CONTROL OVER NANO-CRYSTALIZATION IN TURBULENT FLOW IN THE PRESENCE OF MAGNETIC FIELDS

S. Kobe, G. Dražić, Janez Stražišar, T. Meden

Jozef Stefan Institute, Jamova 39, 1001 Ljubljana, Slovenia.

E. Sarantopoulou, Z. Kollia, A. C. Cefalas

National Hellenic Research Foundation, TPCI, 48 Vassileos Constantinou Ave. Athens 11635, Greece.

IJS Ljubljana Slovenia

Introduction

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 hydro dynamical 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.

Experimental Method

•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 bubbling the suspension with carbon-dioxide gas through a porous frit. As CO_2 is removed from the system, by bubbling air through the solution at a constant flow rate, $CaCO_3$ particles begin to precipitate.

•Experiments were performed in parallel runs.

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 ºC and 40 % relative humidity in a Weiss humidity chamber obtained the crystals of $CaCO_3$.

•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 X-ray powder diffraction patterns of the precipitating samples were recorded on a Siemens D-5000 diffractometer using a reflection geometry (Bragg-Brentano), with a mono-chromatized graphite X-ray source.

•Data were collected in the 2θ angle mode from 20 to 70º in steps of 0.04º; the integration time was 30 s per step. The divergence and anti scatter slits were fixed within 1º and the front slit was 0.2 mm wide.

•For the study of the nucleation and further crystallization of $CaCO_3$ 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 (t_1=5 min; t_2=10 min) 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.

Coupling and transfer of magnetic energy between the molecules and the magnetic field.

•The gap between the ground electronic states of the calcite and the aragonite can be provided by a static magnetic field of ~ 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 ~10^9 Joule/m^3.

•Transfer of energy between a turbulent flow and a spontaneous magnetic field can be described by using the macroscopic approach in a phenomeno-logical way. The interaction of the magnetic field and the flow is described by the Maxwell equation

$$\partial\vec{V}/\partial t + (\vec{V}\bullet \mathrm{grad})\vec{V} = -\frac{1}{\rho}gradP + \frac{\eta}{\rho}\Delta\vec{V} + \frac{1}{\rho}(\zeta + \frac{1}{3}\eta)graddiv\vec{V} + \frac{curl\vec{B}X\vec{B}}{\mu_0\rho}$$

Where η and ζ are the two coefficients of viscosity of the fluid, $\bar{V}$ is the velocity, *P* is the pressure of the fluid, ρ is the density of the fluid, $\bar{B}$ is the magnetic induction and μ_0 is the permitivity of the free space.

Neglecting quadratic terms of the field in the equation of motion :

$$\partial\vec{V}/\partial t + (\vec{V}\bullet grad)\vec{V} = -\frac{1}{\rho}gradP + \frac{\eta}{\rho}\Delta\vec{V}$$

Substituting (½)* curl $\bar{V}$ by $\bar{\Omega}$ and after some algebra we obtain the equation

$$\partial\vec{\Omega}/\partial t = curl(\vec{V}X\vec{\Omega}) + \frac{\eta}{\rho}\Delta\vec{\Omega}$$

By comparing last equation with the equation of Maxwell

$$B=C^*\,\Omega$$

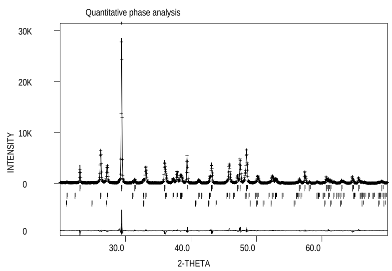
In the case of an incompressible flow

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

U being the change of the mean velocity over a distance L

For energy density of the spontaneous magnetic field ~10^9 joule/m^3, which is required to bridge the energy difference between the two forms of $CaCO_3$, in order to nano-crystallize 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

Experimental Results

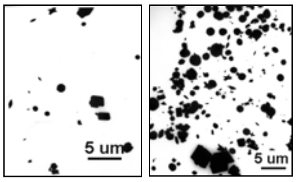


Rietveld plot (R_{wp} = 11). Experimental (crosses), calculated (solid line) and difference (solid line below) Vertical bars denote CuKα$_1$, Θ$_2$ reflection positions of calcite (top row), aragonite (middle row) and vaterite (lower row).

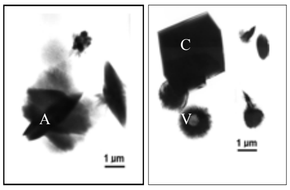
Magn. F. (mT)	Calcite (%)	Aragonite (%)	Vaterite (%)
0	90.2	9,6	0.2
400	80.0	10.4	9.6
1220	28.9	70.6	0.5

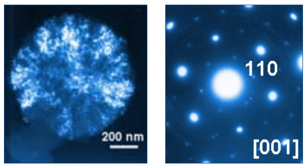
Relative ratio of the three different forms of $CaCO_3$ during the early crystallization stage as a function of the intensity of the external magnetic field.

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

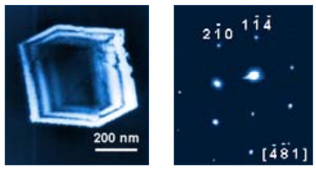


TEM images of crystals formed in the presence of the magnetic field (left), compared to the crystals obtained without the applied magnetic filed (right). A- aragonite, C- calcite, V-vaterite.

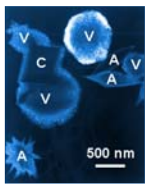




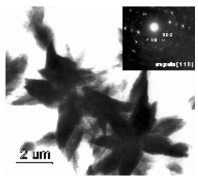
TEM image and a diffraction pattern of Vaterite



TEM image and a diffraction pattern of Calcite



TEM image of different $CaCO_3$ crystals



TEM image and a diffraction pattern of Aragonite

Conclusion

Systematic experimental work showed that magnetic field enhances the formation of aragonite in the early nano-nucleation stages of crystallization of $CaCO_3$ 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 the energy transfer from the turbulent flow to the magnetic field, which is amplified proportional to the change of the kinetic energy of the flow.

Contact:

NATIONAL HELLENIC RESEARCH FOUNDATION

A.C. CEFALAS

Ph: +30-120-7273840

Email: ccefalas@eie.gr