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Influence of magnetic field on calcium carbonate precipitation

Fathi Alimi[a,b]*, Mohamed Tlili[a], Mohamed Ben Amor[a], Claude Gabrielli[b], George Maurin[b]

[a]*Laboratoire de Géochimie et Physicochimie de l'Eau, Centre des Recherches et Technologies des Eaux*
BP 273, 8020 Soliman, Tunisia
Tel. +216 (71) 430-044; Fax +216 (71) 430-934; email: alimi@ccr.jussieu.fr
[b]*Laboratoire Interfaces et Système Électrochimie (LISE), UPR15 du CNRS, Université P. et M. Curie,*
Tour 22, 5e étage, 4 Place Jussieu, 75252 Paris Cedex 05, France

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Abstract

Effect of permanent magnetic field with north and south faces facing each other (0.16 T) on calcium carbonate precipitation type (homogeneous and heterogeneous) and solubility were investigated in different conditions of calcium carbonate water concentration, treatment-pH and water flow rate in the magnetic field. Treated water was exposed to a scaling test by degasifying dissolved CO_2 in water. It was found that magnetic treatment increases the total amount of precipitate and favours the homogeneous nucleation depending on water treatment-pH, water flow rate and the residence time.

Keywords: Magnetic field; Calcium carbonate; Degasification; Homogeneous; Heterogeneous nucleation

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1. Introduction

The magnetic hard water treatment becomes an important alternative to prevent scaling problems in domestic and industrial systems. Indeed, scale precipitation, principally formed by calcium carbonate, under an insulating layer increases the costs of operation and maintenance by lowering the water flow rate and the thermal transfer coefficient in heat exchangers and by increasing the energy consumption of the pumps in drinking water systems. This physical water treatment process was developed to substitute chemical water treatment methods witch employs chemical product harmful to the environment and human health.

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*Corresponding author.

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In the goal to reach good antiscale prevention efficiency, several magnetic devices have been conceived for several decades now [1–3]. In recent years there has been a continued interest in the antiscale magnetic water treatment. Highashitani et al. [4] have found that $CaCO_3$ precipitated in the presence of the magnetic field is marked by a slower nucleation rate and a faster crystalline growth of the formed germs. The aragonite shape is favoured by report on the other calcium carbonate varieties: calcite and vaterite. In addition, the exposure to the magnetic field reduced the rate of coagulation of nonmagnetic colloids by more than 10% and removed the formation of the crystals of $CaCO_3$ though the flow of the magnetic density was not too high. However, an examination of the available literature often introduces contradictory results. Madsen [5] found that magnetic treatment increases nucleation and crystal growth rate. Barrett and Parsons [6] have found that magnetic treatment of $CaCl_2/Na_2CO_3$ and $CaSO_4/Na_2CO_3$ solutions delays the nucleation rate and supports the growth of the existing crystal, produces an effect of memory and influences the formation of $CaCO_3$ under the effect of Na_2CO_3 rather than of $CaCl_2$. In addition, a change in the magnitude of the magnetic field and the water flow rate through the treatment device induce a change in the calcite/aragonite/vaterite proportions [7].

In this paper the effect of magnetic field on calcium carbonate precipitation from calcocarbnic water was studied. This survey consists primarily in distinguishing the effect of magnetic water treatment on calcium carbonate nucleation type and, secondly, the effect of various parameters on this water treatment: water flow rate, water treatment time, water hardness, water pH. For this, a controlled degassing of dissolved CO_2 in water method with assistance of nitrogen was used. This degassing technique, which displaces the calcocarbonic equilibrium, allows the two types of precipitation, heterogeneous and homogeneous, to be effective in various proportions depending on the experimental conditions [8].

2. Materials and methods

In order to avoid any side effect by foreign ions, calcocarbonic pure water, containing only Ca^{2+}, CO_3^{2-} and HCO_3^- ions was used. It was prepared by dissolving reagent grade $CaCO_3$ (powder Carlo Erba Reagenti, 99.9% purity) in deionised water, by bubbling carbon dioxide:

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

In the first stage, before accelerated scaling test, 0.5 L of the tested water was treated magnetically through a magnetic device at different conditions of hardness and flow rate. The $CaCO_3$ concentration, the flow rate and the treatment time chosen were respectively: 300, 400 and 500 $mg.l^{-1}$ of dissolved $CaCO_3$ for the hardness, 0.5, 0.74 and 0.94d $m^3.min^{-1}$ for the flow rate and 15 min for treatment time. This treatment does not affect water pH.

The used magnetic device is detailed in [9]: a series of 5 pairs of permanent magnets with north and south faces facing each other are associated alternately. Each polar piece is the assembly of two rectangular magnets (42×25 mm^2 and 6 mm thickness). The field strength is about 0.16 T in the air gap.

The solutions flowed in a plastic tube (Tygon™ R3606, section area s = 0.38 cm^2, total length 150 cm) placed in the air gap (Fig. 1). The scaling test was done in a 1-L cylindrical cell made of a dense polyamide material and immersed in a thermostatic water bath to maintain the temperature constant (30°C) for about 90 min. For the sake of comparison, experiments were also carried out without passing in the magnetic field (MF).

Calcium carbonate was precipitated from the treated solution by displacement of the calcocarbonic equilibrium by dissolved CO_2 degassing using pure nitrogen according to:

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

After the precipitation test, $CaCO_3$ precipitate

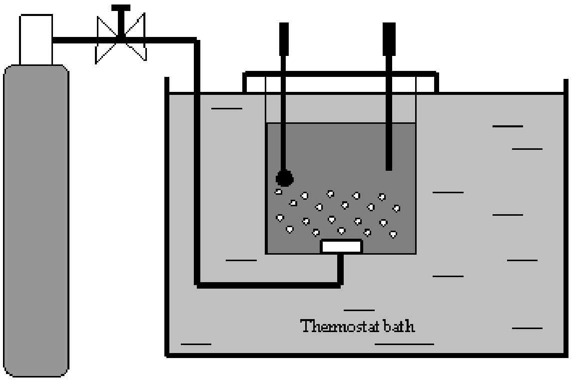

Fig. 1. Experimental treatment system.

in the bulk solution (m_h) was removed by filtering the suspension through 0.45 μm filter medium and the calcium ions remaining in solution were analysed by EDTA complexometry. The precipitation rate or total precipitation ratio and the homogeneous precipitation ratio were determined as follows:

$$\text{Total precipitation ratio }\% = \frac{m_T}{m_I}\times 100$$

$$\text{Homogeneous precipitation ration }\% = \frac{m_h}{m_I}\times 100$$

where m_I is the total calcium carbonate dissolved initially and m_T is the total mass precipitated, determined from calcium analysis.

3. Results

3.1. Effect of magnetic treatment on the total precipitation ratio

These measurements were carried out on 40°F water hardness, in the presence or absence of the magnetic field, for various flow rates, at pH 6 to 7.5.

Fig. 2 shows that, in the absence of magnetic field, the total amount of precipitated $CaCO_3$ did not depend significantly on the flow rate, whatever the pH. In the magnetically treated water, the total amount of $CaCO_3$ precipitate was significantly increased and this effect was intensifying with increasing the water flow rate.

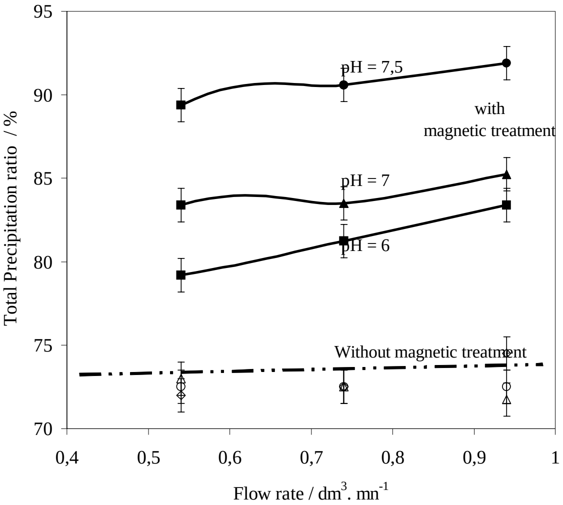

Fig. 2. Variations of the total precipitation ratio in % of the amount of dissolved $CaCO_3$ vs. the flow rate, for treated waters at various pHa in the presence and absence of MT for 400 mg.l^{-1}.

Then, we can conclude that the magnetic field influence by increasing the solubility of $CaCO_3$ in water. In the case of treatment without magnetic field, the solubility of calcium carbonate was usually unchanged some either water pH and flow rate.

3.2. Effect of magnetic treatment on the nucleation type

The determination of calcium carbonate quantity precipitated in the solution shows that magnetically treatment water supports homogeneous nucleation (Fig. 3). This effect is more important when the treatment-pH increases. At pH 6, the homogenous calcium carbonate quantity precipitated, with and without magnetic filed application, increased with the flow rate. This quantity increased by about 10% after magnetic treatment. At pH 7, after magnetic treatment, this homogeneous $CaCO_3$ quantity increased by only 5%.

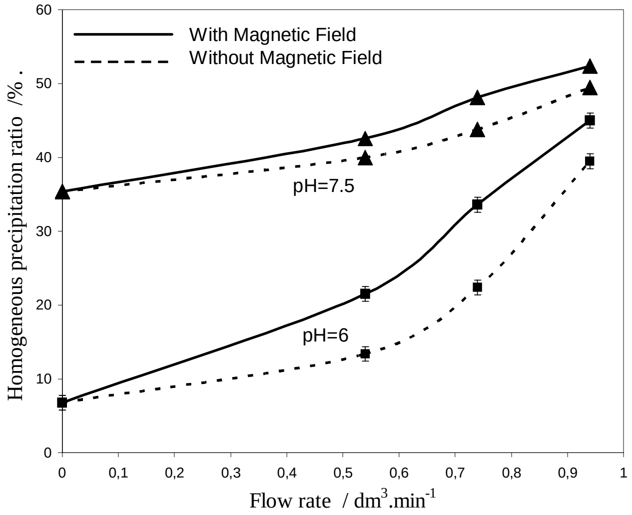

Fig. 3. Variations of the homogeneous precipitation ratio in % of the amount of dissolved $CaCO_3$ vs. the flow rate for 400 mg.l^{-1} $CaCO_3$ concentrations at various treatment pHs.

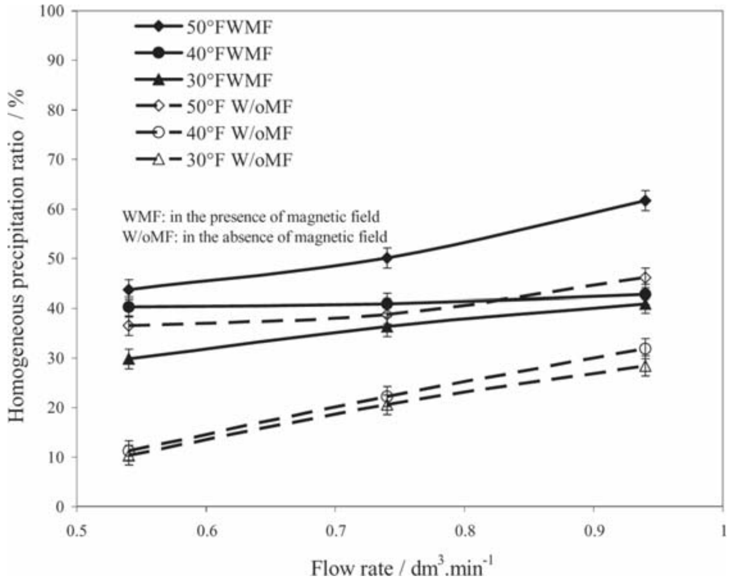

Fig. 4. Variations of the homogeneous precipitation ratio in % of the amount of dissolved $CaCO_3$ vs. the flow rate for treated water of various $CaCO_3$ concentrations at pH =7.

In conclusion, magnetic treatment favoured the nucleation in the bulk solution rather than in the cell wall. This effect on nucleation type (homogeneous or heterogeneous) is more important for lower pH.

To confirm this effect of magnetic treatment on calcium carbonate nucleation type, we have reproduced the same experiments while varying the $CaCO_3$ water concentration. Fig. 4 shows homogeneous $CaCO_3$ percentage as a function of water hardness (300, 400 and 500 mg.l^{-1} as $CaCO_3$) and flow rate. This figure shows clearly and confirms that the precipitated quantity of $CaCO_3$ in the solution increased after magnetic treatment at all water flow rates.

3.3. Effect of residence-time on the magnetic treatment effect

The effect of the residence-time on the $CaCO_3$ precipitation in magnetically treated water was tested by doubling the length of the pipe inserted between the polar pieces in the treatment device. Fig. 5 shows that a double pass favours the bulk solution precipitation.

The increase of homogeneous calcium carbonate precipitated from magnetically treated water, with the same pH, can be attributed to the effect of magnetic field witch can help the formation of clusters in the solution, micelles or ionic pairs such as $(CaCO_3)_n$, $CaHCO_3^+$ or $CaCO_3$. Indeed, the magnetic field influences both the undersaturated water (treatment-pH = 6) and supersaturated water (treatment-pH = 7 and 7.5), we recall that $pH_{equilibrium} = 6.62$. Therefore, the magnetic field could influence the calcocarbonic system in the ionic phase. This result, for undersaturated solutions, is in disagreement with those found by Knez and Pohar [10] and Kney and Parsons [11] who affirmed that the presence of calcium carbonate colloid particles is necessary to obtain an effect of magnetic field.

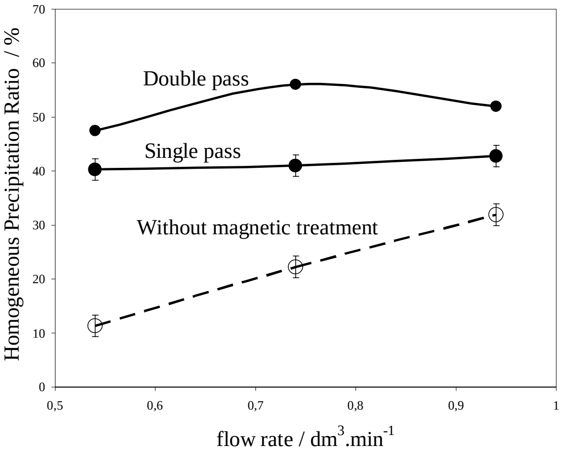

Fig. 5. Variations of the homogeneous precipitation of $CaCO_3$ vs. the flow rate either in the absence of magnetic treatment or after one or two times pass in the magnetic device (pH = 7, $CaCO_3$ concentration = 400 mg.l^{-1}).

The formed micelles, resulting from the magnetohydrodynamic phenomena, are larger in number; this yields smaller precipitation crystals and a larger number of particles. The term magnetohydrodynamic phenomena MHD refers to those influences of the magnetic treatment, which are observable only when both the magnetic field and the flow of the treated fluid are present under the dynamic treatment conditions [12]. The net effect of the application of a magnetic field is the flatness of the velocity profile of the fluid given without MF, which can ultimately result in the formation of a boundary layer near the walls. Formation of this boundary layer results in a larger velocity gradient near the walls than would ordinarily be the case for laminar flow.

4. Conclusion

The influence of the applied magnetic field on the nucleation and the precipitation of calcium carbonate in hard water was confirmed. The treatment-pH and the water flow rate on the magnetic device have an important impact on the nucleation type and on the amount of calcium carbonate precipitated in the end of the scaling test. The higher flow rate and treatment-pH as well as the precipitation rate, the more nucleation is promoted in the bulk solution. It has also been confirmed that the residence time of water under magnetic field has an important influence on the precipitation way.

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