Experimental study on calcium carbonate precipitation using electromagnetic field treatment
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ABSTRACT
The present study investigated the effectiveness of electromagnetic fields in preventing calcium carbonate (CaCO₃) fouling in cooling water. Four different frequencies and two different voltages were adopted to induce electromagnetic fields directly in water with constant water temperature and constant flow velocity. Artificial hard water was used. The solution conductivities decreased by 17–25% from their initial values in the electromagnetic anti-fouling treatment (EAT) cases, depending on different frequencies of electric pulses, whereas the untreated case dropped by 31%. The particle size became small and the crystal structure changed into loose style after EAT. The EAT device independently developed by the State Key Laboratory had been validated as an effective apparatus in preventing CaCO₃ fouling in cooling water.

Key words | calcium carbonate, conductivity, crystal structure, EAT, electromagnetic fields, particle-size distribution

INTRODUCTION
Calcium carbonate (CaCO₃) is one of the most common scales that form on heat transfer surfaces of heat exchangers used in cooling-water systems of thermal power plants (Tijing et al. 2007). When these scales develop, the hydrodynamic performance of heat exchangers will decline with time, thus requiring more pumping power. Moreover, CaCO₃ has a low thermal conductivity of 2.9 W/mK (Incropera & DeWitt 2002), whereas copper, which mostly composes the heat transfer surfaces, has a conductivity of 401 W/mK (Incropera & DeWitt 2002). Thus, these scales result in an increase in energy consumption of cooling-water systems. Mineral fouling is the general term given to scale formation on heat transfer surfaces. The economic cost of cleaning and maintaining heat transfer equipment due to mineral fouling was estimated to be approximately 0.25% of the world gross national product (GNP) (Steinhagen et al. 1993).

Various methods have been employed in preventing or mitigating mineral fouling, which can be classified into physical and chemical methods (Kuppan 2000; Cho et al. 2004). The chemical methods, such as dispersion (Wang et al. 2002), chelation (Chen & Chan 2000), and inhibition (Ketrane et al. 2009), introduce an immediate means of cleaning and have a high success rate in preventing or mitigating mineral fouling. However, the chemical methods have several drawbacks, including water pollution, chemicals storage, chemical residues disposal and other environmental problems. In addition, the chemical methods are expensive when applied at industrial level (Casanueva-Robles & Bott 2005). On the other hand, the physical methods, employing electromagnetic fields (Shahryari & Pakshir 2008; Tijing et al. 2010), catalytic materials, ultrasounds, and sudden pressure changes, have been adopted to solve fouling problems in recent years. No chemical is introduced into the water, i.e. the physical methods are more environmentally friendly than the chemical methods.

Recent research has focused on physical water treatment using electromagnetic fields (i.e. electromagnetic anti-fouling treatment (EAT)) (Lipus et al. 2011). Prevalent studies on EAT usually adopted a very low alternating voltage (e.g. 5, 10, and 3 V) (Xing et al. 2005; Tijing et al. 2010) to generate electromagnetic fields, and the electrodes were various through which the electromagnetic energy was released into the water. Tijing (Tijing et al. 2010) used parallel graphite plate, whereas other researchers (Xing et al. 2005) adopted solenoid coils. In the present study, the processing chamber was a coaxial type and assembled with a central pole and an outer cylinder electrode; these two electrodes composed electric pulses with middle-level

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voltage and frequency on the chamber and induced electromagnetic fields inside the solution. In the present experiment, the artificial hard water was used to investigate the CaCO₃ scaling process due to its easier preparation and more controllable water quality parameter.

The conductivity of artificial hard water was recorded and plotted as a function of time. The particle-size distribution (PSD) in the solution and scanning electron microscope (SEM) photographs of the CaCO₃ scale were analyzed. These three indicators were adopted to prove that present EAT could mitigate or prevent mineral fouling. Furthermore, the experimental data under different pulse frequencies were compared.

**EXPERIMENT FACILITY AND METHOD**

**Facility**

The experimental system (Figure 1) of the present study was composed of a centrifugal pump, constant-temperature water tank (40 L capacity), flow meter, valves, conductivity meter, and EAT device. The temperature of the water tank was kept constant by a U-type thermocouple acting as a high-precision digital thermostat. The sampling port located in the bottom of the tank was used to obtain the solution samples for PSD analysis.

Figure 2 shows the schematic diagram of the present EAT device. The EAT device consisted of two parts: the processing chamber and the electromagnetic signal generator (ESG), independently developed by the State Key Laboratory (Xiong et al. 2011). The core power component of the ESG was metal-oxide-semiconductor field-effect transistor (MOSFET). A higher voltage and frequency pulse was outputted, the higher the temperature the MOSFET had. When the voltage and frequency reached about 120 V and 1.5 MHz respectively, the device attained the limit running temperature. The processing chamber was a coaxial type with two electrodes which were all made of stainless steel. Electromagnetic fields, which acted on the solution inside the processing chamber, were adjusted and controlled by the ESG.

**Figure 1** | Schematic diagram of the present test system.

**Figure 2** | Schematic diagram of the EAT device: (a) side view, and (b) cross-sectional view.
In all tests, the entire experimental system was conducted under rigorous electromagnetic shielding to avoid additional electromagnetic interference.

Method

The test solutions, pumped by centrifugal pump, flowed through the EAT chamber and plastic tubes (cross-sectional diameter = 18 mm; total length = 210 cm) then back to the tank again, as shown in Figure 1. The test water temperature was maintained at 25 ± 0.5°C and the flow velocity was stabilized at 0.8 m/s. Each test continued for 12 hours. Only a few CaCO₃ scales were formed on the inner wall of the tube and the tank which were collected for SEM detection during each test. The tank and tubes were cleaned thoroughly right after each test by draining out the artificial hard water completely, then rinsing with tap water. Subsequently, diluted weak acid (hydrochloric acid volume fraction of 8%) was introduced into the tank and circulated in the system for 1–2 hours. This process was repeated using tap water, and finally, using distilled water. After completed cleaning, the next test would be conducted. In the present study, four frequencies and two voltages were utilized based on the previous experiment experience and on maximum power output. Table 1 shows six experimental groups with different electric parameters. Test-0 was a reference group without treatment to compare with the anti-scaling effect of EAT groups. Test-5 was used to compare the anti-scaling effect at the same frequency but different voltage.

Due the main scale of power plant closed cooling water, the test solution (i.e. artificial hard water) was obtained by introducing calcium chloride (CaCl₂) and sodium bicarbonate (NaHCO₃) powders, with a molar ratio of 1:2, to distilled water. All the time, the initial concentration of Ca²⁺ ions was controlled at 5 mmol/L.

Each test was repeated twice and the significant difference analysis of data utilized by SPSS 11.0 software with Student’s t-test demonstrated these data were valid ($\alpha = 0.05, p < 0.01$).

Conductivity detection

The artificial hard water was analyzed for its characteristic changes every half-hour during each test. The conductivity meter detected electrical conductivity in real-time and recorded at different time intervals. The conductivity reflected the ability of the solution to conduct electricity in accordance with the concentration and mobility of ions and water temperature. In the current study, the water temperature was held stable to guarantee that the conductivity only reflected the actual concentration of ions.

PSD and SEM analyses

The PSD of the particles dispersed in fluid is a mathematical function that defines the relative amounts of particles present, sorted according to size (Jillavenkatesa et al. 2004). The PSD could reflect the size of CaCO₃ crystals formed from the artificial hard water. Undoubtedly, the larger the crystal size was, the higher was the probability that it would create mineral fouling. By the end of each experiment, the PSD was analyzed by collecting water samples at a volume of 200 mL from the sampling port (Figure 1).

SEM images were taken to analyze the surface construction of the CaCO₃ scales. After the solution was completely drained, the deposit subject for SEM analysis was carefully collected from the bottom of the tank at the end of each experiment. Meanwhile, the deposit samples were coated with gold carefully to improve the observation effect.

RESULTS AND DISCUSSION

Water characteristics

Figure 3 shows the test solution conductivity alteration during the experiment. Conductivity directly reflected the number of conductive ions in the solution when the temperature was constant. The initial conductivity value was held stable at 1,200 ± 10 μS/cm. Thus, because of the continuous deposition of CaCO₃ scales, conductivity decreased over time. Figure 3(a) shows the conductivity alteration at the same voltages (100 V) but different frequencies. In the Test-0 group (i.e. untreated case), the value dropped by 31% from its initial value after 12 hours. The conductivities for the EAT cases (from Test-1 to Test-4)
only dropped by 17–25%, corresponding to the different frequencies applied. From the conductivity chart, the decreasing tendency of the EAT cases obviously slowed down more slowly compared with that of the untreated case. One hypothesis (Cowan & Weinritt 1976) on the mechanism of this phenomenon stated that the oscillating electric fields in the processing chamber generated induced electric fields, which provided molecular agitation to the charged mineral ions, i.e. reduced the combination of calcium and bicarbonate ions. Leonard’s experiment (Leonard et al. 2011) with radio frequency but very low voltage (about 5 V) also discovered that the electromagnetic fields could delay the decline of conductivity.

Although the electromagnetic fields reduced the combination of bicarbonate and calcium ions, the conductivity of treatment cases decreased gradually for the high Ca²⁺ ions concentration (5 mmol/L). The chart also shows that the downward tendencies of Test-3 (200 kHz) and Test-4 (400 kHz) were slightly slower than those of the others. In other words, the downward tendency of electrical conductivity was not inversely proportional to the frequency.

Figure 3(b) shows the conductivity measurements at the same frequency (66 kHz) but different voltages. Test-1 (66 kHz, 100 V) decreased by 26% from its initial conductivity value, whereas Test-5 (66 kHz, 50 V) decreased by 28%. The untreated case dropped by 31% after 12 hours from its initial conductivity value. In Test-1, where the voltage was twice that of Test-5, however, the conductivity merely dropped by 2% less than Test-5. The potential explanation is that although the voltage was doubled, the water load was complex, strength of electric field might not be enhanced much in the solution, thus the scale inhibition effect was not significantly shown.

**PSD and SEM analyses**

**PSD in the solution**

A hypothesis was put forward (Kobe et al. 2002) that magnetic fields might affect the nucleation and further crystallization process of CaCO₃. The crystal nucleated more quickly and formed small-size and irregular-shaped particles. Such crystallization was different with the scales, which usually occurred on the surface of the container and could be easily washed away by running solution. Thus, salt crystals had less possibility of forming hard scales. Moreover, Hans (Hans 2004) concluded that the crystal size is reduced by influence of the magnetic field. To test...
and verify these hypotheses, the PSD in the solution was analyzed, as shown in Figure 4(a) and (b). Figure 4(a) shows the PSD in the solution at different EAT frequencies and the untreated case. For the Test-0 (no treatment) case, particles with size range between 14 and 36 μm composed the majority of the total particles in the solution. On the other hand, the percentage of small particles (i.e. below 18 μm) in the EAT cases (Test-1 to Test-4) was more than that of the untreated case. As shown in these curves, a peak exists in the largest proportion. The peaks appear at 16.02% (corresponding to 11 μm), 15.09% (corresponding to 12 μm), 14.56% (corresponding to 11 μm), and 13.62% (corresponding to 11 μm) for Test-3, Test-2, Test-4, and Test-1, respectively. Comparing these EAT cases with the no treatment case, occupancy of particles over 20 μm lessened and the amount of small particle of size less than 12 μm increased. These results verified the hypothesis and indicated that PSD was not proportional to the EAT frequencies.

In order to take the influence of EAT voltage on PSD into account, Figure 4(b) was obtained. The PSD in the solution of Test-1 (66 kHz, 100 V) and Test-5 (66 kHz, 50 V) were similar, although the voltage of Test-1 was twice that of Test-5. On the other hand, Hans (Hans 2004) proved that the crystal size decreases with increasing strength of the magnetic field. The test results showed that electric pulses with the same frequency but different voltages had no significant differences of effect on PSD. The explanation is that although pulse voltage doubled, due to complex water load, electromagnetic field was not enhanced much in the solution, thus the scale inhibition effect was not significantly shown.

**SEM photographs of the scales**

From the above data, EAT actually had a strong effect on slowing down conductivity deduction and reduced the particle size of the crystals distributed in the solution. Thus, it indicated a positive effect on mineral fouling prevention. Based on Kobe’s research (Kobe et al. 2002), magnetic fields led to structure change in CaCO₃ crystals. The
previous tight scale structure gradually became loose under the impact of the magnetic field. Such loose scales were easier to remove under sufficient flow shear forces. To visualize the change of crystal structures, SEM photographs (2,000×) were obtained. Figure 5 shows the SEM images of CaCO₃ crystals formed during the water circulation process with and without EAT, respectively.

The SEM photograph in Figure 5(f) shows that the scales, which formed without the EAT, revealed that the CaCO₃ crystals condensed into big lumps which seemed very dense and adherent. Those of Test-3 and Test-4 cases appeared as loose structures in Figure 5(a) and (b), respectively. The loose structures decreased the possibility of crystals to clog the pipeline. Furthermore, the tendency shows that the crystals gradually condensed into lumps in Figure 5(d) and 5(e), which corresponded well to the decreasing trend of conductivity in the solution.

The Test-3 and Test-4 cases, where the conductivity in the solution had the least reduction, the small-sized particles accounted for the vast majority of total particles by analysis of PSD. Hence, the Test-3 and Test-4 cases were considered as the weakest scaling cases. Moreover, the SEM photographs verified that the crystals structures of the Test-3 and Test-4 cases would not easily form big blocks of scales.

CONCLUSION

The present study investigated the effectiveness of EAT in the prevention of CaCO₃ fouling in a water circulation loop.

The conductivity for the most effective EAT case dropped by 17%, compared with 31% for the untreated case. Analysis of PSD in the solution indicated that the particle size of EAT cases was much smaller than that without treatment. SEM images showed loose structures in the EAT cases compared with the block structure in the untreated case. Tests at the same frequency but different voltages of EAT device were conducted: the results demonstrated that the influence of the EAT device voltage on the test was not obvious. However, 200 kHz was found to be the best working frequency for the EAT device in these tests.

In future, a sweep frequency (around 200 kHz, from 10 to 600 kHz) experiment will be performed to detect the best working frequency scope. Another indicator, the concentration of Ca²⁺ ions will be measured by Ultraviolet Spectrophotometry, which is helpful to observe the chemical process and products.

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