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Original Scientific Paper

Synergistic Application of Chemical and Electromagnetic Water Treatment in Corrosion and Scale Prevention

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The costs of damage caused by scale and corrosion worldwide in cooling towers, boilers and pipes escalated to more than an annual $100 billion in recent years. Neither classical chemical prevention methods nor new alternative electromagnetic water treatment methods have yielded satisfying solutions. We have used a combination of chemical and electromagnetic technologies to prevent scale and corrosion of galvanized zinc coated cooling towers with great success in the last three years. This manuscript describes the physicochemical principles of the approach we employed.

Zinc surfaces were coated with the diaminosilane reagent. This increased a positive charge of the zinc surface and significantly reduced adsorption of calcium cations. Silane coating also protected zinc from corrosion. It was also found that electromagnetic water treatment splits water into atomic hydrogen and hydroxyl ions and acts as a water clusters structure breaker. This prevented buildup of silicate or carbonate scale by increasing the diffusivity of water and ions. When high quantities of calcium and hydrogencarbonate were present, small amounts of partially hydrolyzed polyacrylamide polymeric descalant were added to cooling tower water to prevent calcium carbonate scale buildup through modification of crystal growth. Such synergistic use of chemical and electromagnetic water treatment resulted in no corrosion or scale buildup after three years of plant studies in twenty cooling towers in California.

This article is dedicated to Professor Egon Matijević on the occasion of his 75th birthday.

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INTRODUCTION

Scale and corrosion prevention in cooling towers and boilers are becoming increasingly important industrial issues. The worldwide search for environmentally friendly water treatment technologies is underway due to increased awareness that our ecosystems should be protected from harmful chemicals. Chemicals currently used in scale and corrosion control such as phosphates, phosphonates, molybdates, chromates or aliphatic amines are all toxic to some degree. New, more environmentally friendly technologies could save trillions of liters of water every year.

The main component of scale is usually calcium carbonate in the form of calcite or aragonite. Calcium silicate, silica and calcium phosphate are also present in many geographic areas. Other solids such as hematite, goethite or calcium sulfate are also often present as a component of scale.

Scale comprised of calcium carbonate, calcium silicate and silica is extremely difficult to remove and to prevent from forming. No current technology could handle water rich in both calcium and silicate in a proper way. Silica and silicate scale are particularly unwanted due to their very low thermal conductivity. When such scale is present in more than 100 micron thick deposited layers, heat transfer efficiency is decreased up to 90%.

While phosphonates are commonly used in the US and European Community countries to control calcium carbonate precipitation, no successful way to control silica precipitation on zinc, copper or steel surfaces inside cooling towers and boilers existed until recently.[1] We developed an electromagnetic water treatment device and successfully used it in the control of silica rich scale deposition in the Western United States.[2] Recent fundamental research studies showed that electromagnetic radio frequency radiation modifies the gas/water interface and consequently changes the hydration properties of water.[3] While certain RF signals with high peak to peak amplitudes up to 20 000 V promote the formation of smaller clusters in the bulk water and thicker hydration layer around ions and surfaces,[4] other low amplitude signals promote structuring in the bulk water and decrease the efficiency of hydration of ions and surfaces. It was found that signals which promoted hydration of ions and surfaces also decreased the rate of silica adhesion and increased the rate of silica removal from adhesion columns filled with metallic zinc scrapes. The same type of signal also promoted hydration of calcium and carbonate ions, which resulted in the formation of larger particles due to prolonged nucleation and delayed onset of precipitation. The precipitation step, after all, is the removal of hydration water from nuclei. If ions and nuclei are hydrated more efficiently, water will stick to them until larger nuclei are formed, and the precipitation process starts. And indeed, it was realized that the application of radio frequency water treatment could reduce the precipitation rate of calcium carbonate inside cooling towers up to 50%. Deposition of silica rich scale was reduced up to 90%. Higashitani and coworkers observed similar results with the precipitation of calcium carbonate scale when magnets were used to treat water.[5]

We recently realized that it is the gas/water interface which gets perturbed with the electromagnetic treatment. As in the case of the recently very popular sonoluminescence phenomena (ultrasound treatment of the gas/water interface), it was realized that some splitting of water yielding hydroxyl radicals and atomic hydrogen occurs during electromagnetic water treatment.[6,7] Atomic hydrogen disappears very fast but can get stabilized if some cage-like compounds such as silicates are present.[8] Atomic hydrogen is an ultimate reductant and yields free electrons outside the silicate cage when any oxidative attack occurs. Free electrons are structure breakers and further enhance unstructuring of water clusters in the bulk solution.[9] On the other hand, hydroxyl radicals form hydrogen peroxide which corrodes metal surfaces.

To circumvent problems related to the corrosive behavior of produced hydrogen peroxide when electromagnetic technologies are used, we decided to permanently coat a metal surface with some corrosion protection chemicals. Best results were obtained by coating with self assembled silane multilayers no more than 50 nm thick. The results of studies of synergistic effects of chemicals and electromagnetic radiation are described in this manuscript.

EXPERIMENTAL

Materials and Methods

All salts, acids and bases were purchased from Sigma Chemical Company and were of the highest purity available. Silane reagents were purchased from Gelest Inc. Partially hydrolized polyacrylamide of 7000 molecular mass was purchased from Cytec. Triply distilled, deionized water with a resisitivity of approximately 16.5 MΩ cm was used to prepare solutions and suspensions. The pH was adjusted with additions of 0.1 M of NaOH or HCl. Zinc was obtained from Metal Probes.

The radio frequency (RF) signal was delivered with a helical resonator source as described in Ref. 2. A variable amplitude delivery system at 27 MHz frequency was used. The maximum available amplitude was around 20 000 volts. The RF antenna was a gold coated copper sphere with a diameter of 1 cm connected to a 5 cm diameter helical resonator coil. The antenna was enclosed in a plastic box to prevent dielectric and conductivity losses that result from direct contact with water. The laboratory treatment was performed in the water filled bucket. The RF source was positioned *ca.* 10 cm from closed polypropylene bottles with samples to be treated. The setup minimized the possibility of any contamination. The samples were treated for 30 minutes before the beginning of the physicochemical measurements described below. In cooling towers the RF treatment unit was completely submerged in water near the water inflow pipe. The same setup was used in laboratory flow experiments.

The precipitation of calcium carbonate under a laboratory setting was followed at metal interfaces. Galvanized zinc is used in the industrial application and was chosen as a metal of interest. Saturated calcium bicarbonate solutions were used, and 5 × 1 cm zinc samples with rough metal surfaces were utilized as the substrate. The zinc was placed in a water bath equilibrated at 70 °C with a water flow at *ca.* 0.5 L/min. The weight change of metallic galvanized zinc coupon was measured after 48 hours. The precipitated powder was scraped away, analyzed under optical microscope and dried for X-ray and FTIR analysis to identify a chemical and phase composition.

Metallic surfaces were coated with silane regents obtained from Gelest Inc.[10] One percent aqueous solutions were used, and metal surfaces were completely immersed for 24 hours. After that, the metal surface was washed with deionized water and dried before the experiments with scale precipitation and corrosion rate measurements were initiated. The same approach was used in the cooling towers.

Modifications of the isoelectric point of metallic zinc after coating with different silane reagents were followed with the column method developed by Kallay and coworkers.[11] In short, a column 0.5 cm in diameter and 8 cm in height packed with zinc scrapes (1 mm average diameter) was equilibrated at the desired pH. Then, the column was opened and latex suspension (10 mg/L, 0.3 micron particle size sulfonated latex) was pumped with a peristaltic pump at a flow rate of 0.5 mL/min. The supernatant was collected and the turbidity measured and compared to that of the suspension before passage through the column. The pH of the suspension was then changed, and the turbidity of the collected suspension was measured after pH equilibration. The procedure of pH adjustment and passing of the suspension through the column was then repeated at different pH's to identify the change of adhesion rate and possibly the change in the isoelectric point of zinc. The turbidity ratio of outgoing and incoming suspensions was then plotted against pH for data analysis.

Corrosion rate was measured with a standard corrosion rate meter based on current polarization measurements. Standard metallic corrosion electrodes supplied by the manufacturers were used. Corrosion rates were measured under laboratory and industrial cooling tower conditions and followed for up to three years.

RESULTS

The precipitation of calcium carbonate and other relevant precipitates under laboratory and industrial cooling tower conditions was followed by attaching 5 × 1 cm galvanized zinc coupons to the heat exchange surfaces. Zinc coupons were weighed after 48 hours under laboratory conditions or after one month in industrial cooling towers throughout the Western United States. Under laboratory conditions, saturated solutions of calcium bicarbonate were used as a model system. The water bath was equilibrated at 70 °C and water flow was adjusted at 0.5 L/min. Under such conditions about 52 ± 5 mg of precipitate was collected after 48 hours. When RF water treatment was used, about 25 ± 4 mg of precipitate was collected during the same period of time. When 20 ppm of partially hydrolyzed polyacrylamide, molecular mass 7000, was added to the suspension without RF treatment about 15 mg of precipitate was collected. Finally, when the combination of RF water treatment and polymer treatment at the same dosage of 20 ppm was used only 8 mg of precipitate was collected.

Different samples of silane coupling agents were used to coat the metallic surface and protect it from corrosion. Silane reagents, R_1–Si–$(OR)_3$, contain three siloxane groups Si–OR, which in water hydrolyze to Si–OH and ROH. Silane agents also contain an additional alkyl chain R_1. Si–OH groups produced through hydrolysis can bind to metal oxide groups M–OH which coat most oxides. SiOH groups can also polymerize to form self-assembled mono or multiple layers. Coating and polymerization reactions are schematically depicted as: $\text{M–OH} + \text{Si–OH} \rightarrow \text{M–O–Si} + H_2O$ or $\text{Si–OH} + \text{Si–OH} \rightarrow \text{Si–O–Si} + H_2O$. If R_1 group contains hydrophylic species, silanes are commonly water soluble. Four different water soluble silanes were used in this work: diaminosilane ($R_1 = (CH_2)_3\text{–NH–}(CH_2)_2\text{–}NH_2$); carboxysilane ($R_1 = (CH_2)_{10}\text{– COOH}$); zwitterionic silane ($R_1 = (CH_2)_3\text{–N(COOH)–}(CH_2)_2\text{–N}(COOH)_2$); and (polyethylene glycol)silane ($R_1 = (CH_2)_3\text{–NH–CO–}(CH_2\text{–}CH_2\text{–O})_{4–6}\text{–OH}$). Schematic presentation of these silane molecules is shown in Figure 1. All silanes were applied from 1% water solutions at room temperature. Coating lasted 24 hours. Spectroscopic results[12] indicated the presence of multiple layers with nanometer thickness (no more than 50 nm).

The same precipitation tests as described at the beginning of the »Results« section were used to follow the effects of silane coating on calcium carbonate precipitation. In the absence of silane coating, 49 ± 5 mg of precipitate was collected from the zinc coupons. Diaminosilane coated coupon yielded only 12 ± 2 mg of precipitate. Carboxysilane yielded 110 ± 8 mg of the precipitate. Zwitterionic silane coated zinc coupon mass increased for 52 ± 4 mg. (Polyethylene glycol)silane coated zinc coupon collected *ca.* 45 ± 5 mg of the precipitate.

Since the best results in reducing the rate of calcium carbonate precipitation were observed with the diaminosilane, further experiments were performed with that system. When RF water treatment was used in synergy with diaminosilane coating, only 5 ± 2 mg of precipitate was collected. Finally, when RF water treatment along with the diaminosilane coating and the addition of 20 ppm of partially hydrolyzed polyacrylamide were used no precipitate was observed on the zinc coupons even after 140 hours!

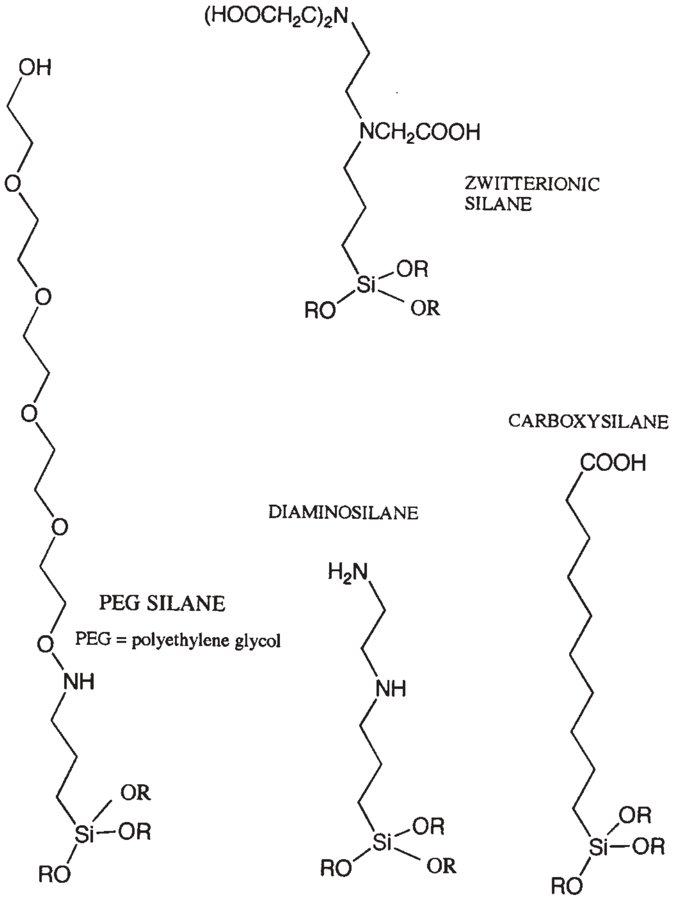

Figure 1. Schematic presentation of the diaminosilane, zwitterionic silane, carboxysilane and (polyethylene glycol)silane molecules used to coat zinc surfaces in this work.

FTIR and X-ray analysis indicated that in the absence of RF, silane coating and polyacrylamide treatment, pure calcite with trace amounts of vaterite and aragonite precipitated on zinc surfaces. In the presence of RF, some aragonite and even calcium oxide precipitated at the zinc surface. The diaminosilane coating as well as the addition of partially hydrolyzed polyacrylamide promoted the precipitation of amorphous calcium carbonate. Detailed spectroscopic and X-ray analysis of the precipitates will be presented elsewhere.[12]

The modifications of the zinc surface after silane coating were followed with changes in the isoelectric point (i.e.p) and corrosion rate. Adhesion col-

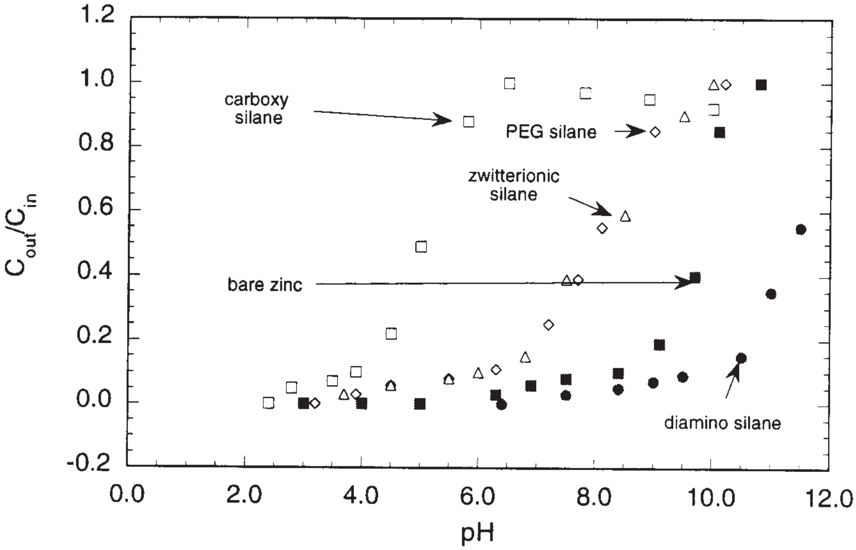

Figure 2. Influence of silane coating on adhesion of sulfonated latex spheres, 0.3 micron diameter on zinc scrapes filled column. Latex suspension was pumped through a column filled with zinc scrapes and equilibrated at desired pH. The turbidity of latex suspension (10 mg/L initial concentration) was measured before and after passage through a column and the turbidity ratio (after and before passing through a column) is plotted *vs.* pH of suspension.

umn experiments were performed according to the method of Kallay, Matijević and coworkers.[13,14] An adhesion column was filled with zinc scrapes, and adhesion of latex particles was followed as described in the experimental materials and methods. As indicated in Figure 2, the isoelectric point of zinc scrapes was found to be around pH = 9.2 The diaminosilane modified zinc surface had an isoelectric point at pH = 10.8. The carboxysilane coated zinc surface had an i.e.p at pH = 3.8. Zinc scrapes coated with the zwitterionic silane showed an i.e.p at pH = 6.8. Finally, the isoelectric point of the polyethylene glycol coated zinc was located at pH = 6.2. The changes in the isoelectric points upon silane coating were also followed with the zinc oxide powders. Remarkably similar results were obtained with the zeta potential measurements on zinc oxide powders and column experiments with zinc scrapes, as indicated in Figure 3.

The influence of silane coating on corrosion rates was followed with the standard industrial corrosion rate meter based on current polarization measurements. Water with 200 ppm of calcium and 100 ppm of hydrogencarbonate was used as a standard model system to follow the rate of corro-

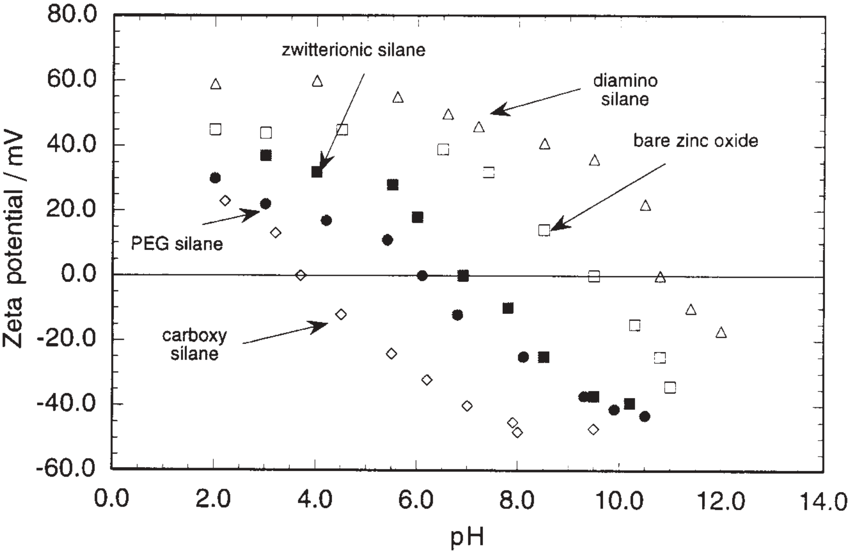

Figure 3. Zeta potential *vs.* pH for the noncoated and silane coated zinc oxide powder. Diaminosilane, carboxysilane, zwitterionic silane and (polyethylene glycol)silane were used to coat zinc oxide powder.

sion of zinc electrodes. The corrosion rate electrodes were placed in water solutions for one month, and corrosion rates were read after that time. A corrosion rate of *ca.* 30 micron/year was observed in the absence of silane coating. This rate was increased to 65 microns per year after RF water treatment. Diaminosilane coating reduced the corrosion rate to below the measurable limit at natural pH of solution used (pH = 8.2). That protective effect disappeared at a pH below 5.5 or above 9.7. Carboxysilane did not protect zinc surface from corrosion. Zwitterionic silane reduced the rate of corrosion from 30 microns/year to 10 microns/year. (Polyethylene glycol)-silane reduced corrosion rate from 30 to 15 microns/year. As in the case of reduction of rate of scaling, diaminosilane produced the superior results. Even in the presence of RF or magnetic water treatment, diaminosilane completely protected galvanized zinc from corrosion.

Long term scale and corrosion measurements in over 25 cooling towers showed the same trend. Best results were obtained when diaminosilane coated zinc surfaces were used along with RF water treatment to prevent scaling and corrosion from occurring. When higher concentrations of calcium and hydrogencarbonate were present in the water, the addition of a small amount of partially hydrolyzed polyacrylamide between 5 and 50 ppm completely prevented calcium carbonate scale formation. Heat exchange surfaces and inserted coupons in cooling towers were scale and corrosion free even after three years. A similar performance was observed with copper surfaces. Mild steel surfaces unfortunately could not be protected from corrosion with silane coating. Studies are underway to understand this behavior.

DISCUSSION

Electromagnetic water treatment has been used increasingly in industrial and biomedical applications in recent years.[15] The molecular mechanisms of the underlying processes are only recently being delineated. We recently showed that the primary receptor of electromagnetic radiation is the water/gas interface.[16] Such water/gas interface changes modify water structure in the bulk as well as at the interfaces. Signals which cause increased thickness of the hydration water and stronger water/ion interactions also promote lesser adhesion of scale components. Unfortunately, same type of signals also produce smaller water clusters and some oxidative free radicals and their products.[16] This increases the rate of corrosion of metallic surfaces which are protected from scaling.

To circumvent this problem, coating of zinc and copper surfaces was successfully attempted in this work. Metallic surfaces were coated with silane coupling agents which are commonly used in paint or powder industry for metal-powder or polymer-powder coupling agents. Corrosion coatings are commonly used to protect different types of surfaces.[17] Yet such coatings are up to 100 microns thick and impede heat transfer in cooling towers or boilers. On the other hand, silane layers used in this work were never thicker than 50 nm and did not interfere with heat transfer. In addition, diaminosilane also successfully reduced the rate of scale deposition.

The question arises as to why diaminosilane caused such a dramatic reduction rate in scale and corrosion processes? Why did other silanes perform much worse or even increase the rate of scaling? All silanes form Si–O–Si bonds except diaminosilane coated zinc with multiple layers up to 50 nm thick. Our preliminary spectroscopic results indicated that other silanes studied in this work were deposited as monolayers. Some errors are always present in any layer, with free Si–OH bonds. Monolayers are therefore less protective than multiple layers. Si–O–Si bonds are hydrophobic and repel water containing dissolved oxidizing species. Si–OH bonds are hydrophilic and act in just the opposite way.

The second question to be answered was why did carboxysilane coating increase the rate of calcium carbonate precipitation while diaminosilane decreased the rate of precipitation, and zwitterionic and (polyethylene glycol)silanes coatings did not modify the rate of precipitation appreciably?

Scientists studying the precipitation of inorganic materials on self-assembled silane layers realized that metal ion adsorption is the crucial step in the precipitation process.[18] Carboxysilane is strongly negatively charged with the isoelectric point of *ca.* pH = 4. At pH = 8, where our experiments were performed, calcium ions are strongly attracted to the negatively charged carboxyl groups. This condition significantly enhances the rate of precipitation. Diaminosilane coated zinc has an isoelectric point at pH = 10.8. At pH = 8 diaminosilane coated zinc is strongly positively charged. This results in the repelling of calcium ions and subsequent reduction in the rate of precipitation. Our preliminary calcium adsorption experiments suggest that the amount of adsorbed calcium is indeed much higher on the zinc surface coated with carboxysilane. RF radiation promotes calcium desorption and subsequently enhances the effects of diaminosilane.

The positive enhancing effects of partially hydrolized polyacrylamide on reduction of scaling rate of the metallic surface is easy to explain. This polymer has the ability to interfere with the normal growth patterns of crystals in supersaturated solutions.[19] This results in the precipitation of more soluble amorphous calcium carbonate which is also of a more soft non-adhering consistency than calcite or aragonite crystals. Consequently, as shown in this work the combined use of RF radiation, silane coating and polymeric antiscalant can result in the enhanced performance of all three methods of scale and corrosion prevention.

CONCLUSIONS

Chemical and electromagnetic methods of water treatment were synergisticaly used to enhance corrosion and scale protection achieved by either approach. Zinc and other metal surfaces such as copper were coated with a diaminosilane agent which shifted the isoelectric point from around 9 to 10.8 and produced a strongly positively charged surface. This significantly reduced calcium adsorption to the metal surface and subsequent scale precipitation. Diaminosilane coating also significantly reduced the rate of zinc corrosion. RF electromagnetic radiation produced thicker hydration layers around surfaces and ions which further enhanced reduction of scale deposition rate. Subsequent addition of partially hydrolyzed polyacrylamide modified crystal growth in the bulk which also reduced the rate of scale deposition. Synergistic use of RF water treatment, metal coating with diaminosilane and bulk addition of polymeric descalant reduced the rate of corrosion and scale in laboratory tests and in the pilot plant studies below measurable levels.

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SAŽETAK

Sinergistička primjena kemijske i elektromagnetske obradbe vode u sprječavanju korozije i nastajanja kamenca

Miroslav Čolić, Allen Chien i Dwain Morse

Troškovi šteta zbog korozije i nastajanja kamenca u tornjevima za hlađenje vode, grijačima i cjevovodima dostigli su u svijetu proteklih godina iznos od preko 100 milijardi USD na godinu. Klasične kemijske metode sprječavanja te pojave, uključujući i nove alternativne metode elektromagnetske obradbe vode, nisu polučile zadovoljavajuće rezultate. U ovom radu korištena je s velikim uspjehom kombinacija kemijske i elektromagnetske tehnologije za sprječavanje nagomilavanja kamenca i korozije u tornjevima za hlađenje vode presvučenim galvaniziranim cinkom. Ovaj rad opisuje fizikalno-kemijske osnove primijenjenog postupka.

Površine cinka bile su presvučene diaminosilanom. To je povećalo pozitivni naboj površine cinka i znatno smanjilo adsorpciju kalcijevih kationa. Presvlaka silanom

također je zaštitila cink od korozije. Opaženo je da elektromagnetska obradba vode razlaže vodu u atomni vodik i hodroksidne ione. To je spriječilo nagomilavanje silikatnog i karbonatnog kamenca povećanjem difuzivnosti vode i iona. U prisustvu velike količine kalcijevih i bikarbonatnih iona, u toranj za hlađenje vode dodane su male količine djelomično hidroliziranog poliakrilamida kao sredstva za uklanjanje kamenca kako bi se spriječilo nagomilavanje kalcijeva karbonata modificiranim kristalnim rastom. Ta sinergistička upotreba kemijske i elektromagnetske obradbe vode nije dopustila koroziju i nagomilavanje kamenca, što je utvrđeno nakon tri godine praćenja rada dvadeset tornjeva za hlađenje vode u Kaliforniji.