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Application of pulsed spark discharge for calcium carbonate precipitation in hard water

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ABSTRACT

The effect of underwater pulsed spark discharge on the precipitation of dissolved calcium ions was investigated in the present study. Water samples with different calcium hardness were prepared by continuous evaporation of tap water using a laboratory cooling tower. It was shown that the concentration of calcium ions dropped by 20–26% after 10-min plasma treatment, comparing with no drop for untreated cases. A laser particle counting method demonstrated that the total number of solid particles suspended in water increased by over 100% after the plasma treatment. The morphology and the crystal form of the particles were identified by both scanning electron microscopy and X-ray diffraction. Calcite with rhombohedron morphology was observed for plasma treated cases, comparing with the round structure observed for no-treatment cases. It was hypothesized that the main mechanisms for the plasma-assisted calcium carbonate precipitation might include electrolysis, local heating in the vicinity of plasma channel and a high electric field at the tip of plasma streamers, inducing structural changes in the electric double layer of hydrated ions.

1. Introduction

According to the U.S. Geological Survey's (USGS) water use survey data (Feeley et al., 2008), thermoelectric generation accounted for 39% (136 billion gallons per day) of all freshwater withdrawals in U.S. in 2000, second only to irrigation. Each kilowatt-hour (kWh) of thermoelectric generation requires the withdrawal of approximately 25 gallons of water, which is primarily consumed for cooling purposes.

Since heat removal from condenser tubes requires the evaporation of pure water, the concentration of mineral ions such as calcium and magnesium in the circulating cooling water increases with time. Even though the makeup water is relatively soft, the continuous circulation eventually increases the hardness of the water due to pure water evaporation. These mineral ions, when transported through piping in ordinary plumbing system, can cause various problems, including the loss of heat transfer efficiencies in condensers and pipe clogging due to scale formation (Somerscales, 1990; Panchal and Knudsen, 1998). Thus, in order to maintain a certain calcium hardness level in the cooling water, one must discharge a fraction of water through blowdown and replace it with makeup water. In a typical cooling tower application, the cycle of concentration (COC) in cooling water is often maintained at 3.5. That means if the calcium carbonate hardness of the makeup water is 100 mg/L, the hardness in the circulating cooling water is maintained at approximately 350 mg/L. If the COC can be increased through continuous precipitation and removal of calcium ions, one can significantly reduce the amounts of makeup and blowdown water, resulting in the conservation of freshwater.

Various chemical and non-chemical methods are used to prevent scaling and thus increase the COC. Among them the scale-inhibiting chemicals like chlorine and brominated

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compounds were the best choice for the control of mineral fouling. Aside from the high cost of chemicals, more stringent environmental laws increased the costs associated with their storage, handling and disposal. These chemicals also pose danger on human health and environment with accidental spills, or accumulated chemical residues over a long period of time (Panchal and Knudsen, 1998; Muller-Steinhagen, 2000). Thus, there is a need for new approach which is safe and economical from both environmental and cost points of view in cleaning and maintenance of heat exchangers. Physical water treatment (PWT) is a non-chemical method to mitigate mineral fouling with the use of electric or magnetic fields, catalytic surfaces, ultrasounds, or sudden pressure changes. Numerous studies have been reported for the effectiveness of ultrasound (Radler and Ousko-Oberhoffer, 2005), solenoid coils (Cho et al., 2003; Cho et al., 2004), magnetic fields (Fathi et al., 2006; Xiaokai, 2008), catalytic material (Coetzee et al., 1998; Lee et al., 2006), and electrolysis (Gabrielli et al., 2006).

In recent years, there is an increasing interest in the study of pulsed electric breakdown in water and other liquids as it finds more applications in both industry and academic researches. High-voltage electrical discharges directly in water have been shown to be able to induce various reactions including the degradation of organic compounds, the destruction of bacteria and viruses, the oxidation of inorganic ions, the synthesis of nanomaterials and polymers (Akiyama, 2000; Sunka, 2001; Locke et al., 2006). The reactions are usually thought to be initiated by various reactive species, UV radiation, shockwaves, high electric field or intense heat produced by pulsed electric discharge. The concentration of the reactive species and the intensity of the physical effects largely depend on the discharge type and solution properties.

Herein the present study reports for the first time the pulsed spark discharge-assisted precipitation of dissolved calcium ions in hard water system. By measuring the variations of calcium and bicarbonate ion concentrations, the solution pH, and the size and number of solid particles suspended in water, the effect of the spark discharge treatment on the nucleation precipitation of calcium carbonate was studied. The morphology of the precipitates was examined by scanning electron microscopy, whereas their crystal structure was identified by X-ray diffraction.

2. Experiment

2.1. Water preparation

To simulate the actual situations in the field, a closed-loop laboratory cooling tower was utilized in the study where Philadelphia city tap water was recirculated to produce concentrated hard water. Fig. 1 shows the schematic diagram of the cooling tower. The recirculation system consisted of a blower to supply air to the cooling tower, a heater to heat the air, a pump to circulate the water, and the cooling tower itself which was filled with Styrofoam balls used as strainers. As pure water evaporated in the cooling tower, the mineral ions such as calcium and magnesium were left behind and collected in the reservoir. Thus, with the continuous recirculation of hard water in the cooling tower, the concentration of mineral ions was gradually increased until desired calcium carbonate hardness of 200–500 mg/L was reached. It usually took several days to obtain the desired concentration. The water pH resulting from this preparation was in the range of 8–10. A total of 100 L of concentrated hard water for each sample was prepared and kept in the reservoir and used for the whole duration of the experiment. The concentrations of cations and anions were analyzed, and Table 1 summarizes the chemical compositions of different water samples collected from the laboratory cooling tower.

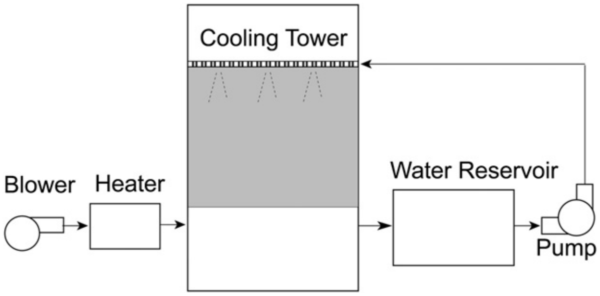

Fig. 1 – Schematic diagram of the laboratory cooling tower.

2.2. Pulsed spark discharge generation system

A pulsed power system was constructed to produce spark discharge directly in water. The system consisted of three components: a high-voltage power supply with a capacitive energy storage, a spark-gap based switch, and a point-to-plain electrode system immersed in water. A schematic diagram of the pulsed power system is shown in Fig. 2. An 8.5-nF capacitor bank was charged by high-voltage pulses provided by a pulsed power supply. When triggered by an air-filled spark-gap switch, spark discharge was initiated between the electrodes from the overvoltage produced by the capacitor. The electrode system included a stainless steel 316-wire electrode as anode, and a stainless steel disk as grounded cathode. The radii of the anode and the disk cathode were 2 and 40 mm, respectively. The radius of curvature at the tip of the anode was 0.2 mm. The distance between the anode and the disk cathode was 10 mm.

Power deposited into water was analyzed by measuring the current passing through the discharge gap and the voltage drop in the gap. For measurements of the current, a magnetic-

Table 1 – Chemical compositions of water sample collected in the simulated laboratory cooling tower.

	Sample 1	Sample 2	Sample 3
Ca^{2+}	96	128	167
Na^{+}	156	230	297
Mg^{2+}	8	13	17
Cl^{-}	98	140	186
SO_4^{-}	176	269	362
HCO_3^{-}	296	392	498
pH	8.67	9.10	9.62
$CaCO_3$ hardness	279	378	492

All values are in mg/L.