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Alternating magnetic field influence on scaling in pump diffusers

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ABSTRACT

This paper examines the influence of alternating magnetic fields on water scale precipitation on diffusers in vertical multistage pumps in real drinking water systems. The exact conditions in pumping stations were simulated in the laboratory using in-house techniques. The testing device consists of two lines, the first a control line and the other for testing, where a permanent magnet was installed. The influence of magnetic fields intensity, post-magnetisation time, temperature and saturation index on calcium carbonate nucleation and crystallisation was studied. The precipitate was analysed using X-ray powder diffraction (XRD) and a scanning electron microscope (SEM). It was found that the precipitate in water from the control line was in the form of calcite, while after the magnet treatment it was in the form of a non-adhesive aragonite powder that could be easily removed with the turbulent flow through the pump diffuser. The results suggest that the magnetic field has a noticeable effect on the transforming process of clusters in the solutions.

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1. Introduction

The build-up of scale deposits is a common problem in water systems (Dobersek and Goricanec, 2014). Calcium carbonate is a dominant component in scale, because natural waters are rich with $Ca²⁺$ ions and carbonic species. The super-saturation to calcium carbonate scale may occur. Chemical additives are the most-often used scale inhibitors for drinking water. Much effort has been expended recently to generate green inhibitors, either from plant extraction or by using natural organic molecules (Chaussemier et al., 2015). The effect of maleic acid on mass and morphology of scale has been studied (Muryanto et al., 2014). The reduction in scale mass suggests that malic acid could be an effective antiscalant for calcium carbonate.

Many factors, such as temperature, pressure, ionic strength, pH, water flow and impurity ions, affect scale inhibition. Magnesium, for example, is readily incorporated into growing calcite crystals at low concentrations but inhibits calcite growth at higher concentrations. A model has been developed to describe crystal growth kinetics. Magnesium may attach to active growth sites and impede crystal growth (Nielsen et al., 2013).

A calcium carbonate crystallisation fouling model on a heat

exchanger surface was developed (Pääkkönen et al., 2015). The best fit was achieved when the model included scaling time and flow velocity factors. In another study, a model was developed where deposition of calcium carbonate mainly depended on temperature and total ionic strength (Kamari et al., 2014). In our previous study, the effect of Zn released from an electro galvanic device onto the calcium carbonate crystal morphology was studied (Simonic and Ban, 2013). It was confirmed that trace amounts of Zn substantially inhibit the nucleation rate of calcium carbonate. The kinetics of scale formation was studied (Zhang et al., 2001) and it was found that as pressure decreases, $CO₂$ solubility in the water phase decrease and raise the pH and increase the saturation index. A similar effect is observed in the turbulent water flow regime.

The use of chemical inhibitors to prevent calcium carbonate scale is not desirable. The influence of weak magnetic fields on the crystallisation and colloidal stability in aqueous systems, which mostly contain non-ferromagnetic compounds, has been investigated over the last few decades. The lowest intensity of the magnetic field that affected the calcite growth rate reported in the literature was 1800 Gauss (0.18 T) (Sohaili et al., 2016) where the solution was subjected to magnetisation and calcite growth rate stopped. The recirculation of water over the permanent magnets with alternating magnetic fields has already been studied (Gabrielli et al., 2001). The effectiveness of this procedure increases with flow velocity up to 1.8 m/s and the number of circulations through the magnetic field. Scaling still occurred, but the scales were less compact and easier to remove. It seems that the nature of the

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precipitation from magnetically treated water may be explained by a modification of crystal seeds (Gabrielli et al., 2001). Calcite growth rates in the presence of the magnetic field have been found to be lower than those in the absence of a magnetic field (Tai et al., 2008). Higher magnetic intensities yield a lower calcite growth rate. The total amount of precipitate depends on the solution pH, the flow rate and the duration of the treatment (Knez and Pohar, 2005). The results suggest that magnetic fields influence calcium carbonate polymorph phase equilibrium either by influencing the $CO₂/water$ interface or through the hydration of carbonate ions prior to the formation of stable crystal nuclei in the solution.

Because of calcium carbonate scale formation, pumps must be frequently stopped and mechanically cleaned. The idea of the present study was to apply permanent magnets to disable calcium carbonate scaling in pump diffusers. Two experimental lines were installed to compare the amounts of scale precipitated in a pump diffuser. The experiment was carried out in a flow system using inhouse techniques, simulating a real pump diffuser; in one-line drinking water was magnetically treated and in the other not. The influence of magnetic fields, post-magnetisation time after water recirculation through the magnetic field, temperature and saturation index on calcium carbonate nucleation and crystallisation was studied. Physico-chemical and microbiological analyses were performed. The precipitate morphology was examined using X-ray powder diffraction and Scanning Electron Microscopy (SEM).

2. Methods

2.1. Sampling and experimental procedure

The pumping station is the last one of a total of five pumping stations on a more than 1500 km water pipeline system. Water samples were taken from a pumping station (Fig. 1a), which is a part of the city water system. The amount of water consumption is $240-280$ m³ monthly. This pumping station supplies only 22 households. The scaling problem occurs in a vertical multistage pump (Fig. 1b), which operates only occasionally because of very low water consumption; water scale builds up on the diffusers and block the pump.

The magnetic water treatment method was tested for effectiveness in experimental lines, in which the problem in the pumping station was simulated.

Two experimental lines were installed to compare the amount of scale precipitated in two identical pipes from magnetically treated (MT) and untreated water (Fig. 2). Both lines were supplied continuously with water from the city water system as it flows through the vertical multistage pump. The water recirculated through the magnet and the water solution was then allowed to precipitate for 1, 2, 3 and 4 h and afterwards analysed with X-ray

Fig. 2. The experimental lines for permanent magnet scale control test.

powder diffraction.

2.2. Methods for precipitate characterisation

The precipitate obtained was washed using milli-Q water and dried under vacuum conditions. X-ray powder diffraction data were collected with an AXS Bruker/Siemens/D5005 diffractometer using Cu-Ka radiation at 293 K. The samples were scanned with a position sensitive detector (PSD) and measured in the range of 10° < 2-Theta-Scale $\langle 80^\circ$, with a step of 0.014 and a scanning speed of 2 s per step. Determination of phases present in the sample was done with the Search/Match program (Kristl et al., 2013).

SEM combined with Energy Dispersive X-ray Spectroscopy (EDS) analysis was used to identify the surface morphologies of carbonate crystals. The precipitate was dried in order to remove the excess surface water. The specimens were attached to a stainless steel carrier and coated with a thin layer of gold under vacuum to increase the electrical conductivity of each sample and to protect the sample's structure from electron beam damage and dehydration within a vacuum. The specimens were observed using a Quanto 2003D FEI scanning electron microscope, equipped with a Sirion 400 FEI energy dispersive microanalysis system (Oxford Instruments, UK) at 15 kV.

2.3. Selected influential factors

Two alternately arranged permanent Neodymium magnets yielding a magnetic field density of 0.6 T and 1.44 T were available to study the effect of magnetic fields.

Five experiments were performed to study the effect of postmagnetisation time on crystal morphology, starting without recirculation, then with 30 min recirculation; the morphology was determined after 1 h, 2 h, 3 h and 4 h with water recirculation. In the MT line, water was recirculated through the magnetic device (Fig. 3). The water was recirculated through the magnetic device to intensify its effectiveness. In our experiment, velocity was set to

Fig. 1. Pumping station (a) and the vertical multistage pump (b).

Fig. 3. The configuration of the magnetic device.

Table 1

Parameters and standard methods used.									
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1.3 m/s in order to fulfil the effectiveness condition of water velocity in the device, based on previous study (Dobersek and Goricanec, 2014). Experiments were performed with the vertical multi stage pump (No 8 in Fig. 2) in order to simulate conditions in the pumping station.

The effect of temperature was studied. The temperature was measured continuously during the whole experiment on both lines before and after the multi stage pump.

2.4. Analyses

The main consideration was to ensure the unchanged quality of water after treatment. Drinking water samples were taken from the pumping station and collected in a reservoir. Both samples were taken for physico-chemical and microbiological analyses. Table 1 presents the measuring parameters and standard methods that were used for physico-chemical water analyses and Table 2 those for microbiological analyses.

Parameters were chosen based on carbonic equilibrium:

$$
Ca(HCO_3)_2(aq) = CaCO_3(s) + CO_2(g) + H_2O(aq) \qquad \qquad (1)
$$

3. Results

3.1. Effect of magnetic field intensity

The exact conditions in the pumping station were simulated in the laboratory. Experimental lines were supplied by the water from the city water system as it flows through the vertical multistage pump with adjusted input running continuously for 30 min.

The X-ray powder diffraction of untreated water precipitate is shown in Fig. 4. The pattern of calcite is clearly seen.

The water was altered by the magnetic field at an intensity of 1.44 T in the second line. The X-ray powder diffraction of treated

Microbiological analyses.

Fig. 4. X-ray powder diffraction spectrograph of scale from pumping station, identifying the sample as calcite.

Fig. 5. X-ray powder diffraction spectrograph of scale of treated precipitate, identifying the sample as aragonite.

sample precipitate is seen from Fig. 5.

The pattern of magnetically treated sample represented aragonite, except the peaks at 32 and 45 on the Theta Scale.

It was assumed that the magnetic field intensity was too high. Experiments with lower intensity of 0.6 T followed at the same conditions. The X-ray powder diffraction pattern of magnetically treated sample confirmed the amorphous structure of calcium carbonate (Fig. not shown). The recirculation time was prolonged to 1 h. The sample pattern of magnetically treated sample was similar to that in Fig. 5. The resulting X-ray powder diffraction of untreated precipitate sample was the same (see $Fig. 4$) showing the pattern of calcite.

Based on X-ray powder diffraction results, scale formation was favourable to aragonite in magnetically treated samples, while in untreated samples it was calcite. The results are consistent with an earlier study in which the authors claimed that magnetisation of the solution favoured the formation of aragonite (Tai et al., 2008). Amorphous calcium carbonate has been found in solution prior to the nucleation of calcium carbonate. According to the literature (Chang and Tai, 2010), it could have been calcium carbonate soluble clusters. The transformation from such clusters to calcite crystals is fast in untreated water, as shown in $Fig. 4$. The transformation to aragonite is slower in treated sample. Based on these results, the mechanism of cluster transformation by a magnetic field explained in literature (Chang and Tai, 2010) is confirmed.

3.2. Effect of post-magnetisation time

The precipitates after the 1, 2, 3 and 4 h of post $-$ magnetisation time were analysed with X-ray powder diffraction. The X-ray powder diffraction spectrograph for treated water after 1 h was not included. The X-ray powder diffraction spectrograph of permanent magnet precipitate after 2 h is the same as that in Fig. 5 and the result for untreated water were the same as that presented in Fig. 4. The difference between the precipitate in untreated and treated water after 2 h of post-magnetisation was determined. While precipitate from untreated water was rough, after the experiment the precipitation was in the form of fine, non-adhesive particles, which is in line with previous studies (Dobersek and Goricanec, 2014; Gabrielli et al., 2001). The X-ray powder diffraction spectrographs of permanent magnet precipitate after 3 h and 4 h were the same as presented in Fig. 5.

SEM micrographs of the same samples once treated with and once without the permanent magnet after 2 h of postmagnetisation were made. The water precipitates from lines with or without magnets were dried and micrographs were made (Fig. 6). The morphology of the precipitate with magnet treatment was considerably different compared to that of the untreated water. SEM micrograph showed that needle-like structures typical of aragonite were formed when the permanent magnet was used, in agreement with the literature (Guo et al., 2011).

The results of the present study are consistent with (Botello-Zubiate, 2004), who find out that calcite became aragonite by action of the magnetic field, what is in accordance with (Coey and Cass, 2000) and (Chang and Tai, 2010). It was also confirmed that magnetisation time has an important influence on calcium carbonate polymorphism (Tai et al., 2008). In the present study, 2 h were necessary for calcium carbonate to precipitate in the form of aragonite at an intensity of 0.6 T, while the time period was shortened at higher intensity. The time period is in accordance with literature kinetic data (Knez and Pohar, 2005), where it has been shown that after around 2 h the calcium carbonate precipitation of nonmagnetic controls occurred while the precipitation in magnetically treated solutions occurred with some 20 min' delay. The precipitate from Fig. 6b in the form of aragonite was powdered and in non-adhesive form, with a distribution of needle-like crystals, while the calcite precipitate formed very adhesive linings.

3.3. The effect of temperature difference

The temperature during the 4 h experiments was recorded. As seen from Fig. 7, the temperature of water from a line without treatment was 9 \pm 0.2 °C and after the pump 9.1 \pm 0.2 °C, which is within the error range. The same temperature was measured on the line with a magnet (0.6 T). Based on these measurements, it can be concluded that temperature difference between pump output and pump input has a minimum effect on water quality and scale formation.

3.4. Physico-chemical analyses and saturation index

The results of our physico-chemical and microbiological analyses of treated samples (0.6 T) after 2 h of post-magnetisation in comparison with tap water are presented in Tables 3 and 4.

Table 4 shows that the water quality remained unchanged after magnetic treatment.

The results for treated water were the same after 3 h and 4 h. It was observed that the quality of water remained unchanged after the treatment. Since the impurities, Zn^{2+} and Mg²⁺, could have some influence on crystal morphology, Zn^{2+} concentration was determined in the water. The value $\langle 0.1 \text{ µg} / \text{l}$ was below the concentration that could reduce the crystal growth rate of calcite (Simonič and Ban, 2013). The Mg^{2+} concentration determined in the water is as high as 0.893 mmol/l, but its influence on crystal morphology did not occur, as seen from EDS analyses in Fig. 8. The result is in accordance with another study (Nielsen et al., 2013).

The Saturating Index according to Langelier (LSI) in untreated water was calculated at 0.74 and in magnet treated water at 0.62. This means that the water was supersaturated and scale forming could occur. The value was a little lower in treated water, which means that supersaturation was lower. According to the literature (Al Nasser et al., 2011) scale rate increases with increasing

Fig. 7. Temperature measurement (line without magnet).

Fig. 6. SEM micrograph of precipitate with (a) no treatment (magnification of 30 μ m) and (b) after the magnet treatment (magnification of 50 μ m).

Table 3 Physico-chemical analyses.

Water	Treated water
$21.0 + 0.2$	$21.0 + 0.2$
$7.58 + 0.2$	$7.60 + 0.2$
$7.6 + 0.2$	$7.6 + 0.2$
$10.3 + 0.2$	$10.3 + 0.2$
$0.4 + 0.1$	$0.4 + 0.1$
$525 + 1$	$525 + 1$
$15.6 + 0.1$	$15.6 + 0.1$
$12.9 + 0.1$	$12.9 + 0.1$
$1.6 + 0.1$	$1.6 + 0.1$
$0.893 + 0.01$	$0.893 + 0.01$
$2.7 + 0.1$	$2.7 + 0.1$
$< 0.1 \pm 0.01$	0.1 ± 0.01

Table 4

Microbiological analyses.

Bacteria	Water	Treated water
Coliform bacteria (CFU/100 ml)		
E. coli (CFU/100 ml)		
Enterococcus (CFU/100 ml)		
Total count of microorganisms (CFU/ml)	10>	$<$ 10

supersaturation. The lower supersaturation in treated water resulted in a lower scale rate.

From these experiments, it can be concluded that nucleation with a permanent magnet is kinetically controlled, since only amorphous calcium carbonate was formed, but during 2 h post- $-$ nucleation period, the aragonite crystal morphology can be seen from Fig. 5.

3.5. Real pumping station precipitate

The transformation from amorphous to crystal form is in accordance with the literature (Knez and Pohar, 2005). Temperature was not changed although the pressure in the diffuser decreased. If the magnet is placed in front of the pump, the temperature also does not change. Thermodynamically, the calcite crystal formation from the amorphous calcium carbonate is favourable. At that stage the magnetic field must have the greatest effect on transforming the clusters in the solutions into aragonite crystal structure and not into calcite, as without the magnet.

From Fig. 8, peaks of Oxygen (O), calcium (Ca) and carbon (C) can

Fig. 9. SEM micrographs of precipitate from basin (left) and pump diffuser (right) at pumping station.

be seen. Both analyses confirmed the calcium carbonate formation. Precipitate from the basin and the diffuser precipitate are the same, according to EDS analyses. This can be explained by the basic concept of the diffuser, where the inlet pressure is high and more $CO₂$ is soluble. After the pump stopped working, because of outlet pressure decrease, the $CO₂$ escaped from the diffuser. Calcium carbonate precipitated in the form of anhydrous calcium carbonate.

Fig. 9 presents X-ray powder diffraction images of precipitate from the pumping station. In Fig. 9a, the precipitate from the basin is seen containing typical calcite cubes, while the calcite crystal growth on the diffuser is seen in Fig. 9b. The surface area of the scale crystals is initially smaller than the total pump tube internal surface area. With time the concentration of scale forming ions at the outlet of the pump will be higher compared to that at the initial stage of scale forming (Zhang et al., 2001). As the size of the nuclei increase with time, the Ca^{2+} concentration gradually decreases until the whole pump is covered with crystals. This is the reason why the pump clogged frequently. The pump was working discontinuously and there was enough time between sequences for the formation of scale on the diffusers.

Based on laboratory scale experiments, this procedure should be tested on real scale; however, the experiment is very delicate, a great deal of documentation needs to be arranged, and unfortunately, an online test is not possible.

4. Conclusion

Alternating magnetic fields had influence on water scale precipitation on diffusers in vertical multistage pumps. In our tests, the water scale in the pump diffuser was initially in the form of calcite, which is difficult to remove. Magnetic treatment is favourable for the formation of aragonite which is powdered, non-adhesive and

Fig. 8. EDS analyses of precipitates from pump diffuser (a) and basin (b) at the pumping station.

can be easily removed by the turbulent flow through the pump diffuser. X-ray powder diffraction and SEM analyses confirm this conclusion. The physico-chemical and microbiological parameters of water quality remained the same after the treatment. It was found that the magnetic treatment did not influence the quality of the water supply. The results suggest that magnetic fields influence the transformation of calcium carbonate cluster in the solution to aragonite crystal structure. Future work will be directed towards testing on real scale.

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