

Influence of alternating electromagnetic field and ultrasonic on calcium carbonate crystallization in the presence of magnesium ions



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ABSTRACT

In the present study the efficiency to the CaCO₃ crystallization caused by the different ordinal combination of alternating electromagnetic field (AEMF) treatment and ultrasonic (US) treatment was investigated by the measurement of the variations of the solution pH, conductivity, turbidity and particle size distribution when Mg²⁺ ions were present, and the crystal phases structure and micrographs of the precipitations obtained from experiments were analyzed by XRD and SEM. The experimental results show that the presence of Mg²⁺ ions can prolong the induction time of the formation of CaCO₃ and make the CaCO₃ particles gradually change into aragonite, the particle size also decreases with the increasing of Mg²⁺/Ca²⁺ ratio. The AEMF + US treatment decreases the size of CaCO₃ particles, and the US + AEMF treatment accelerates the precipitation of CaCO₃. It is interesting that with the presence of Mg²⁺ ions US + AEMF treatment makes the CaCO₃ particles have larger size with looser structure, but at last form completely tiny aragonite needles. The results are advanced in that the proper addition of Mg²⁺ ions combined with the AEMF + US or US + AEMF can significantly improve the physical anti-scaling efficiency.

1. Introduction

Scale problem is a key problem to the industrial heat exchanger and pipe, which roots on using hard water. The traditional chemical descaling methods were used by adding chemicals such as strong acids. But the chemicals are not only corrosive for the industrial systems but also deleterious for the environment. Since these disadvantages of chemical methods, physical descaling methods are gradually being widely used such as AEMF treatment and US treatment.

The application of AEMF treatment has been employed for about 50 years [1,2]. It was first used since the 1960s in the Soviet Union [3]. The AEMF treatment is a very useful physical water treatment method to the scale problem, but the application effect is unsteady. The effect of AEMF treatment can be influenced by many other parameters such as pipe material, foreign ions, temperature and flow velocity etc. [4,5]. The anti-fouling mechanism of this technology is still not all clear as yet. Some studies have concluded that the magnetic field produced by AEMF system can reduce the nucleation time or increase the growth rate of CaCO₃ nuclei [6–10]. But some other studies have come to opposite conclusions, which was claimed that the electromagnetic field can reduce the combination of Ca²⁺ and HCO₃⁻ ions [11–13].

The US treatment is another effective physical water treatment to

the scale problem. The descaling mechanism of US treatment has been considered that US not only can accelerate the formation of CaCO₃, but also can affect its crystal morphology [14–18]. It is considered that the cavitation effect caused by US can make water molecules more active and increase dissolving ability of water, thus more crystals of CaCO₃ will be resolved in solution and the mitigation of scale on tube wall is reached and fouling process is restrained [19]. But the effect of US treatment is not stable because it can be influenced by the acoustic intensity, solution concentration, solution temperature and distance to US transducer [20].

AEMF treatment and US treatment have their own advantages and disadvantages. The AEMF treatment makes a good scale inhibition effect and low power cost, but the electromagnetic field that it produces can be shielded by ferromagnetic pipes such as cast iron pipes which limits the application of AEMF treatment. The US treatment can effectively peel off the old scale on the pipe wall and prevent scale crystals re-depositing by its high frequency oscillation, but the ultrasonic oscillator consumes large quantities of power and it can't work continuously for long time. CaCO₃ crystallization is a very complex process involving several steps. These steps make CaCO₃ precipitate changing from hydrated micelle of disordered pairs into CaCO₃ solid forms [21]. The two physical treatments can affect the different

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steps of CaCO_3 crystallization, which means they have different anti-fouling mechanisms. Therefore combination application of these two physical treatments may produce peculiar effect, but no such study can be found in the literatures at present.

In addition, it is well known that the main scale-forming cation in hard water is Ca^{2+} , but there are always a small amount of other foreign cations such as Mg^{2+} . Mg^{2+} is an important kind of foreign cations in hard water and the ratios of Mg^{2+} and Ca^{2+} are varies greatly with different natural conditions [22,23]. Mg^{2+} ions can affect the CaCO_3 crystallization significantly [24], therefore the presence of Mg^{2+} should not be ignored in the study of physical anti-fouling treatment.

For these reasons, the experimental works presented in this paper were performed with the different ordinal combination of AEMF treatment and US treatment when Mg^{2+} was added in $\text{Ca}(\text{HCO}_3)_2$ solution, and the efficiency to the CaCO_3 crystallization was investigated by the measurement of the variations of the solution pH, conductivity, turbidity and particle size distribution. The crystal phases structure and micrographs of the precipitations obtained from experiments were analyzed by XRD and SEM.

2. Experiment

2.1. Sample preparation and experimental setup

The water used in this study was high-level purified water, which was produced by a Milli-Q Millipore System and had a resistivity of about $18.2 \text{ M}\Omega$, 25°C . The total organic carbon and dissolved oxygen of the water were below 0.05 mg/L and 5.0 mg/L , respectively. The analytically pure MgCl_2 , CaCl_2 , and NaHCO_3 were used for preparing the $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$ solution with concentration of 10 mmol/L . Then the experimental solutions with different ratio of $\text{Mg}^{2+}/\text{Ca}^{2+}$ (0:1, 1/3:1, 0.5:1 and 1:1) were obtained by mixing the $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$ solution.

The experiments were carried out using the setup as shown in Fig. 1. A columniform glass tank with 300 ml experimental solution was wined by the excitation coil (diameter $R = 5 \text{ cm}$, total length $L = 20 \text{ cm}$, turns $N = 100$). The excitation coil was connected with an AEMF generator. The generator's output was an alternating signal with a virtual current of 3 A. The temperature of the experimental solution was controlled at 25°C by a thermostatic water bath. An US oscillator was set under the glass tank. The output frequency of US oscillator was 40 kHz and its power was 300 W .

2.2. Experimental methods

In order to investigate the influence to the process of precipitation in the hard water caused by different $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio, and compare the influence to the hard water of different $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio caused by different physical water treatment methods, the experiments were carry out as two parts.

Part 1, in order to investigate the influence to the process of precipitation in the hard water caused by different $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio, the hard water samples of different $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio were placed for 2 h.

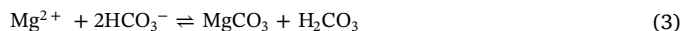
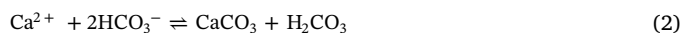
Part 2, in order to compare the influence to the hard water of different $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio caused by different physical water treatment methods, (1) the AEMF was used on the experimental solution at first for 1 h, then the AEMF was stopped and the US was used for the next 1 h. (2) the US was used on the experimental solution at first for 1 h, then the US was stopped and the AEMF was used for the next 1 h.

The pH, conductivity, turbidity and the distribution of particles size were measured every 10 min during each experiment. All the parameters were measured 3 times and the average values were calculated for reducing measurement errors. After each experiment, the precipitations were collected and the crystal phases and the microscopic morphologies were analyzed by X-ray diffraction (XRD) and scanning electron microscope (SEM).

The information of experimental instrument used in present study is shown in Table 1.

3. Results and discussion

The main reaction involved in the precipitation of CaCO_3 and MgCO_3 is governed by the following equilibriums:



At the very beginning of experiment, the concentration of various ions in the solution was higher, HCO_3^- and H_2O had generated H_2CO_3 and OH^- by hydrolysis reaction, therefore the solution was alkaline.

3.1. Influence of Mg^{2+} ions to the process of precipitation

For investigating the influence of Mg^{2+} ions to the process of precipitation in the solution, the hard water solutions of different $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio were prepared and placed for 2 h. Then the pH value,

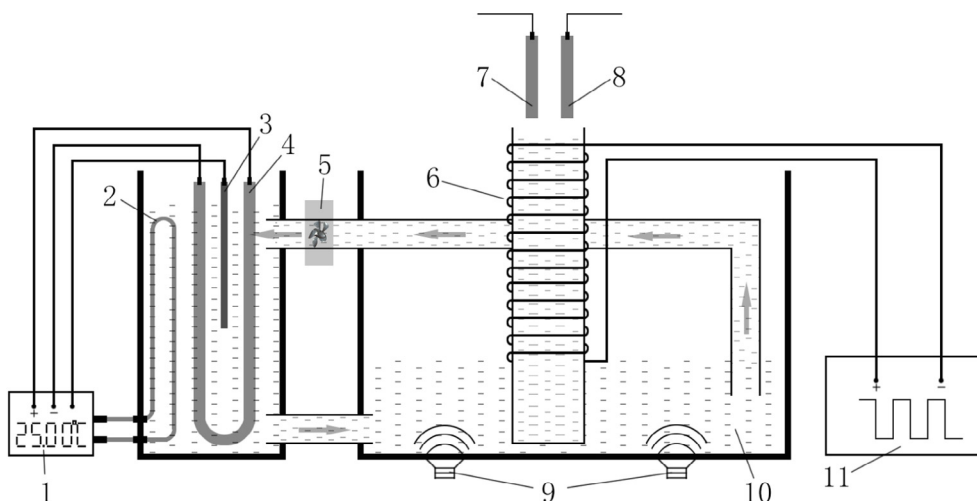


Fig. 1. Schematic diagram of experimental setup. 1-CNC thermostat, 2-Refrigerating tube, 3-Temperature sensor, 4-Electric heating tube, 5-Circulating pump, 6-Excitation coil, 7-PH meter probe, 8-Conductivity meter probe, 9-Ultrasonic generator, 10-Constant temperature water bath, 11-AEMF generator.

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