

**TEM EXAMINATION OF THE INFLUENCE OF MAGNETIC FIELD ON THE
CRYSTALLISATION FORM OF CALCIUM CARBONATE: A MAGNETIC
WATER-TREATMENT DEVICE[†]**

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[†]This paper is dedicated to the memory of Professor Drago Kolar

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Abstract

By using X-ray analysis and a TEM equipped with a Link AN-10000 EDXS analysing system and EDXS with an Ultra-Thin Window Si(Li) detector, different crystal forms of CaCO₃ crystals were characterised. Crystals were grown from tap water and model water both with and without a magnetic field. The formation of separate aragonite crystals was demonstrated in the treated water and clusters of calcite in untreated water. It was determined that under the influence of a magnetic field higher than 500 mT the nucleation and further growth of aragonite can be successfully used as a method against scaling.

The prototype of a magnetic water-treatment device (MWTD) was constructed for testing in a pilot plant for the magnetic treatment of tap water. It has been used for more than two years and the results look very promising for reducing the use of environmentally detrimental chemicals. The weight gains of heat exchangers, which were used in the three parallel pipelines equipped with three different devices against scaling, were followed. The MWTD designed and built in the IJS laboratory showed only a slightly higher weight gain than that achieved with the use of chemicals.

Introduction

CaCO₃ crystallises in three different crystal forms: calcite, aragonite and vaterite. Calcite is usually associated with a hard scale whereas aragonite and vaterite give rise to a softer type of scale that is easily removed.

Anti-scale magnetic treatment has a long and controversial history. The phenomenon of water treatment by an applied magnetic field has been known for several years and has been reported as being effective in numerous instances.¹⁻⁵ It has been established that the nucleation and crystallisation of calcium carbonate in hard water can be influenced by a magnetic field and as a consequence it should no longer be necessary to always look for chemical means to prevent the accumulation of calcium carbonate on surfaces exposed to hard water. This is of great importance in reducing the chemical pollution of the environment.

Different authors have emphasised various parameters (temperature, pH, strength and direction of the applied field, and the impurity elements present in tap water) that influence the efficiency of the treatment with a magnetic field.⁶⁻¹⁰ Many authors have reported large savings in energy, descaling and process-downtime costs after the installation of magnetic water-treatment devices (MWTD) in real systems. However, Baker¹¹ reports that installed MWTDs have also often proved inefficient in real installations, though the precise reasons for their inefficiency are rarely examined in such cases.

In our previous work the influence of different parameters (strength and orientation of the magnetic field, treatment time) on the nucleation and crystallisation of calcium carbonate was studied.¹² For this purpose a special device with permanent magnets based on Sm-Co was developed and constructed.¹³ More recent studies focused on the influence of impurities of different elements on the crystallisation form of calcium carbonate in the presence of an applied magnetic field.¹⁶ Herzog³ and co-workers reported the positive influence of Fe²⁺ on the inhibition of calcite and the promotion of the aragonite crystal form, Coetzee^{14,15} studied the influence of Zn²⁺ ions in ppb quantities on the preferential formation of aragonite in magnetically treated water. Our work confirmed the results of Herzog and Coetzee. We also showed that the same effect observed with Fe²⁺ and Zn²⁺ ions could be obtained with (Cu²⁺).¹⁶ Busch¹⁷ reported a change in the pH difference between the surface and the bulk of the magnetically treated water, which might contribute to the crystallisation changes. The authors claim that the important factors, which promote magnetohydrodynamic forces (responsible for the changes in crystallisation), are the conductivity of the solution, linear flow velocity of the fluid, and the flux density of the field. Recent results reported by Coey,¹⁸ at the 99.9 % probability level, show that drawing water through a magnetic field increases the aragonite/calcite ratio in the deposit.

Experimental

In this study we used model water which was prepared following the literature data of Parsons¹⁹ who reported the optimal concentration of Ca²⁺ ions for the best response

to the magnetic treatment is 300 ppm. Sample solutions of calcium hydrogen carbonate ($\text{Ca}(\text{HCO}_3)_2$) were prepared by dissolving finely ground calcium-carbonate powder of analytical purity in deionised water by 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 of 0,5 l/min), CaCO_3 particles begin to precipitate following the equation:



Experiments were performed in parallel runs. One of the runs was treated with a magnetic field and the other was without. For the magnetic treatment an applied DC field was used (0,5 – 1,3 T). The fluid flow rate was set at 0,03 l/min which corresponds to a velocity of 0,1 m/s and to a low Reynolds number (laminar region). The remaining solids were removed by filtering the suspension through a 0,45 μm filter. The resulting solution is an equilibrium system of $\text{CaCO}_3 - \text{Ca}(\text{HCO}_3)_2 - \text{H}_2\text{O}$.

Crystals of CaCO_3 were obtained by a controlled drying procedure at 70 °C and 40 % R.H. in a humidity chamber (Weiss). The crystals were analysed by X-ray spectroscopy using a Philips X-ray diffractometer and TEM. Samples for the TEM investigation were prepared by the crystallisation of CaCO_3 particles in a magnetic field, directly from tap water on a hollow carbon-coated Cu grid or by filtering of crystals from the model water through a nucleopor (0.2 μm) filter. The parts of the filters containing the crystals were placed on the Cu grid, coated with a thin carbon film and dissolved in chloroform so that only the crystals embedded in the carbon film remained on the Cu grid. The samples were examined using a Jeol 2000 FX transmission electron microscope operated at 200 kV. The chemical compositions of the phases were determined using a Link AN-10000 EDXS system (Energy-Dispersive X-ray Spectroscopy) with an Ultra- Thin Window Si(Li) detector, connected to the TEM.

Results and discussion

Preliminary results from the X-ray analysis showed a difference in the amount of the three crystallographic forms of CaCO_3 if the model water was treated with the magnetic field.

Figure 1. shows the diffraction spectra of the crystals obtained from magnetically treated and nontreated samples. The results of the quantitative analysis of these spectra are in Table 1.

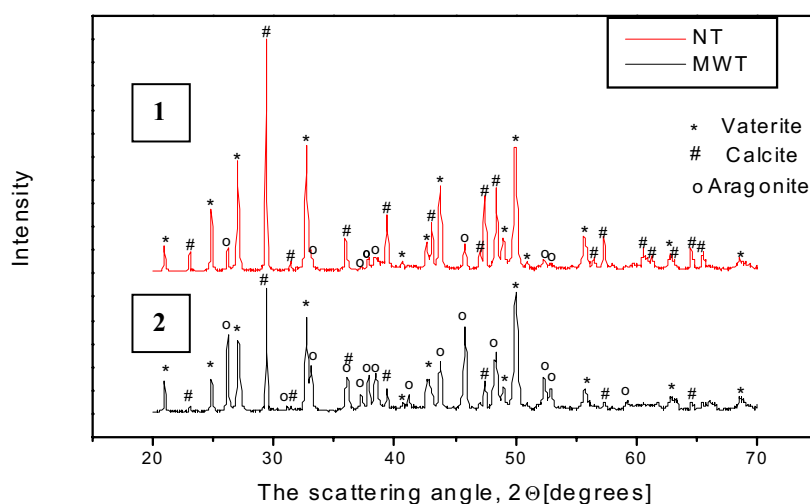


Figure 1. Diffraction spectra of nontreated (1) and magnetically treated (2) model water

Table 1: Mass percentages of different crystal forms of calcium carbonate for samples in Figure 1.

Crystal form	Calcite (%)	Aragonite(%)	Vaterite (%)
Nontreated sample	34	14	52
Treated sample	14	44	42

The results of the diffraction analysis show:

- significantly more aragonite in the magnetically treated sample;
- relatively high proportions of vaterite in both samples.

Vaterite is a metastable crystal modification of calcium carbonate that often precipitates first, but usually transforms quickly to calcite. According to the data of Coetzee^{14,15} the treated solutions consistently produced aragonite and occasionally treated and untreated solutions gave rise to CaCO₃ precipitating in the vaterite form.

TEM observations

Samples prepared in a magnetic field.

In samples prepared with crystallization in a magnetic field of 500 mT rectangular shaped calcium-carbonate particles with sizes up to a few microns were found. In Figure 2 A, a dark-field TEM micrograph of a six-angled CaCO_3 particle is shown. In Figure 2 B, where a region of the particle at higher magnification is shown, we can see that the particle consists of very fine crystallites with sizes between 1 and 5 nm. From the selected-area electron-diffraction patterns (Fig 3 A) where more or less uniform and slightly diffuse rings were found it was concluded that the crystallites were randomly oriented in the particle. To identify the form of calcium carbonate that was present in the particles grown in the magnetic field we simulated (calculated) electron-diffraction patterns for various phases and compared them to the experimental electron-diffraction patterns. For calculations the EMS computer program package (Electron Microscopy Simulation program from P. Stadelmann, EPFL - CIME, Lausanne, Switzerland) was used.²⁰ In Figure 3 B, the comparison of the experimental (a) and calculated diffraction patterns (b) where a mixture of aragonite and vaterite phases in the ratio 1:1 with a crystallite size of 5 nm were used in the calculations are shown. The match between both patterns was partial. The match between the experimental (a) and simulated (b) pattern for the calcite phase was worse, as shown in Figure 3 C. It was concluded that during the crystallization of CaCO_3 in a magnetic field, the majority of particles consisted of a mixture of aragonite and vaterite crystals.

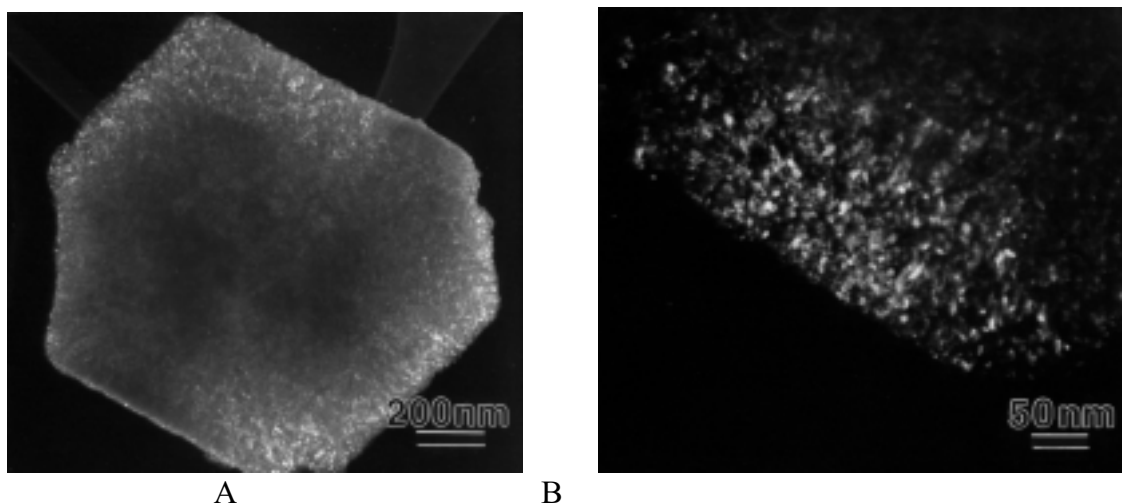


Fig. 2: Dark-field TEM micrograph of a regularly shaped CaCO_3 particle crystallized in a magnetic field (A) consisting of crystallites up to 5 nm large (B).

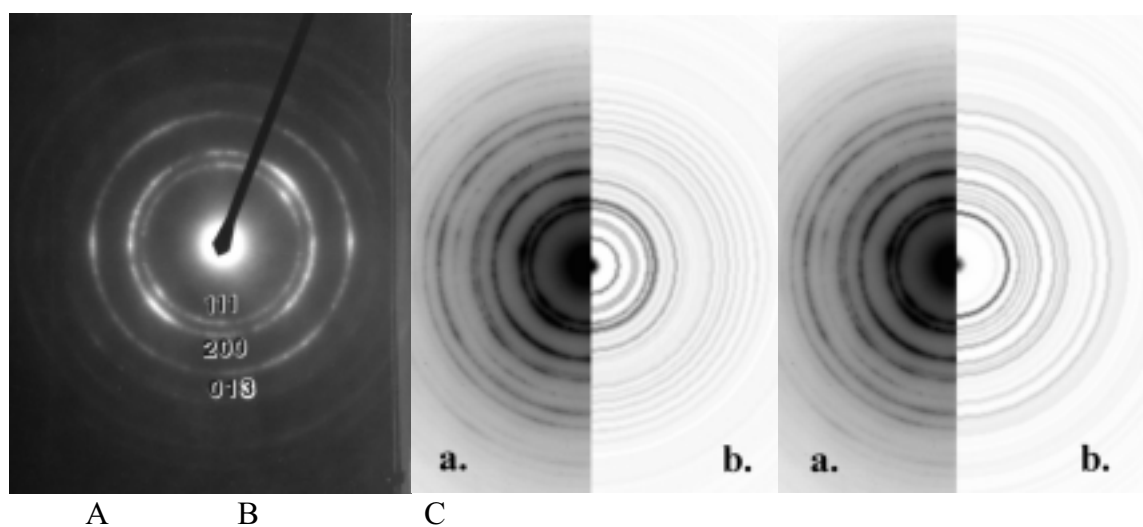


Figure 3: A- experimental selected-area electron-diffraction pattern (indexed as aragonite); B- the comparison of the experimental (a) and calculated diffraction pattern (b) for a mixture of aragonite and vaterite phase (1: 1) (particles size 5nm); C– the comparison between experimental (a) and simulated (b) electron-diffraction patterns for calcite phase (with particle size 5nm).

A. Samples prepared without a magnetic field

In samples prepared without a magnetic field we observed more spherically shaped CaCO_3 particles with a size of approximately one micron (Fig. 4 A). From dark-

field TEM imaging (Fig. 4 B) and electron diffraction patterns it was found that the particles consisted of larger crystals of calcite. In Fig. 5 A an experimental SAED pattern of the calcite phase in the [021] zone axis, and in Fig. 5 B, a simulated diffraction pattern of calcite in the same zone axes are shown. The position and the intensity of the diffraction spots in the experimental and simulated patterns match very well.

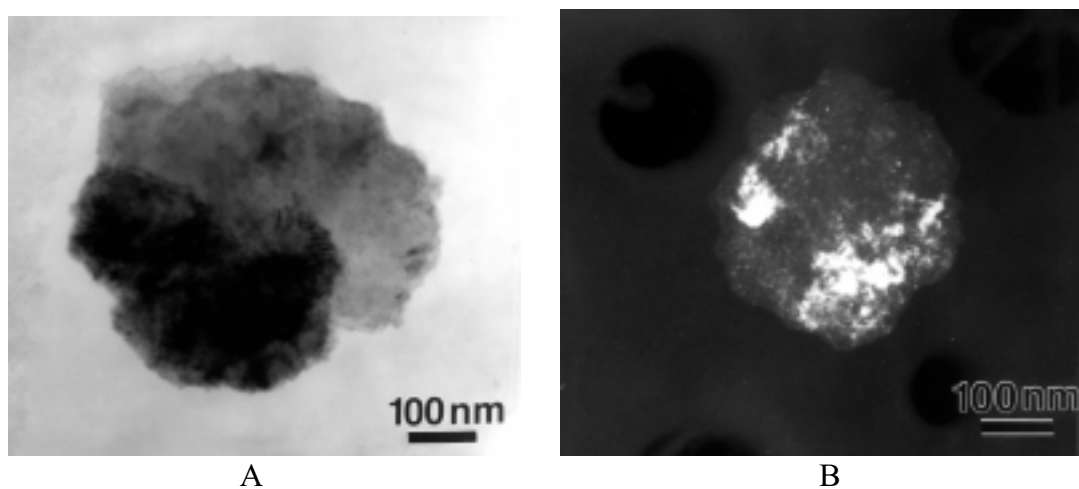


Figure 4. TEM micrograph (A bright field) (B dark field) of CaCO_3 particle, crystallized without magnetic field.

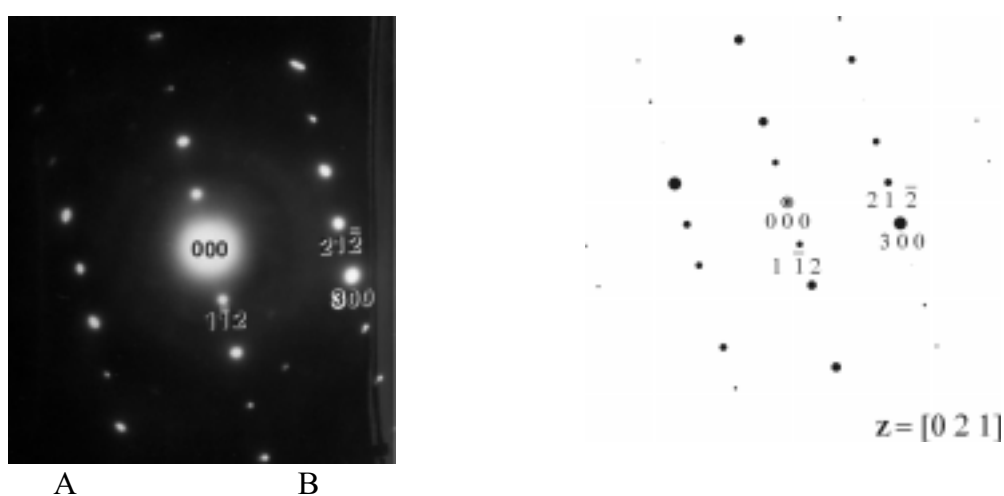
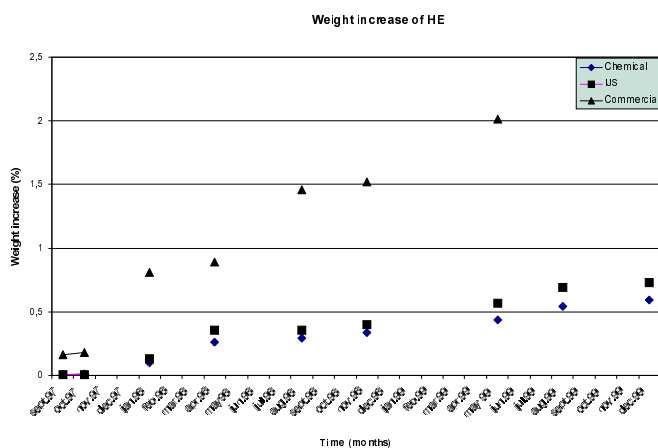


Figure 5. Experimental (A) and calculated (B) SAED patterns of calcite in zone axis [021].

Application

Besides the basic research in the laboratory, a pilot plant for magnetic water-treatment was constructed. This pilot plant consists of three different lines for tap-water treatment: a standard chemical treatment; a magnetic water treatment (MWT) with a commercial device; a magnetic water treatment with the device constructed in our laboratory. The pilot plant has been used for more than two years and the results look very promising for reducing the use of environmentally detrimental chemicals. The level of Zn and Cu impurities in the water used in the apartment-block testing was found to be 0.02 and 0.2 mg/litre.

Figure 6 A shows the results obtained from a pilot plant in a district-heating system (Figure 6 B). The weight gains of the heat exchangers, which were used in the three parallel pipelines equipped with three different devices against scaling, were followed. The commercial MWTD failed after one year of use and the water pressure in the pipeline decreased to such a level that it had to be excluded from the testing system. The MWTD constructed in our laboratory showed only a slightly higher weight gain than that achieved by the chemicals.



A

B

Figure 6. Weight gain of heat exchangers (A) in three different pipelines equipped with three different devices for the treatment of hard water; pilot-plant installed in a district heating system. Three parallel pipelines equipped with two different devices for MWT compared with chemical treatment. (B).

Conclusions

Comparing calculated and experimental SAED patterns it was concluded that particles of calcium carbonate, crystallized in the presence of a magnetic field, mainly consisted of a mixture of aragonite and vaterite. The match between calculated and experimental patterns is not complete indicating that some other phases, possibly calcite, were also present. Another reason for the mismatch could be the poor crystallization of the phases and numerous defects due to its size. Particles crystallized in the absence of the magnetic field were found to be the well-crystallized calcite phase.

The formation of aragonite rather than calcite under the influence of an applied magnetic field has been demonstrated. It has proved the existence and preferential growth of the crystal form, which does not cause scaling, or at least not to such an extent as calcite.

Our work has also shown a very promising practical application of this effect in a district-heating system in the city of Ljubljana. The water hardness in Ljubljana is ~14°dH and it also has an appropriate chemical composition for using the magnetic devices instead of chemicals or at least to diminish their use to a significant extent.

There is no doubt that magnetic water treatment works, however, more widespread acceptance of MWTDs would result from a more comprehensive understanding of the mechanism by which the process operates.

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Povzetek

Z uporabo rentgenske difrakcije in TEM opremljenega z analitskim sistemom Link AN-10000 EDXS smo določevali različne kristalne oblike CaCO₃. Kristale smo pripravili s kontroliranim sušenjem iz surove in modelne vode, ki smo ju obdelovali z magnetnim poljem primerne jakosti in smeri. Rezultate smo primerjali z rezultati analiz kristalov pripravljenih iz neobdelane vode. Ugotovili smo, da magnetno polje vpliva na tip kristalizacije in da se spremeni razmerje aragonit/vaterit/kalcit.

Izdelali smo prototip naprave za magnetno tretiranje vode in ga preizkusili v pilotni postaji, kjer smo obdelovali sanitarno vodo dve leti. Rezultati so pokazali, da prirastek teže na toplotnih izmenjevalci zaradi nastanka oblog, ni bistveno večji kot pri uporabi kemijskih mehčalcev trde vode.

Pri uporabi magnetnega polja za obdelovanje trde vode, kalcijev karbonat kristalizira pretežno v kristalnih oblikah, ki ne tvorijo trdnih oblog in je tak način tretiranja vode primeren za uporabo v praksi. Obloge, ki nastanejo, so pretežno aragonit, vaterit in v majhnih količinah kalcit in so lahko odstranljive. Obdelovanje trde vode s fizikalno metodo je ekološko pomembno saj se je mogoče na ta način izogniti uporabi kemikalij ali pa jo vsaj bistveno zmanjšati.