NANOCRYSTALIZATION OF CALCIUM CARBONATE IN MAGNETIC FIELD.

Cefalas, A. C. (1), Kobe, S. (2), Sarantopoulou, E. (1), Kollia Z. (1), Stražišar, J. (3), Meden, A. (4)

(1)National Hellenic Research Foundation, TPCI, Athens, Greece. (2)Department of Nanostructured Materials, Jozef Stefan Institute, Ljubljana, Slovenia

(3)Department for Geotechnology and Mining, University of Ljubljana, Slovenia (4)Faculty of Chemistry and Chemical Engineering, University of Ljubljana, Slovenia

Abstract

The crystallographic point symmetry group of precipitating particles on flow surfaces during the initial stage of nucleation depends besides other factors on the intensity of external magnetic fields and the state of flow during the initial stage of nucleation. Scanning electron microscopy and quantitative X-ray analyses verify that Ca^{2+} and CO_3 2- ions in water flow systems and under constant magnetic field of ~ 1.2 T, precipitate as $CaCO_3$ crystals with the ratio of aragonite-vaterite to calcite higher than ~ 7 . The experimental data can be explained with the application of a quantum mechanical model, which predicts that magnetic fluctuations inside the flow of ionic liquids can be amplified to high values by taking energy from an external magnetic field through the angular momentum of the rotating water molecules. Results are in agreement with recently developed macroscopic magnetohydrodynamic models of nano-crystallization .

Introduction

The formation of precipitated deposits on the surfaces of water and fuel flow systems (pipes, tanks, etc) is commonly known as "scaling" [1]. Scaling deposits significantly increase operating and maintenance costs in industrial plants by slowing down the efficiency of the energy transfer between industrial blocks

The physical anti-scale magnetic treatment (AMT) has been reported as being effective, but no explanation on its cause exists yet, as the existing theories are based on phenomenological macroscopic physicochemical models. In this communication we discuss the coupling of the magnetic fields to a molecular system, in two different pictures (macroscopic and microscopic approach).

Experimental

In an effort to understand the experimental results of the scaling process in water flow systems in the presence of magnetic fields [2-4], we have studied experimentally the crystal form of the precipitated $CaCO_3$ in their early stage of crystallization by using quantitative X-ray analyses and SEM. The experimental procedure has been described previously [4]. The same conditions were used for all experiments.

The X-ray powder diffraction patterns of the precipitated particles 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 2è 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 10 and the front slit was 0.2 mm wide.

For the study of the nucleation and further crystallization of $CaCO_3$ also the analytical SEM (JEOL JSM 5800) together with EDXS was used to characterize the chemical composition.

Experimental results

In previous work we were following how the amount of different crystal symmetries of precipitated calcium carbonate depends on the intensity of the magnetic field. The present work was to confirm the reproducibility of the experiment itself and field of 1,3 T was used in all experiments. Crystalline forms of $CaCO_3$ (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 [7]. The program DBWS [8] was used for the refinement of typically 22 variables. The agreement between the experimental and the calculated patterns were within accepted limits (Rwp ~10 -15). Literature data [1] claim that the AMT in not widely used in the practice because of very low reproducibility, but our results completely disprove these claims. They show that the reproducibility of experiments is very good and the amount of precipitated calcium carbonate in the aragonite + vaterite crystal forms, which do not form a scale on exposed surfaces, is between 87,5 and 96,4.

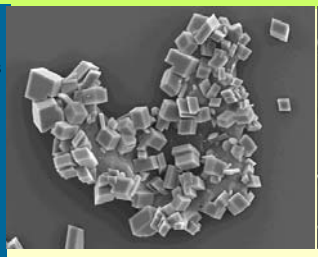


Fig. 1. SEM images of the precipitated particles. Without magnetic field the formation of calcite (trigonal structure) is predominant. (Magnification 200 X)

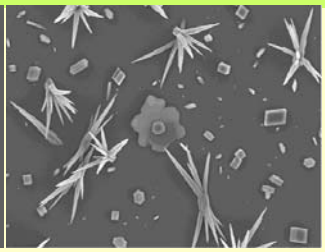
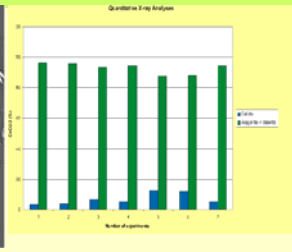


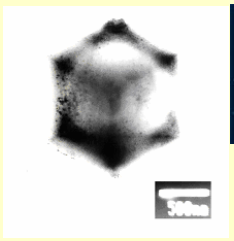
Fig.2 With the application of 1.2 T magnetic fields the main crystal forms are aragonite and vaterite. (Magnification 200 X)



Quantitative X-ray analyses of seven experiments under the same experimental conditions showing the enhanced ratio of aragonite+vaterite to calcite, in the presence of magnetic field.

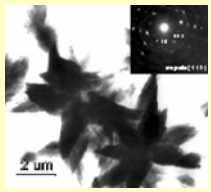
An obvious difference in the crystal forms and their amount per square unit of the treated and non-treated samples is evident. Crystals formed in the presence of the magnetic field are mostly in aragonite and partly in vaterite form, crystals obtained without the applied magnetic field are predominantly calcite.

TEM and Diffraction Patterns

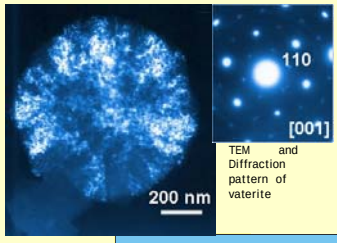


TEM image of calcite

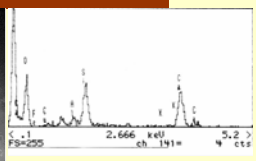
Diffraction pattern of calcite



TEM image and a diffraction pattern of aragonite



TEM and Diffraction pattern of vaterite



Figs 7 a,b TEM image and diffraction pattern (SEAD) of amorphous phase found in the magnetically treated samples.

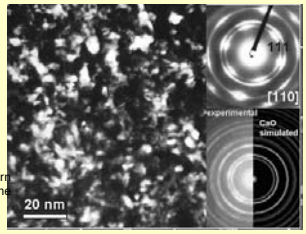


Fig.5 Dark-field TEM image of decomposed vaterite. Insets (upper): SAED patterns of decomposed vaterite crystal where spots (arcs) indicate textured CaO in [110] zone axis. Circles correspond to randomly oriented nanocrystals of CaO. Lower inset: comparison of experimental and simulated SAED patterns for cubic (Fm3-m) CaO

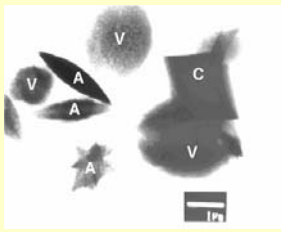


Fig.6 TEM image of various crystals obtained in treated samples: C – calcite, A – aragonite, V - vaterite

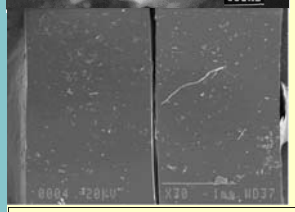
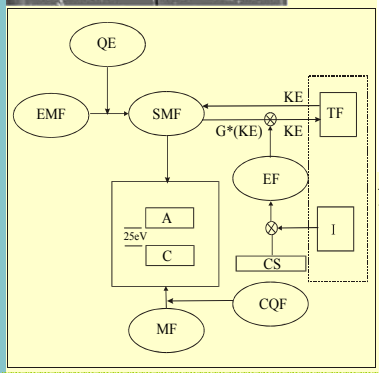
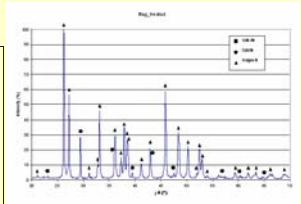
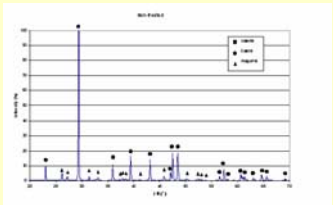


Fig. 8. SEM image of the inner surface of the Si tube used for the experiment





The diffraction spectrum of precipitated CaCO3 obtained from water treated with the applied magnetic field.



The diffraction spectrum of precipitated CaCO3 obtained from non-treated water.

Applied Magnetic Field (T)	Calcite (%)	Aragonite+Vaterite (%)
0	90.2	9.8
1.2	6.5	93.5

Table1

$$H=\sum_k \hbar\omega_K \hat{\alpha}^{+}_{k\lambda}\hat{\alpha}_{k\lambda}+\frac{1}{2}\sum_j \hbar\omega_j \hat{\sigma}^{Z}_{ja}+\frac{1}{2}\sum_j \hbar\omega_j \hat{\sigma}^{Z}_{jf}+\hbar\sum_j K_{aj}(\hat{\sigma}^{+}_{ja}\hat{\alpha}_{k\lambda}+\hat{\sigma}^{-}_{ja}\hat{\alpha}^{+}_{k\lambda})+$$
$$+\hbar\sum_j K_{fj}(\hat{\sigma}^{+}_{jf}\hat{\alpha}_{k\lambda}+\hat{\sigma}^{-}_{jf}\hat{\alpha}^{+}_{k\lambda}) \quad (4)$$

$$\alpha(t)=\exp(-i\omega t+\frac{\gamma}{2}\sigma^{z}_{jf0}t)\,\alpha(0)+\sum_j \frac{k_{jf}e^{-i\omega_{jf}t}\left\{1-\exp\left[i(\omega_{jf}-\omega_l)t+(\frac{\gamma}{2})\sigma^{z}_{jf0}\right]\right.}{(\omega_{jf}-\omega_l)-i\frac{\gamma}{2}\sigma^{z}_{jf0}}\sigma^{-}_{jf} \quad (21)$$

References

1. Baker, J. S., Judd, S. J., Parsons, S. A. *Desalination* V110, (1997) 151.
2. S. Kobe, G. Dražić, E. Sarantopoulou, A. C. Cefalas. *Mat. Sci. and Eng. C*, V23, (2003) 811.
3. S. Kobe, G. Dražić, P.J. McGuiness, J. Stražišar, *J.M.M.M.*, V236, (2001) 71.
4. S. Kobe, G. Dražić , A.C. Cefalas , E. Sarantopoulou , J. Stražišar , *Crystal Eng.*, V5 (2002) 243.
5. Radiation and noise in quantum electronics, W.H. Luisell, Mc Grow hill, 1962.
6. Electrodynamics of continuous media", L.D. Landau and E. M. Lifshitz, Pergamonpress V8, 1981, p181.
7. Inorganic Crystal Structure Database, release July 2002, Fachinformationszentrum Karlsruhe, Germany and U.S. Department of Commerce, USA, 2002.
8. R.A. Young, A. Sakthivel, T.S. Moss and C.O. Paiva-Santos, *J. Appl. Cryst.* V28, (1995) 366.

Conclusions

•A quantum two level molecular system, in its initial stage as a function of the magnetic field is described by the same Hamiltonian as the MASER amplifier.
In this case one fluctuating mode of the magnetic field at a frequency ù, can be amplified to high values by taking its energy from the constant magnetic field through the angular momentum of the two level atomic system.
•In the case of a turbulent flow, the kinetic energy of the flow is transferred to the magnetic mode even in the absence of magnetic field.
•Transfer of energy from the magnetic field to the two level system changes the free energy of the system during the initial stage of crystallization forcing the molecular system to crystallize in a different structure.

•Theoretical results are in a good agreement with experimental data of nano-crystallization of CaCO3 in water flow systems obtained by the quantitative X-ray analyses and SEM equipped with EDXS.
•The reproducibility of experiments is very good.
• The amount of precipitated CaCO3 in water flow systems obtained by the quantitative X-ray analyses and SEM equipped with EDXS.