

Influence of magnetic field on the aragonite precipitation

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Abstract

Many laboratory investigations of magnetic water treatment (MWT) for scale control explained the formation of less compact scales by raised portion of aragonite, which is needle-like and less adhesive than rhombohedral calcite crystals, while our experiment was conducted with tap water, which contains Mg^{+2} and Fe^{+2} ions in concentrations exceeding thresholds for calcite inhibition, common for major tap waters. MWT efficiency was evaluated by amounts of scale precipitated in boilers and pipes during three-weeks run of two parallel experimental lines—one with and another without magnetic treatment. All scales were identified by X-ray diffractometer to be aragonite, but in the case of magnetic treatment, scales occurred in much smaller amounts: the scale on heating copper-pipe spiral was 2.5-times thinner due to MWT and in zinc-coated steel pipe occurred as very thin powder-like coating, while in the line without the treatment abundant hard lining was formed. The scales' morphology was observed by scanning electron microscope: the husks from both lines consisted of parallel distributed needles, but these crystals were about four times thinner in the case of MWT. The present work demonstrates that hard scale deposits can form even under conditions where aragonite precipitates predominantly, and that MWT can also affect the crystallization of this polymorph in a manner conducive to scaling control.

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1. Introduction

Effects of magnetic field on water dispersion and crystallization processes are interesting not only from fundamental studies point of view but also from practical one. The build up of scale deposits is a common and costly problem in many industrial processes using natural water supplies. Different traditional chemical methods are used for the scale prevention: either the pre-precipitation of the scale former with lime or soda ash, the addition of scale inhibiting reagents, or the replacement of the scale former with soluble ions by ion exchange. These methods are effective, but they can be expensive and substantially change the water chemistry.

Environmental and economical considerations are strong motivations for developing methods which would prevent hard scales just by modifying the way of the precipitation.

Such a method is magnetic water treatment (MWT), which is widespread used in recent years. It is possible to find different kind of MWT devices on the market. These commercial devices consist of either electromagnets used for high water flow capacities in industrial plants, or of permanent magnets for lower capacities.

Magnetic fields in these devices are either static or dynamic and are relatively weak (from 0.05 to 1 V s/m^2). Although the velocity of water flow through a magnetic field is recommended to be from 0.5 to 2 m/s, some interesting results were also found at hydrostatic exposition of laboratory prepared solutions and dispersions to a static magnetic field (Higashitani et al., 1993, 1995). Exposition times, recommended for the effective treatment, in the cases of pulsating magnetic fields or flows of water through the gap between alternating magnets are of order 10^{-1} s (Oshitani et al., 1999a), but in the cases of stationary exposition to the static magnetic field they should be much higher (Higashitani et al., 1993).

Practical use of MWT devices has shown that the scaling still occurs, but scales are in smaller amounts, less compact and removable.

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The influence of weak magnetic fields on the crystallization and colloidal stability in aqueous systems has been investigated by many authors, for the last few decades.

Although the existence of MWT effects seems to be now well documented, this issue is still controversial one. While some authors (Grimes, 1988; Parsons et al., 1997) report about scale reduction by MWT, some others have found only minor or non-influence (Busch et al., 1997).

There are some evidences that nucleation and crystal growth of calcium carbonate in hard water can be influenced by magnetic field.

First, some researchers have found that the portion of aragonite was raised after MWT at very different conditions: hydrostatic or hydrodynamic exposition to static magnetic field of either pure solution or tap water (Grimes, 1988; Higashitani et al., 1993; Barret and Parsons, 1998; Kobe et al., 1998, 2001; Coey and Cass, 2000; Bottello-Zubiate et al., 2004; Knez and Pohar, 2005). For *static treatment* (i.e., static exposition of water solution to static magnetic field), suppressed nucleation, but enhanced crystal growth was indicated (Higashitani et al., 1993; Barret and Parsons, 1998). The nucleation rate depends on the way and on the time of the solution exposure to the magnetic field (Holysz et al., 2002).

Other researchers have found that the nucleation of CaCO₃ in the bulk of the solution was enhanced by *dynamic treatment*, which was carried out by passing pure solution or tap water through a static magnetic field (Martynova et al., 1967; Kronenberg, 1985; Bogatin et al., 1999) or by static exposition of pure solution to an alternating magnetic field (Wang et al., 1997).

Gabrielli et al. (2001) have electrochemically confirmed that the precipitation of CaCO₃ was occurring in whole volume in the case of pure or salted solution. **Tested solutions were circulated along permanent magnets.** Magnetic field yield by alternately arranged magnets was more effective than homogeneous magnetic field. Furthermore, the effectiveness was higher with increasing the flow velocity up to 1.8 m/s and the number of circulations through the magnetic field.

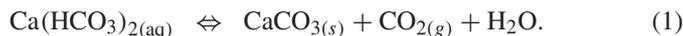
Until now, no definite theory of these effects has been presented, but several explanations have been proposed. The mechanism is not related to the magnetic attractions amongst colloidal particles as the applied magnetic fields are weak and most of particles are non-magnetic. Hypothetically, the mechanism comprises at least two types of interactions:

- magnetically modified hydration of ions and surfaces of dispersed particles (Higashitani et al., 1993, 1995; Oshitani et al., 1999a,b), and
- Lorentz force effects (Tombacz et al., 1991; Lipus et al., 2001).

At static magnetic treatment the hydration can be affected while at dynamic magnetic treatment Lorentz force action additionally can appear. Modified hydration may last several days (Higashitani et al., 1993) and Lorentz force modification of the electric double layer on solid surfaces is estimated to last a few hours after the treatment (Lipus et al., 2001). Both modifications may affect the crystallization and coagulation processes during and after MWT.

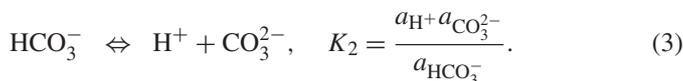
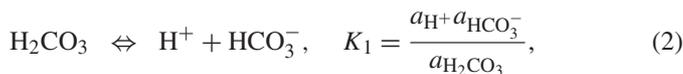
2. Scale-control by morphology modification

In most scales, calcium carbonate is a dominant component, because natural waters are rich with Ca²⁺ ions and carbonic species (CO₂, HCO₃⁻, CO₃²⁻) and usually have pH values less than 9. In this range, the over-saturation to CaCO₃ may occur by different causes (Stumm and Morgan, 1996; Kristiansen, 1975). Calcium carbonate is only slightly soluble in pure water, but more soluble when carbon dioxide is present in water:

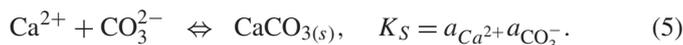
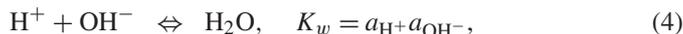


As the solubility of CO₂ gas decreases with increasing Temperature or decreasing pressure, the solution tends to restore the equilibrium (1) by the shift toward CaCO₃ precipitation.

Simultaneously, the equilibrium (1) depends on pH. A small part of dissolved CO₂ forms carbonic acid, which weakly dissociates in two steps (Eqs. (2) and (3)) and determines pH:



When dissociated hydrogen ions are neutralized by an addition of OH⁻ ions (Eq. (4)), the solution tends to restore the equilibrium (Eqs. (2) and (3)) with higher concentrations of HCO₃⁻ and CO₃²⁻ ions. As the solubility of CaCO₃ directly depends on CO₃²⁻ concentration (Eq. (5)), pH rise causes the precipitation:



Theoretically, the equilibrium concentration of Ca²⁺ at particular pH and Temperature can be determined from upper equilibria. Eq. (8) is derived from electro-neutrality equation (6), where the concentration of CO₃²⁻ is expressed from (5), the concentration of HCO₃⁻ from (3) and of OH⁻ from Eq. (4). The activity factors $f_z = a/c$ (where z is ion valence) depend on ionic strength I of the solution and can be calculated by Eq. (7) for diluted solutions.

$$2c_{\text{Ca}^{2+}} + c_{\text{H}^+} = 2c_{\text{CO}_3^{2-}} + c_{\text{HCO}_3^-} + c_{\text{OH}^-}, \quad (6)$$

$$f_z = 10^{-0.5z^2\sqrt{I}/(1+\sqrt{I})}, \quad I < 0.02 \text{ mol/l}, \quad (7)$$

$$c_{\text{Ca}^{2+}} = \frac{\frac{K_w}{f_1^2} - c_{\text{H}^+}^2 + \sqrt{\left(\frac{K_w}{f_1^2} - c_{\text{H}^+}^2\right)^2 + 8K_S c_{\text{H}^+}^2 \left(\frac{c_{\text{H}^+}}{K_2 f_2} + \frac{2}{f_2^2}\right)}}{4c_{\text{H}^+}}. \quad (8)$$

Some water supplies are already over-saturated when entering the pipeline systems; others may get over-saturated during processing them through the systems. The resulting precipitation leads to numerous technical and economical problems in industrial plants and domestic equipment due to blocking the flow of water in pipes and limiting heat transfer in heat exchangers.

Precipitated CaCO_3 may be a mixture of various phases: crystalline phases, amorphous and hydrated phases. The crystalline phases are (Lippmann, 1973):

- calcite (with trigonal structure, usually in form of rhombohedral crystals),
- aragonite (with orthorhombic structure, often in form of needle-like crystals) and
- vaterite (with hexagonal structure, often in form of spherical crystals).

Among these phases calcite is thermodynamically the most stable at ambient Temperature and atmospheric pressure and usually prevails in the precipitation from pure $\text{Ca}(\text{HCO}_3)_2$ solutions (Rudert and Müller, 1982).

Aragonite and vaterite are kinetically favorable and may appear as a first form, recrystallizing to calcite during the aging of the precipitate. Vaterite is the least stable anhydrous polymorph (Wolf et al., 2000), while aragonite is quite stable when precipitates from hot waters (Rudert and Müller, 1982).

In water processing systems, which are usually supplied with natural waters containing different ions and dispersed particles, the nucleation as the first step of the crystallization process is important. It mostly occurs on surfaces of dispersed minerals and especially on walls of pipeline and heating equipment. This is a result of lower surface energy of nuclei on the wall or a result of higher over-saturation degree at the wall, at which water is heated or used as a coolant. Consequently, the composition and structure of the scale depend also on the material on which it has arisen (Kozic et al., 2004). On steel and zinc-coated steel, some aragonite appears even from pure solutions; its portion rises with increasing Temperature up to about 50% at 90 °C (Rudert and Müller, 1982).

Furthermore, natural waters contain some ions which are capable to retard the formation of calcite and consequentially give the priority to the formation of aragonite even at room Temperature. The majority of terrestrial waters, for instance in the USA (Stumm and Morgan, 1996), contains Mg^{2+} and Fe^{2+} with concentrations that exceed the threshold for the calcite inhibition, which is 10^{-8} mol/l for Fe^{2+} and 10^{-4} mol/l for Mg^{2+} (Gutjahr et al., 1996). The same ions may also have an important role in scale-control by MWT. Holysz et al. (2003) observed combined effect of static magnetic treatment and presence of Mg^{2+} or Fe^{2+} ions on calcium carbonate precipitation.

3. Experimental

Two experimental lines (Fig. 1) were installed to compare the amounts of the scales precipitated in two identical boilers and pipes from magnetically treated (MWT line) and untreated water (blank line). Both lines were supplied by tap water at adjusted input (0.2 l/min) running continuously for three weeks. In MWT line, water was circulated through the magnetic device to intensify its effectiveness and to fulfill the effectiveness condition of water velocity in MWT device, which is from 0.5 to 2 m/s. In our case, the velocity through the gape of the magnetic device was adjusted on 1.25 m/s (water circulation flux

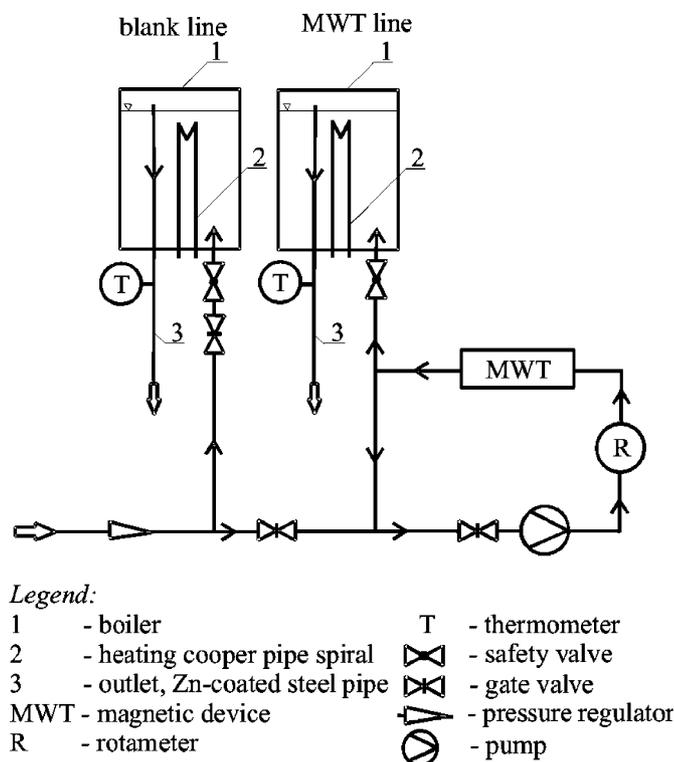


Fig. 1. Scheme of equipment for MWT—scale control test.

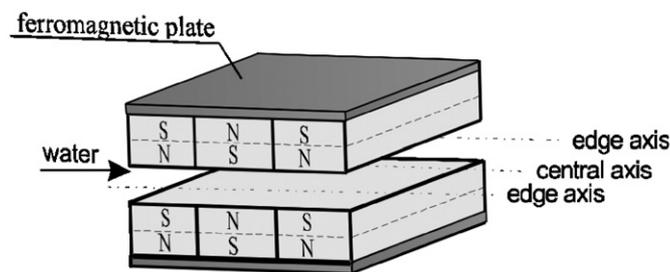


Fig. 2. The arrangement of magnets in MWT device.

5.3 l/min). The retention time of water in the magnetic field was 0.1 s. The water was heated in boilers from 16 to 70 °C. Some parts of the equipment in which an abundant precipitation was expected, such as heating copper-pipe spirals and some segments of zinc-coated steel pipes for hot water conduction, were weighted before and after the experiment.

The applied MWT device was constructed with alternately arranged permanent Neodim magnets (Fig. 2), yielding a magnetic field with three maximums of density 0.6 and 0.8 V s/m² (Fig. 3a). Density curve along the axis at the edge of the gap (indicated as edge axis in Fig. 2) is only slightly lower than the curve along the center axis. Data in Fig. 3 were monitored by Hall effect method with a microprobe point-measurements (Goričan et al., 2000).

Tap water had a total hardness of 14 German degrees, pH of 7.5, electrical conductivity of 485 $\mu\text{S}/\text{cm}$, turbidity of 0.35 NTU and concentrations given in Table 1.

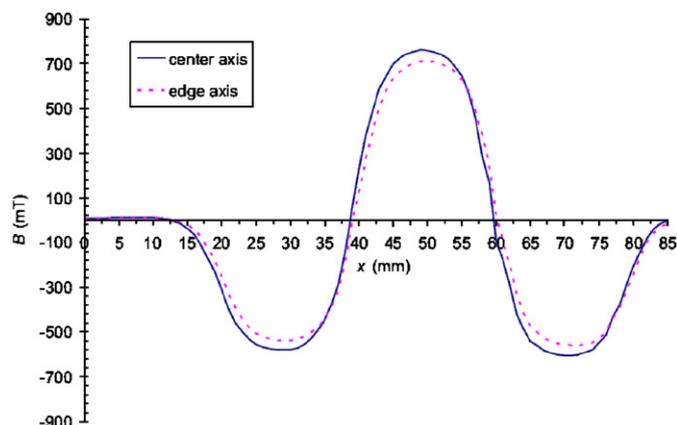


Fig. 3. The distribution of magnetic field density in the gap of MWT unit.

Table 1
The composition of tap water in our test

Cations	<i>c</i> (mmol/l)	Anions	<i>c</i> (mmol/l)
Ca ²⁺	1.80	Cl ⁻	0.61
Mg ²⁺	0.71	NO ₃ ⁻	0.34
Na ⁺	0.04	SO ₄ ²⁻	0.10
K ⁺	0.02	free CO ₂	0.45

4. Results and discussion

The scale precipitated on hot surface of the heating spiral in both lines. After the lining had reached the particular thickness, it started to crack and husks were accumulated on the bottom of the boiler. Photographs of scales are presented in Fig. 4.

In the blank line, scale on the heating spiral was 3.5 mm thick in average. On the boiler's bottom, the sediment consisted of well-formed crystals (diameter 2–3 mm) and scale husks (also 3.5 mm). The outlet pipe was almost blocked by the abundant and compact scale (Fig. 4c).

In MWT line, lining on heating spiral was also present, but the amount of sediment on the bottom was much smaller—for about 70%, and it consisted only of husks, which were about 2.5-times thinner than those in the blank line (Fig. 4a and b).

Secondly, the major difference was inside the outlet steel piping (Fig. 4d), where only a small amount of powder-like coating was found in L-segment of the pipe in MWT line. It was wiped out easily and its amount was negligible in comparison to the abundant scale from untreated water.

Considering the over-saturation in the boilers, a diagram, presented in Fig. 5, was estimated by Eq. (8) taking the values for the equilibrium constants from Table 2.

During the run, inlet and outlet calcium concentration was being determined periodically by EDTA titration. With certain timely variations, the inlet data were 16 °C, 1.8 mmol/l Ca²⁺ and pH = 7.5; and the outlet data were 70 °C, 1.0 mmol/l Ca²⁺ and pH = 7.5, for both lines. The concentration varied up to ±0.1 mmol/l and pH up to ±0.2. The inlet concentration was slightly below the solubility point (that is 1.88 mmol/l from

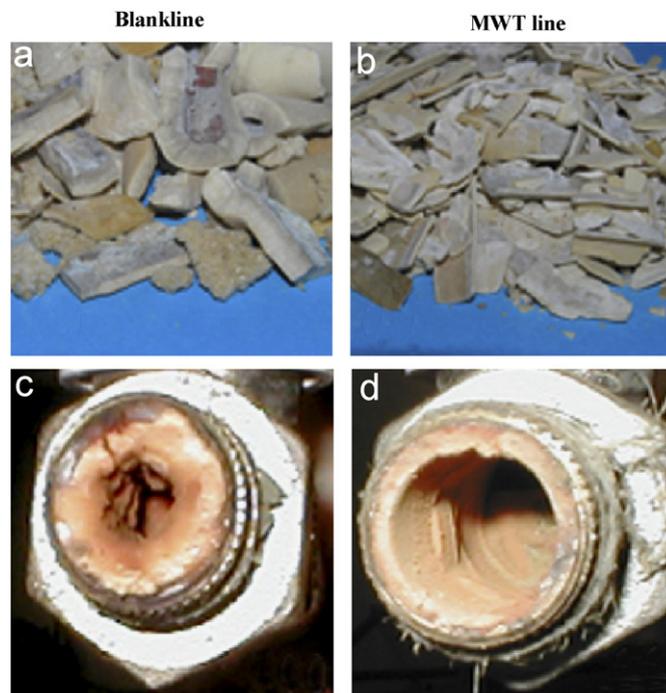


Fig. 4. Photographs of scales: (a,b) sediments in the boilers; (c,d) L-segments of Zn-coated steel pipes.

the isotherm at 16 °C); and in boilers, 3.6 higher than the solubility point at 70 °C, while in the outflow, it was double higher.

According to the outlet calcium concentrations similar from both lines, and the weight difference between the scales, we can conclude that certain part of CaCO₃ was somehow washed away by water flow.

After the first experiment was completed, two additional runs were performed in MWT line. For the first additional run, the scaled pipe from the blank line (Fig. 5c) was installed into MWT line and then the test was conducted at the same conditions as in the first run. The old scale was gradually disappearing; for about 2 mm in 10 days. This result is consistent with some other reports (Grimes, 1988) and with our further industrial experiences with the MWT device applications. For instance, a pipe-shell heat exchanger was supplied with tap water, which had similar composition as the one in our laboratory. The water was used for cooling with outlet Temperature 40 °C. The water was not pretreated properly and scaled up the inner side of pipes in the heat exchanger drastically. After the installation of our devices at the entrance of the exchanger, the scale completely disappeared in a few months. Secondly, an article on reduction in the surface tension of water due to magnetic treatment and hydrodynamic treatment was published recently (Amiri and Dadkhah, 2006). In that report, a circulation of pure and tap water through plastic Tygon pipe affected the surface tension similarly as MWT. To find out the portion of possible hydrodynamic effect due to the circulation on our results in MWT line, we repeated the run in the line with the circulation, but without MWT unit, which was replaced by a

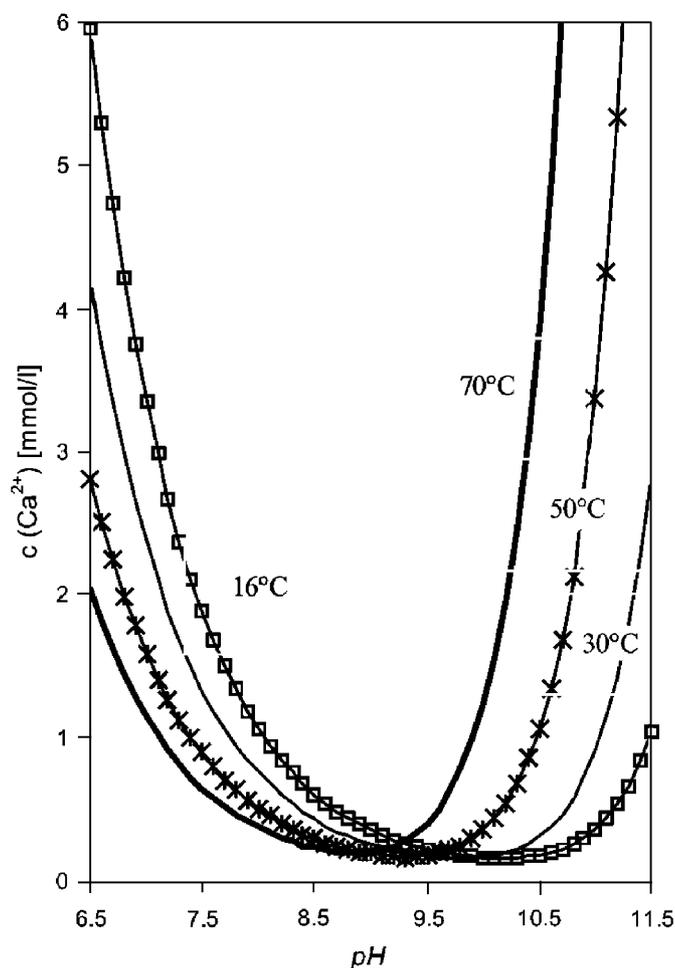


Fig. 5. CaCO_3 solubility isotherms for our tap water composition ($I \approx 7 \text{ mmol/l}$, $f_1 \approx 0.9$, $f_2 \approx 0.7$).

Table 2
The calcium carbonate equilibrium constants at different Temperatures (Kristiansen, 1975)

T ($^{\circ}\text{C}$)	K_2	K_S	K_w
16	3.82×10^{-11}	5.99×10^{-9}	5.28×10^{-15}
30	5.14×10^{-11}	4.03×10^{-9}	1.46×10^{-14}
50	6.74×10^{-11}	2.37×10^{-9}	5.46×10^{-14}
70	7.50×10^{-11}	1.38×10^{-9}	1.99×10^{-13}

blank pass. The scaling was quite similar to the scaling in the blank line from the first run; an abundant blockage in outlet pipe occurred. Some thickness and amount differences of sedimented husks in both latter tests appeared, but these were rather a result of slightly different fluctuations of tap water composition than in the first test.

Tap water in our experiment had the concentration Fe^{2+} ions less than $2 \times 10^{-6} \text{ mol/l}$. The concentration of Mg^{2+} was higher than the minimal concentration required for the efficient calcite inhibition (McLester et al., 1970; Meyer, 1984). According to the magnesium concentration and high-temperature conditions

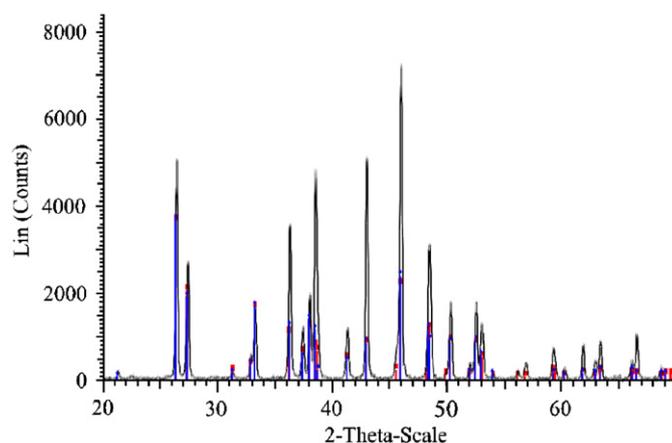


Fig. 6. X-ray diffraction spectrograph of scale from outlet pipe in the blank line, identifying the sample as aragonite.

(Grimes, 1988), all samples from both lines were identified as aragonite.

Samples' data were collected with AXS-Baker/Siemens/D5005 X-ray powder diffractometer (using $\text{Cu K}\alpha$ radiation). Phases were determined by Search/Match program (Ban et al., 2004).

Spectrographs are practically identical for all samples and one of them is presented in Fig. 6.

In world literature, there is a general opinion that calcite is responsible for hard scales because it forms rhombohedral crystals, which are highly adhesive, while the presence of needle-like crystals of aragonite is the main factor for the formation of softer, porous, more soluble deposits. This explanation is reasonable for many laboratory results of magnetically raised ratio aragonite/calcite, but in our case deposits in the blank line were already aragonite, which was surprisingly hard and tenacious. Obviously, in practical water-processing cases, some thermal and hydrodynamic factors affect the radial development of aragonite needles.

Fig. 7 presents micrographs of scale samples from the first experiment, observed by FEI-QUANTA 200 3D Environmental Scanning Electron Microscope.

Fig. 7a presents the cross-section morphology of the compact, but porous scale from the outlet pipe. Aragonite needles can be seen in small voids.

Fig. 7b presents cross-section morphology of a crystal from the blank-line sediment. These crystals were formed in less rigorous conditions on the boiler's wall. They were well developed, but very brittle. The radial development of needles can be seen in the cross-section of the crystal.

Figs. 7c and d compare cross-section morphology of a husk from the blank line and one from MWT line. Parallel development of orthorhombic needles, in the radial direction from the heating surface, close to each other, gave a compact lining.

The needles are in the case of MWT approximately four times thinner than in the case without the treatment. This can be a result of enhanced nucleation or retarded growth of aragonite crystals, somehow caused by MWT.

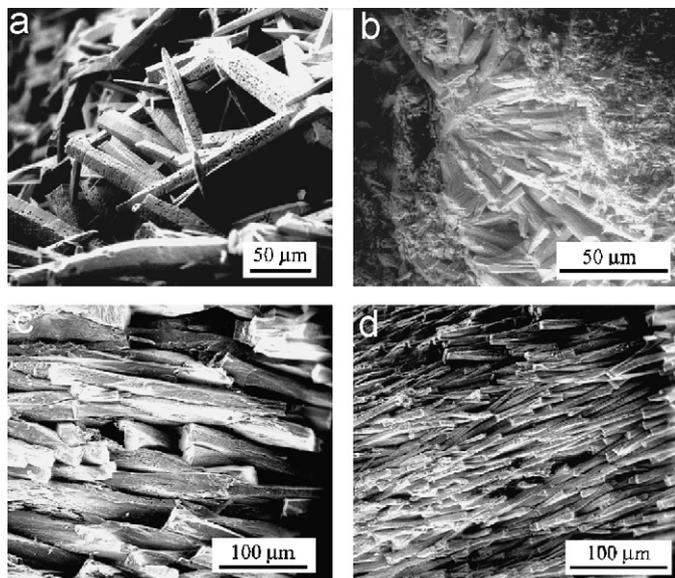


Fig. 7. Cross-section morphology of: (a) the hard scale from the pipe (Fig. 4c), (b) a sedimented crystal (Fig. 4a), (c) a husk from the blank line (Fig. 4a), (d) a husk from MWT line (Fig. 4b).

5. Conclusion

The comparison of scales from two parallel experimental lines with boilers, one supplied by untreated tap water and another by the water circulated through the magnetic device, shows that **MWT can reduce the thickness of scale on high-temperature heating surfaces and protect the hot water conducting pipes from scale completely and even dissolve an old scale.** Two and a half times thinner scale on heating surface, such as occurred in the experiment with MWT, would in industrial heat exchangers at common conditions provide about 50% higher heat exchange.

The nature of scaling reduction in our experiment was not a result of magnetically raised portion of aragonite, as it was in many cases conducted in well-controlled laboratory conditions (Grimes, 1988; Higashitani et al., 1993; Kobe et al., 1998, 2001; Coey and Cass, 2000; Bottello-Zubiate et al., 2004; Knez and Pohar, 2005), because the aragonite already dominated in the precipitate from untreated tap water due to Mg^{2+} presence, exceeding the threshold for the calcite inhibition, and, first of all, due to high-temperature conditions. Smaller amount of the sediment and thinner aragonite crystals in the husks from the boiler with MWT point on magnetically altered rate ratio of nucleation and crystal growth. **The deficit in scale mass indicates a formation of fine-suspended particles, washed away by water flow. The results are in some extent consistent with the report (Gabielli et al., 2001) and other reports about the dynamic magnetic treatment (Martynova et al., 1967; Kronenberg, 1985; Bogatin et al., 1999; Wang et al., 1997).** Some additional experiments are needed to find out whether these fine-suspended particles are the result of much more easily removable deposits due to MWT or the result of enhanced precipitation on suspended seeds in the bulk of the flowing water.

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