

IDENTIFICATION OF CRYSTALLIZATION FORMS OF CaCO₃ WITH FTIR SPECTROSCOPY

IDENTIFIKACIJA KRISTALIZACIJSKIH OBLIK CaCO₃ S FTIR SPEKTROSKOPIJO

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It has been established that nucleation and crystallization of calcium carbonate in hard water can be influenced by magnetic fields. In this study NGIA (Near Grazing Incidence Angle) reflectance FTIR (Fourier Transformed Infrared) spectroscopy has been used for the identification and characterization of the crystallization forms of calcium carbonate influenced by magnetic field treatment. Spectra obtained from thin films of calcium carbonate crystals, grown from hard water on different substrates, have been studied. The influence of impurity ions, which are usually present in ordinary tap water (such as iron, copper and zinc) and appear to favor the formation of aragonite rather than calcite crystals after the magnetic treatment, was confirmed. The morphological differences between magnetically treated and untreated samples, i.e. crystals grown from these samples, were investigated by means of scanning electron microscopy (SEM).

Key words: magnetic water treatment, FTIR spectroscopy, calcite, aragonite

Ugotovljeno je bilo, da je na nukleacijo in kristalizacijo kalcijevega karbonata v vodi mogoče vplivati z delovanjem zunanega magnetnega polja. Za identifikacijo in karakterizacijo kristalizacijskih oblik kalcijevega karbonata po tretiranju vode z magnetnim poljem smo uporabljali NGIA (Near Grazing Incident Angle) refleksijsko FTIR (Fourier Transformed Infra Red) spektroskopijo. Snemali smo spektre na tankih filmih kalcijevega karbonata, ki smo jih dobili s sušenjem trde vode na različnih substratih. Tako smo študirali vpliv elementov v sledovih, kot so železo, baker in cink, ki so navadno prisotni v vodovodni vodi, na prednostno tvorbo aragonita namesto kalcita ob istočasnem delovanju magnetnega polja. Morfološke razlike med magnetno obdelanimi in neobdelanimi vzorci, to je med kristali dobljenimi s kontroliranim sušenjem netretirane in tretirane modelne vode smo opazovali z vrstičnim elektronskim mikroskopom.

Ključne besede: tretiranje trde vode z magnetnim poljem, FTIR spektroskopija, kalcit, aragonit

1 INTRODUCTION

A number of investigations have been carried out on the effects of magnetic field on hard water¹⁻⁵. It has been established that nucleation and crystallization of calcium carbonate from hard water can be influenced by a magnetic field and it is no longer necessary to always apply chemical methods for water softening.

Calcite, the stable crystal modification of calcium carbonate, grows from hard water in clusters, which after a certain time form a solid scale firmly attached to the surface where the nucleation of crystals started. Aragonite, identified in the magnetically treated water, grows in unattached orthorhombic crystals, which are easily removed from the surface. Under normal temperature and pressure conditions, aragonite is an unstable crystal modification which spontaneously transforms into calcite. Another crystal modification of CaCO₃ is vaterite, which is the least stable of the three anhydrous calcium carbonate polymorphs and is gradually transformed into either calcite or aragonite.

Different authors have emphasized various parameters (temperature, pH, strength and direction of the applied magnetic field, impurity elements, etc.), which influence the efficiency of the treatment with the magnetic field⁶⁻¹⁰. In our previous work the influence of different parameters on the nucleation and crystallization

of calcium carbonate was studied¹¹. For this purpose a special device with permanent magnets based on Sm - Co was developed and constructed¹². In the present study we have focused on the influence of impurities of different elements on the crystallization form of calcium carbonate in the presence of an applied magnetic field. Herzog and coworkers reported the influence of ferro ions on the inhibition of calcite and promotion of the aragonite crystal form³. Coetzee and coworkers^{13,14} studied the influence of Zn²⁺ ions, in ppb quantities, on the preferential formation of aragonite in magnetically treated water. There are other authors too, who have studied the influence of a great number of different trace elements, such as Fe²⁺ (3,18), Fe³⁺ (3,18), Mn²⁺ (18), Mg²⁺ (18,19,20,21,22,23), Zn²⁺ (13,14,24), Cu²⁺ (17) as impurities in the water system.

Our interest was to find an explanation for the changes in the crystallization form of calcium carbonate (crystals grown from the hard water) in the presence of an applied magnetic field.

2 EXPERIMENTAL

For the experimental work a model system based on bidistilled deionized water with a maximum resistivity of 18 MΩ/cm was used. Solutions of 0.035 M

concentration Na_2CO_3 and CaCl_2 were added to the water as precursors for obtaining calcium carbonate (based on the literature data of Higashitani et al.⁶). The concentration of Ca was 350 ppm¹⁵.

To study the influence of impurity ions in ppm quantities, we used polished platelets of different metals (5 x 2.5 cm) as substrates for FTIR (Fourier Transformed Infra Red) spectroscopy thin films analyses as well as glass substrates covered by a thin layer of $\text{SnO}_2\text{:F}$. The metal platelets were made of Fe, Cu and Zn. These platelets were then covered with a thin film of model water solution and the samples were dried under controlled conditions (70°C and 40% humidity). For every substrate we prepared a treated and untreated sample. Treated water was exposed to a magnetic field of 200 - 280 mT during drying using permanent magnets based on Sm - Co. The crystals obtained by evaporation of water were analyzed by NGIA (Near Grazing Incident Angle) FTIR spectroscopy and scanning electron microscopy (SEM).

A Perkin Elmer Spectrometer Model 2000 equipped with Spectra Tech NGIA, which enables measurements at 80° with P-polarized radiation has been used to characterize the thin films of deposited material.

For scanning electron microscopy we prepared samples of model water and water with 10 ppm Cu^{2+} ions on a graphite substrate. We used a JEOL JSM - 5800 scanning electron microscope and analyzed samples by qualitative and semiquantitative EDS analysis.

To follow the differences between the chemical method of water treatment with phosphates and water treatment with magnetic devices we constructed a pilot station with three simultaneously operating lines. In the first line a chemical softener was used, in the second a commercial magnetic device and in the third line a magnetic treatment device based on Sm - Co permanent magnets which was manufactured at our institute. To study the effectiveness of our own magnetic device the heat exchangers from every line were weighed several times during a two year period to check how much calcium carbonate was deposited inside.

3 RESULTS AND DISCUSSION

Each vibrational spectrum consists of a set of internal modes for each crystallographically distinct anion, with frequencies perturbed only slightly from the free ion values, and a set of low frequency lattice modes characteristic of the particular crystal structure¹⁶. The mid-infrared spectra of all carbonate minerals tend to look alike so an IR spectrum is a useful identification tool for this anion. The spectrum obtained from a thin film grown on Cu platelets (**Figure 1**) shows only the internal modes which appear in the normally accessible region of the infrared. On the spectrum of the untreated sample the fundamental bands of calcite can be seen at: 708 cm^{-1} (ν_4 - in-plane bend), 883 cm^{-1} (ν_2 - out-of-plane

bend) and at about 1400 - 1500 cm^{-1} (ν_3 - asymmetric stretch). The frequency for asymmetric stretching absorption is very broad and intense, so the band assignment is not precise. In contrast, the spectrum of magnetically treated water displays split bands for out-of-plane bending vibration and asymmetric stretching which is characteristic for the aragonite crystal structure. It is hard to say for sure, because of the overlapping of the bands, but it appears that there are also bands of vaterite. Vaterite has a band at ~750 cm^{-1} which can be seen in the spectrum of the treated sample only. The bands of aragonite and vaterite can not be seen in the spectrum of calcium carbonate obtained from the untreated model water. Similar results were obtained with iron and zinc substrates but when the spectra of calcium carbonate were obtained from water deposited on the $\text{SnO}_2\text{:F}$ coated glass (**Figure 2**) there was no evidence of the influence of the applied magnetic field. Both spectra were almost identical showing only characteristic bands of calcite.

The influence of metal impurities from the metal substrates on the crystallization of calcium carbonate is obvious. Those metals are almost always present in tap water too and they impact on the crystallization of calcium carbonate contained in it.

It should be noted that small frequency shifts of the observed LO modes in the spectra of the thin films were expected and are attributed to the observed LO modes which systematically appear at wave numbers higher than the corresponding TO modes detected in the IR absorption and/or diffuse reflection spectra. They correspond fairly well to the already known LO modes of calcite and aragonite monocrystals¹⁶. In addition, their relative intensities conform to observed TO spectra,

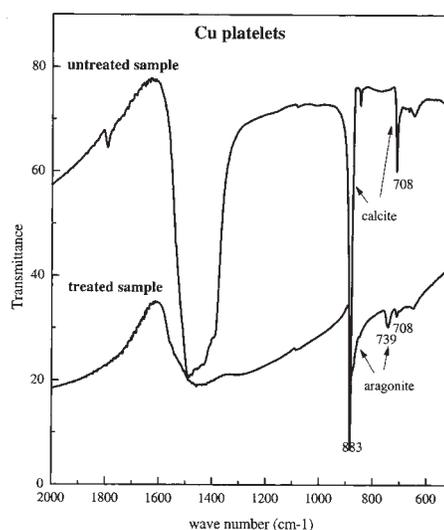


Figure 1: NGIA FTIR spectra obtained from a thin film of calcium carbonate crystals grown from treated and untreated water on a copper platelet

Slika 1: NGIA FTIR spektri tankih filmov kalcijevega karbonata dobljenega z sušenjem netretirane modelne vode

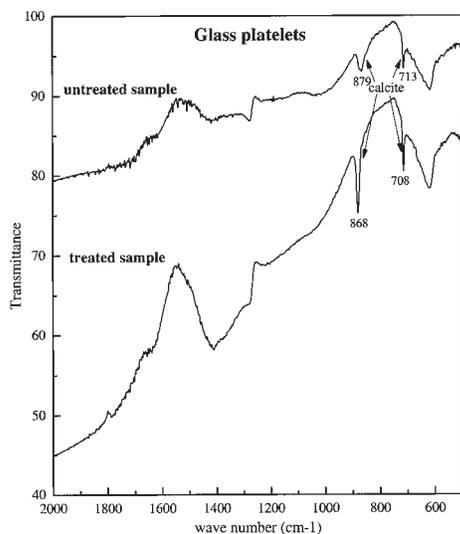


Figure 2: NGIA FTIR spectra obtained from a thin film of calcium carbonate crystals grown from treated and untreated water on a glass platelet

Slika 2: NGIA FTIR spektri tankih filmov kalcijevega karbonata dobljenega z sušenjem tretirane modelne vode

undoubtedly proving the presence of the aragonite in the spectra of magnetically treated samples.

The changes which appear in the model water after magnetic water treatment can also be followed with scanning electron microscopy. In **Figure 3 and 4** there are SEM micrographs of calcium carbonate crystals obtained from untreated and treated model water, respectively, and it is clear that the crystals grown from the treated sample are bigger than those which crystallized from the untreated sample which is in accordance with the existing data^{2,25}. An increase in the size of particles can have two beneficial effects². First, the larger crystals will not coagulate to form scale in the same way that smaller crystals would. This is the

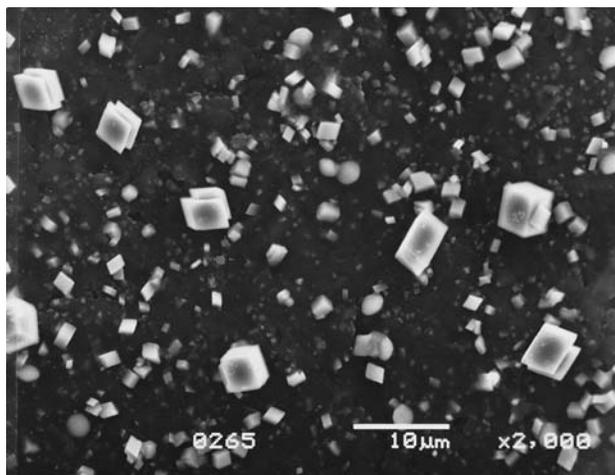


Figure 3: SEM micrograph of calcium carbonate crystals obtained from untreated model water

Slika 3: SEM slika kristalov kalcijevega karbonata dobljenega iz netretirane modelne vode

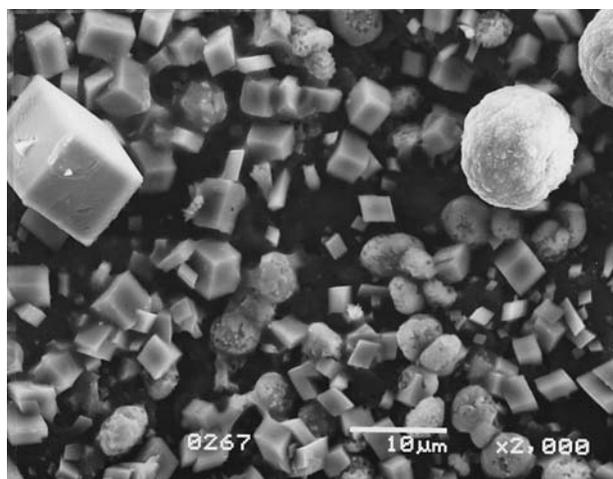


Figure 4: SEM micrograph of calcium carbonate crystals obtained from treated model water

Slika 4: SEM slika kristalov kalcijevega karbonata dobljenega iz tretirane modelne vode

purpose of the magnetic water treatment units. Secondly, the presence of the larger crystals disrupts the equilibrium between the fluid and any existing scale. Smaller particles, in general, dissolve more easily so larger particles will reduce the local concentration of calcite in the solution and remove the existing scale.

If we add copper ions to the model water (10 ppm Cu^{2+} solution) and treat it with a magnetic field, we obtain a lot of spherules (**Figure 5**) which are due to vaterite formation¹⁴. The cubes and spherules are much bigger than in the untreated sample, particularly when compared with crystals from pure water. EDS analysis of the cubes reveals just calcium carbonate, while the spherules appear to be composed of calcium carbonate with copper ions accumulated in them (**Figure 6**). This indicates that trace amounts of copper in hard water

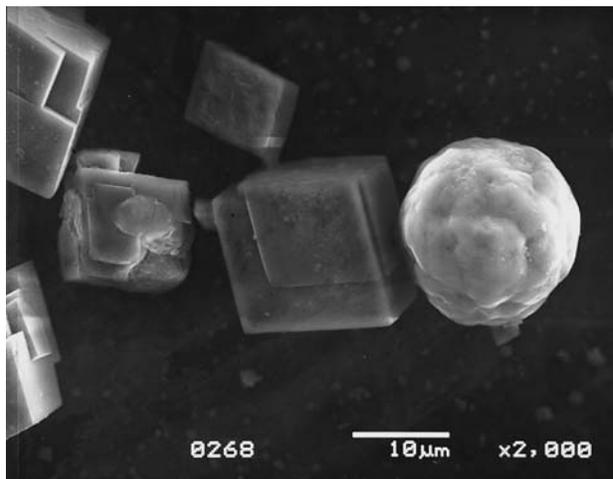


Figure 5: SEM micrograph of calcium carbonate crystals obtained from treated model water with copper impurities

Slika 5: SEM slika kristalov kalcijevega karbonata dobljenega iz tretirane modelne vode z dodatkom 10 ppm Cu

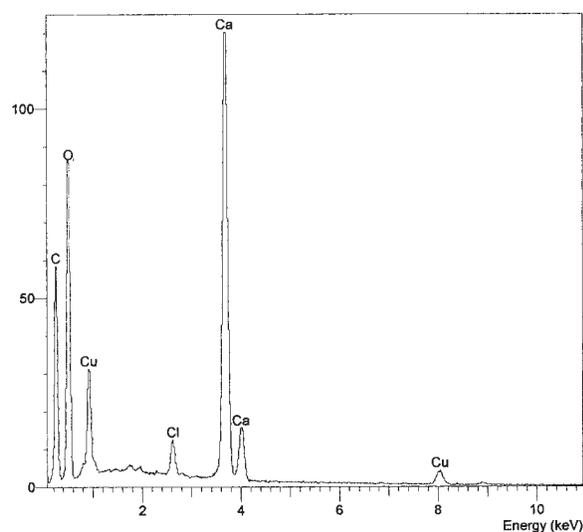


Figure 6: EDS analysis of spherulites
Slika 6: EDS analiza kroglic

alters the nucleation and crystallization of calcium carbonate.

The results of weighing the calcium carbonate deposits from the heat exchangers are shown in Figure 7. The weight increase of the heat exchanger in the chemical treatment line and the line with the magnetic water treatment device constructed in our laboratory does not differ significantly. In the case of the commercial magnetic treatment device the weight of the heat exchanger increased rapidly and the device had to be removed from the line because it lowered the water pressure.

4 CONCLUSIONS

It is already known, and indeed been confirmed several times, that it is no longer necessary to always apply chemical means to prevent the accumulation of calcium carbonate on surfaces exposed to hard water, which is of great importance in reducing the chemical pollution of the environment.

The application of a magnetic field to hard water successfully prevents the growth and agglomeration of calcium carbonate as calcite, but to obtain optimal results it is very important that the magnetic field has the proper strength and direction^{4,6,15}.

The most important aspect of the present work is the new approach of using FTIR spectroscopy as a method for characterizing thin films, which gives the possibility of rapid qualitative analysis of water treated with an external magnetic field.

FTIR spectroscopy appears to be a useful method for characterization and identification of different forms of calcium carbonate. With a new approach and the application of FTIR spectroscopy for thin film characterization, the crucial influence of impurity

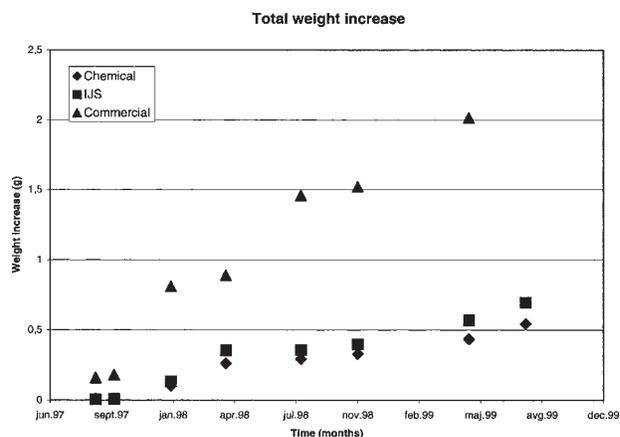


Figure 7: Diagram of effectiveness of water softening methods (pilot station)

Slika 7: Diagram učinkovitosti metode mehčanja trde vode (pilotna postaja)

elements on the crystallization of calcium carbonate under the influence of the applied magnetic field was confirmed. Trace elements, such as iron, copper and zinc inhibit the growth of certain crystal planes and promote others.

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