Nanocrystallization of CaCO₃ at solid/liquid interfaces

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ARTICLE INFO

Article history:
Received 30 July 2007
Accepted 15 April 2008
Available online xxx

PACS:
68.35.Rh
81.65.kn
47.27.wb
67.70.DV
61.14.x

Keywords:
Calcium carbonate
Turbulent flow
Scaling
Solid–liquid interface
Water
Nanocrystals
Calcite
Aragonite
Vaterite

ABSTRACT

With the application of 1.2 T external magnetic field, 90% of CaCO₃ soluble molecules in water flow precipitate on stainless steel 316 solid/liquid interface in the form of aragonite/vaterite. The magnetic field increases locally the thermodynamic potentials at interface, favoring the formation of aragonite than calcite, despite the fact that the field-free ground electronic state of aragonite is situated higher than of calcite. A quantum mechanical model predicts that magnetic fluctuations inside the liquid can be amplified by exchanging energy with an external magnetic field through the angular momentum of the water molecular rotors and with the macroscopic angular momentum of the turbulent flow. The theoretical model predicts that the gain is higher when the magnetic field is in resonance with the rotational frequencies of the molecular rotors or/and the low frequencies of the turbulent flow and that aragonite concentration is increasing at 0.4 T in agreement with the experimental results. Contrary to calcite, aragonite binds weakly on flow surfaces; and hence the process has significant industrial and environmental impact.

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1. Introduction

The formation of precipitated deposits at the liquid/solid interface of industrial flow systems is commonly known as “scaling”. It is one of the most common processes in nature and the cause of water corrosion in industrial flow systems. Despite the simplicity of chemical reaction of forming CaCO₃ and other precipitants on the surfaces of the water flow elements, scaling by itself is a complex process as the deposition rate and the cohesion of the precipitated particles on the flow surfaces is proportional to the strength and the type of the chemical bonding between the particles and surfaces, which mainly depend on the chemical composition of the particles, the electro-kinetic potentials of the agglomerations at the nucleation point, the type and roughness of the flow surfaces, the presence of crystal growth modifiers and surface functionalizers [1–5], etc. In addition, the strength of chemical bonding of crystal nanocomposites of similar chemical structure depends on their symmetry (crystallographic point group). It is now widely accepted that initial stage of nucleation is crucial for driving the chemical reactions to a certain direction, with sound environmental, technological and economical impact, as it forms the crystal seed, on which the scaling products will further continue to agglomerate in crystal form. As the strength of attachment of the precipitating nanocrystals on flow surfaces depends on the symmetry of the initial crystal seed, the degree of scaling depends as well on the initial stage of crystallization of the precipitating products. In addition, the first stage of nucleation and crystalization depends besides the catalyzing atomic/molecular blocks of flow surfaces, on additional factors, such as the presence of magnetic fields during the first stage of nucleation, and the initial state of atoms and molecules in the flow (energy, momentum, state of flow, etc.) [6–18]. Furthermore, strong
magnetic fields can be generated within the turbulent flow of ionic liquids [19], which alter the local thermodynamical equilibrium of the liquid/solid interface. The most common example of industrial corrosive scaling agent is CaCO₃, which naturally exists in three different crystal forms. At normal conditions the most stable form is calcite (rhombohedral-hexagonal unit cell), mostly found in nature. Aragonite has lower symmetry with orthorhombic unit cell. Hardly ever CaCO₃ is found in the less stable form of vaterite, which eventually undergoes phase transition to calcite or aragonite. Contrary to calcite, aragonite bounds weakly at liquid/solid interfaces and scaling can be minimized provided that aragonite will be formed instead of calcite.

Traditional chemical methods of scale control involve either the pre-precipitation of the scale former with lime or soda ash, the addition of scale inhibiting reagents [21–23] or the replacement of the scale former with soluble ion exchange [24]. All of these methods though effective in scale control, substantially change the physicochemical properties of solutions.

As an alternative to chemical de-scaling, the magnetic anti-scaling has been reported as being effective by limiting the scale deposition rate, removing existing scale, or producing a softer and less tenacious surface effects [1–56]. Many reports claim large savings in energy, cleaning and process downtime costs from the installation of magnetic water conditioners in real systems [1–4]. The investigations on the influence of magnetic field on scaling is mainly focused on the process of nucleation and/or crystallization of CaCO₃ [10,32–35], the crystal structure of CaCO₃ [10,18,31,34–36,25], the colloidal aqueous dispersions stability [17,24,26,23,39], the change of the zeta potential (ζ) of colloidal particles [21,22,34,35,38,39] and the physical-chemical properties of the water or its solutions, such as the surface tension, etc. [25,44].

The first systematic investigation on the effect of magnetic fields on zeta potential of suspensions of CaCO₃ was performed by Q1 Krylov et al. [22]. It was shown that an externally applied magnetic field is lowering the zeta potential (ζ) of CaCO₃ and the influence of field on zeta potential is increasing with time. The effect of magnetic field in water flow systems under well-controlled laboratory conditions showed that there was a significant effect on the precipitation rate of CaSO₄ crystals. Conductivity, calcium solubility, and zeta potential were decreased, whereas the amount of total suspended solids was increased [22].

Furthermore Tombácé et al. studied the effect of weak magnetic fields on the aggregation state and electrophoretic mobility of hematite soils in flowing systems as a function of time and electrolyte concentration [23]. While enhanced aggregation of hematite was observed following application of magnetic fields (change in turbidity, scattered light intensity, and photon correlation), little effect on aggregation state was observed for the static systems or for the flowing systems in the absence of magnetic field. Mobility also increased during the initial phase of static and dynamic application of magnetic fields. Changes in both mobility and particle aggregation states indicated a significant dependence on electrolyte concentration. These effects were discussed in terms of a magnetohydrodynamic interaction between the magnetic field and ions: Busch et al. [24] investigated the aggregation state of flowing colloidal dispersions of polystyrene latex microspheres. Comparable effects were noted when cholesterol suspensions were recirculated in the absence of magnetic field or when the suspensions were exposed to an equivalent magnetic field in the absence of flow. For cholesterol suspensions, the increment of particle dimensions was most pronounced between 0.15 and 1.0 T. Aggregation effects were also observed for both types of suspensions, in the regions near to critical concentration of coagulation. The rates of precipitation and sedimentation of CaCO₃ in magnetic fields were significantly different from solution at zero field intensities [25]. Also zeta potentials, nucleation rates and surface tension of the entire in situ precipitated nucleus were significantly affected in comparison to the reference system.

Additional investigations by Chibowski et al. [26] confirm different crystal forms and rates with the application of external magnetic fields and a systematic study on the nucleation of various crystals such as Na₂CO₃ in water and electrolyte solutions with magnetic fields was done by Higashitani et al. [1]. Similarly, the same authors investigated the effect of dynamic magnetic fields on Na₂O₃, CaCl₂ and CaCO₃ precipitated from solutions, and the effect of static magnetic field on the zeta potential and the diffusion of the colloid particles in electrolyte solutions [10]. All of the above studies clearly indicate the correlation between the crystal forms of the precipitating particles and the magnetic field and the state of flow.

However, despite the large number of experimental results, which identified conditions of 90% reduction in CaCO₃ scale formation under magnetic fields [19–20,27–30], the interpretation of the process is still an open issue.

Indeed, up to now various mechanisms to interpret physical anti-scaling have been proposed [23,31–35,25]. None of them however is fully comprehensive to account for all the experimental effects. Early work, which claimed changes in the structure of water resulting from magnetic exposure, has now been revised. In addition the influence of contaminants (Fe²⁺ or Zn²⁺, etc.) introduced by magnetically induced corrosion has been thoroughly considering together with surface effects [50–56]. Other workers have more recently proposed models to support the theory of enhanced nucleation in the bulk solution. However, on the basis of current crystallization theories, any effects on heterogeneous nucleation would have nanosecond relaxation time and homogeneous nucleation would be unlike, even after exposure to a reasonably strong (0.5 T) magnetic fields.

Solesly magnetically induced changes in crystal structures, i.e. calcite to aragonite, through hydrodynamic interaction between the magnetic field and the flow [20,53] could interpret experimental results provided that strong magnetic fields can be developed within the flow [57]. Magnetic induced changes on crystal structure at interfaces, imply that strong magnetic fields are developed locally, which alter the field-free thermodynamic potentials of the system changing thus the crystal structure of the precipitating particles.

However, none of these theories are able to explain the reduction of scaling in a coherent way, because only classical theories have been applied up to now.

Along these lines and in order to explain the formation of aragonite in the presence of magnetic fields at interfaces, calculations regarding the structure of the ground electronic states for the two structural forms of CaCO₃ were performed [19]. Ab initio calculations for the ground electronic states of aragonite and calcite suggest that the ground electronic state of aragonite is placed as high as 28 eV above the ground electronic state of calcite. On the other hand, the slope of the ground electronic state of aragonite is much stiffer than that of the calcite, and therefore the Ca²⁺ and CO₃²⁻ ions should have higher kinetic energies to overcome the repulsive forces of the potential barrier. Therefore, the formation of calcite is energetically in favor of that of aragonite.

The theoretical results are in agreement with experiments that aragonite is formed at high temperature and pressure from melts. The required kinetic energy of the ions can be provided by an external magnetic field. In this case the localized free energy F per unit volume is larger than the free energy in the absence of external magnetic fields.

Previous calculations suggest that the energy of 28 eV, which is required to bridge the gap between the ground electronic states of calcite–aragonite, can be provided by a magnetic field of 45 T within a typical internuclear distance of 0.5 nm between Ca$^{2+}$ and CO$_3^{2-}$ ions. The formation of the aragonite was explained by assuming that energy transfer is taking place between the magnetic field and the turbulent flow and it was quantitatively described with the Navier–Stokes and Maxwell’s equations [58].

According to this model, the magnetic field can be amplified to high values as the kinetic energy of the turbulent flow is transferred to the magnetic field [19,20]. The transfer of energy is enhanced around conductive surfaces, and the theoretical predictions are in agreement with experimental results [41].

In this communication, we report on the influence of the magnetic field on the initial state of nucleation of CaCO$_3$ at the solid/liquid interface of a stainless steel 316 tube under well-defined conditions by applying an external magnetic field of 1.2 T. Transmission and scanning electron microscopy and quantitative X-ray diffraction analysis was used and it was found that under the presence of magnetic fields 93.2% of CaCO$_3$ mainly crystallizes in the form of aragonite and vaterite rather than calcite, in agreement with previous investigations [19,20].

Furthermore, the appearance of large magnetic fields, which are required to form aragonite, was interpreted by applying a quantum mechanical microscopic approach for the first time to our knowledge. The coupling of the magnetic field to the molecular system was described by quantizing the flow, the electromagnetic field, and the molecular system. A simplified two level atomic/molecular system, within the turbulent flow and in the presence of a constant magnetic field, is described by the same set of equations of motion, which describe the MASER amplifier. According to this model, one magnetic fluctuating mode at a given frequency $\omega$, can be amplified to high values by absorbing energy from an existing constant external magnetic field. The coupling and transfer of energy is taking place through the angular momentum of the three entities: the water molecules, the magnetic field and the flow.

Using the quantum mechanical approach, the amplification of magnetic field within the flow can be derived from first principles bypassing thus the ad hoc assumptions of the macroscopic hydrodynamic theory [19,20]. The theoretical model predicts that the gain is high when the magnetic field is in resonance with the rotational frequencies of the molecular rotors or/and the low frequencies of the turbulent flow. The aragonite concentration is constantly increasing with the intensity of magnetic field and the gain is high at 0.4 T, in agreement with the experimental results where the aragonite concentration is higher than 80% at 0.6 T. Results are in agreement with recent experiments, which claim that quantum effects within the flow should be taken into consideration to interpret CaCO$_3$ nucleation [57].

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 deionized water with the resistivity of $\rho = 18$ M$\Omega$. Due to its very low solubility (3.8 $\times$ 10$^{-3}$) CaCO$_3$ was dissolved in the so called “model water” by blowing CO$_2$ through a porous frit. The resulting solution is an equilibrium system CaCO$_3$–Ca (HCO$_3$)$_2$–H$_2$O. 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 solution was then exposed to a constant applied magnetic field (DC) of 1.2 T (field was measured using a Gaussmeter) for all the experimental trials, contrary to previous trials with changing magnetic field [19,20]. 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. In addition parallel comparative trials were performed without the field. Following the experimental procedure with and without magnetic field, forced precipitation of the dissolved CaCO$_3$ was accomplished by passing nitrogen gas through the systems. The remaining solids were removed by filtering the suspension through 0.45 $\mu$m filter medium. Solid particles were separated from the solution by centrifugation and were dried at 40 °C and 70% R.H. The morphology of the precipitated particles was analyzed by using scanning electron microscopy (SEM – JOEL 5800) and X-ray diffraction analysis was performed to determine the crystal form. For the preliminary study of the nucleation and further crystalization 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 gridfoundered into the solution for different times (5 and 10 min after the beginning of the process). 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 characterize the chemical composition. X-ray powder diffraction patterns of the samples were recorded on a Siemens D-5000 diffractometer with the reflection (Bragg-Brentano) geometry using graphite monochromatized Cu K$_\alpha$ radiation. Data were collected in the 2$\theta$ range from 20 to 70° in steps of 0.04°; the integration time was 30 s per step. The divergence and anti-scatter slits were fixed (1°); the receiving slits were 0.2 cm; a quantitative X-ray analysis was performed supported by the software program. The mass fractions were determined by Rietveld refinement. The structural models of all three phases were taken from the ICSD standards. To determine the accuracy of the experimental set-up five trials were performed under the same conditions for each experiment and the results of the X-ray analyses were compared.

3. Results and discussion

The effect of static magnetic field on crystal morphology and structure of precipitating aggregates on the liquid/solid interface in water flow is shown in Figs. 1 and 2 for 0 and 1.2 T field intensities, respectively. CaCO$_3$ crystals under zero external magnetic field precipitate at the liquid/solid interface as
homogeneous agglomerations of calcite (Fig. 1). The size of the crystals at 1.2 T magnetic field was smaller, the agglomerations were well separated and exhibited needle-like and flower shaped aragonite structures (Fig. 2) which were not observed at zero magnetic field. Following TEM imaging (Figs. 3 and 4) of the precipitating particles during the early stage of crystallization, calcite, aragonite and vaterite, were detected at significantly different concentration levels. The vaterite was decomposed to form 5–10 nm wide CaO particles under the effect of the electron beam. The dark-field TEM image of decomposed vaterite is shown in Fig. 5. The upper inset of Fig. 5 exhibit SAED-like patterns of decomposed vaterite crystal shapes with spots (arcs) of CaO texturing in [1 1 0] zone axis. Circles correspond to randomly oriented nanocrystals of CaO. The lower inset indicates the results between the experimental and the simulated SAED patterns for cubic (Fm$ar{3}$m) CaO. The bar size is 20 nm.

600 nm x 200 nm. In the case of the application of strong external magnetic fields, the amorphous agglomerating phases contain higher amount of Si contaminants. Si was found in the crystalline structure of vaterite, especially in samples investigated immediately after the application of the external magnetic field. This is in agreement with recent results, where the effect of magnetic fields in industrial flow systems was enhanced with the addition of Si [21]. The presence of Si in our experiments was due to the use of silicon rubber tubes in certain parts of the circulating line of water flow system. The SEM images of the inner pipe surfaces suggest that Si particles were peeled-off in the flow at higher rates under the magnetic field. The diffraction patterns of precipitated particles at zero and 1.2 T magnetic fields, respectively, are indicated in Figs. 7 and 8. The predominating peaks of aragonite in Fig. 8 can be clearly identified, while in Fig. 7 mainly CaCO$_3$ in the form of calcite is present. For all the experimental conditions with external magnetic field in water flow, the concentration of aragonite/vaterite crystals in the precipitating samples was higher than...
90% and it was constantly increasing with the intensity of the magnetic field (Table 1).

For describing the formation of aragonite (and/or vaterite) instead of calcite in flow systems in the presence of magnetic fields calculations have to be carried out for the relative position of the ground electronic states of different structural forms of CaCO₃. Preliminary calculations for the ground electronic states of aragonite suggest that it is placed 28 eV above the ground electronic state of the calcite [19,20]. However, the situation is completely different when CaCO₃ is dissolved in water. The required energy to reach the ground electronic state of the aragonite is provided by either steady state or time dependent magnetic fields.

In the absence of static magnetic fields electromagnetic fluctuations always accompany the flow of a conductive fluid, and spontaneous magnetic fields can be amplified to large values. When a conductive fluid moves under external magnetic field, electric currents accompany the flow, which is modified. On the other hand, energy is feedback from the flow to the magnetic field and the complex situation is described by Maxwell’s, Navier Stocks and the equations of heat transfer [19,20].

They are form a complete set of equations, which fully describe the interaction of electromagnetic fields with the turbulent flow and the transfer of energy. The main question during the exchange of energy is whether an electromagnetic fluctuation can be amplified or dumped by the turbulent flow in the lapse of time. When the magnetic field interacts with the flow, its energy is dissipated within the flow, and the currents tend to diminish the field. On the other hand, it can be shown [58] that when a fluid is in motion, the lines of the magnetic

<table>
<thead>
<tr>
<th>Applied magnetic field (T)</th>
<th>Calcite (%)</th>
<th>Aragonite + vaterite (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>90.2</td>
<td>9.8</td>
</tr>
<tr>
<td>0.6</td>
<td>17.50</td>
<td>82.5</td>
</tr>
<tr>
<td>1.2</td>
<td>6.5</td>
<td>93.5</td>
</tr>
</tbody>
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Fig. 6. TEM images of different size agglomerations of aragonite at 1.5 T. The size of the left and right bars is 200 and 500 nm, respectively. The two images were taken at different times, a fact which suggests that CaCO₃ continues to grow around the crystal form of the initial crystal seed. The average crystal size of the needle-like shapes of aragonite crystals of left image is 200 nm × 100 nm, while the average size after 30 min is 600 nm × 200 nm.

Fig. 7. X-ray diffraction spectrum of precipitated CaCO₃ with zero magnetic field.

Fig. 8. X-ray diffraction spectrum of precipitated CaCO₃ at 1.2 T.
forces follow the lines of flow and the magnetic field is proportional to the stretching of the lines. In a turbulence flow any two points move apart in time, and therefore as the lines of the magnetic forces stretched the magnetic field is strengthened in time as well. Under certain conditions these two opposite tendencies are balancing each other and a criterion can be provided distinguishing the two cases of damping or amplification of spontaneous magnetic field. The threshold condition for amplification is [58]:

\[ \eta \sigma \mu_0 > 1 \]  

(1)

where \( \eta \) is the coefficient of viscosity of the fluid, \( \sigma \) is the fluid conductivity, \( \rho \) is the fluid density and \( \mu_0 \) the vacuum permittivity.

The exchange of energy between the magnetic field and the turbulent flow is given by

\[ B^2 \sim U^2 \rho \mu_0 \]  

(2)

Eq. (1) states that in the case of amplification, the energy density of magnetic fields developed within a flow volume \( \sim \lambda_0^3 \), is proportional to the kinetic energy of the flow within the same volume. The dimension \( \lambda_0 \) is the length where the energy dissipation and the viscosity of the fluid become important.

The energy density of amplified spontaneous magnetic fields grown in a turbulent flow near the liquid/solid interface with \( \sim 1 \mu m \) surface roughness, is of the order of \( 10^{15} J/m^3 \), when the velocity fluctuations within \( \lambda_0 \), are 10 m/s. Similarly, the Reynolds number \( R \) is \( \sim 10 \), and \( \lambda_0 \sim 0.1 \mu m \). It is obvious therefore that for an energy density of the spontaneous magnetic field of the order of \( 10^{15} J/m^3 \), which is required to bridge the energy gap between the two structures of CaCO\(_3\) fluctuations of velocity of the order of \( 10^3 \) m/s should be generated within the turbulent flow. These values of velocity fluctuations in principle could be developed at the interface of conductive surfaces from local ion acceleration and from local thermal fluctuations. The key point in the above macroscopically classical treatment is that the exchange of energy between the magnetic field and the flow is taking place through the angular momentum of the turbulent flow. A microscopic approach on the molecular level will require a quantum mechanical treatment. In this case, the exchange and transfer of energy between the external magnetic field and a fluctuating magnetic mode is taking place through the angular momentum of the rotating water molecules.

The process is described by the same set of equations as for the parametric amplification and the theory of MASER by quantizing both the field and the molecular water rotors.

In the general case where a molecular system with momentum \( \hat{p}_0 \) interacts with an electromagnetic field, \( \hat{A} \equiv (\hat{E}, \hat{H}) \), the total Hamiltonian \( \hat{H} \) of the system can be written in a variety of equivalent forms,

\[ \hat{H} = \frac{1}{2m} \left( \hat{p}_0^2 + \hat{A}^2 (\hat{r}_c, t) \right) + \frac{1}{2} \int \left( \epsilon_0 \hat{E}^2 + \mu_0 \hat{H}^2 \right) dt - \frac{1}{2} \int \left( \hat{E}_0 \right)^2 dt - e \sum_j \hat{\psi}(\hat{r}_c) + Ze \hat{\psi}(0) \]  

(3)

where the first term represents the kinetic energies of electrons and the energy of interaction with the field \( \hat{A} \), the second term is the energy of field, and the three last terms are the static potential energy of the electrons and nucleus. The system of reference in this case is the fixed coordinate system \( \hat{r}_c : x, y, z \) rotating with the molecule. In the Coulomb gauge and after some elaborate algebra Eq. (3) becomes:

\[ \hat{H} = \frac{1}{2m} \left( \hat{p}_0^2 + \hat{A}^2 (\hat{r}_c, t) \right) + \frac{1}{2} \int \left( \epsilon_0 \hat{E}^2 + \mu_0 \hat{H}^2 \right) dt - \frac{1}{2} \int \left( \hat{E}_0 \right)^2 dt - e \sum_j \hat{\psi}(\hat{r}_c) + Ze \hat{\psi}(0) \]  

(4)

where the symbols have their usual meaning and the summation is over the external electrons. Since the \( \hat{r}_c \) is of the order of Bohr radius, and the gradient operator is of the order of the wavenumber \( k \) of the field \( (\hat{E}_0, \hat{H}) \), the successive terms in the expansion of the exponential diminish rapidly and only the first non-vanishing terms of \( \hat{H}(0) \) and the first two non-vanishing terms of \( \hat{E}_0 \) are retained.

With conversion to quantum mechanics and termination of the exponential expansions, the Hamiltonian can be written:

\[ \hat{H} = \hat{H}_k + \hat{H}_R + \hat{H}_\parallel \]  

(5)

where \( \hat{H}_k \) is the Hamiltonian of the single molecule

\[ \hat{H}_k = \frac{1}{2m} \sum_j \hat{\psi}^2(\hat{r}_c) - \frac{1}{2} \int \psi(\hat{r}_c) \left( \frac{\hbar^2}{2m} \nabla^2 \hat{\psi}(\hat{r}_c) \right) dt \]  

(6)

\( \hat{H}_R \) is the Hamiltonian of the field

\[ \hat{H}_R = \frac{1}{2} \int \left( \epsilon_0 \hat{E}^2 + \mu_0 \hat{H}^2 \right) dt \]  

(7)

The vector potential operator \( \hat{A} \) of the field in the second quantization form is the sum of field harmonic oscillations and is given by the equation.

\[ \hat{A}(\hat{r}, t) = \sum \alpha_k \left( \frac{\hbar}{2 \sqrt{2 m \omega_0}} \right)^{1/2} \left( i \hat{a}_k \right) \hat{a}_k \exp(i \hat{K} \cdot \hat{r} - \alpha_k t) \]  

(8)

where the summation of \( k \) is taking place over all the modes of the field at frequencies \( \omega_k \) and within a volume element \( \tau \) of the interaction. \( \hat{r}_e \) are the polarization vector operators, \( \left\{ \hat{a}, \hat{a}^\dagger \right\} \) are the annihilation and creation field operators, respectively. The Hamiltonian of the field in this case is becoming

\[ \hat{H}_R = \sum \hbar \omega_k \hat{a}_k \hat{a}_k^\dagger \]  

(9)

The interaction Hamiltonian \( \hat{H}_i \) of the molecule with the magnetic field contains four contributions:

\[ \hat{H} = \hat{H}_D + \hat{H}_Q + \hat{H}_{MD} + \hat{H}_{NL} \]  

(10)

Where \( \hat{H}_D, \hat{H}_Q, \hat{H}_{MD}, \hat{H}_{NL} \) are the electric dipole, electric quadrupole, magnetic dipole and non-linear interactions, respectively.

The magnetic dipole interaction is given by

\[ \hat{H}_{MD} = \frac{\mu_0}{2m} \hat{H} \times \hat{J}_c \]  

(11)

where \( \hat{J}_c \) is the angular momentum operator of the molecular system.

The non-linear term is proportional to the square of the magnetic vector operator \( \hat{H}(0) \)

\[ \hat{H}_{NL} = \frac{e^2 \mu_0^2}{8m} \hat{H}^2 \]  

(12)

The next step will be to describe the energy transfer between the magnetic field and the molecular rotor and to investigate the
The eigenstates where \( \omega \) along the molecular principle axis, the second term has two contributions from the fast rotation of the inertial frame of reference includes three components; the first one is the magnetic dipole interaction term. 

It can be proved easily with the use of the closure theorem that the angular momentum operators are the generating functions of the finite rotations and make the change of notation

\[
\tilde{\sigma}^+ i \tilde{\sigma} = (\psi(\theta, \varphi, \chi_i) \psi(\theta, \varphi, \chi_j)).
\]

The molecular Hamiltonian can be written

\[
\hat{H}_{\text{ang}} = \sum \hbar \omega \tilde{\sigma}^+ \tilde{\sigma}.
\]

Let us find now the physical interpretation of the operators \( \tilde{\sigma}^+ \tilde{\sigma} \). The matrix elements of the rotation operator \( D(\theta \varphi \chi) \) are eigenfunctions of Eqs. (18) and (19). The angular momentum operators are the generating functions of the finite rotations and

\[
D(\theta \varphi \chi) = \exp \left( \frac{i \hbar}{\ell \mu_\ell} \right) \exp \left( \frac{i \hbar}{\ell \mu_\ell} \right) \exp \left( \frac{i \hbar}{\ell \mu_\ell} \right)
\]

Therefore, the operators \( \tilde{\sigma}^+ \tilde{\sigma} \) are the corresponding angular momentum creation and annihilation operators

\[
\tilde{\sigma}^+ = \int \hat{\sigma}^+ = \hat{\sigma} - \hat{\sigma}.
\]

The magnetic interaction part \( \hat{H}_M \) of the total Hamiltonian \( \hat{H} \)

\[
\hat{H}_M = \frac{\hbar}{\ell \mu_\ell} \sum_{\ell \mu_\ell} \left( \frac{\hbar^2}{2 \mu_\ell \ell \hbar \omega} \right) \left( \hat{\sigma}_\ell \hat{J}_\ell - \hat{J}_\ell \hat{\sigma}_\ell \right)
\]

Eqs. (22) and (23) have been derived provided that the dipole approximation is valid and only the terms \( \kappa = 1 \sim 1 \) are surviving the exponential series expansion.

We change now the frame of reference from the fix coordinate system to the inertial one and the angular momentum \( \hat{J}_e \) becomes

\[
\hat{J}_e = \hat{J}_e + \hbar \omega \hat{\sigma} \times \hat{r} ^{\text{rot}}
\]

The term \( \hat{J}_e \) is the contribution to the angular momentum from the internal rotations of the molecule. The matrix elements of the rotation operator \( D(\theta \varphi \chi) \) are the eigenfunctions of the angular momentum operator \( \hat{J}_e \), Eqs. (23) with the use of Eq. (24) and after some algebra becomes

\[
\hat{H}_M = \frac{\hbar}{\ell \mu_\ell} \sum_{\ell \mu_\ell} \left( \frac{\hbar^2}{2 \mu_\ell \ell \hbar \omega} \right) \left( \hat{\sigma}_\ell \hat{J}_e - \hat{J}_e \hat{\sigma}_\ell \right)
\]

Let us consider now the effect of the general combination

\[
| \psi(\theta, \varphi, \chi_i) \rangle \langle \psi(\theta, \varphi, \chi_j) |
\]

which we denote for simplicity [1] (2). The effect of [1] (2) on another rotational eigenstate [3] changes the state to [1] if the [3] state is the original [1], but gives zero otherwise. In other words, [1] (2) is an operator whose application to an atom in a rotational state [2] removes it from that state and put it into state [1]. We can say that [1] (2) destroys rotational state [2] and creates rotational state [1]. It is usual to replace the operator [1] (2) by the notation similar to that used for the operators which create and destroy photons. We define \( \tilde{\sigma}^+ \tilde{\sigma} \) as the creation and annihilation operators, respectively.
The operator $\hat{J}_i = \hat{J}_i - \hat{J}_{i,\text{eff}}$ is analyzed as follows:

$$\hat{J}_i = \hat{J}_i - \hat{J}_{i,\text{eff}} = \hat{J}_i + \hat{J}_i + \hat{J}_i = \left(\hat{J}_i - \hat{J}_{i,\text{eff}}\right) + \left(\hat{J}_i + \hat{J}_i\right)$$

$$= \hat{\sigma}^+ (\hat{i} + \hat{j}) + \hat{i} \hat{\sigma} (\hat{j} - \hat{i}) + \hat{j} \hat{\sigma}^+ (\hat{i} + \hat{j})$$

(26)

A similar expression is derived for the operator $\hat{J}_{i,\text{eff}}$:

$$\hat{J}_{i,\text{eff}} = \hat{J}_{i,\text{eff}} + \hat{J}_{i,\text{eff}} + \hat{J}_{i,\text{eff}}$$

$$= \hat{\sigma}^+ (\hat{i} + \hat{j}) + \hat{i} \hat{\sigma} (\hat{j} - \hat{i}) + \hat{j} \hat{\sigma}^+ (\hat{i} + \hat{j})$$

(27)

where the operators $\hat{\sigma}^{\pm}$, $\hat{\sigma}$ are the creation and annihilation operators of the angular momentum operator $\hat{J}_{i,\text{eff}}$ having in general a different set of eigenvalues than $\hat{J}_i$. The generating function of infinitesimal rotations in this case is the $D(\hat{\omega},\hat{\sigma})$.

Let us suppose now that the magnetic field is applying along the $Z$-axis of the inertial system. In this case the vectors $\hat{\omega}_i, \hat{\omega}_k$ are in the $(X, Y)$ plane and in the $(i, \hat{j})$ directions and only the $\hat{J}_i, \hat{J}_{i,\text{eff}}, \hat{J}_{i,\text{eff}}$ components will survive. In addition we will retain only the terms $\hat{\sigma}^+, \hat{\sigma}, \hat{\sigma}^+ \hat{\sigma}_d, \hat{\sigma} \hat{\sigma}_d^+$. In this case Eq. (25) becomes:

$$\hat{H}_M = \sum_{\alpha_k} \left\{ \frac{\hbar^2}{2m} \left( \frac{\hbar^2}{2m\tau_{\text{CF}}} \right)^{1/2} \left[ i^2 + i \hat{\sigma}^+ \hat{\sigma}_d \exp(\hat{a}_k \hat{\sigma} \hat{\sigma}_d^+ \exp(\hat{a}_k \hat{\sigma} \hat{\sigma}_d^+)) \right] + 2 \left[ i + \hat{\sigma} \hat{\sigma}_d^+ \exp(\hat{a}_k \hat{\sigma} \hat{\sigma}_d^+ \exp(\hat{a}_k \hat{\sigma} \hat{\sigma}_d^+)) \right] \right\}$$

(28)

The total transition probability $w$ between molecular rotational states induced by the external magnetic field is given by the Fermi Golden rule:

$$w = \frac{2\pi}{\hbar} \left| \langle f | H_M | i \rangle \right|^2 \rho(E_f)$$

(29)

where $|f\rangle$ and $|i\rangle$ are the final and initial rotational states of the molecule. It is plausible to consider transitions between a large number of very closely spaced intermediate rotational states. In the last case, the transition probability is given by the summation of all the transition probabilities between the intermediate states $w_i, w = \sum_i w_i$. This is similar to multiphoton absorption of photons through intermediate electronic states in atoms and molecules and it is valid for either time dependent or static magnetic fields.

From the previous equations, the total Hamiltonian of the system now becomes in the second quantization form:

$$\hat{H} = \sum_k \hbar \omega_k \hat{a}_k \hat{\sigma}_d^+ + \sum_i \hbar \omega_i \hat{\sigma}_i$$

$$+ g \left\{ \sum_k \left[ (\hat{f} + \hat{\sigma}^+ \hat{\sigma}_d \exp(\hat{a}_k \hat{\sigma} \hat{\sigma}_d^+ \exp(\hat{a}_k \hat{\sigma} \hat{\sigma}_d^+)) \right] + 2 \left[ \hat{\sigma} \hat{\sigma}_d^+ \exp(\hat{a}_k \hat{\sigma} \hat{\sigma}_d^+ \exp(\hat{a}_k \hat{\sigma} \hat{\sigma}_d^+)) \right] \right\}$$

(30)

and

$$g = -\sum_k \left\{ \frac{\hbar^2 \alpha^2}{8m^2 \tau_{\text{CF}}} \right\}^{1/2}$$

(31)

where the summation over $i, k, l$ is over the number of the molecules, which are within a small volume $\tau$, the number of modes of the field and of the number of the polarizations $\hat{\sigma}_i$.

Eq. (30) is our final result. The first term of Eq. (30) is the Hamiltonian of the magnetic field, the second term is the Hamiltonian of the two level quantized molecular system of $\hat{\sigma}$, the third term is the interaction Hamiltonian between the magnetic field and the molecular system and the fifth term is the interaction Hamiltonian between the magnetic field and the molecular system due to molecular rotations. The physical interpretation of Eq. (30) is that the magnetic field interacts with the rotational levels of the molecular system through the angular momentum of the molecules. The efficiency of the energy transfer between magnetic field and the molecules depends on the coupling with the angular momentum of the molecule. Eq. (30) is similar to the equation, which describes the operation of a MASER amplifier where a large number of spin 1/2 particles interact with an external magnetic field $B$ oscillating with frequency $\omega_B$ along the $z$-axis and when the coupling coefficients $K_{ij}, K_{ij}$ are small ($k < \omega_B$) the Hamiltonian of the system is given by the equation:

$$H = \hbar \omega_B \hat{a}^+ \hat{a} + \sum_j \hbar \Omega_{ji} \hat{a}^+ \hat{a} + \sum_j K_{ji} (\hat{a}^+ \hat{a} + \hat{a} \hat{a}^+)$$

(32)

The next step is to solve the Heisenberg equation of motion. Since the boson and angular momentum operators commute, we obtain in a usual way the Heisenberg equations of motion:

$$\frac{d\hat{\sigma}_i}{dt} = -i \omega \hat{\sigma}_i - i \sum_j \sum_{\alpha_k} g_{\alpha_k \alpha} \hat{\sigma}_j$$

(33a)

$$\frac{d\sigma_{ij}}{dt} = -i \omega \sigma_{ij} - i \sum_{\alpha_k} g_{\alpha_k \alpha} \sigma_{ij}$$

(33b)

$$\frac{d\sigma_{ij}}{dt} = -2i g (\sigma_{ij} \omega + \sigma_{ij} \omega^*)$$

(33c)

$$\frac{d\sigma_{ij}}{dt} = -i \omega \sigma_{ij} - i \sum_{\alpha_k} g_{\alpha_k \alpha} \sigma_{ij}$$

(33d)

$$\frac{d\sigma_{ij}}{dt} = i \omega \sigma_{ij} + \sum_{\alpha_k} \sigma_{ij} \sigma_{ij}$$

(33e)

Where now the operators $\sigma_{ij}^\alpha$ are defined as

$$\sigma_{ij}^\alpha = (\hat{f} + \hat{\sigma}^+ \hat{\sigma} \hat{\sigma}_d \exp(\hat{a}_k \hat{\sigma} \hat{\sigma}_d^+ \exp(\hat{a}_k \hat{\sigma} \hat{\sigma}_d^+)))$$

(34)

Eqs. (33a-e) cannot be solved analytically because they contain non-linear terms such as $\sigma_{ij} \omega \sigma_{ij}$, etc. We must therefore make a linear approximation if the model is going to describe linear coupling and transfer of energy and magnetic field amplification. When the energy is transferred from molecules to the magnetic field, the two level rotor flips from its upper quantum state to the lower one followed with the emission of one rotational quantum and, which its energy, is transferred to the magnetic field. In the case of a week coupling between the molecules and the magnetic field (non-magnetic liquid) the initial thermal equilibrium of $\sigma_{ij}$ entities does not change appreciably and it can be substituted by its constant equilibrium value $\sigma_{ij}^0$. For according to Eq. (33), the change in $\sigma_{ij}$ is proportional to $\tau$ which makes the term $g \sigma_{ij} \omega$ of the order of $\tau$. We may therefore have a system of linear equations by replacing $\sigma_{ij}$ by its equilibrium value $\sigma_{ij}^0$. This approximation decouples Eq. (33) and we are left with an infinite set of linear equations:

$$\frac{d\sigma_{ij}}{dt} = -i \sum_{\alpha_k} g_{\alpha_k \alpha} \sigma_{ij}$$

(35)

$$\frac{d\sigma_{ij}}{dt} = -i \sum_{\alpha_k} g_{\alpha_k \alpha} \sigma_{ij} + i \sum_{\alpha_k} g_{\alpha_k \alpha} \sigma_{ij}^0$$

(36)
Since the equations are linear the solution for \( \alpha(t) \) is of the form:

\[
\alpha(t) = u(t)\alpha(0) + \sum_j u_j(t)\sigma^j
\]  

(37)

where \( \alpha \) and \( \sigma^j \) are the operators in the Schrödinger picture at \( t = 0 \). From the commutation relation of the operators we have:

\[
|\alpha(t),\alpha^+(t)| = 1 = |u(t)|^2 - \sum_j |u_j(t)|^2 \sigma^j
\]  

(38)

We must solve Eqs. (37 and 38) by means of Wigner–Weisskopf approximation [60]. By omitting the details, and for \( g < (\omega, \omega, \omega) \) the result is:

\[
u_j(t) \cong \exp\left(-io\omega + \frac{\gamma}{2}\sigma^j_0t\right)\frac{g e^{-i\omega\sigma^j_0 t}}{(\omega_j - \omega - i\gamma/2\sigma^j_0)}
\]  

(39)

where

\[\gamma = 2\pi g^2(\omega_1)\rho(\omega_1)\]

(40)

Here \( \rho(\omega) \) is the density of the angular momentum states of molecular rotor modulated by the magnetic field at frequency \( \omega \) and \( \omega_1 = \omega + \Delta \omega \sigma^j_0 \)

The small frequency shift is given by:

\[\Delta \omega = \sqrt{\int_{-\infty}^{\infty} \rho(\omega)\omega^2 d\omega - \omega_1^2} \sigma^j_0 \]

(41)

where \( \sigma^j_0 \) is the Cauchy's principal value and

\[\sigma^j_0 = \tan^\beta h\omega \right \frac{2\pi}{\hbar}\]

(42)

where \( T_\alpha \) is the temperature of the rotational states, which can be either positive or negative. Eq. (39) describes the amplification of an initially weak field \( \alpha(0) \) in the presence of an external magnetic field \( B \), through the coupling with a rotating molecular rotor \( \sigma^j_0 \) in our case the water molecules. Eq. (39) has a general validity and it is not restricted to a specific system. The molecular parameters enter in Eq. (39) through the angular velocity terms \( \omega^j_0 \) which depend on the specific molecular system.

Now, let us consider a two level angular momentum system in an external constant magnetic field in the Z-axis, and a weak RF field \( B_1 \cos \omega t, B_1 \sin \omega t \) in the X, Y-axis the mean value of the z component of the spin operator \( \sigma_z \) (in the direction of the constant magnetic field) is given by:

\[\langle \sigma_z \rangle = \cos \left(\frac{\Omega}{2}\right)t + \sin \left(\frac{\Omega}{2}\right)t \cos \theta \]

(43)

where

\[\Omega = \left[\omega - \Omega_b \right]^2 + \left(\frac{G_B B_1}{\mu} \right)^2 \right]^{1/2}, \quad \Omega_b = \frac{G_B B^2}{\hbar \mu}
\]

(44)

\[\sin \theta = \frac{G_B B_1}{\hbar \mu}
\]

(45)

B is the intensity of the static external magnetic field, \( \mu \) is the permeability of the medium, \( B \) is the Bohr's magnetron equal to 9.27 \times 10^{-24} \text{ T}^{-1}, G_B \) is the gyromagnetic ratio depended on the angular momentum \( J \) of the molecular rotor [61].

In the case of resonance where \( \omega_{JR} = \omega = \Omega_b \equiv (G_B B/\hbar \mu) \) and for weak RF magnetic field, the angular momentum processes through many cycles before \( \langle \sigma_z \rangle \) changes its value [60].

For weak coupling Eq. (39) becomes:

\[\langle \alpha(t) \rangle \approx \langle \alpha(0) \rangle\]

\[\langle \alpha(t) \rangle^+ \langle \alpha(0) \rangle = \langle \alpha^+ \rangle \langle \alpha(0) \rangle \]

(46)

(47)

Where \( \langle \alpha(t) \rangle \) is the mean number of field quanta in the cavity. Eq. (46) is the final result. It describes the time evolution of a small electromagnetic field fluctuation \( \alpha(0) \). It can be amplified to large values by taken energy from the constant magnetic field through the coupling term \( \gamma^2 \). In the case of the absence of the external magnetic field, \( \alpha(0) \) fluctuates at the random frequency \( \omega_0 \) as is expected. In the case of high external magnetic field \( (G_B B > 2\hbar \mu \kappa T) \), \( \alpha(t) \rightarrow \exp(-i\omega_0 t + (\gamma/2) t) \alpha(0) \) and the fluctuating frequency \( \omega_0 \) is modulating by the coupling between the magnetic field and the two level system through \( \gamma \). In this case the average number of quanta of the electromagnetic field, and thus of the magnetic field is given by the equation

\[\langle \alpha(t) \rangle \approx \langle \alpha(0) \rangle \approx \langle \alpha(0) \rangle \]

(48)

in agreement with the classical theory of quantum amplifiers. The gain \( G \) in this case is,

\[G = \sqrt{\left(\frac{\omega_0^2 + \omega_0^2}{4}\right)^2}
\]

(49)

For weak coupling and for a constant magnetic field, the gain coefficient \( G \) of a fluctuating magnetic mode at frequency \( \omega_0 \) is independent from the rotational states of the molecular rotors and thus independent from the type of liquid medium. At resonance \( \omega_0 = \omega \equiv \left(\frac{G_B B}{\hbar \mu} \right), \gamma \rightarrow \infty \), and hence \( G \rightarrow \infty \). Thus, when the intensity of a static external magnetic field is in resonance with the rotational states of a molecular rotor, a fluctuating magnetic mode at this frequency can be amplified to high values. As an example, for the water molecule the \( 5.5 \rightarrow 6.5 \) transitions involve levels with rotational frequencies \( \omega_{J} = 2.2 \times 10^{11} \text{ MHz} \), for \( J = 5, 6 \), and then \( B \sim 0.4 \text{ T} \). This is in agreement with our experimental results where for this value of the external magnetic field the formation of aragonite starts to increase (Table 1). The quantum model predicts that high magnetic fields can be amplified in the turbulent flow as well. In this case the energy a magnetic fluctuation can be amplified from the external magnetic field through the low frequency angular velocity \( \Omega_b \) of the turbulent flow. It is expected therefore a magnetic field in a turbulent flow to be amplified to its highest possible value when the external magnetic field is oscillating at the high frequency of the molecular rotors and at the low frequencies of the turbulence.

Finally, in order to have a more realistic quantitative model, a loss mechanism should be introducing in addition to the amplified mechanism and the feeding a small time fluctuating signal into the cavity should be introduced. The cavity now acts as a negative resistance device by operating just below oscillating threshold and we might get a high gain in line with the general theory of negative resistance amplifiers. The average number of quanta inside the cavity at the time \( t \) is in this case,
where

\[ \eta = Y_L - Y_G(\sigma_2), \quad Y_L = \frac{1}{T_c} \exp\left(\frac{-h_0}{kT_c}\right) \]

\[ Y_G = \exp\left(-\frac{h_0}{kT_c}\right) \]  

\[ (51) \]

and the small input signal, which is provided by the constant magnetic field fluctuation is

\[ \alpha(t) = A e^{-\frac{i}{2} q \omega \Delta t} \]  

\[ (52) \]

4. Conclusions

By applying a moderate magnetic field of 1.2 T in water flow systems, more than 90% of CaCO₃ nano-crystallizes at the solid/liquid interface of non-magnetic stainless steel 316 pipes in the form of aragonite. Nucleation as aragonite is taking place provided that magnetic fields were developed within the flow. Transfer of energy from the magnetic field to the flow drives the system to a state of higher energy during the initial stage of crystallization, favoring crystallization of CaCO₃ in the form of aragonite. A quantum mechanical model predicts that a fluctuating magnetic mode inside the fluid can be amplified to high values by taking its energy from an external magnetic field through the angular momentum of the molecular rotors and/or the turbulent flow in the case of resonance, the amplification coefficient attains its maximum value and the concentration of aragonite is expected to be enhanced in comparison to calcite. The theoretical results are in agreement with present and previous experimental data of nanocrystallization of CaCO₃ in water flow systems.

Q2 Uncited reference

Acknowledgment

Authors would like to acknowledge Dr. Zoran Samardžija for the analytical work on SEM/EDXS.

References


