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THEORY OF ELECTRONIC ANTI-FOULING TECHNOLOGY TO CONTROL PRECIPITATION FOULING IN HEAT EXCHANGERS

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ABSTRACT

This paper provides a scientific explanation for the operating principle of the electronic anti-fouling (EAF) technology. The EAF technology produces an oscillating electric field via Faraday's law to provide necessary molecular agitation to dissolved mineral ions. Through improved collisions, they precipitate to insoluble mineral crystals, a process called "controlled precipitation." Hence, the level of supersaturation of the hard water significantly decreases, and new scale deposits are prevented inside heat transfer equipment. © 1997 Elsevier Science Ltd

Introduction

Scales are formed when hard water is heated (or cooled) in heat transfer equipment such as heat exchangers, condensers, evaporators, cooling towers, boilers, and pipe walls. The type of scales differs from industry to industry, depending on the mineral content of available water. Scales often observed in industry include calcium carbonate, calcium sulfate, barium sulfate, silica, iron scales, and others. One of the most common forms of scales is calcium carbonate ($CaCO_3$), which occurs naturally as an ingredient of chalk, limestone, and marble. Acidic water passing over and permeating through rocks dissolves limestone into calcium and bicarbonate ions, thereby making water hard. When the hard water is then pumped into heat transfer equipment, the calcium and bicarbonate ions precipitate due to the changes in the solubility, forming hard scales on the heat transfer surfaces, and clogging pipes and manifolds. When scales deposit in a heat exchanger surface, it is traditionally called "fouling" [1-3].

Fouling problems are of major concern to many industries using water and heat. Examples include process, petroleum, food, utility, marine, mining, air compressor and air separation industries. If one can reduce or prevent fouling in heat transfer equipment in these industries, the savings in energy, maintenance, replacement of equipment, etc. will be truly significant. With this new technology, heat exchangers can perform at their initial maximum capacity all the time, conserving energy without polluting the environment.

Once scales build up in a heat transfer surface, at least two problems associated with scales occur. The first problem is the degradation in the performance of the heat transfer equipment. Because the thermal conductivity of scales is much smaller than that of pipe materials, a thin coating of scales on the heat transfer surface will greatly reduce the overall heat transfer performance. For example, the thermal conductivity of calcium carbonate is approximately 0.8 W/mK [4], while that of copper is 401 W/mK [5]. The second problem is that a small change in tube diameter substantially decreases the flow rate or increases the pressure drop across the heat transfer equipment. For example, a 5% reduction in diameter results in a 22-30% increase in pressure drop [6]. This is due to the fact that the pressure drop across a tube is inversely proportional to the fourth power of the tube diameter in laminar flow, and almost the fifth power of the inside diameter in turbulent flow.

The current technique in preventing fouling is the use of scale-inhibiting chemicals such as dispersing or chelating agents [7]. The anionic 'claws' of these agents chemically grip dissolved cations, thus neutralizing them. Ion exchange and reverse osmosis are also used to reduce water hardness, alkalinity, and silica level. However, these equipment are expensive in industrial scale and require heavy maintenance for proper operation. Once fouling occurs in heat exchangers, scales are removed by using acid chemicals, which shorten the life of heat exchanger tubes, thus requiring premature replacement. When acid cleaning is not desirable, scraping, hydro-blasting, sand blasting, metal or nylon brushes are used, operations which incur downtime and repair costs. If an electronic anti-fouling (EAF) technology can be used, one can discontinue the use of scale-inhibiting chemicals or chemicals to remove scales, thus preserving a clean environment. The primary benefit of the EAF technology, if proven, will be in maintaining the initial peak performance of a heat exchanger indefinitely.

Alternative Solutions

There have been a number of alternative solutions to the chemical treatment of water for the purpose of fouling control. History shows that Egyptians used permanent magnets two to three thousand years ago in an attempt to reduce scale deposits in pipes carrying hard water [4]. In the

United States, there have been numerous efforts for the past 150 years to introduce permanent magnets or electromagnetic devices as manifested by the long list of patents awarded by the U.S. patent office [4]. More recently, a number of devices using electromagnetic field or sound waves have appeared in the market.

One of the major problems of these alternative solutions is the lack of understanding of the operating principle (or theory). Currently there are more than 50 companies marketing different types of non-chemical methods in the world. Some of the claims made by these companies are correct and acceptable while many show a lack of understanding of the principle of fundamental physics and chemistry. Furthermore, most claims are testimonial statements. Although these statements collected from field applications are valuable and helpful in understanding the principle, they do not add much in understanding the theory of the alternative methods.

This paper focuses on an EAF technique, which is one of the most recent alternative solutions and an environmentally clean technology. The objective of this paper is to propose a theory of the electronic anti-fouling technology. Due to the limited space, other alternative methods are not discussed in the present study.

Background

The scale deposition mechanism is often explained by a process that includes the dissolution of minerals, supersaturation, nucleation, precipitation, crystal growth, and, finally, scale deposition. The scale deposition mechanism is controlled by many variables, which include fluid temperature, surface temperature, flow velocity, pressure, pH, etc. Each of these variables affects the solubility of scale-causing minerals, thus the scale deposition mechanism.

The solubility of calcium carbonate decreases with increasing temperature and pH, whereas it decreases with decreasing pressure [8]. When conditions such as temperature, pressure, and pH change in a flow system such that the solubility of calcium carbonate decreases, calcium and bicarbonate ions precipitate to form $CaCO_3$ crystals. This happens usually on heat transfer surfaces because water temperature suddenly changes as the water makes contact with the heat transfer surfaces. Furthermore, the heat transfer surfaces are negatively-charged (i.e., in a solution whose pH is greater than 7.0); thus, positively-charged ions such as calcium and magnesium line up against the negatively-charged heat transfer surfaces within a distance of approximately 10-30 angstrom, a phenomenon known as "the electric double layer" [9]. Subsequently, the electrostatic Coulombic attraction force between the dissolved mineral ions and heat transfer surfaces makes these mineral ions adhere to the surfaces as $CaCO_3$ crystals

(dissolved calcium ions)

$$Ca^{++} + 2HCO_3^- \xrightarrow{\text{Uncontrolled precipitation}} CaCO_3 + H_2CO_3$$

Scale build-up ↓

Calcium salts stick to
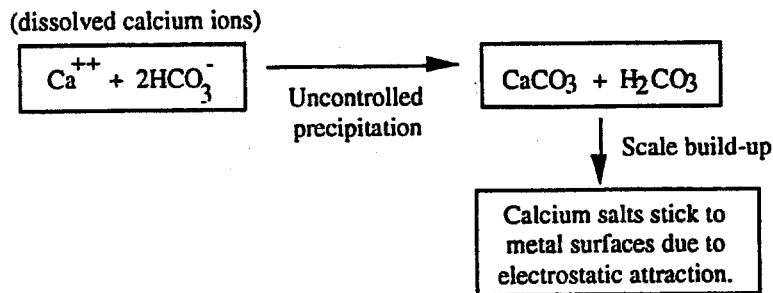metal surfaces due to
electrostatic attraction.

FIG. 1

Block diagram showing uncontrolled precipitation of calcium and bicarbonate ions and
subsequent adhesion of $CaCO_3$ crystals to heat transfer surface.

precipitate. This is why scale deposits are unavoidable when hard water is used in heat transfer
equipment. Figure 1 shows a chemical reaction of $CaCO_3$ precipitation occurring inside a heat
exchanger, a phenomenon which is called "uncontrolled precipitation" in the present study.

Calcite and Aragonite

There are two types of calcium carbonates, $CaCO_3$: calcite and aragonite as shown in Fig. 2.
Calcite is a calcium carbonate which is formed at room temperature (i.e., below 30°C), easily
removable with weak HCl acid, less-adherent than aragonite [4], having a hexagonal crystal
shape and a specific gravity of 2.71. Aragonite, also a calcium carbonate, is formed at high
temperature (i.e., above 30°C) and is difficult to remove [4], having an orthorhombic crystal
shape, and a specific gravity of 2.94. Specifically, the aragonite is a more troublesome form of
calcium carbonate than calcite because it forms a harder and denser deposit than calcite in boilers
and other heat transfer equipment [4]. When calcium carbonate is formed at temperature above
30°C, both aragonite (~80%) and calcite (~20%) are formed.

When hard water is heated inside heat transfer equipment, the aragonite type of calcium
carbonate is formed due to elevated temperature, thus adhering to heat transfer surfaces.
Therefore, if one can precipitate calcium carbonate to form the calcite type of calcium carbonate
before the hard water enters heat transfer equipment, one can reduce or prevent scale deposits.
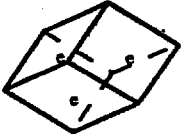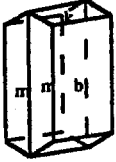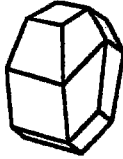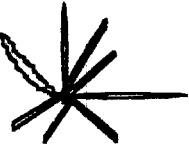This is the key concept of the electronic anti-fouling technique.
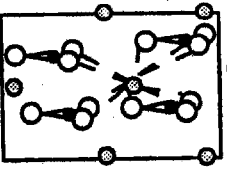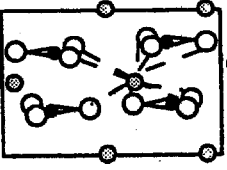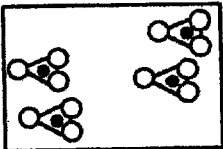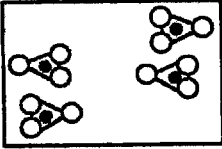
Calcium Carbonates / Compared items	Calcite	Aragonite
Specific Gravity	2.71	2.94
Adhesiveness	less-adherent to pipe & heating surface	adherent to pipe & heating surface
Crystal Form	 Hexagonal	 Orthorhombic
Visualization through Microscope	 Round shape	 Needle shape
Carbonate layer orientation (side view)	O Ca ● Carbon O Oxygen CO3 groups in same direction	O Ca ● Carbon O Oxygen CO3 groups in opposite directions
Carbonate layer orientation (top view)	⊗ Ca (not shown) ● Carbon O Oxygen CO3 groups in same direction	⊗ Ca (not shown) ● Carbon O Oxygen CO3 groups in opposite directions

FIG. 2

Two types of calcium carbonate: Calcite and Aragonite

The Principle of the Electronic Anti-Fouling Technology

Figure 3 shows a schematic diagram of the operation of an electronic anti-fouling unit. A 18 (or 14) gauge single stranded wire is wrapped around a feed pipe to a heat exchanger. Two ends of the wire are connected to the electronic anti-fouling control unit. The EAF unit produces a pulsing current to create time-varying magnetic fields inside the pipe. Subsequently, the time-varying magnetic field creates an induced electric field inside the pipe, a phenomenon which can be described by the following Faraday's law [10]:

$$\int E \cdot ds = -\frac{\partial}{\partial t} \int B \cdot dA \qquad (1)$$

where E is an induced electric field vector, s is a line vector along the circumferential direction, B is a magnetic field strength vector, and A is the cross sectional area of pipe. In order to maximize the induction, a pulsing current having a square-wave signal was used.

The induced electric field which oscillates with time provides necessary molecular agitation to charged mineral ions such that calcium and bicarbonate ions collide and precipitate (see Fig. 4). Once dissolved ions are converted to insoluble mineral crystals, the level of supersaturation of the water significantly decreases; thus new scale deposits on the heat transfer surface are reduced or prevented.
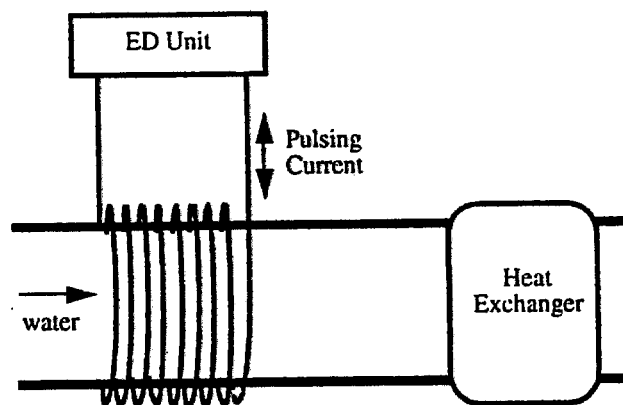

FIG. 3

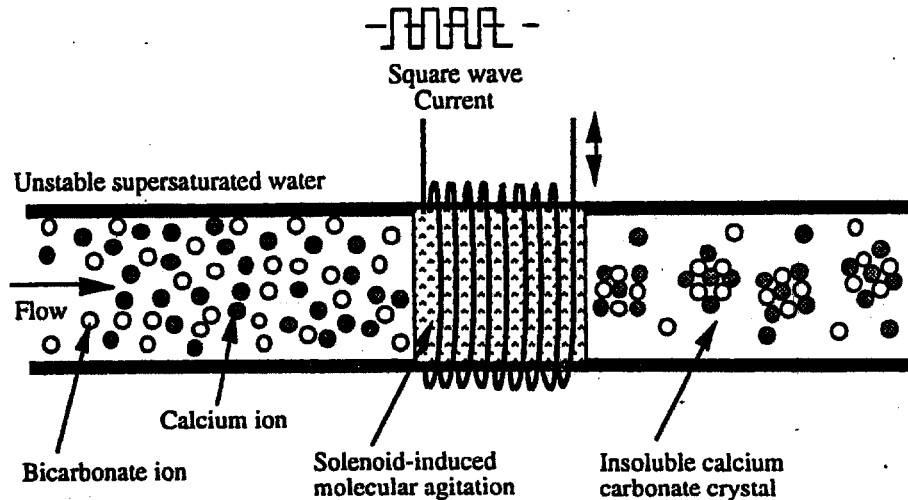Schematic diagram of the operation of an electronic anti-fouling unit

FIG. 4

Schematic diagram of controlled precipitation through electronic anti-fouling technology.

Hard Water as the Culprit of Fouling

Hard water has excess dissolved mineral ions well above the saturation limit of each dissolved ion, and hence the water becomes unstable. If one leaves the supersaturated water in the atmosphere for one or two days, most mineral ions precipitate as dissolved CO_2 escapes slowly from the surface of the water, and the level of supersaturation decreases accordingly [7]. However, since the natural precipitation process takes place very slowly, it can not be used in most heat transfer systems.

It is this supersaturated and unstable nature of hard water that causes fouling in a heat exchanger. Fouling also occurs with saturated water because the saturated water becomes locally supersaturated when it makes contact with a heat transfer surface. In this case, the fouling problems occur slowly over a period of years.

The fouling problems of the present interest occur in a time period of days, weeks or months, which can be attributed to the use of supersaturated water from the beginning. For example, when one has supersaturated water with a supersaturation level of six (i.e., hardness of approximately 350 ppm as $CaCO_3$) [8], the level of supersaturation further increases well

beyond six inside the heat exchanger as the water makes contact with heat transfer surfaces. The supersaturation level (or similarly the Langelier index) of water is the key factor which determines how fast scaling takes place [4].

Hypothesis of Electronic Anti-Fouling Technology

To understand the mechanism of electronic anti-fouling technology, we will begin with a discussion of the energy of nucleation. In order to understand the process of nucleation, which can be either homogeneous or heterogeneous, it is necessary to introduce the concept of Gibbs free energy [11]. The Gibbs free energy of the formation of a substance, ΔG, is defined as the heat content for the formation of the substance minus the product of the temperature and the entropy. This function is often used to evaluate thermodynamic equilibrium. A spontaneous reaction will result in a reduction in the change in the Gibbs free energy, i.e., a negative ΔG.

The Gibbs energy of nucleation is the summation of two distinct portions, a bulk energy term and a surface energy term [11].

$$\Delta G(\text{nucleation}) = \Delta G(\text{bulk}) + \Delta G(\text{surface}) \tag{2}$$

The bulk energy term can be defined as

$$\Delta G(\text{bulk}) = - jkT \left[\frac{a}{a_0}\right] = -\frac{4}{3}\pi r^3 \Delta G_v \tag{3}$$

where j is the number of molecules in the nucleus, k is the Boltzmann constant, T is absolute temperature, r is the radius of the nucleus, ΔG_v is the free energy change of transformation per unit volume, and a/a_0 is the ratio of the actual and equilibrium activities. a/a_0 can be considered as the degree of supersaturation. Note that $\Delta G(\text{bulk})$ is always negative, indicating that the bulk energy term drives the reaction forward spontaneously. This is the energy released during crystallization from the making of bonds. The surface term can be defined as

$$\Delta G(\text{surface}) = 4\pi r^2 \gamma \tag{4}$$

where γ is the interfacial tension. The $\Delta G(\text{surface})$ term is the energy required to make the surface of the nucleus and is always positive in sign.

At the initiation of nucleation, the number of molecules in the nucleus is small such that the surface energy term (i.e., a function of radius^2) is larger than the bulk energy term (i.e., a

function of radius[3]), making the overall Gibbs free energy positive in sign. Thus, the reaction will not occur spontaneously without energy input from outside the system. However, as the crystal grows, the bulk term will become more dominant, making the overall Gibbs free energy negative in sign. Subsequently, the reaction will continue spontaneously.

Figure 5 shows how the Gibbs free energy of crystallization is affected by the size of the nucleus and the degree of supersaturation. Assuming the solution is supersaturated, the nucleus must grow beyond a critical size in order for the nucleus to continue to grow. In other words, the bulk energy term must be larger than the surface term so that ΔG(nucleation) becomes negative and the crystallization reaction proceeds spontaneously. The energy that must be supplied into the system before this happens can be considered the activation energy of nucleation. Generally, the rate of nucleus formation can be expressed as [11]:

$$J \text{ (Rate of Nucleation)} = A \exp[\frac{-\Delta G}{kT}] = A \exp[\frac{-16 \pi \gamma^3 v^2}{3k^3T^3 (\ln S)^3}] \qquad (5)$$

where A is similar to the frequency factor in the reaction rate equation, S is the supersaturation factor, which is essentially the same as a/a_0, and v is the molecular volume. The frequency factor adjusts for the number of effective collisions as related to the total number of collisions. In this manner, it can be seen that the rate of nucleation is dependent on four basic quantities; the
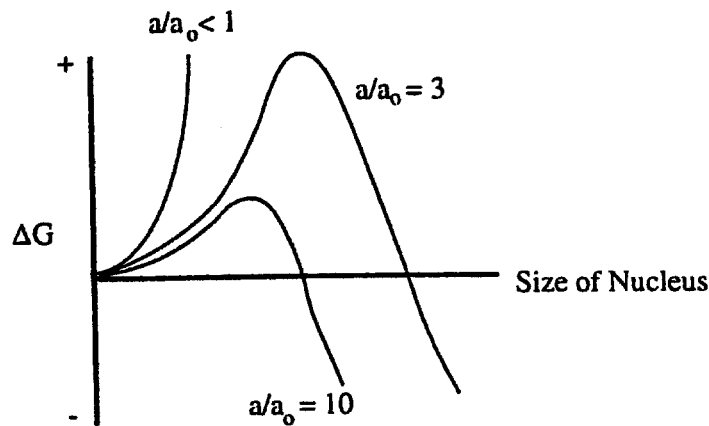

FIG. 5

Profiles of Gibbs free energy at three different supersaturation ratios
(i.e., a/a_0 <1, 3, and 10)

frequency factor, the temperature, the interfacial energy, and the degree of supersaturation [11].

For example, one can have the following constants for calcium carbonate precipitation, assuming that water temperature is 25°C and the degree of supersaturation of water is $S = 3$:

γ (interfacial tension) $= 0.011 \times (12.21 - \frac{1}{2} \ln S)$ J m^{-2}

v (molecular volume) $= 6.13 \times 10^{-29}$ m^3 (6)

k (Boltzmann constant) $= 1.38 \times 10^{-23}$ J/K

and

$J = A \exp[-1,576] = \sim 0$ (7)

This clearly demonstrates that the homogeneous nucleation can not take place in the precipitation of calcium carbonate particles. In other words, the precipitation must be heterogeneous. Of note is that similar results (i.e., $J \sim 0$) were obtained for different degrees of supersaturation. For example, J becomes $A\exp[-84]$ for $S = 50$. It is well accepted that the nucleation that occurs in natural water is predominantly from heterogeneous nucleation [4,11]. Any foreign material which will reduce the interfacial tension between the solid and liquid phase will promote nucleation.

Discussion

Any theory of the electronic anti-fouling (EAF) technique must be able to explain two distinct phenomena. The first is the immediate forced precipitation of calcium carbonate from water, and the second is the predominant formation of the calcite (non-adherent) form of calcium carbonate.

The forced precipitation is explained by heterogeneous nucleation theory. Dissolved ions are constantly participating in collisions with the impurities in the water phase. The small percentage of the collisions that are effective in nucleation are statistically accounted for by the frequency factor previously described. The oscillating electric field produced by the EAF treatment changes the effectiveness of the collisions, increasing the number of collisions that result in nucleation.

The change in the frequency factor can be explained by the weakening of the hydrogen bond between the ion and the surrounding water molecules. The oscillating electric field produced by the EAF treatment orients the charges of the ions (both positive and negative). Along with an increase in the kinetic energy of the colliding ions, the oscillating electric field also increases the

Coulombic attraction of the ions by increasing their dipole moments. If the standard dipole moments of the ions are disturbed by the EAF treatment, the solvated ion will have a different energy with the evolving nucleus. Just as the heterogeneous nucleation rate increases due to lowered interfacial energy, a shift in dipole moment also results in increased nucleation. All of these factors improve the efficiency of the collisions, resulting in a larger number of resulting nuclei such that the ΔG(nucleation) becomes negative, leading to the spontaneous crystallization. This is the basis for the immediate precipitation that is observed from the EAF treatment.

The above-mentioned hypothesis of the improved collision efficiency by the EAF technology needs to be verified experimentally. However, since the collision occurs at molecular levels, it may not be possible to prove this experimentally in engineering laboratory. Therefore, we have attempted to indirectly prove this by conducting crystal growth experiments with samples treated by the EAF technology as summarized in Fan and Cho [12]. Furthermore, the above hypothesis was validated through filtration experiments where precipitated calcium carbonate particles by the EAF technology were removed using a filter. The alkalinity of filtrates were measured using the standard titration technique. Details of the alkalinity experiment carried out to prove the above hypothesis were given elsewhere [13].

The explanation of how the EAF treatment of water results in the formation of calcite is explained as follows: The EAF treatment provides the necessary energy for the scale-causing mineral ions to nucleate in the solution (i.e., at the inlet pipe). Once the nucleus has reached a critical mass, the crystallization continues spontaneously until the precipitate is visible. This crystallization occurs within the liquid phase. Therefore, the precipitates that are formed do not adhere to the heat transfer surfaces or pipe walls because of the lack of the electrostatic force between the precipitates and heat transfer surfaces, but are suspended and move with the carrier fluid.

In addition to the change in nucleation site (i.e., nucleate in the solution not on the heat transfer surfaces), the EAF treatment also affects the crystal structure of $CaCO_3$. Under the EAF treatment, the calcium and bicarbonate ions are converted to the calcite form of $CaCO_3$ particles at room temperature, which are powdery and fluffy, and easily removed by turbulence and routine blowdowns. On the contrary, without the EAF treatment, the calcium and bicarbonate ions are converted to the aragonite form of $CaCO_3$ particles at elevated temperature inside a heat exchanger, which easily adhere to the heat transfer surfaces and form hard scales requiring acid cleaning for removal.

The formation of calcite by the EAF treatment can also be explained by the lattice energies of crystals. When pure calcium carbonate precipitates naturally under typical environmental conditions, the predominant crystalline form can either be the aragonite or the calcite form depending on temperature or pressure. The difference in Gibbs free energy between the formation of calcite (-269.78 Kcal/mole) and aragonite (-269.53 Kcal/mole) is only -0.25 Kcal/mole. For the untreated water, scale crystals in general will grow at the surface of a heat exchanger in layers by forming a lattice structure which depends on temperature at the heat transfer surface. This structure is the aragonite form, which is dendritic, dense, and adherent. In this structure, adjacent carbonate ions in each crystal layer are oriented in opposite directions as shown in Fig. 2. On the other hand, the oscillating electric field produced by the EAF treatment precipitates calcium carbonate particles at room temperature, where adjacent carbonate ions in each crystal layer are oriented in the same direction due to an induced electric field which oscillates along the circumferential direction but remains uni-directional along the radial direction, resulting in the formation of calcite.

When we get a calcium carbonate particle whose size is 1 mm in diameter, the question of how many calcium and bicarbonate ions are converted into the 1 mm size $CaCO_3$ particle will be addressed next. Based on the molecular weight of $CaCO_3$ of 100 g/mole, a specific gravity of 2.71 (i.e., calcite), and the Avogadro number, the number of $CaCO_3$ molecules in a 1 mm size $CaCO_3$ particle was calculated to be 8.5×10^9, almost ten billion $CaCO_3$ molecules. In other words, the EAF treatment converts dissolved mineral ions into mineral salt crystals through controlled precipitation at a rate of ten billion calcium and bicarbonate ions per 1 mm size $CaCO_3$ particle. This is an extremely efficient way to neutralize the dissolved mineral ions and to prevent them from depositing on the heat transfer surface or pipe walls.

Conclusions

This paper provides a scientific explanation for the operating principle of the electronic anti-fouling (EAF) technology. The EAF technology produces an oscillating electric field via Faraday's law to provide necessary molecular agitation to dissolved mineral ions. Through improved collisions, they are converted to insoluble mineral crystals, a process called "controlled precipitation." Hence, the level of supersaturation of the hard water significantly decreases, and new scale deposits are prevented inside heat transfer equipment. It is hoped that the present paper will help promote further studies on the electronic anti-fouling technology and other non-chemical methods to control precipitation fouling.

Final Remarks

As a result of the controlled precipitation by the EAF treatment, the supersaturation level in the water is significantly reduced. Since the fouling rate is the deposition rate minus the removal rate, the fouling rate can be negative when the EAF treatment eliminates the new scale deposits, suggesting that the existing scales can be removed over a period of time.

The present paper uses calcium carbonate as an example of the mineral scales. However, the electronic anti-fouling technique is not limited to the calcium carbonate scale. The EAF treatment utilizes the electrical charges of dissolved ions. Since all the dissolved ions have the electrical charges, the EAF treatment is effective for any dissolved inorganic ions, including calcium, magnesium, barium, silica, bicarbonate, sulfate, etc. In particular, it is worth mentioning on silicate scales. The solubility of silicate decreases with decreasing temperature such that dissolved silica ions precipitate as water is cooled. The silica scale problems are commonly seen in geothermal plants where heat is extracted from silica-loaded hot water through a heat exchanger.

The issue of whether the EAF treatment lasts indefinitely should be addressed. Since the mineral crystals like calcium carbonate are insoluble, they will not be redissolved to water unless there is a significant change in pH, temperature, or pressure. Details of the optimum operational conditions and the effectiveness of EAF treatment in an actual heat exchanger are given elsewhere [13,14].

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