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The influence of the magnetic field on the crystallisation form of calcium carbonate and the testing of a magnetic water-treatment device

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Abstract

By using X-ray analysis and a TEM equipped with a link AN-10000 EDXS analysing system and an ultra-thin-window Si(Li) detector, different crystal forms of CaCO₃ crystals were characterised. These crystals were grown from tap water and model water both with and without a magnetic field. Separate aragonite crystals were formed in the treated water and clusters of calcite in the untreated water. We observed that under the influence of a magnetic field higher than 500 mT, the nucleation and subsequent growth of aragonite could be successfully used as a way of preventing scale. The prototype of a magnetic water-treatment device (MWTd) was constructed for testing in a pilot plant that treats tap water. It has been in use for more than 2 years and the results look very promising for reducing the need for chemically treated water. 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 MWTd designed and built in the IJS laboratory, showed only a slightly higher weight gain than that achieved with the use of chemicals. © 2001 Elsevier Science B.V. All rights reserved.

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1. 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 with an applied magnetic field has been

known for many 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 use chemicals to prevent the accumulation of calcium carbonate on surfaces exposed to hard water. This could have a significant impact on reducing the chemical pollution of the environment.

Different authors have emphasised various parameters including temperature, pH, strength and direction of the applied field, and the impurity elements present in tap water, that can influence

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the efficiency of water treatment with a magnetic field [6–10]. Some of these authors have reported large savings in both energy and the costs of descaling and process-downtime after the installation of magnetic water-treatment devices (MWTDD) in real systems. However, Baker [11] reports that installed MWTDDs have also often proved inefficient in real installations, though the reasons for their inefficiency were not examined in this case.

In some of our earlier work, we studied the influence of different parameters: strength and orientation of the magnetic field, and treatment time, on the nucleation and crystallisation of calcium carbonate [12]. In order to do this, we developed a MWTDD with Sm–Co [13]. Our more recent studies focused on the influence of different impurity elements on the crystallisation form of calcium carbonate in the presence of an applied magnetic field [16]. We are not the only group working on these effects; Herzog [3] and co-workers reported the positive influence of Fe^{2+} on the inhibition of calcite and the promotion of the aragonite crystal form, and Coetzee [14,15] has studied the influence of Zn^{2+} ions in ppb quantities on the preferential formation of aragonite in magnetically treated water. Our results agreed with those of Herzog and Coetzee, but we also showed that the effect observed with Fe^{2+} and Zn^{2+} ions could also be obtained with Cu^{2+} [16]. Other opinions exist, Busch [17] et al. reported a change in the pH difference between the surface and the bulk of the magnetically treated water which, they suggested, 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, the 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.

2. Experimental

In this study, we used model water that was prepared following the method of Parsons [19],

who reported that the optimum concentration of Ca^{2+} ions for the best response to the magnetic treatment was 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 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 of 0.5 l/min, CaCO_3 particles begin to precipitate according to the following equation:



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, we used an applied DC field of between 0.5 and 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 was an equilibrium system of CaCO_3 – $\text{Ca}(\text{HCO}_3)_2$ – H_2O .

A controlled drying procedure at 70°C and 40% relative humidity in a Weiss humidity chamber obtained the crystals of CaCO_3 . The crystals were analysed with an X-ray diffractometer and a TEM. Samples for the TEM investigation were prepared by crystallising the CaCO_3 particles in a magnetic field; this was directly from tap water on a hollow carbon-coated Cu grid or by filtering the crystals from the model water through a 0.2- μm nucleopore filter. In the later cases, 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. Both types of samples were examined using a Jeol 2000 FX TEM operated at 200 kV. The chemical compositions of the phases were determined using a Link AN-10000 energy-dispersive X-ray spectroscopy (EDXS) system with an ultra-thin-window Si(Li) detector that was connected to the TEM.

3. Results and discussion

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

Fig. 1 shows the X-ray diffraction spectra of the crystals obtained from magnetically treated and untreated samples; the results of the quantitative analysis are in Table 1.

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 CaCO_3 precipitating in the vaterite form.

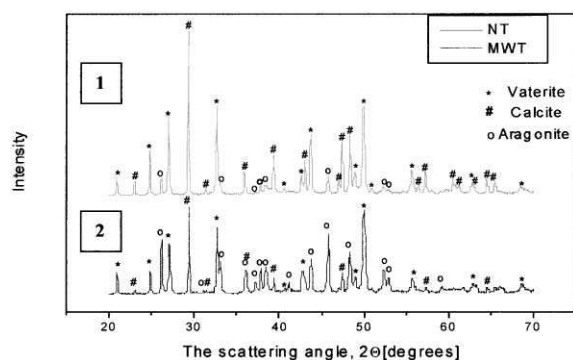


Fig. 1. X-ray diffraction spectra of: (1) untreated and (2) magnetically treated model water.

Table 1

Mass percentages of the different crystal forms of calcium carbonate for the samples in Fig. 1

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

3.1. TEM observations

3.1.1. Samples prepared in a magnetic field

For the samples crystallised in a magnetic field of 500 mT, rectangular calcium carbonate particles of a few microns were found. In Fig. 2A, a dark-field TEM micrograph of a six-angled CaCO_3 particle is shown. In Fig. 2B, which shows a region of the same particle at a higher magnification, we can see that the particle consists of very fine crystallites between 1 and 5 nm. From the selected-area electron-diffraction patterns (Fig. 3A), 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 the electron-diffraction patterns for various phases and compared them to the experimental electron-diffraction patterns. For these simulations, we used the EMS computer-program package (electron microscopy simulation program from P. Stadelmann, EPFL-CIME, Lausanne, Switzerland) [20]. In Fig. 3B, we show the comparison of the (a) experimental, and (b) simulated diffraction patterns. For the simulated pattern, we used a mixture of aragonite and vaterite phases in the ratio 1:1, and crystallites of 5 nm. The match between both the patterns was partial. However, as we can see from Fig. 3C, the (a) experimental and (b) simulated patterns for the calcite phase was not as good as for the aragonite. From this, we can conclude that during the crystallisation of CaCO_3 in a magnetic field, the majority of particles consist of a mixture of aragonite and vaterite crystals.

3.1.2. Samples prepared without a magnetic field

In samples prepared without a magnetic field, we observed rounded CaCO_3 particles of approximately $1\ \mu\text{m}$ (Fig. 4A). From dark-field TEM imaging (Fig. 4B) and from electron-diffraction patterns, we found that the particles consisted of large calcite crystals. In Fig. 5A, we can see an experimental SAED pattern of the calcite phase in the $[021]$ zone axis, and in Fig. 5B, a simulated diffraction pattern of calcite in the same zone axes. The position and the intensity of the diffraction spots in the experimental and simulated patterns match very well.

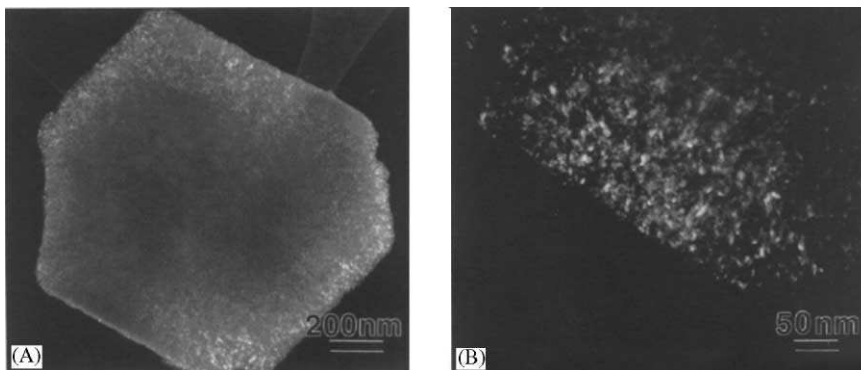


Fig. 2. Dark-field TEM micrograph of a regularly shaped CaCO_3 particle crystallised in a magnetic field (A); consisting of crystallites up to 5 nm (B).

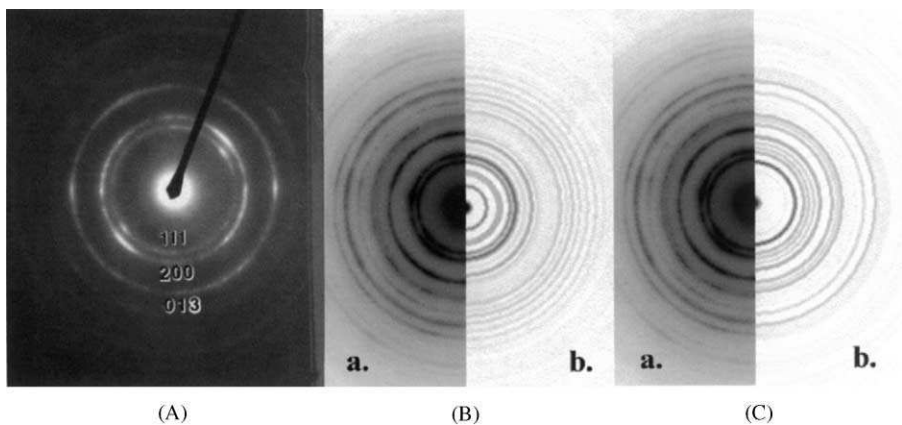


Fig. 3. (A) Experimental selected-area electron-diffraction pattern (indexed as aragonite); (B) the comparison of the experimental (a) and calculated diffraction pattern (b) for a mixture of aragonite and vaterite phase (1 : 1) (particle size 5 nm); (C) the comparison between experimental (a) and simulated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

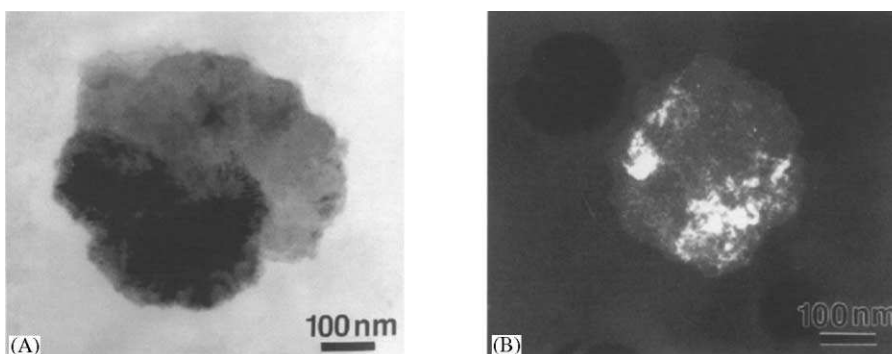


Fig. 4. TEM micrograph (A—bright field, B—dark field) of CaCO_3 particle, crystallised without magnetic field.

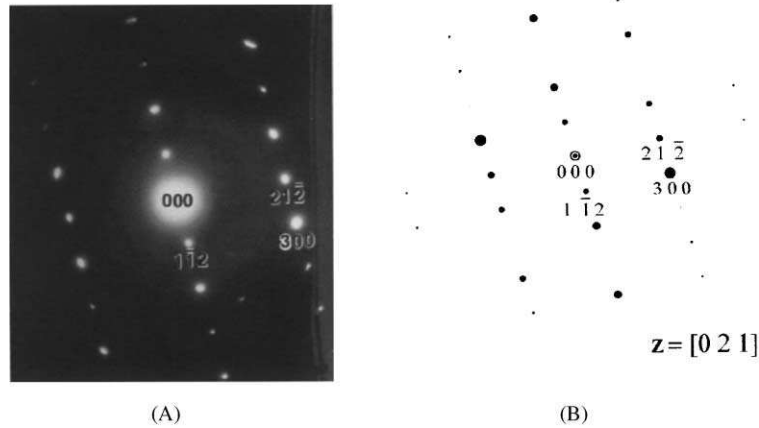


Fig. 5. Experimental (A) and calculated (B) SAED patterns of calcite in zone axis [0 2 1].

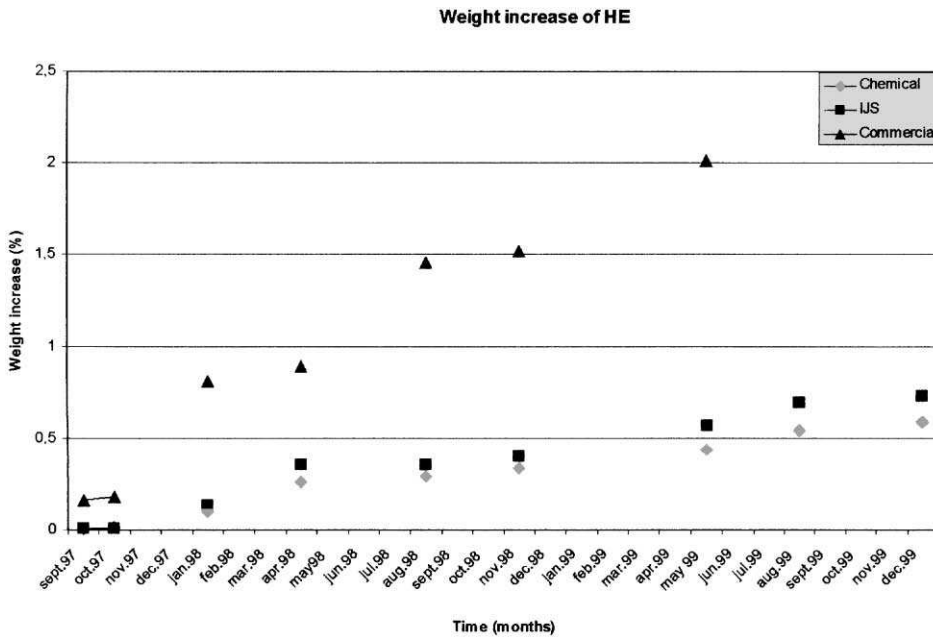


Fig. 6. Weight gain of heat exchangers in three different pipelines equipped with three different devices for the treatment of hard water.

3.2. Application

Besides doing basic research in our laboratory, we have constructed a pilot plant for magnetic water treatment in an apartment block in Ljubljana, Slovenia. This pilot plant consists of three different lines for tap-water treatment: a standard chemical treatment; magnetic water treatment

(MWT) using a commercial device; and magnetic water treatment using the device constructed in our laboratory. 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/l.

The pilot plant has been in operation for more than 2 years and the results look very promising for reducing the need for chemically treated water.

Fig. 6 shows the results obtained from the pilot plant. We followed the weight gains of the heat exchangers used in the three parallel pipelines. The commercial MWTD failed after 21 months, and the water pressure in the pipeline decreased to such an extent 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 with the use of chemicals.

4. Conclusions

Comparing calculated and experimental SAED patterns, we can conclude that the particles of calcium carbonate which were crystallised in a magnetic field, consisted mainly of a mixture of aragonite and vaterite. The match between simulated and experimental patterns was not complete, indicating that some other phases, possibly calcite, were also present. Another reason for the mismatch could be the poor crystallisation of the phases and numerous defects. Particles crystallised in the absence of the magnetic field were found to be in the well-crystallised calcite phase.

The formation of aragonite rather than calcite under the influence of an applied magnetic field has been demonstrated. We have 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 an apartment-block heating system in the city of Ljubljana. There is no doubt that magnetic water treatment works; however, more widespread acceptance of MWTDs would result from a better understanding of the mechanism by which the process operates.

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