increase of pH until a maximum value was observed which defines the precipitation time, t_p .^[46] This step was associated to the homogeneous CaCO_3 nucleation process.^[47] The second step was characterized by a pH decrease due to the calcium carbonate precipitation in the tested solution.^[43] In a third step, the degassing of CO_2 and the precipitation of CaCO_3 in solution tend to equilibrate so a stabilization of the pH was observed. The solutions have been previously treated with the magnetic field during different times, as indicated, before a FCP test. When the tested solution was not treated by a magnetic treatment (Fig. 1A, blank solution, black curve), t_p was 51 min. When the solutions were treated by the magnetic field, the t_p values increased with the exposure time. For instance, t_p increased from 67 min to 86 min, for an exposure of 15 min and 18 h respectively (Fig. 1A and Table 1). This result shows the longer the solution is exposed, the more the nucleation step is longer.

The evolution of the resistivity over time for untreated and treated solutions with a magnetic field was shown in Fig. 1B. Without magnetic treatment (Fig. 1B, black curve), the resistivity increases significantly and linearly after a period of 51 min which corresponds to the homogeneous precipitation of CaCO_3 in the tested solution.^[47] The results show that r_p decreases when the magnetization time increases. When the magnetization time increases from 15 min to 18 h, the precipitation rate decreases from 14 $\Omega \cdot \text{cm} \cdot \text{min}^{-1}$ to 11 $\Omega \cdot \text{cm} \cdot \text{min}^{-1}$. The calculation of the inhibition efficiency, E_{FCP} , depending on the exposure time shows that E_{FCP} increases from 24 % to 60 % (Table 1). It is noteworthy that the application of a magnetic field did not inhibit completely the formation of CaCO_3 even after 18 h of exposure. Consequently, the increase of the exposure time of the tested solution to the magnetic field promotes a delay in the formation of calcium carbonate in solution, a decrease of the precipitation rate and an increase of the inhibition efficiency correlated to t_p , r_p and E_{FCP} respectively. It is noteworthy that the application of a magnetic field did not inhibit completely the formation of CaCO_3 even with 18 h of exposure.

Furthermore, it is observed that at $t=0$, the resistivity decreases when the exposure time increases (Fig. 1B). This result is confirmed by the work of Szcześ et al.^[40] In their study, with 15 mT of MF during 5 min, the conductivity (which is inversely proportional to the resistivity) increases significantly.

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This effect might be interpreted on the basis of stronger hydrogen bonds and from gas/liquid interface perturbation. Numerous mechanisms explaining the influence of the magnetization phenomena on CaCO_3 precipitation have been reported in

literature. Salman et al. have determined that the Ca^{2+} concentration decreased slower when a solution was treated with a magnetic field compared with a non treated solution.^[48]

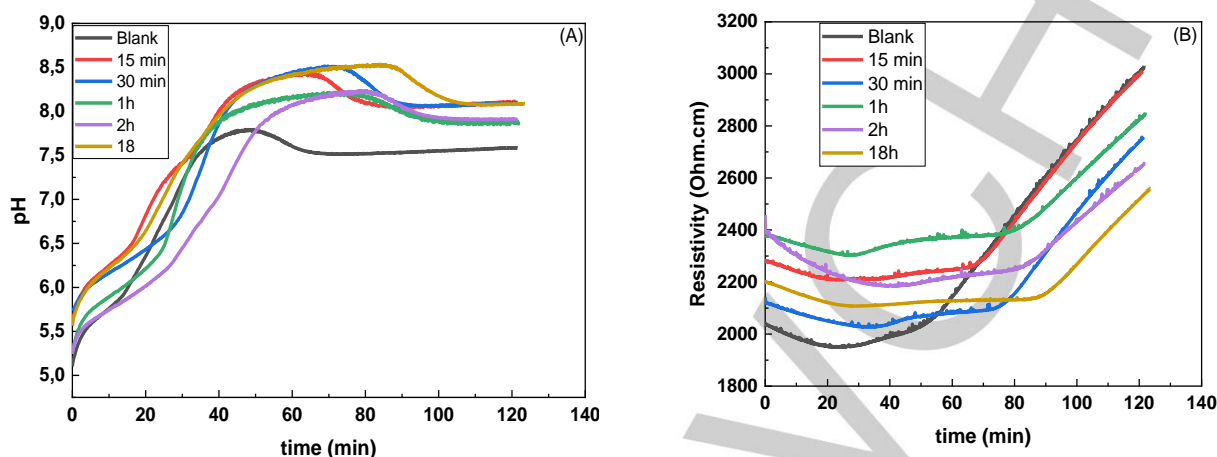


Figure 1. Evolution of the (A) pH and (B) resistivity over time obtained by FCP after a magnetic treatment of 0.7 T during different exposure times in a synthetic solution at 25 °F and 30 °C.

Table 1. Results obtained by FCP tests without and with magnetic treatment in synthetic water 25 °F and 30 °C.

Magnetization time	t_p ^[a]	r_p ^[b]	E_{FCP} ^[c]
0 (Blank)	51±1	14±1	-
15 min	67±1	14±1	24±4
30 min	74±1	13±1	36±4
1h	78±2	11±1	50±7
2h	80±1	11±1	53±3
18h	86±2	11±1	60±5

[a] precipitation time; [b] precipitation rate ($\Omega \cdot \text{cm} \cdot \text{min}^{-1}$); [c] inhibition efficiency (%).

By this way, it proved that magnetic treatment affects the CaCO_3 formation by retarding its precipitation in solution. According to Prykarpatsky et al., the reduction of the scaling rate in the treated solution by MF may be explained by the intermolecular separation of Ca^{2+} and HCO_3^- ions present in solution caused by the Lorentz force when they pass through a magnetic field.^[49] Higashitani et al. have shown that the nucleation rate was decreased but the growth of nucleated crystals was accelerated at values of B above 0.30 T.^[30] In another study, Lundager Madsen explained that the increase of the nucleation and growth rates was correlated to a faster proton transfer from hydrogen carbonate ions to water, due to the proton spin inversion in the magnetic field.^[50] It was also found that the precipitation rate depends on the method and the time of the solution exposure to the magnetic field.^[51]

In order to assess the persistence of the antiscaling properties of the magnetic treatment (called memory effect), FCP tests were carried out on magnetically treated solutions after different rest times. The solutions were treated by the MF during three magnetization time, t_m : 15 min, 30 min and 2 hours. Then, they were rested at ambient temperature for a given rest time, t_r , from 15 min to 24 h after magnetization and before FCP tests. It is assumed that the composition of the tested solutions did not vary during the stagnation time.^[30]

Table 2 present the three scaling parameters, t_p , r_p and E_{FCP} , obtained from FCP measurements after different rest times, t_r (0, 30 min, 2 h and 24 h) and different magnetization time, t_m (15 min, 30 min and 2 h). A decrease of the precipitation time, t_p , is observed when the rest time, t_r , increases, whatever the time of magnetization, t_m , is. For instance, for 15 min of magnetization, the precipitation time, t_p , varies from 67 min to 61 min for a rest time of 0 min and 24 h respectively. Similarly, for 30 minutes and

Memory effect of the magnetic treatment

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2 hours of magnetization, after 30 min of stagnation, t_p decreases from 74 min to 62 min and from 80 min until 71 min, respectively (Table 2). These results show that the nucleation process is accelerated as the MF effect decreases over time. Surprisingly, the precipitation rate, r_p , remains quite constant (Table 2). For example, for 15 min of magnetization, r_p values are 12 and 13 $\Omega \cdot \text{cm} \cdot \text{min}^{-1}$ for a rest time of 30 min and 24 h respectively. It seems that the MF continues to act on the homogeneous precipitation process for a long time, acting differently on the various parameters of the scaling process. According to Table 2, the inhibition efficiency, E_{FCP} , decreases when the rest time, t_r , increases, for each time of magnetization.

For instance, at 15 min of magnetization, the inhibition efficiency decreases when the rest time, t_r , increases until reaching 24% with $t_r = 24$ h. However, when the magnetization time increases, the inhibition efficiency, E_{FCP} , remains high regardless of the rest time. The longer the magnetization time, the greater the inhibition efficiency is. Thus, the influence of the MF on the CaCO_3 formation decreases over time but it can persist until 24 h. It is noteworthy that the inhibition effect of the MF lasts for a long time, even until 24h.

Table 2. FCP results after different magnetization times and rest times.

$t_m^{[a]}$	15 min			30 min			2 h		
	t_p	r_p	E_{FCP}	t_p	r_p	E_{FCP}	t_p	r_p	E_{FCP}
0	67±1	14±1	24±4	74±1	13±1	36±4	80±1	10±1	59±3
30 min	64±1	12±2	32±7	67±1	14±1	18±1	77±1	11±1	53±3
2h	61±1	10±1	40±4	64±1	13±1	25±3	76±1	13±1	40±4
24h	61±1	13±1	24±3	62±1	12±2	35±3	71±1	11±1	44±1

[a] magnetization time; [b] rest time.

It can be found in the literature that memory of magnetic treatment can last up to 200 h.^[32] Higashitani et al. have demonstrated by measuring the absorbance of the solution that the magnetic effect remained for at least 120 h after magnetization.^[30] Mascolo verified the persistence of the magnetic treatment for 14 days.^[52] Silva et al. explained that when the separated ions (Ca^{2+} and HCO_3^-) pass through magnetic field, the tendency of the solution to form scale is inhibited.^[24] The process by which ionic species of opposite charge remain separated is called the memory effect, this ability to separate decreasing as time passes after the magnetic exposure. These results prove that magnetic treatment produce a memory effect and influences the CaCO_3 precipitation as well as its crystal forms (shown after), which was confirmed by some authors.^[21, 26, 32]

Effect of MF on the heterogeneous CaCO_3 precipitation on a metallic surface

Chronoamperometry was used to examine the MF effect on the heterogeneous calcium carbonate precipitation on stainless steel for different magnetization times. It consists of precipitating calcium carbonate on a metallic surface by applying a cathodic potential (-1 V/SCE).^[53, 54] The potential generates O_2 reduction according to the following electrochemical reaction (Eq. 2):



The local pH at the electrode surface increases significantly and the reaction rate of solid calcium carbonate formation is therefore enhanced by the excess OH^- according to the following equations (Eq. 3 and 4):^[55]



As shown in Fig. 2, the electrochemical current is normalized by I_0 , the current value at the maximum of the curve, in order to facilitate the comparison between the different experiments. These experiments were performed at 30 °C and 60 °C (Fig. 2A and B). To compare the scaling potentiality of each tested solution untreated and treated by the MF, two scaling parameters were extrapolated from chronoamperometric results: the scaling time, t_s , corresponds to the intersection between the tangent of the decreasing linear part of the curve and the time axis and the scaling rate, r_s , is determined from the slope of the linear part of the current-time curve.^[53, 56] The inhibition efficiency, E_{CA} , of the magnetic treatment was also calculated from the chronoamperometry measurement according to the following equation (Eq. 5):

$$E_{\text{CA}} = \frac{r_{s0} - r_{si}}{r_{s0}} \times 100 \quad (5)$$

where r_{s0} and r_{si} were the scaling rates of CaCO_3 precipitation on a metallic surface from the tested solution without and with the magnetic treatment, respectively. The corresponding values were regrouped in Table 3. Without magnetic treatment a classical chronoamperometric curve was observed, where the reduction current of dissolved dioxygen decreases over time (Fig. 2A and B, black curve).^[17] This is related to the precipitation of CaCO_3 on the active surface of the electrode which generates an insulating barrier against dioxygen diffusion. The scaling time, t_s , was found

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to be 62 min at 30 °C (Fig. 2A and Table 3). When the tested solutions were treated with a MF, t_s increases with the magnetization time (Fig. 2). For instance, at 30 °C, t_s increases up to 341 min when the solution was magnetically treated during 18 h (Table 3). This result shows that the MF is efficient to delay the scaling process on the electrode surface. For the longer time, the full curve is not shown here for practical reason. The scaling rate, r_s , was determined from the slope of the linear part of the curve current against time.

According to Table 3, the r_s values decrease when the magnetization time increases. The MF slows down the

heterogeneous precipitation on the surface electrode. The application of a magnetic field strength of 0.70 T during a magnetization time of 18h, leads to an increase of the scaling time until 341 min and a decrease in the precipitation rate from 0.024 to 0.003 A·min⁻¹. Moreover, the efficiency, E_{CA} , reaches a value of 88 % (Table 3). The inhibition efficiency increases with the magnetization time. Several authors have shown that magnetic field would tend to reduce the nucleation rate and to accelerate the crystal growth.^[29, 30] Gabrielli et al. confirmed that the concentration of calcium ions decreased when the solution was exposed to a magnetic field, preventing calcium carbonate formation.^[17]

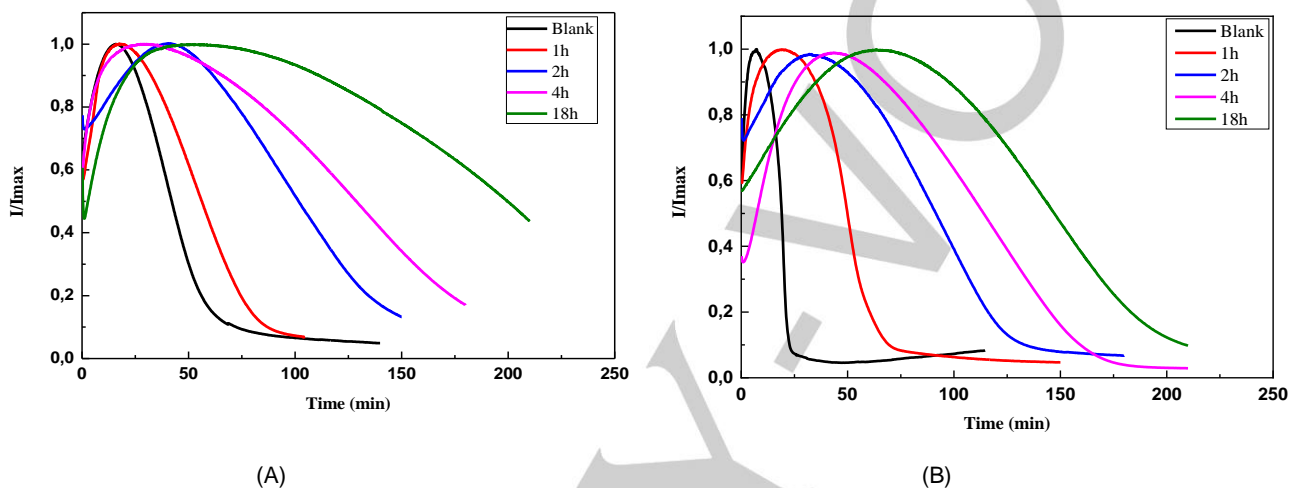


Figure 2. Evolution of the electrochemical current versus time of the tested solution at (A) 30 °C and (B) 60 °C, for different times of a magnetic treatment at 0.70 T, -1 V/SCE, rotation speed of the working electrode at 1200 rpm in synthetic water with a hardness 25 °F.

Table 3. Results obtained by chronoamperometric tests without and with magnetic treatment of 0.70 T in synthetic water 25 °F.

T		30 °C			60 °C		
t_m [a]	t_s [b]	r_s [c]	E_{CA} [d]	t_s	r_s	E_{CA}	
0	62±1	0.024±0.001	-	24±1	0.104±0.001	-	
1h	85±1	0.017±0.002	30±6	62±1	0.030±0.001	71±2	
2h	154±1	0.009±0.002	58±6	127±1	0.012±0.001	88±1	
4h	169±1	0.005±0.001	80±2	161±1	0.010±0.001	90±1	
18h	341±2	0.003±0.002	88±5	181±1	0.010±0.001	90±1	

[a] magnetization time (h); [b] scaling time (min); [c] precipitation rate (min⁻¹); [d] inhibition efficiency (%).

The effect of temperature on the formation of scale in the absence and presence of magnetic treatment at intensity of magnetic field of 0.70 T is shown in Figure 2. Without magnetic treatment, the current density decreases rapidly from 62 min at 30 °C until 24 min at 60 °C to reach a residual value reflecting a blocked surface. For the same experiments performed at 60 °C and 0.70T by varying each time the magnetization time, the results show that the scaling time, t_s , decreases gradually with the increase of temperature. Indeed, for example, according to Table 3 and, for 1 h of magnetization time, t_s decreases from 85 min to 62 min, for 30 °C and 60 °C respectively. However, the

scaling rate, r_s , increases from 0.017 to 0.030 A·min⁻¹ for 1 h of magnetic treatment at the two temperatures. It is important to note that the effectiveness of the magnetic treatment increases when the temperature increases as shown in Table 3. The effect of temperature on scale formation has been investigated by Boulahlib et al. They confirmed that the increase of the temperature decreases the solubility of dissolved oxygen in water which decreases the scaling time.^[57]

Effect of MF on the morphology of CaCO₃ crystals

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One of the differences of the MF effect on CaCO_3 formation is its influence on the morphology of CaCO_3 crystals obtained by homogeneous and heterogeneous precipitation.

Morphology of the CaCO_3 crystals obtained by homogeneous precipitation

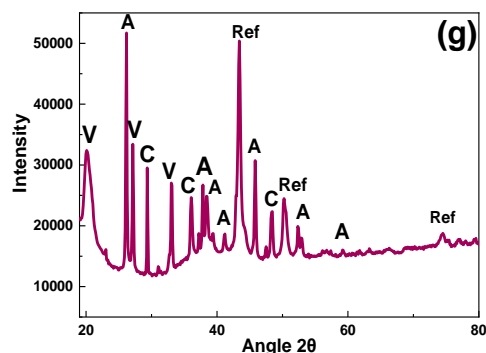
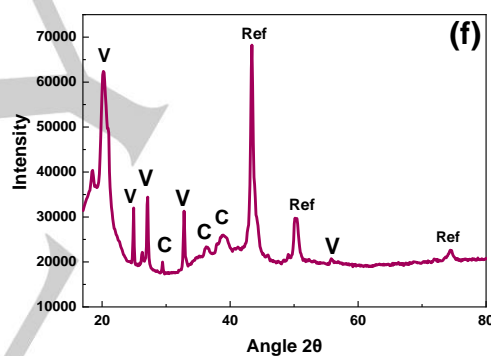
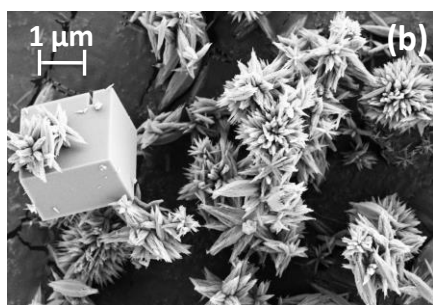
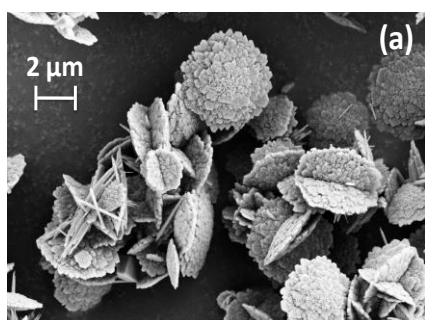
After evaluating the influence of the magnetic field on CaCO_3 formation in solution by using FCP method as discussed in previous section, the morphologies of the CaCO_3 crystals, formed in solution after a magnetic treatment, were observed by SEM and the crystalline phases were investigated by XRD for different magnetization times, t_m (Figure 3). In order to quantify the molar fraction of calcite X_C , vaterite X_V and aragonite X_A , respectively, the calculation of the molar fraction of each crystalline variety is given by the following equations (Eqs. 6, 7 and 8):^[58]

$$\frac{I_C^{104}}{I_A^{221}} = 3.157 \times \frac{X_C}{X_A} \quad (6)$$

$$\frac{I_C^{104}}{I_V^{110}} = 7.691 \times \frac{X_C}{X_V} \quad (7)$$

$$X_C + X_V + X_A = 1 \quad (8)$$

Results show a difference in the type of the crystallographic forms of CaCO_3 . Indeed, without magnetic treatment, mostly vaterite polymorph (the metastable form of CaCO_3) and some calcite crystals were observed which were confirmed by XRD spectrum (Fig 3a and Fig 3f). Peronno et al.^[47] proved that the FCP method leads to vaterite formation when the tested solution was not treated with an inhibitor. Otherwise, when the tested solution was treated by a magnetic field for different times of exposure, t_m , the aragonite form appears in the solution (Figure 3). The magnetic field leads to the formation of a mixture of vaterite, calcite and a predominant part of aragonite. It seems that a part of vaterite was transformed into aragonite. This result was confirmed by XRD spectrum (Figure 3) which revealed characteristics peaks of aragonite, calcite and vaterite. Surprisingly, after 18h of exposure, it is noteworthy that the vaterite appears again in the solution. As noted above, the magnetic field modified the crystalline structure from vaterite into aragonite and calcite, but after 18 h of magnetization, only vaterite was formed, like in untreated solution. It seems that 18 h is the cut-off time after which the magnetic effects were negligible. The molar ratios of observed crystal forms of calcium carbonate were calculated according to Eq. 6, 7 and 8, when the synthetic water was exposed to a magnetic field at different times.



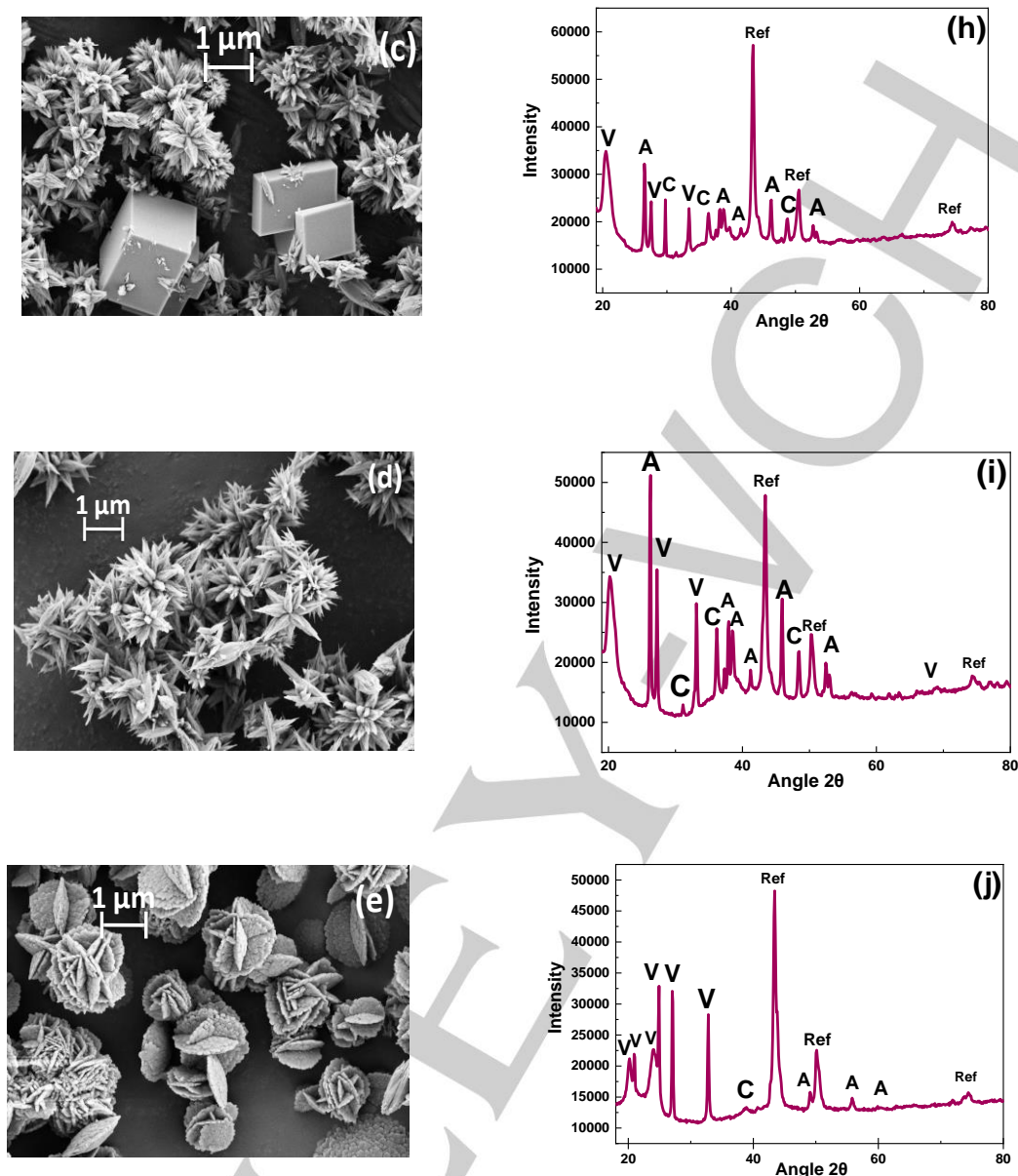


Figure 3. SEM images and XRD spectra of the CaCO_3 scales formed by FCP method after magnetic treatment of 0.70 T at 30 °C for different magnetization times: (a and f) without MT, (b and g) 15 min, (c and h) 30 min, (d and i) 2 h, (e and j) 18 h. (A: aragonite; C: calcite; V: vaterite; Ref: reference).

Table 4 shows that the values of these molar fractions depend on the exposure time. Indeed, in the untreated solution, the molar ratios of the vaterite and calcite forms are about 93 % and 7% respectively (Table 4). In this case, the aragonite is not present at all. When the exposure time increases from 15 min to 2 h, these molar ratios decrease because of the formation of aragonite: calcite proportion is less than 10 %, the vaterite slightly increases up to 60 % and the aragonite slightly decreases from 42 to 32 %. However, for an exposure time of 18 h, the vaterite appears as the main component with a percentage of 64%. These results are

in agreement with the researches of Coey et al. and Tai et al. who have demonstrated that magnetic field might inhibit CaCO_3 precipitation and promote the formation of aragonite rather than vaterite and calcite.^[32, 21] In another study, it has been demonstrated that aragonite formation was accelerated by the magnetic exposure.^[30] Lundager Madsen noted that the influence of a magnetic field of 0.27 T at 25 °C on inorganic salts promoted the formation of smaller crystals of calcite compared to solution without magnetic exposure.^[50] Some studies have shown a size reduction of vaterite and calcite crystals in the presence of magnetic fields.^[50, 59]

Table 4. Molar ratios of the different crystalline forms present in the synthetic solution after a FCP test.

Magnetization time	Calcite (%)	Vaterite (%)	Aragonite
0 (Blank)	7	93	-
15 min	13	45	42
30 min	12	51	37
1h	8	60	32
2h	8	60	32
18h	7	64	29

In addition, the MF memory effect over the crystal morphology, obtained through the FCP method, was analyzed with SEM and XRD. Results show that even after a while of stagnation, the aragonite was still observed with the others forms (vaterite and calcite). Indeed, Table 5 presents the percentage of each form. After 15 min of magnetic treatment, the molar fraction of vaterite is about 45 % and 42 % of aragonite. While after 30 min of stagnation, the aragonite percentage begins to decrease little by little until 24h of stagnation and it returns into vaterite with a

percentage of 70 % and 25 % aragonite. The molar fraction of vaterite polymorph increases from 51 % to 59% for 30 min of magnetization and from 48 % to 81 % for 2 h, between 0 and 24 h of stagnation time respectively. In the opposite way, the aragonite percentage decreases from 37 % to 36 % and from 46 % to 16 % at 24 h of stagnation (Table 5). Thus, it was found by comparing with the previous results that the antiscaling properties of magnetically treated water were persistent for approximately 24 hours after treatment.

Table 5. Molar ratios of the different crystalline forms present in solution before and after stagnation at 15 min, 30 min and 2h of magnetization time and 0, 30 min, 2h and 24h of stagnation time.

t_m	15 min			30 min			2h		
t_r	$X_v^{[a]}$	$X_c^{[b]}$	$X_a^{[c]}$	X_v	X_c	X_a	X_v	X_c	X_a
0	45	13	42	51	12	37	48	6	46
30 min	75	5	20	57	6	37	57	6	37
2h	70	5	25	70	5	25	75	5	20
24h	70	5	25	59	5	36	81	3	16

[a] Molar ratios of vaterite; [b] Molar ratios of calcite; [c] Molar ratios of aragonite.

Morphology of the CaCO_3 crystals obtained by heterogeneous precipitation

After each chronoamperometric experiment, the CaCO_3 crystals formed on the surface of the working electrode were observed by SEM and characterized by XRD (Figure 4). The deposits consisted of two crystalline varieties: calcite and vaterite. The percentage of each form has been calculated from Eq. 6, 7 and Eq. 8.^[58] The scale formed after a CA experiment (25 °F and 30 °C) and when the solution was exposed at a MF during 18 h. Without magnetic treatment, the deposit is mainly constituted by vaterite form (87 %) as given by the SEM images and the XRD spectrum (Fig. 4a and 4c). However, with the magnetic field strength at 0.70 T, the percentage of vaterite decreases more to 62 % which was transformed into calcite (38 %). This result was confirmed by SEM and XRD spectrum (Fig. 4b and 4d). These

results are in agreement with those obtained from other works. Indeed, Rodriguez-Blanco et al. who have suggested that the application of magnetic field may stabilize vaterite and accelerate calcite growth.^[60] In addition, Tai et al. noted that a magnetic field of high intensity was more effective on calcite nucleation/growth than on the other species.^[21] The lowest intensity of the magnetic field to affect the calcite growth rate reported in previous literature was about 1000 Gauss (0.1 Tesla) when the solution was subjected to magnetization for 2h.^[61] Liu et al. have also found an increase of the aragonite forms compared to the blank solution when a magnetic field at 0.6 T was applied to water at pH 7.3 and at 40 °C. These results prove that magnetization has an effect on both heterogeneous and homogeneous nucleation.^[41]

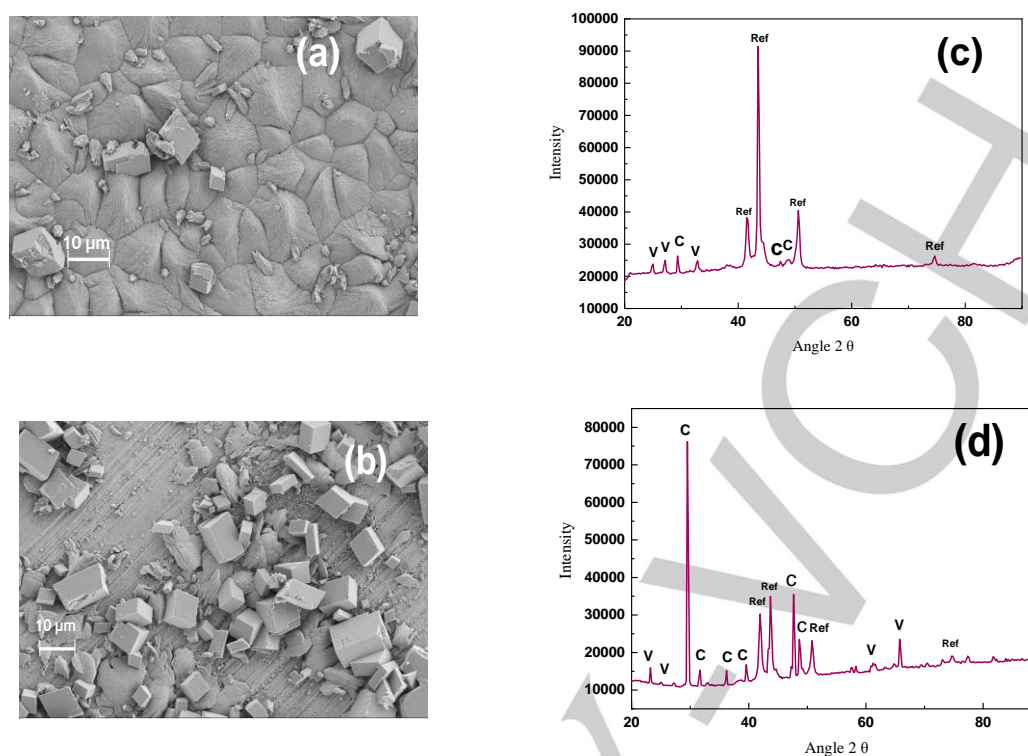


Figure 4. SEM images and X-ray diffraction spectra of the CaCO_3 scale formed by chronoamperometry (a and c) without treatment and (b and d) after 18h of magnetization at 0.70 T, in a synthetic solution at 25 °F and 30 °C.

By comparing the scale inhibition effectiveness of magnetic water treatment between FCP method and CA, it was found that under the same conditions (30 °C, 25 °F), the optimal time of exposure to the magnetic field was 18 hours obtained for both methods of scale generation. In the one hand, they are in good agreement and sensitive to investigate the effect of MF. On the other hand, according to the experimental results, the inhibition of calcium carbonate formation is more effective for the electrochemical method (CA) than the non-electrochemical method (FCP). Indeed, the study of CA, shows that in the presence of magnetic field the precipitation time increases and can reach 341 minutes with a maximum efficiency of 85 %, this is consistent with the results already published by Gabrielli et al. and Barret.^[17, 29] Moreover, XRD and SEM results show that different forms of CaCO_3 exist after the magnetic field was applied. Thus, in the FCP method the magnetization would favor the formation of aragonite which is the more stable phase besides the presence of cauliflower-shaped crystals characteristic of vaterite and the calcite.^[21, 32] Nevertheless, the aragonite quantity decreases over the magnetization time as it is shown here. However, the deposit formed on the surface by chronoamperometry consists of a mixture of vaterite and calcite without any observed aragonite under our experimental conditions, where the percentage of the calcite phase increases gradually with the increasing in the magnetic field intensity.^[21] Many studies of magnetic water treatment for scale control explained the formation of less compact scales by the increase amount of aragonite, which is less adhesive than calcite crystals.^[62]

Conclusion

Magnetic treatment was performed to evaluate its influence upon homogeneous and heterogeneous CaCO_3 precipitation in 25 °F carbonically pure water. The obtained results from FCP and CA investigations lead to the following conclusions. In the one hand, the scale inhibition dependent on the exposure time to the magnetic field. It was proved that magnetic field affects the calcium carbonate formation by retarding its precipitation. The magnetic field effect increased with increasing exposure time. In the other hand, the results confirmed that magnetic treatment creates a memory effect, which means that inhibition efficiency can be maintained for at least 24h after treatment. FCP experiment (30 °C, hardness 25 °F), showed that the precipitation of CaCO_3 was delayed until 86 minutes for 18 h of magnetic treatment (60 % of inhibition efficiency). To conclude, when the solution was rested at ambient temperature without a magnetic field, the magnetic effect can persists until 24 h after the exposure but it decreases over time. In addition, the results of SEM and XRD showed that the FCP method promotes mainly the formation of vaterite form, but after magnetic treatment aragonite were produced rather than vaterite and calcite.

Experimental Section

Scaling solution

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All experiments were performed in synthetic carbonically pure water, only containing Ca^{2+} and HCO_3^- ions. The initial concentration of Ca^{2+} in all tested solutions was 100 mg.L^{-1} (equivalent to a hardness of 25°F). This scaling solution was prepared by dissolving calcium carbonate (CaCO_3) powder (AnalaR NORMAPUR VWR, 99.7% purity) in pure water (Milli.Q water, $18.2 \text{ M}\Omega \text{ cm}$ resistivity and $\text{TOC} < 5 \text{ mg.L}^{-1}$). To achieve a complete dissolution of CaCO_3 , carbon dioxide CO_2 gas was added in the solution for 12 h, accompanied by a moderate mechanical stirring (450 rpm). After this dissolution phase, the pH of the solution was around 5.5–5.7. Spontaneous precipitation of calcium carbonate does not take place under these conditions, due to a very low level of supersaturation. Afterwards, the solution was filtered using a polyamide filter with a porosity of $0.45 \mu\text{m}$ (Whatman) to remove any impurities.^[47,63]

Magnetic field devices

The magnetic treatment was carried out using a device delivering a static magnetic field from permanent magnets (Delta Water Co., Egypt) with an average flux density of 0.70 T. This technology has been established as a method for evaluating its ability to prevent scale precipitation in hard water.^[17, 51, 4] Indeed, the synthetic water solutions were exposed to the magnetic field at different times from 15 minutes up to 18 hours before a scaling test. In this configuration, the direction of the magnetic field was perpendicular to water exposure which led to a greater efficiency as noticed by some authors.^[25, 51]

Fast controlled precipitation (FCP) method

The fast controlled precipitation (FCP) method is an accelerated scaling test which consists on a moderate degassing of dissolved CO_2 leading to an accelerated CaCO_3 precipitation in solution. This method has been previously described elsewhere.^[47] The nucleation and the homogeneous precipitation could be followed by monitoring simultaneously the pH and the resistivity of the tested solution versus time.

For a FCP measurement, 400 mL of the tested solution with a hardness of 25°F ($[\text{Ca}^{2+}] = 100 \text{ mg.L}^{-1}$) is transferred into a Teflon beaker placed in a bath thermostatically controlled at 30°C . The stirring speed is set at 850 rpm which allows the CO_2 degassing. A pH meter (PHM210 Radiometer Analytical) and a conductivity meter (CDM210 Radiometer COPENHAGEN) were used to measure the pH and resistivity values simultaneously. To ensure a good repeatability, all experiments were performed in triplicate.

After each FCP experiment, the CaCO_3 crystals formed during the test were collected by filtration in order to analyze the morphology by scanning electronic microscopy (SEM) and X-ray diffraction (XRD) analysis.

Chronoamperometry

For these experiments, CaCO_3 deposition was generated by chronoamperometry (CA) at a cathodic potential of -1V/SCE . This method was used to evaluate the scaling power of different waters.^[53] It was often used to study scaling kinetics, and the antiscaling efficiency of organic inhibitors, plant extracts and polymers.^[35, 53, 63, 65, 66, 67]

A three-electrode cell was used with a rotating stainless steel disk as a working electrode. Its speed of rotation was fixed at 1200 rpm. A saturated calomel electrode (SCE) and a platinum grid were used as reference and counter electrodes, respectively.

Before each experiment, the surface of the working electrode, with 0.2 cm^2 active area, was polished with a silicon carbide paper up to 1200 grade, washed with distilled water, degreased with acetone, dried and finally immersed in the scaling solution. Scaling accelerated tests were carried out with a Princeton Applied Research, AMETEK, model 616B potentiostat monitored by Versa STAT 4 software.

Characterizations of CaCO_3 crystals

The scale formed in the tested solutions at 25°F and 30°C , was examined by scanning electronic microscopy (SEM) and X-ray diffraction (XRD). The SEM pictures were obtained with a FEG-SEM Zeiss Ultra55 microscope model.

The XRD spectra were recorded at 2θ angle in the range of $20\text{--}80^\circ$ with an X-ray diffractometer type X-Empyrean Panalytical employing $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). Intensities of the diffraction peaks obtained by XRD at the angles $2\theta = 25^\circ$ (I_V^{110}), $2\theta = 29.5^\circ$ (I_C^{104}) and $2\theta = 46^\circ$ (I_A^{221}) were used to quantify the molar fraction of calcite (X_C), vaterite (X_V) and aragonite (X_A), respectively.^[58]

Acknowledgements

This work was supported by PHC-Utique program. The authors thank Françoise Pillier, Stéphanie Delbrel, Cyrille Bazin and Axel Desnoyers de Marbaix (LISE) for technical assistance. We acknowledge and thank Dr. Anis Elaoud for providing us magnetic devices.

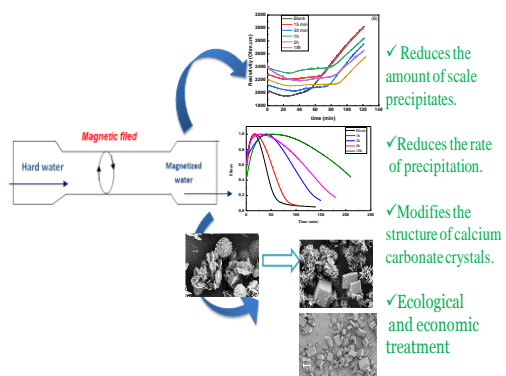
Keywords: Chronoamperometry • Fast controlled precipitation • Magnetic treatment • Memory effect • Scale inhibition

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RESEARCH ARTICLE

Entry for the Table of Contents



Magnetic water treatment: is an ecological and interesting method to prevent scaling in hard water. It contributes to the inhibition of the homogeneous (FCP) and heterogeneous (CA) germination, a decrease in the kinetics of scale nucleation and a modification of the morphology of calcium carbonate crystals.