Nucleation and crystallization of CaCO$_3$ in applied magnetic fields

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Abstract

The formation of calcium carbonate is not only a common ionic reaction that takes place in natural processes, but also creates a problem known as scaling, which is present in our every day life and in various industrial processes and technologies. In spite of the simplicity of the reaction there is considerable variability in the properties of the solid product, such as: crystal form, particle size distribution, electro-kinetics potential, etc. The influence of the magnetic field on calcium carbonate precipitation has been known for a long time but despite a lot of effort, which has been made to explain this effect, researchers still disagree on the mechanism(s) responsible for it. The focus of our research work was to follow systematically the influence of the magnetic field on the crystal form of calcium carbonate precipitated from low concentration water solutions. By changing the strength of the field and the flow rate of the water through the system the calcite/aragonite/vaterite ratio varied. The crystal form and the particle-size distribution of the precipitated calcium carbonate were determined by using X-ray analyses and TEM. The theoretical part of the work was to study the mechanism of the influence of the magnetic field on the nucleation and further crystallisation of calcium carbonate. Starting from ab initio calculations the fundamental physics knowledge was used to propose a mechanism for a better understanding of the phenomena.
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1. Introduction

The magnetic treatment of water is becoming an important alternative to the chemical treatment in preventing a scale formation in industrial and some other commercial water systems (e.g. heating boilers). Scale deposits increase operating and maintenance costs by lowering the flow capacities and increasing the energy consumption of pumps in cool water systems and by lowering the heat transfer in hot water systems with heat exchangers and evaporators. Chemical treatment of water by using polyphosphates is in a long term detrimental for the environment and due to the constant changes in the water hardness it is not possible to exactly determine the dose of chemicals. This can be harmful for human health too, if such water is drinking water.

Magnetic water treatment devices for scale prevention have been in use for several decades now. The first such commercial device was patented in Belgium in 1945 [1]; in the former Soviet Union powerful electromagnets have been used in hot water systems since the 1960s [2]; in the USA the use of magnetic water treatment devices has been spreading since 1975 [3]. However, a review of the available literature is rather confusing due to the often contradictory results that were reported. [4–11]. The main drawbacks mentioned in the literature are: complicated physicochemical phenomena that occur simultaneously, no reliable theoretical models available for optimization, difficulty in getting reproducible results on a laboratory scale, so the most positive results have been reported in large scale industrial applications [7]. However, the available literature generally agrees on some principal operating conditions for such devices. The fluid flow must be orthogonal in respect of the direction of the applied magnetic field. Magnetic field strength of at least 500 mT is required for successful treatment (though some commercial devices operate at lower strengths) although this depends on the composition of the water and the type of device. Relatively high flow rates (corresponding to velocities of 0.5–2 m/s and Reynolds numbers in the turbulent region) and long residence times are required, hence the need for re-circulating systems [6–8]. Many studies concerning the magnetic treatment of water suspension systems report that the effect depends very much on the nature and the condition of the solution e.g. pH, presence of impurities e.g. Fe^{2+} [4], Cu^{2+} [12], Zn^{2+} [13], and some lighter metals like Mg^{2+} and Si^{4+} [14]. Our previous research [15,16] has shown that the formation of the hard calcite scale on the surfaces exposed to hard water can be successfully prevented with the applied magnetic filed. The explanation of the phenomena is not yet offered and the purpose of this work is to try to understand the mechanism of the beneficial influence of the magnetic treatment, which is the objective of this paper.

2. Experimental

Using X-ray diffraction analysis on a Philips X-ray diffractometer it is possible to follow the influence of the applied magnetic field on the phase compositions. Sample solutions of calcium hydrogen carbonate ($Ca\,(HCO_3)_2$) were prepared by

dissolving finely ground calcium carbonate powder of analytical purity in deionised water and by bubbling the suspension with CO_2 through a porous frit. The resulting solution is an equilibrium system $CaCO_3$–$Ca(HCO_3)_2$–H_2O. For the further precipitation of $CaCO_3$, CO_2 was removed by heating and the air was blowing through the solution (0.05–0.5 l/min). The applied magnetic field used for the treatment was between 0.4 and 1.5 mT and was measured using a Gauss-meter. The experimental set-up was described in details previously [16]. The remaining solids were removed by filtering the suspension through 0.45 μm filter medium. The fluid-flow rate was 0.87 m/s and Reynolds numbers in the turbulent region (~6000). The solution was re-circulated for 8 h. Solid particles were separated from the solution by centrifugation and were dried at 40 °C. X-ray diffraction analysis was performed to determine the crystal form. For the preliminary study of the nucleation and further crystallization of different forms of $CaCO_3$ an analytical electron microscopy was used. A sample for the TEM observation and analysis (Jeol 2000 FX, Jeol 2010 F (FEG)) was prepared by using a C/Cu grid foundered into the solution for different times (t_1, t_2). In a specially constructed cell where various parameters could be controlled the nano-sized particles were collected on the grid and examined under the electron microscope. EDXS was used to characterise the chemical composition.

3. Results and discussion

3.1. Experimental results

Fig. 1 shows the comparison of the spectra of non-treated and magnetically treated model water and the difference between the recrystallization products. The quantitative analyses of the final recrystallization products showing the influence of the
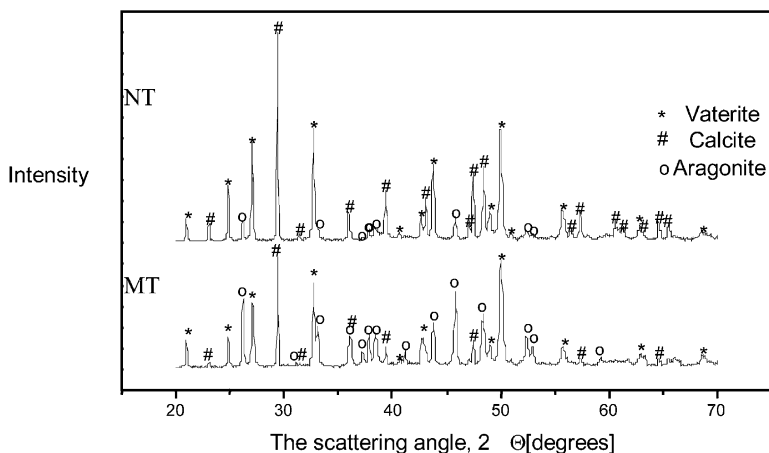

Fig. 1.　XRD spectra of treated samples: MWT—in magnetic field (1.4T) and NT—without the magnetic field.

applied magnetic field and its strength on the amount of different fractions of calcite, aragonite and vaterite crystals is shown in Table 1 where the results of the quantitative evaluation of X-ray spectra are quoted (unpublished results).

With the high-resolution electron microscopy and microanalyses the nucleation and early stages of crystallization were observed by phase identification and determination of the chemical composition (elemental analyses). The fractions of various phases in the recrystallization products were also estimated. Particles of calcite, aragonite and vaterite, which were detected in different amounts, are shown together with their diffraction patterns on Fig. 2. Under the electron beam the decomposition of vaterite phase was observed (formation of CaO). Fig. 3 shows the comparison between the crystallization products at the time t_1 and t_2 with and without the magnetic field. An obvious difference in the amount of crystals per square unit and in the particle size of treated and non treated samples is evident.

In magnetically treated samples an amorphous phase containing a high amount of Si was also detected (Fig. 4). Si was found in many other crystalline particles (vaterite) exclusively the ones that were obtained after the treatment in a magnetic field. According to the literature [14] a very successful application of a magnetic water treatment device (MWTD) on the industrial level was attributed to the presence of Si as an impurity in treated water. In our experiment Si ions impurities come from the silicon rubber tubes used for the water flow system.

3.2. Proposed mechanism

To explain the formation of aragonite in the presence of magnetic fields it is necessary to perform calculations regarding the structure of the ground electronic states for the two structural forms of $CaCO_3$. Ab initio calculations for the ground electronic states of aragonite and calcite (unpublished data) suggest that the ground electronic state of aragonite is placed 28 eV above the ground electronic state of calcite, Fig. 5. On the other hand, the ground electronic state of aragonite is much stiffer than that of the calcite, and therefore the Ca^{2+} and CO^{2-} ions should have higher kinetic energies to overcome the repulsive forces of the potential barrier, in order to form aragonite rather than calcite. Therefore the formation of calcite is energetically in favour of that of aragonite. These theoretical results are in agreement with the fact that aragonite is formed from liquid which melts only at a very high temperature and pressure. However the situation is completely different when $CaCO_3$
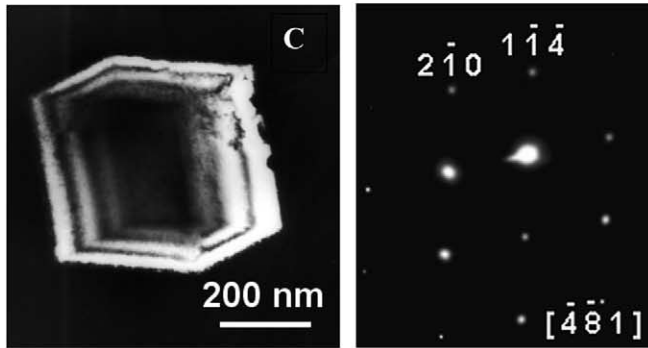
Table 1
The comparison of the amount of recrystallization products obtained without the magnetic field and at different strengths of the applied magnetic field
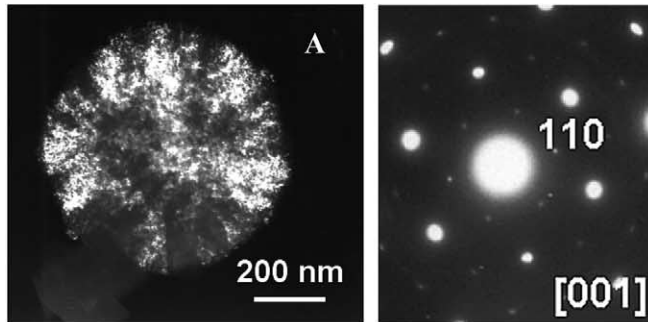
Sample	Magnetic field	Calcite (%)	Aragonite (%)	Vaterite (%)
C1N5	No	90.2	9.6	0.2
C1M5	400 mT	80.0	10.4	9.6
MP2C1	1220 mT	28.9	70.6	0.5
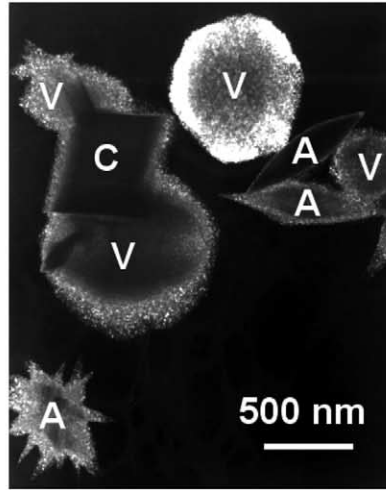
(a)

(b)

(c)

Fig. 2. TEM image of various crystals obtained in treated samples and corresponding SEAD patterns: C—calcite, A—aragonite, V—vaterite (a); calcite (b); vaterite (c).
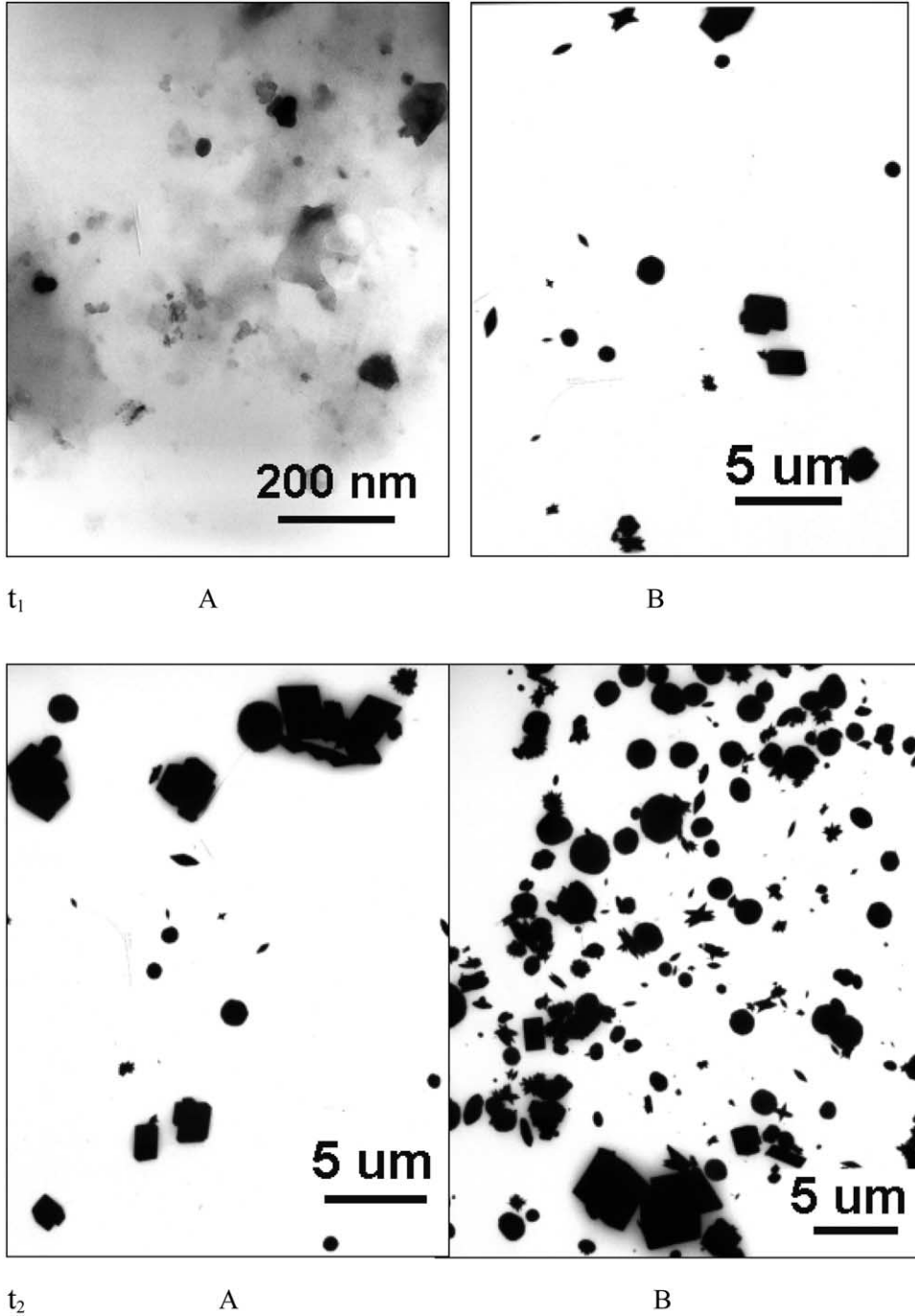
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t$_1$ A   B

t$_2$ A   B

Fig. 3.   Crystals obtained at the time t$_1$ and t$_2$ with (A) and without (B) the magnetic field.
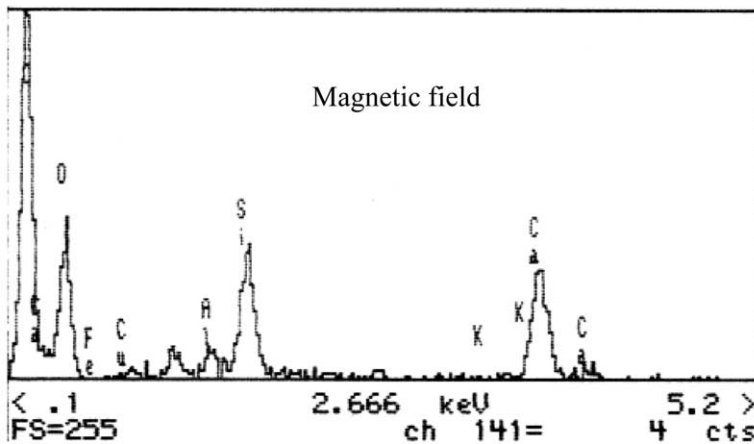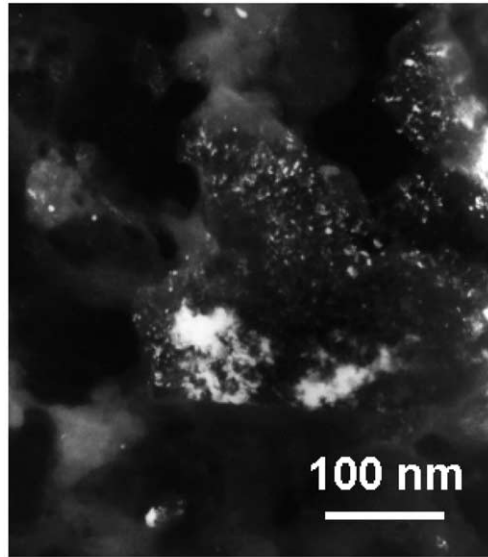
Fig. 4.   A TEM image and the EDXS spectrum of amorphous phase found in treated samples.

is dissolved in water. The kinetic energy of the ions, which is required, first to achieve the energy of the ground state of the aragonite, and then to overcome the potential barrier of the ground electronic state could be provided by a magnetic field.

Indeed, in the presence of a typical magnetic field, the energy dE/dV of the electro-magnetic field per unit volume is given by the formula:

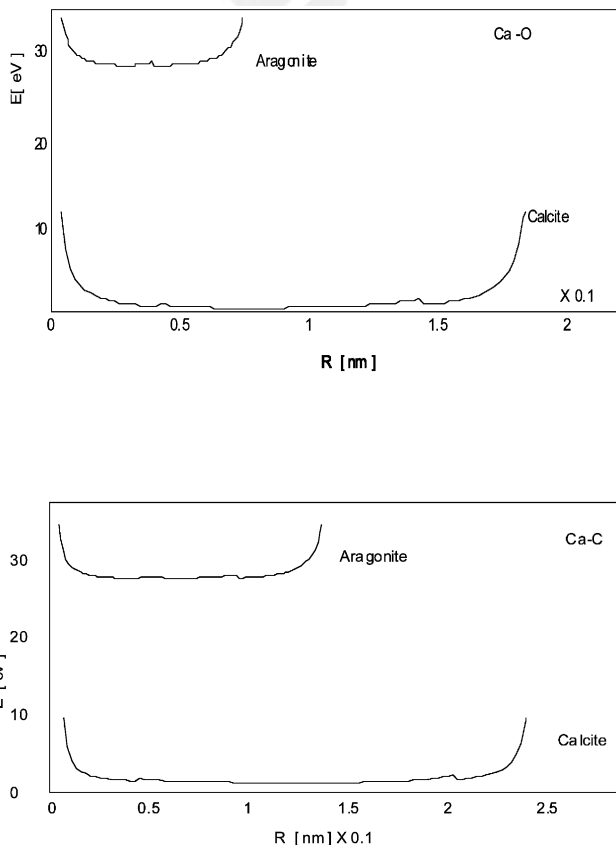$$\frac{dE}{dV} = \frac{1}{2\mu_0}B^2 + 2\varepsilon_0 E^2 \qquad (1)$$

Fig. 5. Ground electronic states of the Ca-O and Ca-C bond calculated for calcite and aragonite. The inter-nuclear distance R has been chosen arbitrarily to 2 nm to indicate the difference between the potentials of the ground electronic states of calcite and aragonite. The ground electronic state of aragonite is placed 28 eV above that of calcite.

where B is the magnetic induction and E the intensity of the electric field, μ_0 and ϵ_0 are the permitivity and permeability of the free space respectively.

Now in the presence of an electromagnetic field the free energy F per unit volume of the $CaCO_3$ molecules is given by the equation:

$$F(T,P) = F_0(T,P) + dE/dV \tag{2}$$

where $F_0(T,P)$ is the free energy in the absence of any magnetic or electric fields.

From Eqs. (1) and (2) a simple calculation suggests that the energy of 28 eV, which is required to bridge the gap between the ground electronic states of the calcite and the aragonite can be provided by a magnetic field of 45 T within a typical inter-nuclear distance of 0.5 nm between Ca and CO_3 ions for the $CaCO_3$ molecule. The formation of the aragonite in the presence of electromagnetic fields can be explained if we take into consideration that the electromagnetic field fluctuations in the presence

of flow, and high electric fields near conductive surfaces could well exceed the average field values even by a small order of magnitude [17].

3.2.1. Electromagnetic fluctuations in the presence of flow

When a conducting fluid moves in the presence of a magnetic field, electric currents accompany its motion and therefore electric fields are induced on it as the electric current flows. The magnetic field by itself exerts quite strong forces on those currents, which might considerably modify the flow. Conversely, the currents themselves modify the local magnetic field, and thus a complex interaction between the magnetic field and the flow is taking place. The phenomenon can be described by comparing the field equations with those of fluid dynamics. For example, it is well known that turbulent motion of a conducting fluid has the remarkable property that it might be accompanied by the growth of spontaneous magnetic fields, which might be quite strong [17]. Even in the absence of any electromagnetic field, there are always small perturbations in a conductive fluid, resulting from reasons not related to the fluid motion itself, and accompanied by very weak electric and magnetic fields. These perturbations can be amplified to very high values or damped, depending on the conditions of the flow and the magnitude of the local magnetic field [17]. The presence of very high electric and magnetic fields is inherent in the motion of the fluid and the fluid can exchange energy with the electromagnetic field. It is evident therefore that in order to have the energy requirement for the formation of the aragonite, the required magnetic field of 45 T, is easily met in the presence of a typical magnetic field of 1–1.5 T.

3.2.2. Electric fields near conductive surfaces

Close to the surface of a conducting pipe and around sharp edges the electric field can be as high as 10^6 V/m [17]. Such high fields modify the electronic structure of the molecules and usually lower the energy position of the excited electronic states relative to the ground state. Therefore it is expected that near conductive surfaces the required energy gap between the ground electronic states be further reduced, and this can explain why aragonite is formed even in the presence of low intensity magnetic fields. The local electric field could be further enhanced in the presence of metals having ground state electrons with d electronic configurations, or internal d electronic configurations with orbital radii greater than those of the ground state due to the polarised nature of the d electronic configuration. The mixing of the electronic states further facilitates the formation of the aragonite. On the other hand, it is easily proved that a charged particle near the surface of a conductive plate is bound by a potential energy of 6.8 eV. This energy is transformed in to kinetic energy, and it is enough to overcome the potential barrier of the ground electronic state of the calcite or the aragonite and subsequently to form the molecule.

4. Conclusions

The strong influence of the applied magnetic field on the nucleation and further crystallization of calcium carbonate in hard water was confirmed. The density of the

magnetic field has an important impact on the amount of different crystal forms of $CaCO_3$. It is also confirmed that the presence of impurity ions such as Cu shown in our previous work or Si in the described experimental conditions are additionally needed for the effective preferential formation of aragonite or vaterite. There is no doubt that magnetic water treatment works in practice, and the mechanism by which the process operates is proposed.

Acknowledgements

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