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The influence of electrogalvanic device on scaling

Research Article

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Abstract: The use of an electrogalvanic device for scale neutralisation is descibed in this paper. Physico-chemical analyses were performed before and after the treatment. The results were compared with those obtained by using magnetic water treatment device. By measuring some individual parameters and the implementation of chemical analysis, the satisfactory functioning of the electrogalvanic device was demonstrated. The quality of drinking water did not change much after the water treatment method. The results of determination of calcium carbonate saturating index showed that the raw drinking water is in carbonate equlibrium as well as both treated water samples. The calcite/aragonite ratio was studied by means of microscopy and X-ray powder diffraction. Inspection of crystals formed during the experiments with microscopy indicated that aragonite crystal structure of the precipitates prevailed over the calcite stucture. The diffractograms showed that the share of aragonite increased after using the electrogalvanic device compared with raw drinking water samples where the share of calcite was higher.

Keywords: *Water treatment • Electrogalvanic device • Calcite • Aragonite*

1. Introduction

Scale control is very important in cooling because of the effects of the deposits on heat transfer, corrosion of metals and fouling of cooling tower film fill. Scale deposits are mainly composed of calcium carbonate. By «carbonate system» we mean the set of species produced by the equilibria:

$$H_2O + CO_2 \leftrightarrow HCO_3^- + OH^- \leftrightarrow CO_3^{2-} + H_2O \quad (1a)$$

$$H_2CO_3 \leftrightarrow HCO_3^- \leftrightarrow CO_3^{2-} \quad (1b)$$

If water is alkaline the equlibrium will be shifted to the right. Water containing carbonate will continue to absorb carbon dioxide until the solubility limits of the cation salts are reached. If water is acidic the equlibrium is shifted to the left. Calcium ions are always present in some concentration in natural waters. They react with CO_3^{2-} to form insoluble $CaCO_3$. Calcium carbonate eqilibria is defined by equation:

$$CaCO_{3\,(s)} + H_2O_{\,(l)} + CO_{2\,(g)} \leftrightarrow Ca(HCO_3)_{2\,(aq)} \quad (1c)$$

In alkaline solutions HCO_3^- is converted to CO_3:

$$Ca^{2+} + HCO_{3\,(aq)}^- + OH^- \leftrightarrow CaCO_{3\,(s)} + H_2O_{\,(l)} \quad (1d)$$

$CaCO_3$ is mostly found in the form of polymorphs: calcite, aragonite and vaterite. The crystal structures are rhomberic, orthorombic and hexagonal respectively. $CaCO_3$ precipitation in water is mostly a mixture of calcite and aragonite which differs on the ratio between them. The ratio is affected by temperature, pH, ion concentration and suspended solids [1]. The carbonate group fits more into aragonite than into calcite network, which is why aragonite is denser (2.93 g cm^{-3}) than calcite (2.71 g cm^{-3}). In aragonite the Ca^{2+} ion is surrounded with nine oxygen ions, but in calcite only with six. However, calcium ions are more distant from the oxygen, the bond is weaker and the structure is thermodynamically less favourable. Aragonite forms needle crystal [2].

Of the three polymorphs vaterite is the least stable, aragonite is metastable and calcite is the most stable. Calcite is less soluble compared with aragonite, yet aragonite precipitates first and then recrystallizes into calcite. The recrystallization rate depends on pH,

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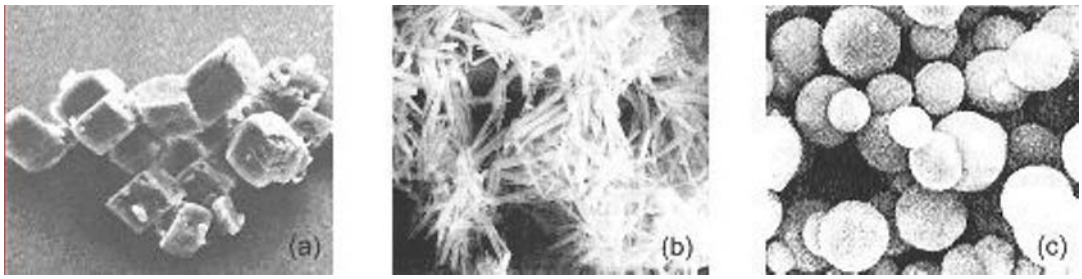

Figure 1. Microscopic observations of a) calcite, b) aragonite, c) vaterite (1000x magnification) [3].

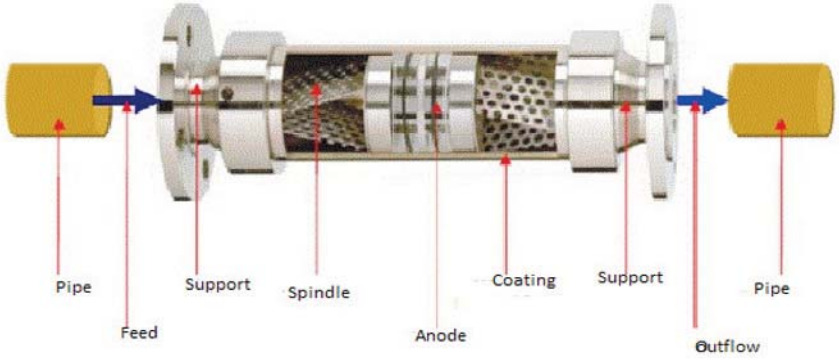

Figure 2. Electrogalvanic device [3].

temperature and impurities in water. Calcite is solid scale, aragonite crystalls are softer [1]. Microscope images of $CaCO_3$ polymorphs are presented in Fig. 1.

The fact that ionic impurities can influence crystallization reactions, is well known. Calcium carbonate precipitation can also be reduced or delayed by using so-called crystallization inhibitors [4]. These substances prevent or disturb precipitation by adsorbing onto the surfaces of nuclei as they form or onto the faces of growing crystals, respectively, thereby modifying the kinetics of crystallization. A number of metal and non-metal ions were tested, such as Zn^{2+}, Pb^{2+}, Cd, Cu^{2+}, all showing different efficiencies in influencing crystal growth rates [5]. In the absence of such processes, absorbed Zn^{2+}, Pb^{2+}, and Cu^{2+} remain coordinated at the calcite surface as mononuclear inner-sphere complexes during extended reaction periods [6]. Trace amounts of Zn in particular, can slow down the nucleation rate of calcium carbonate and also promote its crystallization in the aragonite rather than the calcite form even under conditions where calcite would be the preferred crystal form. Mg^{2+} also reduces the calcite crystallization [2]. It was reported that 2 ± 10^{-7} mol L^{-1} of Zn^{2+} ions can reduce the crystal growth rate in calcite by 80% [7].

If water is saturated with $CaCO_3$, $Zn(OH)_2$ on the steel surface is formed which protect the pipe from further corrosion. Such galvanic protection mechanism under thin layer of electrolyte was proposed by some authors [8,9].

The main objective of the work reported herein, was to study the effect of electrogalvanic device on scaling. The effect of Zn which is released from the device on the $CaCO_3$ crystal morphology was studied. The calcite/aragonite ratio was studied by means of a chemical analysis and X-ray powder diffraction. A mechanism has been proposed that the surface reaction of Zn-ions with $CaCO_3$ might be rate determining step in the crystallization process.

2. Experimental procedure

The electroglavnic device (EGD) used in the study is presented in Fig. 2.

The effect of water treatment unit is based on an electrogalvanic principle in which a conducting connection between two non-similar metals, due to the different reduction potentials of these metals, causes one of the metals as the reacting anode to release its Zn-ions into the water. It has been shown that such metal ion release causes positive effects by agglomeration (deposition) of scale forming substances contained in the water. Consequently these substances can not deposit themselves within water piping network. Without such a water treatment unit, there is a recognizable tendency for precipitation of calcium carbonate inside water pipes from the outer edge towards their center.

Table 1. The methods and apparatus used for water analyses.

Parameter	Standard	Method/Apparatus
***T* (°C)**	ISO 10523	Thermometer
pH	ISO 10523	Electrochemical/pH-meter, MA 5740
χ (μS cm^{-1})	ISO 7888	Electrochemical/WTW conductometer LF 537
***TH* (°d)**	38409-H6 (1986)	Titration
***CaH, MgH* (°d)**	38406-E3 (1982)	Titration
$\gamma(CO_{2free})$ (mg L^{-1})	38409-H7 (1979)	Titration
γ(Zn) (μg L^{-1})	ISO/DIN 11885 (1993)	ICP-MS/Parkin-Elmer Elan 6000
Aragonite, Calcite	Rapid test	Colorimetry

2.1. Sampling and physico-chemical analyses

The first set of drinking water samples (1) was taken from the Maribor waterworks. Second set of samples is denoted by 2 and means the treated samples using EGD. Third set of experiments denoted by No3 means the drinking water samples taken at the entrance to a hotel. No4 denotes treated water using EGD, which were taken immediatelly after treatment, and samples No5 were taken from the pipe, after the treated water flows through the waterpipes for five minutes. Samples No6 represent boiled untreated water and No7 treated water. Physico-chemical analyses were performed for all samples at room temperature (22±1°C). Table 1 represents the methods and apparatus used for water analysis. Each experiment was repeated several times and the reproducibility of results was satisfactory.

pH_s is the pH measured after $CaCO_3$ saturation and is can be calculated by Eq. 2:

$$pHs = -log \frac{K_{a2} \cdot \gamma(Ca^{2+}) \cdot c(Ca^{2+}) \cdot \gamma(HCO_3^-) \cdot c(HCO_3^-)}{K_p} \quad (2)$$

Where:

K_{a2} = equilibrium constant; $\gamma(Ca^{2+})$ = activity coefficient regarding calcium ions; (Ca^{2+}) = calcium ion concentration (mmol L^{-1}); $\gamma(HCO_3^-)$ = activity coefficient regarding hydrogen carbonate ions; $c(HCO_3^-)$ = hydrogen carbonate concentration (mmol L^{-1})

The Langelier Saturation index *LSI* is determined as a difference between experimentally determined *pH* and *pH*s:

$$LSI = pH - pHs \quad (3)$$

If

LSI > 0 Scale can form and $CaCO_3$ precipitation may occur

LSI ~ 0 carbonic equlibria

LSI < 0 no scale potential.

Borderline scale potential, water quality and temperature changes, or evaporation could change the index.

The symbols in Table 1 represent:

T = temperature (°C), pH = pH value, χ = the electrical conductivity (μS cm^{-1}), *TH* = total hardness (°d), *CaH* = calcium hardness (°d), *MgH* = magnesium hardness (°d), $\gamma(CO_{2free})$ = mass concentration of CO_2 (mg L^{-1}) and γ(Zn) = concentration of Zn-ions (μg L^{-1}).

2.2. Methods of characterization

X-ray powder diffraction data were collected with an AXS-Bruker/Siemens/D5005 diffractometer, using Cu-Kα radiation at 293(1) K. The samples were scaned with position sensitive detector (PSD) and measured in the range of 10°<2Θ<80, with a step of 0.014 and a scanning speed of 2 s per step. Determination of phases present in the samples was done with Search/Match program.

2.3. Crystal morphology

Crystal morphology is an important parameter in determining the properties of scale. Calcite is usually associated with a hard scale, whereas aragonite and vaterite could give rise to a softer type of scale that is easily removed. Crystals were collected when the crystallization process was completed, vacuum-dried and small amounts mounted for SEM analysis. Olympus SZX 16 stereo optical microscope was used, connected with Olympus DP72 high resolution camera. The magnification used for evaluation was 400x.

3. Results and discussion

Physico-chemical analyses are presented in Table 2. Samples were analysed at room temparature.

In all experiments the pH increased due to the lack of CO_2 in equilibrium, therefore the reaction 2 turned

Table 2. Physico-chemical analyses of treated samples taken from Maribor waterworks.

No	1	2
pH	7.7±0.1	7.9±0.1
χ/(μS cm^{-1})	582±3	580±3
TH (°d)	18.4±0.1	18.2±0.1
CaH (°d)	13.4±0.1	13.2±0.1
MgH (°d)	5.0±0.1	5.0±0.1
$\gamma(CO_{2free})$/(mg L^{-1})	8.0±0.4	5.2±0.4
γ(Zn) (μg L^{-1})	36±11	79±1

Table 3. Physico-chemical analyses of boiled treated samples taken from Maribor waterworks.

No	6	7
pH	8.3±0.1	8.4±0.1
χ/(μS cm^{-1})	506±3	475±3
TH (°d)	14.9±0.2	14.5±0.2
CaH (°d)	9.9±0.2	9.5±0.2
MgH (°d)	5.0±0.2	5.0±0.2
$\gamma(CO_{2free})$/(mg L^{-1})	<0.5	<0.5
γ(Zn) (μg L^{-1})	36±5	79±5

left in order to increase the CO_2 concentration. At the same time $CaCO_3$ should increase which is recognised from the small decrease in calcium hardness (*CaH*). The magnesium hardness (*MgH*) remained the same. We can assume that scale formation was predominantly due to formation of aragonite not hard calcite. Since aragonite is precipitated, less CO_2 was determined in treated water. The equilibria (see Eq. 1d) is shifted to the left in order to increase the CO_2 concentration, at the same time, $CaCO_3$ precipitates. However, Zn^{2+} formed by the anodic reaction:

$$Zn \rightarrow Zn^{2+}+2e^- \quad (4)$$

is released from electrogalvanic device. Some CO_3^{2-} reacts with Zn^{2+} to form amorphous $ZnCO_3$, and it is a host for $CaCO_3$ which can not crystallize as calcite and remains in the aragonite form. At the same time the H_2CO_3 (CO_2) concentration is decreasing as it is presented in Table 2. The equilibria (Eq. 1c) is shifted to the left in order to increase the CO_2 concentration. Therefore, the tendency for $CaCO_3$ precipitation is increasing and pH is increasing which is also seen from Table 2.

If water is saturated with $CaCO_3$, $Zn(OH)_2$ on the steel surface is formed which can protect the pipe from further corrosion. Such a galvanic protection mechanism under thin layer of electrolyte was proposed by Yadav [8].

Table 3 presents the analyses of the boiled water samples. The analyses were performed after cooling to room temperature.

The hardness of the untreated samples was already lower for around 0.7 mmol L^{-1} Ca^{2+} compared with the room temperaure samples. Mg-hardness remained the same. CO_2 concentration (determined in cooled samples) decreased below the detection limit due to evaporation at 100ºC.

LSI indexes were determined in drinking water from 0.59-0.63, while in treated samples were between 0.82 and 0.91. This means that a slight tendency for scaling is presented. The LSI was slightly lower after treatment which means that the tendency of $CaCO_3$ precipitation is lower. The obsevation of the scale showed the different solidness of the precipitation: if the precipitation in the treated samples was touched it felt soft. The precipitation in drinking water samples was hard to the touch.

3.1. Rapid test

The results of rapid test are presented in Fig. 3. No1 sample is drinking water, No2 treated water and No3 is boiled treated water cooled to room temperature. The experiment starts and after two minutes samples from Maribor waterworks showed the presence of aragonite due to a brown color developing in all samples. If the calcite would be predominant the colour would remain light grey.

Drinking water samples from another location were taken. The sampling site was a small hotel in our city where an electro-galvanic device is installed. The water analyses are presented in Table 4.

Samples 3 and 5 are identical, although water (sample 5) was treated and flowed for a few minutes to reach the sampling point. In the 4th sample the decrease in CO_2 concentration is seen, similar as to that observed in samples 1 and 2. It suggests that the equilibrium (Eq. 1b) was shifted to the left and some $CaCO_3$ precipitated. Due to the rapid test results we assume that aragonite was formed and not calcite. In order to prove this hypothesis further research steps were made: X-ray analyses and microscopic observations.

If solid-state diffusion was an operative mechanism in metal sequestration by calcite under ambient conditions, it is reasonable to expect that the formation of octahedral Zn^{2+} surface complexes would facilitate movement of Zn^{2+} into the bulk, whereas the tetrahedral coordination was observed in powder experiments and Zn^{2+} movement would be hindered. [6] Mechanistic differences in metal coordination may be of particular importance in the case of Zn^{2+}. Surface complexes and movement of the metals into the calcite structure is hindered, consequently calcite growth is inhibited,

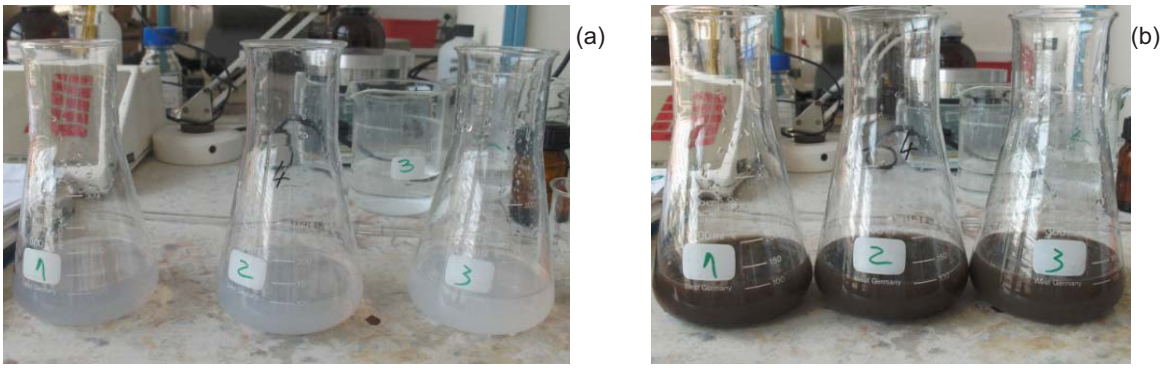

Figure 3. Rapid test a) begining of the test b) after 2 min.

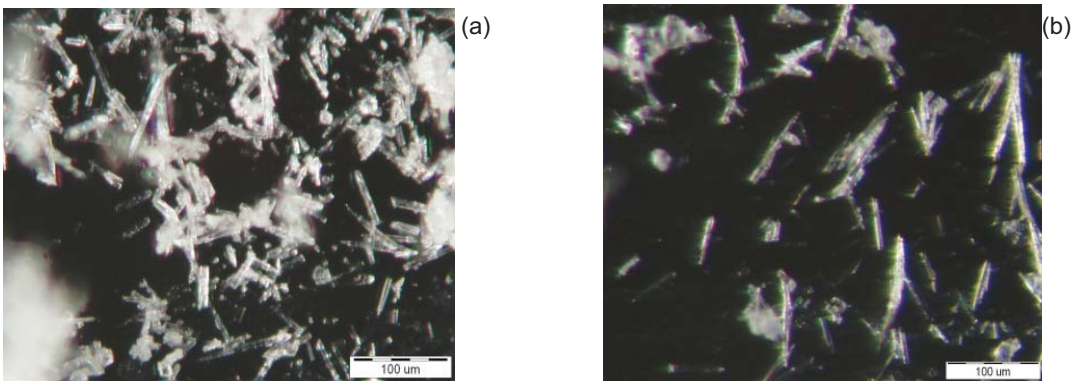

Figure 4. $CaCO_3$ crystall forms under microscope (a) drinking water, b) treated water).

Table 4. Physico-chemical analyses of treated samples taken from hotel sample.

No	3	4	5
pH	7.5±0.1	7.6±0.1	7.5±0.1
χ/(*μ*S cm^{-1})	543±3	539±3	543±3
TH (°d)	16.1±0.1	16.0±0.1	16.1±0.1
CaH (°d)	11.8±0.1	11.7±0.1	11.8±0.1
MgH (°d)	4.3±0.1	4.3±0.1	4.3±0.1
γ(CO_{2free})/(mg L^{-1})	10.65±0.4	8.58±0.4	10.65±0.4
γ(Zn) (*μ*g L^{-1})	23±1	85±1	76±1

which is attributed to blocking of these high energy sites. In our experiments, the concentration of Zn^{2+} after electrogalvanic device increased (see last row, Table 4). Zn^{2+} was most probably adsorbed onto the calcite structure and calcite growth was inhibited according to Elzinga [6].

Microscope observations showed the form of $CaCO_3$ in drinking water. The results are presented in Fig. 4.

Aragonite crystal forms were easily identified by recognising aragonite needles while the calcite rhombohedrons were harder to find. It was not possible to estimate the percentage composition in samples where mixtures of crystal morphologies occurred. We found more white aragonite crystals however, these observations are of course somewhat subjective. Visual inspection of crystals formed during the course of experiments, however, provided an early indication of what the crystal structure of the precipitates might be.

Crystal forms were also confirmed by X-ray analysis. In order to compare the achievement of EGD with another anti-scaling method, the experiment was performed using a magnet. Drinking water circulated with average velocity of 1 m s^{-1} through the magnet yielding a magnetic field with three maximums of density 0.6 and 0.8 Vs m^{-2}. Fig. 5 represents the powder diffraction patterns of $CaCO_3$, from drinking water samples taken at Maribor waterworks (the highest), EGD (in the middle) and magnetically treated water (at the bottom in Fig. 5). Calcite peaks are denoted by «C», all other peaks represent aragonite. The peak heights represent the quantity of fractions: the higher the peak the bigger the fraction present in the water. In the upper pattern the heights of the calcite (denoted by «C») peaks were much higher compared with both treated samples since the maximal number of counts reached 1600. The diffractograms of the EGD treated water (in the middle) and magnetically treated water (at the bottom) did not differ much one from another, however, the heights of all peaks are lower in EGD treated samples: the maximal

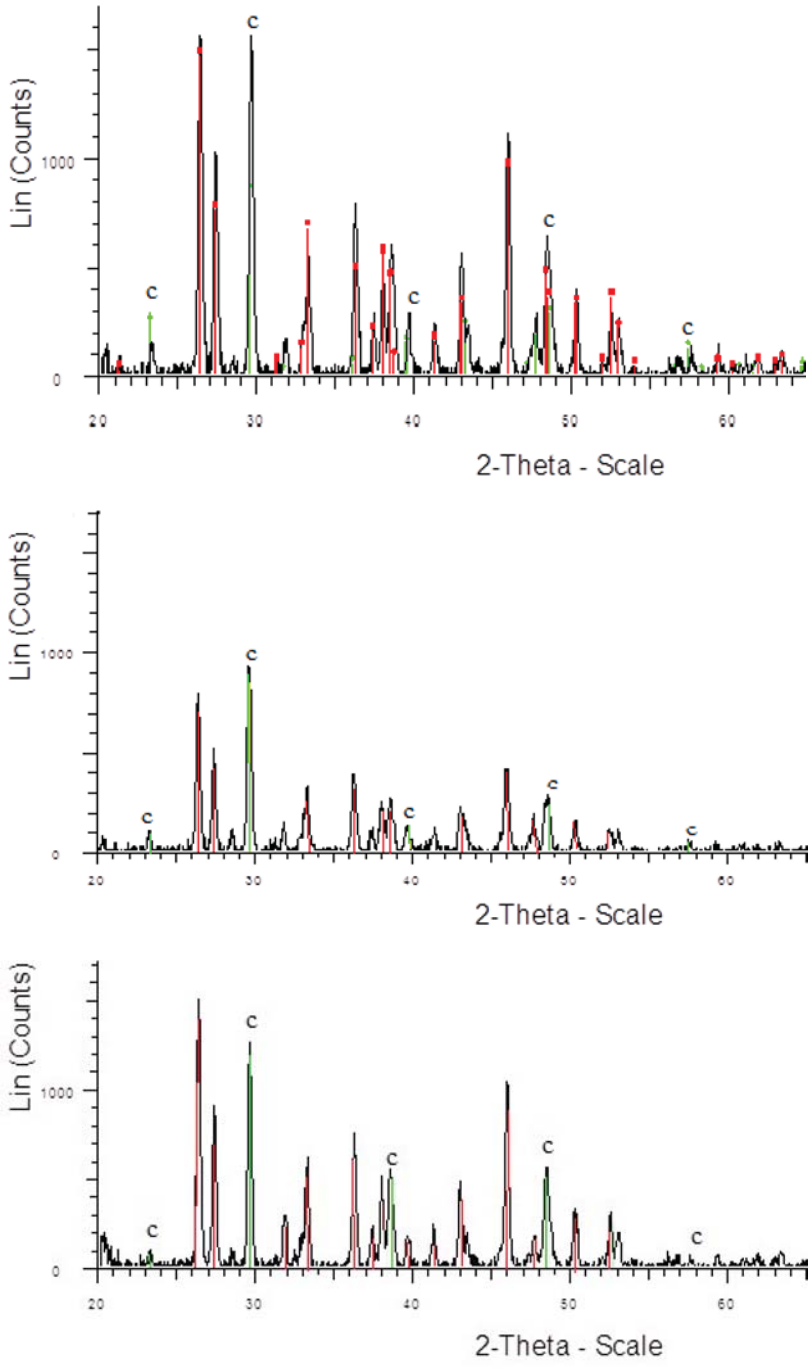

Figure 5. Powder diffraction patterns of $CaCO_3$: C denotes calcite peak (marked green), aragonite peaks are marked red; The highest pattern: untreated water, in the middle: water treated with EGD and the lowest pattern: magnetically treated water.

peak heights for calcite at 30 on 2-Theta-Scale was 950 counts for EGD treated sample and 1250 counts for magnetically treated water, respectivelly. It is obvious that calcite in not predominant fraction. The diffractograms of the precipitate from water treated by EGD and a magnet still show some calcite fraction peaks, but the number of these peaks is lower compared with the number in untreated water precipitate. Therefore we can conclude that in untreated water (the upper sample) higher calcite/aragonite fraction is obtained compared with the treated samples. Fig. 6 represents the powder diffraction patterns of $CaCO_3$ from hotel pipeline samples: upper is made in sample of untreated water and the lower of EGD treated water. Peaks denoted by «C»represent

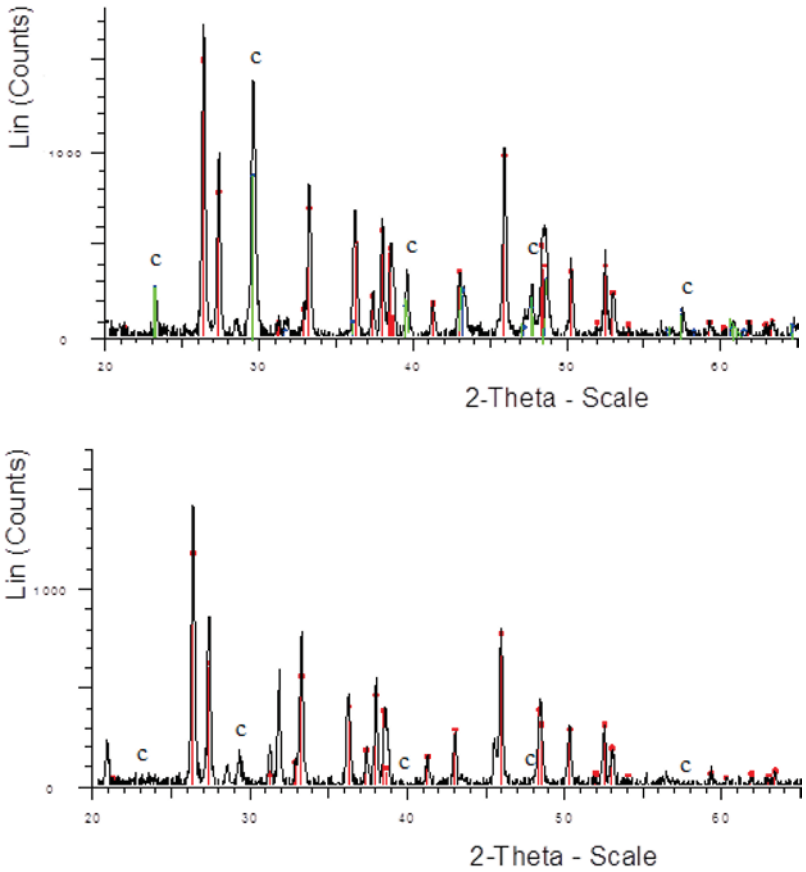

Figure 6. Powder diffraction analysis of $CaCO_3$ (upper pattern denotes the untreated water, lower one EGD treated water; C- calcite (marked green), aragonite peaks are marked red).

the calcite fraction, all other peaks represent aragonite fraction. From Fig. 6 it is clearly seen that the number of calcite fraction peaks as well as their heights are much larger compared with EGD treated water. The peak height at 30 on 2-Theta-Scale was around 1400 counts for untreated water and only 200 counts for EGD treated respectivelly, while all other peaks were too low to be observed. Thus, the most important conclusion is that the aragonite is favourisable cabonate form which precipitates in treated samples.

It was not possible to detect neither magnesium calcite $Ca_{1-x}Mg_xCO_3$ nor $CaSO_4$.

The formation of aragonite rather than calcite is demonstrated to occur when the Zn/Ca concentration ratio is greater than 0.06×10^{-3} [10]. The Zn/Ca concentration ratio calculated in this study was from 0.17×10^{-3} to 0.33×10^{-3} in drinking water (see Tables 3 in 4, last row, first column). The Zn/Ca concentration ratio increased from 0.3×10^{-3} to 0.68×10^{-3} (see Tables 3 in 4, last row, second column). Therefore, we can conclude that the formation of aragonite is favourable. This hypothesis was was proved by x-ray analysis, rapid tests and microscopic observations. We can assume that Zn-ions released from the electrodevice adsorb onto $CaCO_3$ crystals and at the same time inhibit the calcite crystals' growth. Further, the measurements of Zn concentration immediatelly after the device was done and again in the bathroom which was the most distant from the device (see Table 4, last row, second and third columns). The difference between the measured Zn-concntrations is 9 μg L^{-1}. If the Zn/Ca concentration ratio is calculated, the result 0.065×10^{-3} is obtained which is greater than 0.06×10^{-3}. Again, it is in accordance with Freijs' claim that such environment is favourable for the aragonite formation.

The evidence of the reduced scale formation is seen from Fig. 7 which shows photographs before the device was installed (a) and after installation (b). Inside the steel pipe $CaCO_3$ in the form of calcite is accumulated on the inner surface. On the contrary the right photograph shows the improvement of the pipes' surface with the usage of EGD. Obviously, the scale was removed because the device favoured aragonite formation over calcite.

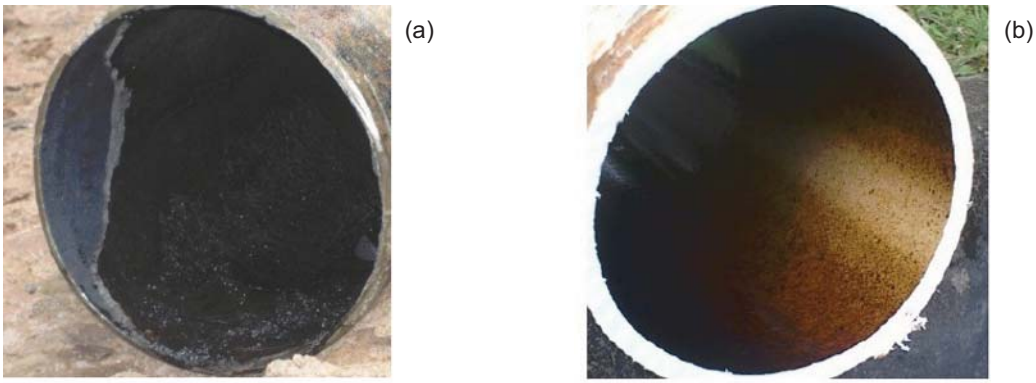

Figure 7. Photographs of scales in steel pipe before (a)) and after (b)) the EGD was installed.

4. Conclusion

It is evident from the results that trace amounts of Zn can substantially inhibit the nucleation rate of $CaCO_3$. This effect has been quantified in terms of delay time. The formation of aragonite rather than calcite is demonstrated to occur when the Zn/Ca concentration ratio is greater than 0.06×10^{-3}. We have also demonstrated that these effects can cause reduction in scaling in a simple laboratory application. Aragonite crystal forms were easily identified by recognising aragonite needles while the calcite rhombohedrons were harder to find during microscopic observations. X–ray powder diffraction showed that the calcite/aragonite ratio was favorable to aragonite in EGD treated samples.

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