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INFLUENCE OF MAGNETIC FIELD ON CALCIUM CARBONATE PRECIPITATION IN THE PRESENCE OF FOREIGN IONS

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1. Introduction

Calcium carbonate precipitation has been the subject of numerous investigations because of its importance in several industrial processes. Its scale deposition at the liquid/solid interface of flow systems induces important damage in the domestic or industrial installations using natural waters (pipe blocking, membrane clogging, efficiency decay of heaters or heat exchangers …). The main reaction involved in the precipitation of CaCO3 is governed by the following equilibrium called calcocarbonic equilibrium:

$$Ca^{2+} + 2HCO_3^- \leftrightarrow CaCO_{3(s)} + CO_2 + H_2O \qquad (1)$$

Depending on the temperature, ion concentration, pH, and flow rate of the solution, equilibrium Eq. 1 can be shifted in the forward or backward direction. Three crystalline forms of $CaCO_3$ exist: calcite, which has a cubic shape; vaterite, which has a spherulite, hemispherical flowers, or lenses morphology; and aragonite, which is recognized as needles. Each $CaCO_3$ variety is stable depending on thermodynamic conditions.

Various methods are used to prevent scaling, for example water decarbonation using electrochemical processes, seeding or acid addition. However these chemicals are generally deleterious for human health and their use is forbidding in drinking water.

Thus, environmental protection and economic considerations are two strong motivations for developing various types of physical antiscale methods (ultrasonic, ultraviolet radiation, electric and magnetic treatment). Magnetic methods attract a special attention due to their ecological purity, safety, and simplicity. This technique was widely employed on the treatment of irrigation water [1], industrial water [2] and in numerous other cases.

Natural water contains particles charged in the form of positive and negative ions. Taking into account this fact, various studies related to the effectiveness of the magnetic field (MF) on the calcium carbonate precipitation in the presence of foreign ions were done. The effect of a static magnetic field on the precipitation of $CaCO_3$ was studied in the presence of Mg^{2+}, Fe^{2+} and SO_4^{2-} [3–5]. The found results showed that the MF affects the zeta potential, the pH, and the speed of precipitation. The presence of Fe^{2+} maintains the zeta potential positive, however the presence of SO_4^{2-} make it negative. The effect of Fe^{2+} and SO_4^{2-} on the zeta potential of $CaCO_3$ probably results from their specific adsorption on $CaCO_3$ surface. While the effect of Mg^{2+} is less clear. For Herzog et al. [6], it is the addition of particles of ferric hydroxide in the water which is responsible for the MF effect on $CaCO_3$ precipitation.

In a previously study [7], the effect of a magnetic treatment on a calcocarbonic water was largely tested. It was observed that the effectiveness of the magnetic treatment on the precipitation of calcium carbonate is depending on various parameters such as pH of solution, hardness of water, flow rate and time of treatment. The results indicated that the MF enhanced the precipitation of $CaCO_3$ in bulk-solution instead of heterogeneous one and decreases its solubility. It was advanced that the main magnetic effects concern the associations of ionic species which are present in the solution and which are involved in the nucleation process of $CaCO_3$ precipitation.

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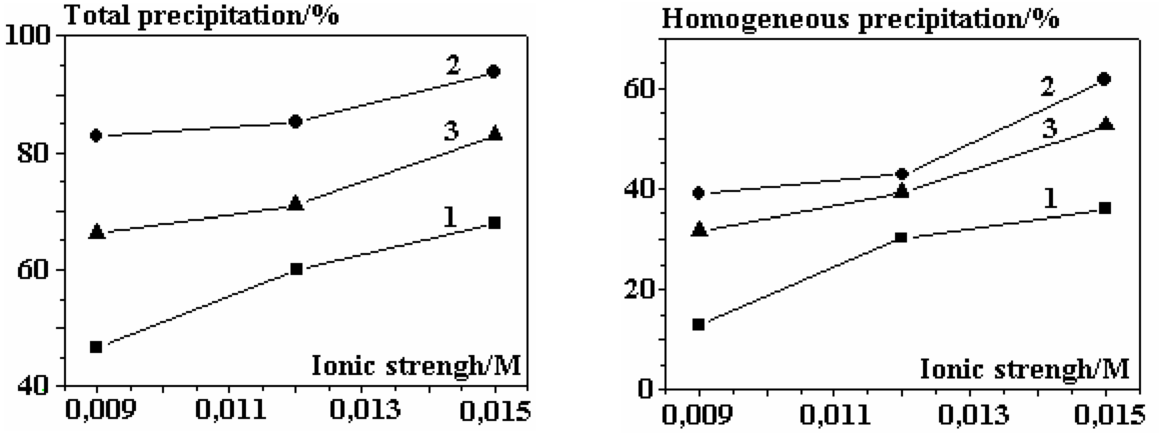
The properties of aqueous ionic solutions have been extensively researched in recent years since it has been shown that the presence of ions modifies the properties of water. In this reason, the application of a permanent MF on a more complex system remains very interesting. In this paper the experimental results on the effect of a MF on the precipitation process of calcium carbonate scale from calcocarbonic pure water containing Mg^{2+}, SO_4^{2-} or Na^+/Cl^- are reported.

2. Experimental

The synthetic treated water was prepared by adding Mg2+, SO_4^{2-} and Cl-/Na+ to a calcocarbonic pure water (water containing only Ca2+, CO32- and HCO_3^- ions), prepared by dissolving 0.4 g.dm-1 reagent grade CaCO3 in deionized water, by bubbling carbon dioxide during a full day. The solutions, containing one of the foreign ions at the desired concentration, were prepared by dissolving Na_2SO_4, $MgCl_2$ or NaCl in bidistilled water and added to the calcocarbonic solution just before treatment. Three level of ionic strength (*IS*) are tested for each ion: 0.015, 0.0195 and 0.027 M, the reference solution is calcocarbonic pure water (*IS*=0.012M). The initial pH was adjusted at 7 and the temperature was maintained at 30°C.

The treatment of a volume of $V = 0.50$ dm^3 of prepared water, through the permanent magnetic device, was applied in a pipe made of Tygon material. The magnetic device was described in details in the paper of Gabrielli et al. [8]: a series of 5 pairs of permanent magnets with north and south faces facing each other are associated alternately. The magnetic circuit of each pair was closed with a U shaped iron yoke. The field strength was about 0.16 T in the air gap. The choice of Tygon is due to that this material gives the higher amount of $CaCO_3$ precipitated by homogeneous way [7, 9]. The total time of treatment t_T was maintained for 15 minutes and the flow rate was moderate in order to have a laminar regime (0.74 dm^3 min^{-1}), the degassing test is for about 90 minutes. For every case of *IS*, two tests were made: treatment with circulation in the presence and absence of MF. All the experiments were replicated 3 times and average values were calculated (~3%). After each test the tubing was thoroughly cleansed, first, by recirculating a low-concentration acid solution for about 0.5 h, after which deionised water was recirculated for 0.5h. After each experimental series the tubing was replaced. The effect of MF on calcium carbonate precipitation from a pure calcocarbonic solution was, also, tested and three level of *IS* were chosen: 0.009, 0.012 and 0.015M. In this part, three types of pipe material were tested: Tygon, PVC and W PTFE (White PTFE).

The experiment apparatus of magnetic treatment and of degassing technique employed in this study were described in previous articles [7].



a *b*

Fig. 1. Effect of hardness of solution on (a) total and (b) homogeneous precipitation of $CaCO_3$ for a various material pipe of treatment

3. Results and Discussion

3.1. Effect of hardness

As illustrated in fig. 1, the total and the homogeneous precipitation ratio are increased, in the presence of MF, with increasing the water hardness and it’s also influenced by the nature of the pipe material, especially for the total precipitation ratio. This effect could be attributed to the composition of the material. As reported by Parker and Ranney [10], Barcelona et al. [11] and by Curran and Tomson [12], the pipe could release solid particle on solution due to the erosion mechanism occurring at the polymer/water interface. The amount of these particles depends significantly on the nature of pipes. For these researchers, it was shown that Tygon leach substantial quantities of constituents and that PTFE do not appear to leach any constituents. These particles, in the step of degassing test, will support the nucleation of calcium carbonate, so, the amount of homogeneous precipitation increase with the number of constituents.

In presence of MF, this effect is amplified by the magnetohydrodynamic effect especially for the homogeneous amount of precipitation (fig. 2). The most important effect was observed for the Tygon pipe. This result is in agreement with the results observed by Amire and Dadkhah [13] who suggested that MF increased the amount of impurities leaded by the Tygon pipe in solution and with the observation cited before [10–12].

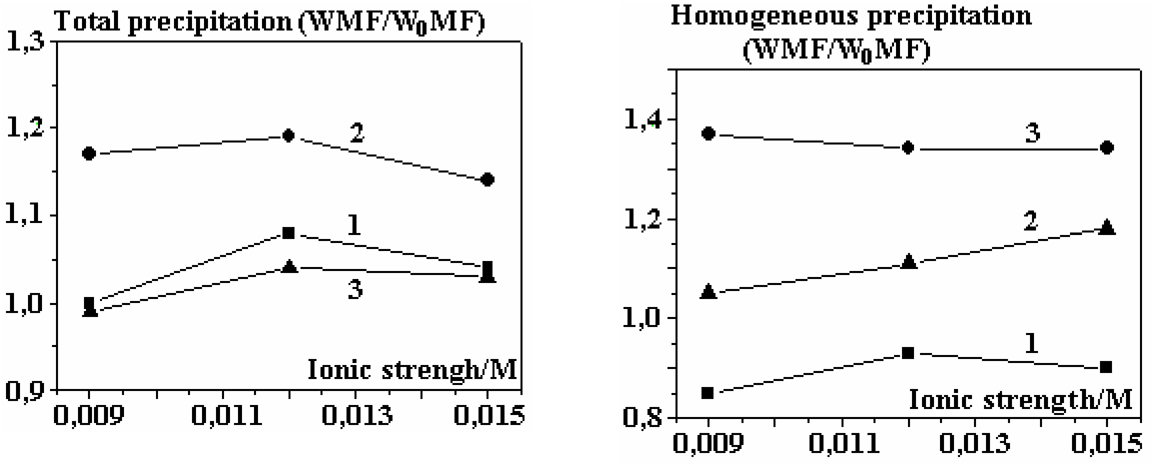


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Fig. 2. Effect of hardness of solution on (a) total and (b) homogeneous precipitation of $CaCO_3$ for a various material pipe (WMF: With Magnetic Field, WoMF: Without Magnetic Field)

3.2 Efficiency of magnetic field in the presence of foreign ions

The results obtained in absence of magnetic field and in presence of foreign ions, on the induction time, total amount of precipitation and the homogeneous amount of precipitation are presented on table 1.

Table 1. Effect of foreign ions on t_{ind}, total and homogeneous precipitation ratio of $CaCO_3$

Ionic Strength / M	Ion	Induction time (t_{ind}) / min	Total precipitation (*TP*) / %	Homogeneous precipitation (*TH*) / %
0.012	------	10	72.5	22.8
0.015	NaCl	12	55	21.2
	$MgCl_2$	13	50	20.1
	Na_2SO_4	13	53.6	19.5
0.0195	NaCl	16	52.5	20.4
	$MgCl_2$	20	35	17
	Na_2SO_4	16	47.5	15.7
0.027	NaCl	16	50	18.6
	$MgCl_2$	26	17.5	13.3
	Na_2SO_4	17	44	11.1

The results presented in this table showed that NaCl slow down nucleation and decrease the rate of total precipitation. The more the quantity of this salt is added, the more this effect is accentuated until reaching an IS of 0.02M after which NaCl loosed its effect. For the homogeneous precipitation, the addition of NaCl hasn't any influence.

For the sulfate, the application of treatment, haven't great effect on the total precipitation some either the IS (~50%) but show a higher effect on the homogeneous precipitation. this amount decreased from 19.5% 11%for 0.015 and 0.027 M, respectively.

The presence of Mg^{2+} in solution prolongs the induction period of $CaCO_3$, which also increased with increasing Mg^{2+} concentration as observed by Tai and Chien [14]. Pokrovsky [15] showed, also, that the induction period of $CaCO_3$ increases with increasing Mg^{2+}/Ca^{2+} activity ratio in solution. The increase in t_{ind} is due to an increase in the crystal-solution interfacial tension at higher Mg^{2+}/Ca^{2+} ratio and due to an increase in the activity of Mg^{2+} at lower Mg^{2+}/Ca^{2+} region. In our study the t_{ind} passed from 10 min, in absence of Mg^{2+}, to 13 min for Mg^{2+}/Ca^{2+}=0.25 and reach 26 min for Mg^{2+}/Ca^{2+}=1.25.

The presence of MF causes further changes in the determined parameters. This effect depends on the nature and the concentration of the foreign ions used. Fig. 3 showed that MF reduces the nucleation time of $CaCO_3$ some either the composition or the *IS* of treated solutions. Moreover, the degree of MF effect on t_{ind} is water composition-dependent. Indeed, with respect to reference solution (pure calcocarbonic water), the effect of MF on t_{ind} is more pronounced in presence of foreign ions until an *IS* value about 0.02 M. Beyond this IS value, MF effect on t_{ind} become less important. Also, it should be noted that MF effect on nucleation time is more important in the presence of Mg^{2+} or SO_4^{2-} ions.

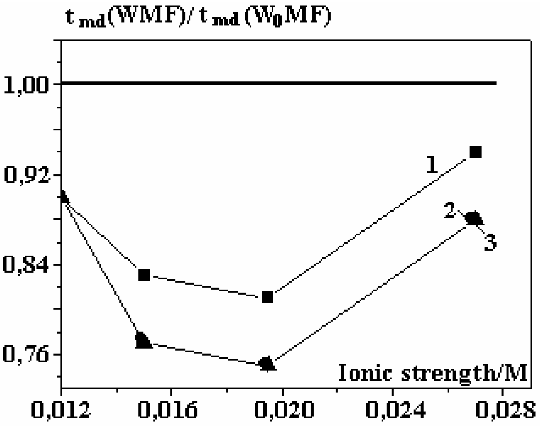


Fig. 3. Effect of MF on induction time of $CaCO_3$ in presence of foreign ions

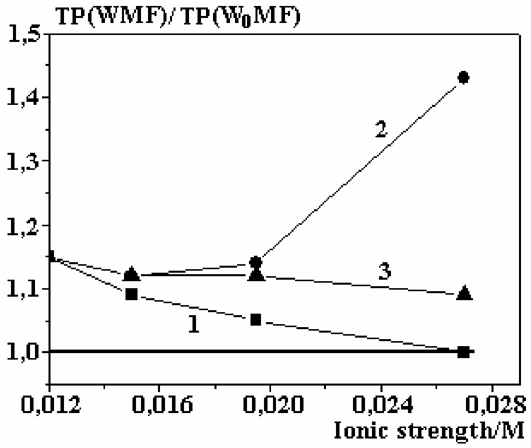


Fig. 4. Effect of MF on total precipitation ratio of $CaCO_3$ in the presence of foreign ions

For the *TP* of calcium carbonate in the presence of foreign ions, fig. 4 presents the obtained results versus the tests made without magnetic field. This curves showed that *TP* decrease in the case of NaCl and this reduce is more important for the higher *IS*. The opposite effect is observed in the case of magnesium. While, in the presence of sulfate, the effect of MF is almost constant whatever the *IS*.

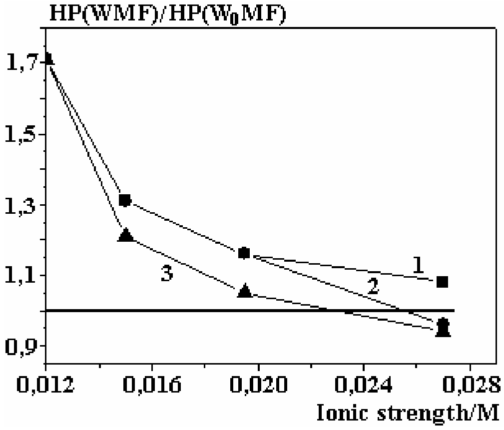
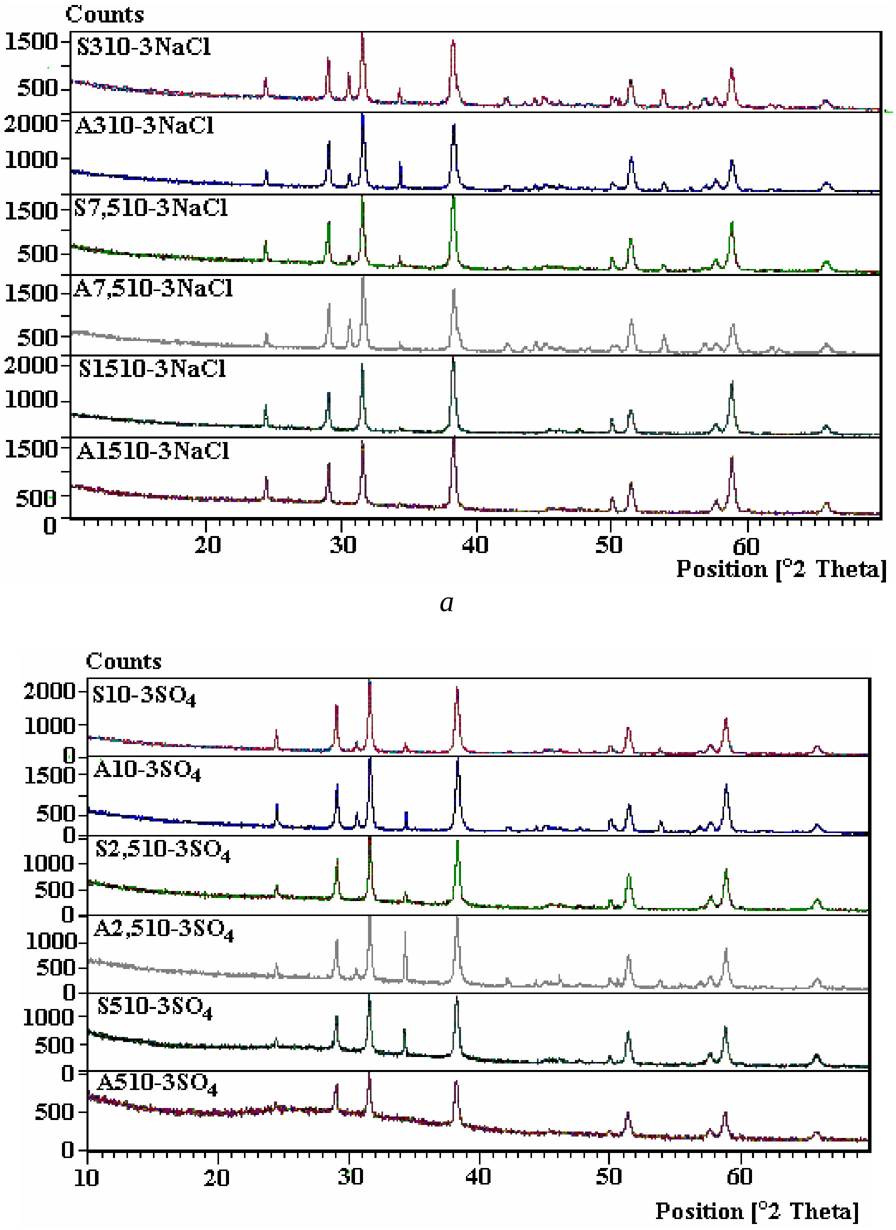


Fig. 5 Effect of MF on homogeneous precipitation ratio of $CaCO_3$ in the presence of foreign ions



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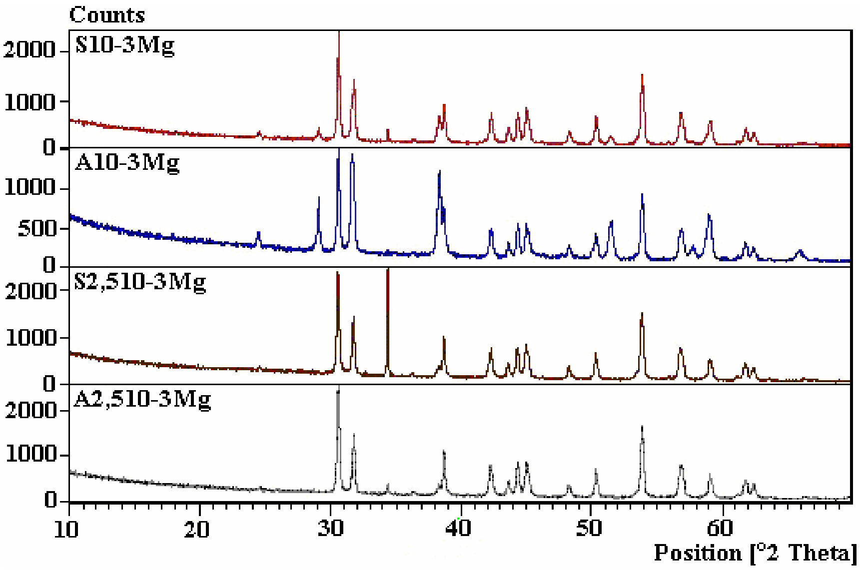

c

Fig. 6. X-ray diffraction patterns for $CaCO_3$ precipitated in presence of (a) NaCl, (b) sulfate and (c) magnesium with and without magnetic treatment

In fig. 5 is presented the effect of MF treatment on homogeneous precipitation. It's shown that MF treatment favoured the precipitation of calcium carbonate in the bulk of the solution by homogeneous process. The presence of foreign ions inhibits his effect and a contradictory effect is registered for higher *IS* (>0.024 M) in the presence of Mg^{2+} and SO_4^{2-} ions.

3.4 Effect of magnetic field on the morphology of $CaCO_3$ formed in the presence of foreign ions

In fig. 6 are reported the X-ray diffraction patterns for the $CaCO_3$ precipitated by degassing test, in the bulk of solution, in presence of NaCl, Na_2SO_4 or $MgCl_2$ for treated and untreated solutions.

It was shown that in the presence of NaCl, MF don't influence on the morphology of $CaCO_3$ precipitate either the concentration of NaCl added. In presence of magnesium, with application of MF, the amount of formed aragonite was increased and the precipitation of vaterite and calcite were inhibited. When the *IS* is high (*IS*>0.02), only aragonite was precipitated. For the sulfate, the pattern of the deposit from the treated water shows that MF inhibits the formation of calcite for the high IS and favoured aragonite in the other case.

In this paper, it has been proved that magnetic water treatment has effect on calcium carbonate crystallization by increasing the total precipitate amount and by favoured its formation in the bulk-solution instead of its incrustation on the walls. It was, also, proved that water composition and its *IS* has a noteworthy effect on $CaCO_3$ precipitation. Magnetic filed effectiveness is foreign ions-dependent, this effect is inhibiting with the presence of NaCl and encouraged in the presence of magnesium whereas the sulfate has no effect. These observations are not valid for the obtained results of homogeneous precipitate. The main difference is that the homogeneous precipitation is inhibited with *IS*. The morphology of $CaCO_3$ formed with MF is influenced by the nature of foreign ions, MF has as effect to favour the precipitation of vaterite in the case of sulfate and NaCl and the precipitation of aragonite in the presence of magnesium.

This effect is explained by the magnetically modified hydration of ions and solid surfaces and Lorentz force effects on ions and dispersed particles. Which effect would prevail depends on the magnetic treatment regime and on the composition of the treated system [16].

Bush et al. [17] have assumed that the Lorenz forces exerted on charged species induce local convection movements in the liquid which could contribute to accelerate associations between ions or colloidal particles. According to these authors, magnetohydrodynamic (MHD) phenomena induce eddy currents which flattened the fluid velocity profile in the tube. This effect would result in a larger velocity gradient, along the walls. In addition, the streaming potential along the walls which is velocity dependent should increase with the magnetic field. This phenomenon, by changing the surface charge, could throw out of balance the water composition equilibrium in the vicinity of the tubing walls [17–19].

MF effects were also often explained in terms of magnetically induced changes in the hydration of ions or solid surfaces. According to Lungader Madsen [20–21] MF induces faster proton transfer from hydrogen carbonate to water, due to proton spin inversion in the field of diamagnetic salts. The increased formation of CO_3^{2-} ions would explain the beneficial effect of MF on the amount of precipitate. Another explanation proposed by Higashitani et al. [22] is related to the specific influence of MF on the hydration of CO_3^{2-} ions which could directly modify the polymorph phase equilibrium during the precipitation. The same phenomenon could also affect the dehydration process of the ionic pair associations and the hydrated calcium carbonate forms which act as precursors for the formation of the anhydrous forms which constitute the calcium carbonate precipitate.

4. Conclusion

Permanent magnetic treatment (0.16 T) of duration 15 min of calcocarbonic solution in the presence of Na2SO4, MgCl2 or NaCl affects properties of CaCO3 formed. It appears in changes of induction period, total and homogeneous precipitation ratio of calcium carbonate formed by degassing test of treated solution. The effects depended on the kind of the foreign ions present in the treated water. This effect is, also, influenced by the hardness of water and by the nature of the pipe material. Finally, MF influence the morphology of calcium carbonate precipitate by increasing the precipitation of vaterite and aragonite in the presence of magnesium and by suppressed the formation of calcite.

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Summary

The study of magnetic effect on the precipitation of calcium carbonate was widely studied. The main objective was to prevent the mineral scales deposits on the walls of industrial or domestic equipments. Magnetic water treatment for scale prevention has been around and has been reported as being effective in many instances. This investigation focused on MF effect on $CaCO_3$ in presence of foreign ions. Because of their abundance in natural waters Mg^{2+}, SO_4^{2-}, Na^+ and Cl^- were chosen for this study. It was shown that MF application reduces the induction time (t_{ind}) some either the water composition or the ionic strength (*IS*). With respect to reference solution, the effect of MF on t_{ind} is more pronounced in presence of foreign ions until *IS*= 0.02 M. Beyond this value, MF effect on t_{ind} become less important. Moreover, it was shown that MF effect on total and homogeneous precipitation ratios decreases with *IS* increasing. This inhibitory effect of magnetic treatment, with *IS*, is water composition-dependent. The presence of NaCl has the most effect on total precipitation whereas $MgCl_2$ and Na_2SO_4 inhibit the precipitation of calcium carbonate in bulk of the solution.