CONTROL OVER NANO-CRYSTALIZATION IN TURBULENT FLOW IN THE PRESENCE OF MAGNETIC FIELDS
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Abstract
The influence of the magnetic field and the water flow on the crystal form of calcium carbonate precipitated from low-concentration water solution was followed systematically. By changing the strength of the field 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. A simple hydrodynamical model, using the Navier-Stoke’s and Maxwell’s equations predicts that there is a strong energy coupling and transfer between turbulent flow and the magnetic fields and they can be amplified to high values. Since the formation of aragonite is enhanced in the presence of magnetic field, scaling is prevented in turbulent flow.

Index Terms — scaling, magnetic water treatment, magneto hydrodynamics, turbulent flow.

1. Introduction
The formation of calcium carbonate is not only a common ionic reaction that takes place in natural processes, it also results in a problem known as scaling, which is present in our everyday lives and in various industrial processes and technologies. In spite of the reaction’s simplicity there is a considerable variability in the properties of the solid product, such as crystal form, particle size distribution, electro-kinetics potential, etc. Magnetic treatment of water for scaling control and prevention represents one of the most promising water treatment technologies today. The promise of this technology lies mostly in its ecological importance and relatively low cost of its implementation and maintenance, in comparison with
classical – chemical water treatment methods. The chemical treatment of water using polyphosphates is, in
the long term, detrimental to the environment and because of constant changes in the water’s hardness, it is
not possible to determine exactly the correct dose of chemicals. This can also be harmful to the health of
humans, if such water is used as drinking water. A satisfactory explanation of the scaling process under
various conditions is not available yet in the literature [1-5]. However it is obvious that a thorough
understanding of the scaling process in the presence of magnetic fields should involve a description of the
physical processes, which influences the nucleation of the calcium carbonate in the early stages of the
formation of the crystals. In an effort to interpret and understand the experimental results of the scaling
process in water flow systems in the presence of magnetic fields [6,7], we have studied the crystal form and
the size distribution of the precipitated calcium carbonate particles in their early stage of crystallization by
using X-ray analyses and transmission electron microscopy (TEM). It was found that the formation of
aragonite is enhanced as much as 70%. In addition, by using a simple hydro dynamical model, it is
predicted that there is a strong energy coupling and transfer between the kinetic energy of a turbulent flow
and the magnetic field. Therefore the magnetic fields can be amplified to high values, and even in the case
of absence of external magnetic fields, they can be generated within the turbulent flow, preventing scaling.

2. Experimental

The experimental procedure has been described previously [7] Sample solutions of calcium hydrogen
carbonate (Ca(HCO₃)₂) were prepared by dissolving finely ground calcium-carbonate powder of analytical
purity in demonized water and bubbling the suspension with carbon-dioxide gas through a porous frit. As
CO₂ is removed from the system, by bubbling air through the solution at a constant flow rate, CaCO₃
particles begin to precipitate. The experimental evidences were based on over 5 years of intensive
experimental evidences with hundreds of experiments and analyses of results and the experimental error in
the concentration of C/A/V was ~ 10%. Experiments were performed in parallel runs and were repeated for
each condition until the results were reproducible. One of the runs was treated with a magnetic field and the other was not. For the magnetic treatment an applied DC field of between 0.5 and 1.3 T was used. The remaining solids were removed by filtering the suspension through a filter. A controlled drying procedure at 70 °C and 40 % relative humidity in a Weiss humidity chamber obtained the crystals of CaCO3.

Determination of the amount of calcite, vaterite and aragonite crystals precipitated from the treated water shows the importance of the strength of the applied magnetic field on the quantity of different crystal forms. The system was cooled so the eventual heating of water due to the high magnetic field was prevented and the constant temperature of water was enabled. The same conditions were used for all experiments; the only variable was the strength of the applied field. Each experiment was repeated until the system was stabilized and the results were reproducible. The X-ray powder diffraction patterns of the precipitating samples were recorded on a Siemens D-5000 diffractometer using reflection geometry (Bragg-Brentano), with a monochromatized graphite X-ray source. Data were collected in the 2θ angle mode 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 within 1° and the front slit was 0.2 mm wide. For the study of the nucleation and further crystallization of CaCO3 we used analytical electron microscopy. Samples for the TEM observation and analysis (Jeol 2000 FX and Jeol 2010 F (FEG)) were prepared using a C/Cu grid that was immersed into the solution for different times (5 and 10 minutes after the beginning of the process). The nano-sized particles were collected on the grid and examined under the electron microscope. EDXS was used to characterize the chemical composition.

3. Results and discussion

1.1 Experimental results

Following the experimental procedure the amount of precipitated calcium carbonate particles depends on the intensity of the magnetic field. All the three crystalline forms of CaCO3 (calcite, aragonite and vaterite) were identified in the powder samples and the mass fractions were determined by Rietveld refinement. The
structural models of the three phases were taken from the ICSD 8] (standards 16710, 15194 and 15879 for calcite, aragonite and vaterite respectively). The program DBWS [9] was used for the refinement of typically 22 variables (3 scale factors, 3 background terms, 1 zero correction, 2+3+2 unit cell parameters, 1 overall temperature factor – common for all 3 phases and 3+2+2 profile width parameters). In some cases additional variables were needed to account for individual profile features. The agreement between the experimental and the calculated patterns were within accepted limits (Rwp ~10 -15), Fig 1. The results of the quantitative X-ray analysis are shown in Table 1. With TEM and EDXS microanalysis the nucleation and early stages of crystallization were studied. The particles of calcite, aragonite and vaterite were detected in different amounts. Fig. 2 shows the comparison between the crystallization products 10 minutes after the beginning of the crystallisation with and without the magnetic field. An obvious difference in the amount of the crystals per square unit of the treated and non-treated samples is evident. TEM images of crystals formed in the presence of the applied magnetic field, compared to the crystals obtained without the field are shown in Fig 3. Crystals formed in the presence of the magnetic field are mostly in an aragonite form, crystals obtained without the applied magnetic field are predominantly calcite, but also aragonite and vaterite could be observed.

1.2 The equations of motion of a fluid in a magnetic field

For describing the formation of aragonite 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 the two structural forms of CaCO₃. It was found that the ground electronic states of the Ca-C and Ca-O bonds in the aragonite crystal were placed ~ 25 eV above the ground electronic state of the calcite. In water flow systems were carbon carbonate is dissolved in water the required energy to bridge the energy gap between the two crystalline forms of calcium carbonate can be provided by external magnetic fields. The main theoretical issues which have to be addressed are coupling and transfer of magnetic energy between the molecules and the magnetic
field. In the presence of magnetic fields the free energy \( F \) per unit volume of a molecular system is given by the equation 
\[
F(T, P) = F_0(T, P) + \frac{dE}{dV}.
\]
Where \( F_0(T, P) \) is the free energy in the absence of any magnetic or electric field, and \( \frac{dE}{dV} \) is the energy density of the magnetic field. The formation of crystals in one or the other form depends on the initial conditions of crystallization, which on its turn depends on the free energy of the molecular system. If for example only one molecule of aragonite could be formed somewhere on the boundary of the flow with a solid surface, the accumulation of Ca and CO\(_3\) ions around the initial crystal seed will be followed by crystallization in the same structural form. In addition if the energy density of \( 25\text{eV per molecular volume} \) could be provided to the molecular system, then accumulation of additional Ca and CO\(_3\) ions around the initial seed, will have higher probability to give structural forms crystallized with hexagonal symmetry (aragonite). From the above equations the required energy to bridge the gap between the ground electronic states of the calcite and the aragonite can be provided by a static magnetic field of \( \sim 45 \) Tesla within a typical inter-nuclear distance of 0.5nm between the ions of Ca and CO\(_3\). This value corresponds to an energy density of \( \sim 10^9 \) Joule/m\(^3\). Previous long standing experimental results suggest that aragonite can be formed on conducting surfaces in flow systems in the presence of static or time dependent magnetic fields smaller than 45 Tesla. In addition the flow conditions should play a significant role besides the magnetic field, to modify the initial nano-crystallization phase of CaCO\(_3\). Indeed, 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 [10]. The coupling of the magnetic fields to a conductive flow, is describing in two different pictures. In the first which is the macroscopic one, the coupling of the electromagnetic energy to the flow is described by the Navier-Stokes and Maxwell’s equations. In this case energy transfer is taking place between spontaneous magnetic fields and turbulent flow. In the second microscopic approach the coupling of the radiation to the flow is described by fully quantizing both the flow and the electromagnetic field. In this
communication we will discuss only the transfer of energy between a turbulent flow and a spontaneous magnetic field using the macroscopic approach in a phenomenological way. This picture can be quite instructive for the further development of any quantum mechanical theory. When a conductive fluid moves under the influence of a magnetic field, the flow is modified. On the other hand energy is transferred from the flow to the magnetic field and backwards and this complex situation is described by the equations of flow together with the Maxwell’s equations. The interaction of the magnetic field and the flow is described by the equation

\[
\frac{\partial \vec{V}}{\partial t} + (\vec{V} \cdot \text{grad}) \vec{V} = -\frac{1}{\rho} \text{grad}P + \frac{\eta}{\rho} \Delta \vec{V} + \frac{1}{\rho} (\zeta + \frac{1}{3} \eta) \text{grad} \text{div} \vec{V} + \frac{\mu_0}{\rho} \text{curl} \vec{B} \times \vec{B} 
\]

Where \(\eta\) and \(\zeta\) are the two coefficients of viscosity of the fluid, \(V\) is the velocity, \(P\) is the pressure of the fluid, \(\rho\) is the density of the fluid, \(\vec{B}\) is the magnetic induction and \(\mu_0\) is the permitivity of the free space.

Now, there always exist small perturbations in a conductive fluid resulting from reasons not connected to the flow itself. These perturbations are connected with fluctuations of the vacuum energy of the magnetic field [11]. The main question is whether or not fluctuations can be amplified or dumped by the turbulent flow in the lapse of time. The following arguments show that either case may occur depending on the properties of the field itself. When the magnetic field interacts with the flow its energy is dissipated within the flow, and the induced currents tend to diminish the field. On the other hand it can be shown [10] that when a fluid of sufficient conductivity is in motion, the lines of the magnetic forces are following 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 are stretched the magnetic field is strengthened in time as well. Under certain conditions these two opposite tendencies can be balanced and
a criterion can be provided distinguishing the two cases of damping or amplification of the spontaneous magnetic field. While the magnetic field resulting from the motion remains weak, its effect on the motion itself is small and it can be neglected. That is, we may consider fluid turbulence as providing the intermediate medium where magnetic perturbation can be developed. We assume a steady turbulent velocity distribution and we neglect quadratic terms of the field in the equation of motion. In this case eqn. 1 takes the form of the simplified Navier-Stokes equation for a incompressible fluid

\[
\frac{\partial \mathbf{V}}{\partial t} + (\mathbf{V} \cdot \nabla) \mathbf{V} = -\frac{1}{\rho} \nabla P + \frac{\eta}{\rho} \nabla V
\]  

(2)

Substituting \((\frac{1}{2}) \nabla \times \mathbf{V}\) by \(\boldsymbol{\Omega}\) and after some algebra we obtain the equation

\[
\frac{\partial \mathbf{\Omega}}{\partial t} = \nabla \times (\mathbf{V} \times \mathbf{\Omega}) + \frac{\eta}{\rho} \Delta \mathbf{\Omega}
\]  

(3)

By comparing equation 3 with the equation of Maxwell for \(\mathbf{B}\), it can be seen that \(\mathbf{B}\) and \(\mathbf{\Omega}\) satisfy similar differential equations, which can become identical provided that \((\eta/\rho) = (\sigma \mu_0)^{-1}\). In this case a specific solution of the equation 3 exist such that \(\mathbf{B} = C^* \mathbf{\Omega}\) where \(C\) is a constant. Therefore in this case there is only one value of the magnetic field, which is independent on the constant value, and where the magnetic field does not either increases or decreases. This situation corresponds to the case of equilibrium. When the conductivity of the fluid exceeds its equilibrium value then the dissipative loss of the electromagnetic field will be insufficient to compensate the increase of the magnetic field due to the stretching of the lines and in this case spontaneous amplification of the magnetic field from small magnetic perturbations is taking place. Obviously the threshold condition for amplification is: \((\eta \sigma \mu_0 / \rho) \geq 1\).
Next step it will be to estimate the order of magnitude of the magnetic field as it is growing from small perturbations and this can be done by referring to the fluid-mechanical properties of the turbulence itself and eqn 2. Turbulent flow can be regarding as a superposition of turbulent regions of different dimensions, from the largest $L$, which represents the external scale of the turbulence, to the smallest $\lambda_0$, which represents its internal scale, and its physical interpretation is that it is connected to the length dimension where the energy dissipation and the viscosity of the fluid become important. Its value can be expressed in terms of $L$ and the Reynolds’s number $R$, where $R \sim UL\rho/\eta$ of the turbulent flow as a whole ($U$ being the change of the mean velocity over a distance $L$), and $\lambda_0 \sim \frac{L}{R^{1/4}}$. The spontaneous magnetic fields should follow the same correlation low as the angular velocities of the flow, and for distances greater than the length $\lambda_0$ their relative directions are random. It is obvious therefore that the order of magnitude of the last term on the right hand side of eqn1 should be of the order of $\sim B^2/\rho\mu_0\lambda_0$. Similarly the term $(\nabla \times \mathbf{V}) \times \mathbf{V}$ is of the order of $\sim U^2/\lambda$, where $U$ been the change in the velocity over a distance $\lambda$. In the case of an incompressible flow the two terms are comparable and we have

$$B^2 \sim U^2/\rho\mu_0$$

Eqn 4 is our final result and tell us that the energy density in a turbulence flow of the spontaneous magnetic fields, as they are developed within the volume $\sim \lambda_0^3$, is of the same order of magnitude as the fluctuations of the kinetic energy of the flow within the same volume. It is obvious therefore that in order to have an energy density of the spontaneous magnetic field of the order of $\sim 10^9$ joule/m$^3$, which is required to bridge the energy difference between the two forms of CaCO$_3$, in order to nanocrystallize it as aragonite, the turbulent flow should generate velocity fluctuations of the order of $10^3$ m/sec. Such values of velocity
changes could be achieved by thermal fluctuations and/or on the boundary of a conductive surface from ion acceleration by mirror charges on the conductive surfaces.

4. Conclusions

It was found experimentally that magnetic field enhances the formation of aragonite in the early nano-nucleation stages of crystallization of CaCO₃ in water flow systems, reducing thus scaling. The formation of aragonite in the presence of magnetic fields is enhanced when the flow is turbulent. This is due to energy transfer from the turbulent flow to the magnetic field, which is amplified proportional to the change of the kinetic energy of the flow.

5. References


Figure Captions

**Fig. 1** Rietveld plot ($R_{wp} = 11$). Experimental (crosses), calculated (solid line) and difference (solid line below) Vertical bars denote CuKα₁, Θ₂ reflection positions of calcite (top row), aragonite (middle row) and vaterite (lower row).

**Fig. 2.** Crystals obtained at time $t_2$ with (left) and without (right) the magnetic field

**Fig. 3** TEM images of crystals formed in the presence of the magnetic field (a), compared to the crystals obtained without the applied magnetic filed (b); the three crystallization forms can be observed: A-aragonite, C-calcite, V-vaterite.

**Table 1.** Relative ratio of the three different forms of CaCO₃ during the early crystallization phase as a function of the intensity of the external magnetic field.

<table>
<thead>
<tr>
<th>Magnetic filed (mT)</th>
<th>Calcite (%)</th>
<th>Aragonite (%)</th>
<th>Vaterite (%)</th>
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<tr>
<td>0</td>
<td>90.2</td>
<td>9.6</td>
<td>0.2</td>
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<td>10.4</td>
<td>9.6</td>
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<tr>
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<td>28.9</td>
<td>70.6</td>
<td>0.5</td>
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</table>
Figure 1
Figure 2
Figure 3