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WATER CONDITIONING DEVICES - AN UPDATE

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Despite adverse evaluations by corrosion engineers and water technology experts, non-chemical devices claimed to function by electronic, electrostatic, magnetic and other physical principles continue to be promoted for prevention of scale and deposits, microbiological growth and corrosion mitigation in water-using systems. There is an urgent need for factual information and validated performance data on such systems. These data are needed to permit economic and technical evaluation by owners and engineering staffs of industrial, institutional and commercial installations, for whom safe, efficient operation and continuous availability of costly steam generating and cooling systems are of critical importance.

A study now in progress by a Technical Practises subcommittee of the National Association of Corrosion Engineers⁽¹⁾ already has identified and listed nearly 100 non-chemical devices now being marketed for water treatment applications. Many of these are similar or identical in design and construction, but are sold under different tradenames by their promoters. In these times of growing fuel shortages and burgeoning regulation by local, State and Federal agencies, the promotional claims of minimum energy requirements, elimination of chemical feed and control requirements, reduced pollution, and potential water conservation are increasingly attractive to owners and engineers whose facilities include costly utility systems - heating and cooling.

The promotion of non-chemical devices to replace conventional water treatment approaches is far from new. Over two decades ago (at the Fourteenth Annual Water Conference) Welder and Partridge presented a thoughtful evaluation of typical devices^(2,3). Characteristics and principles of more than 50 different systems dating back to 1865 were listed and described. This landmark publication included a useful bibliography of 106 references and patent citations, plus case histories of recorded performance on several devices. Eliassen, Uhlig, Skrinde and Davis described and critically evaluated several electrical 'water conditioners' in laboratory studies and a series of papers^(4,5,6).

General characteristics and benefits claimed for many present-day devices include:

1. Prevention of corrosion, scale and deposits, and microbiological growth in water-using systems by physical forces (non-chemical methods).

2. Operating results not reflected by changes in water composition, as determined by standard chemical analyses.
3. Little or no technical control required.
4. Minimum or no energy (power) input required.
5. Elimination of potential pollution from system discharges, since conditioning method is non-chemical.
6. Further energy savings through elimination or reduction of utility system blowdown/bleedoff requirements.

At odds with such claimed benefits are less desirable characteristics of equal concern, such as:

1. Unpredictable and erratic performance in field applications.
2. Rarely supported by results of properly designed operating tests, conducted under supervision of unbiased water technology/corrosion scientists.
3. Operating data and results of scientific evaluations rarely are adequate to account for apparent good results in certain cases, or failure in others.
4. Claims of effective performance too often are supported only by testimony from uncritical, non-scientific observers.
5. Promotional literature often includes extravagant, unsupported claims, and utilizes pseudo-scientific terminology, essentially unintelligible to knowledgeable engineers, scientists and water technologists.

Our objectives in this update are to discuss operating principles of 'new generation' non-chemical devices now being marketed, as described in manufacturers' trade literature. To view these devices in perspective, they will be compared with established electrical/magnetic water conditioning systems of proven performance, and which:

1. Produce predictable, reproducible results.
2. Require appreciable energy input for operation.
3. Have demonstrated consistent effectiveness in corrosion control and water or waste treatment applications.
4. Are based on accepted scientific principles.

With respect to 'new generation' devices, we hope to initiate thoughtful discussion on questions such as these:

1. Do the principles by which non-chemical devices are claimed

to operate include a factual nucleus from which consistent, reproducible benefits may be predicted?

2. What significant performance in scale/corrosion control can be expected, in view of the limited energy inputs typical of most devices?
3. Do additional corrosion products traceable to deterioration of dissimilar metal couples in conditioner water passages, or metal hydroxides produced by sacrificial components modify normal scale formation processes on heat transfer surfaces, or otherwise contribute to reduction in scale deposit formation?
4. If so, what reproducible results in characteristics and magnitude of scale/deposit control process results may be obtainable with electrical or magnetic water conditioners?

Let us seek to penetrate the smoke screen of ignorance, mystery and pseudo-scientific jargon which pervades the marketing of many devices now being offered, and find the germs of truth (perhaps still unrecognized and unidentified) which might offer potential future utility.

A partial listing of established electrical/magnetic/physical systems employed in water/waste treatment applications might include these examples:

1. Ozone generators - for sterilization, BOD reduction, micro-biological growth control, and oxidation of heavy metals, etc.
2. Cathodic protection for preservation of metal structures, using driven or sacrificial anodes.
3. Sacrificial anodes as source of iron and aluminum ions, for coagulation.
4. Electrolysis of brine and brackish supplies to produce chlorine for biofouling control.
5. Electrolytic reduction of Cr^{+6} , by forced oxidation (corrosion) of iron.
6. Electrodialysis and ion exchange membrane processes for desalting water.
7. Reverse osmosis - pump power being employed to force water through micropore membranes or hollow fibers, to remove large amounts of dissolved salts.
8. Magnetic separators and high gradient magnetic filters, to remove magnetic iron particles in boiler feedwater, or in waste treatment applications.

Note that:

1. All these processes require not only substantial capital investment, but also have substantial power demands.
2. All work on known, accepted principles; produce reproducible results; and have been evaluated objectively and reported in engineering studies.
3. All require careful control, monitoring and continuous maintenance.

In this presentation we will consider four types of ~~the~~ chemical conditioning systems, some of which have been proved extensively in recent years. These are Electrostatic Water Treatment Units, Electrostatic/Ultrasonic Systems, Magnetic Water Treatment Devices, and a provocative newcomer - Scale Deposit Control by Ozone. Performance case histories have been compiled on several systems in these categories.

Electrostatic Water Treatment Systems

Units claimed to operate on electrostatic force field principles are marketed under tradenames such as AQUATROL, AQUATRONIC, CORROTROL, HANLEY, PROGRESSIVE, SULLECTRON and ULTRASTAT. Also using this principle but no longer being marketed are the Ingersoll-Rand ELECTROSTATIC WATER TREATERS and the Worthington ELECTROSTATIC SCALE CONTROLLER. These devices include a positively charged, insulated electrode centrally located in a grounded cylindrical casing which acts as the negative electrode. When high voltage is developed on the positive electrode, an electrostatic field is established across the water-filled annular space between the electrodes. Untreated water passes rapidly through the force field and on to the water-using system, being exposed to electrostatic forces only briefly. Operating on 110-120 V 60 HZ power, these controllers typically draw less than 1/10 ampere, indicating that little or no work is done. Current flow usually is accounted for by dielectric leakages and a low-wattage "ON" signal lamp.

The theoretical basis of scale control by electrostatic water conditioners is linked with the assumption that water molecules (which are polar) become oriented into an ordered array between the positive and negative electrodes; and the scale-forming ions then become surrounded with dipole clouds of water molecules, preventing migration to heat transfer surfaces, or to the oppositely charged electrode.

In several scholarly publications discussing the composition of water substance, Buswell and Rodebush (7,8) pointed out that water is an associated liquid, a heterogeneous fluid structure of single H₂O molecules, groups (or clumps) of such molecules,

and a few (H^+) or (OH^-) ions (about 1 in 555 million at pH7). Liquid water is said to consist of ice-tridymite structures, quartz-like structures, and close-packed ammonia-like structures. Under the influence of a short term electrostatic field exposure, orientation of such 'clumps' and ice-like structures into an orderly array is highly unlikely.

Buswell and Rodebush also pointed out that most anions do not form large envelopes of water molecules, since the hydrogen bond does not propagate through several water molecules. However, cations smaller than (K^+) attract the oxygen of the water molecule and make the hydrogens more acidic. They bond to oxygens of other water molecules so polarization extends through at least two layers, and may involve 10 or more water molecules. This suggests that the orientation of water molecules around ions of scale forming salts does not prevent their migration to heat transfer surfaces. It is recognized that water molecules do act to separate (+) and (-) ions, and partly neutralize attraction between these electrical charges.

Electrostatic treatment literature claims that water exposed briefly to the electrostatic force field will exhibit residual scale-prevention and scale-removal effects in water-using equipment far downstream. This claim is questioned; electrostatic effects, if confirmed, should apply only during the few seconds of passage through the lower energy field. Since no current flows other than dielectric leakages, little or no work can be done - either in polarization of water molecules, or suggested migration of microcrystals of scaleformers to the (+) electrode. The scale control mechanism proposed is in conflict with long-established mechanisms of 'in situ' scale formation, as elucidated by Hall et al (9) and other early investigators. Their work showed that salts having retrograde solubility with increasing temperature form 'in situ' scale deposits directly on the heat transfer surface, when concentration of ions involved exceed solubility product limits of the salt, in the viscous film of concentrated boiler water contacting the heated surface.

In cooling towers, where water evaporates and concentration occurs, ion of scale-forming salts also reach concentration limits (governed by solubility product consideration) beyond which 'in situ' precipitation on heat transfer surfaces occur. Solubility of $CaCO_3$ is reduced, and precipitation accelerated by factors such as temperature rise, alkalinity increase, and CO_2 loss.

The mechanisms of 'in situ' scale formation are governed by ion concentrations and temperatures at heat transfer surfaces in such evaporative systems. The concentrations of scaling ions can be altered or controlled by chemical additions and bleedoff, but not by upstream exposure of makeup water to electrostatic force fields. No doubt electrostatic forces cause temporary drift of ions toward an oppositely charged electrode or shell. But since such forces cannot remove scale-forming ions or reduce their concentrations, their ability to combine or recombine with other ions to form insoluble salts (scale)

when solubility product limits are exceeded is not altered. No proof has been offered to confirm residual effects in water downstream from point of exposure to an electrostatic field.

Promotional literature from some suppliers of electrostatic treaters claim corrosion control by utilization of dissolved oxygen to form a thin protective coating on internal metal surfaces of water-using equipment. Years of field experience and corrosion research have shown that dissolved oxygen in water accelerates corrosion in boilers and cooling systems. Oxygen acts to depolarize protective hydrogen films on cathodic surfaces, to allow continuation of corrosion processes. It also reacts with water, using electrons liberated when metals corrode to produce hydroxyl ions. Oxygen, ferrous ions and hydroxyl ions combine to cause precipitation of ferric hydroxide, building up deposits of corrosion products which further stimulate localized attack.

Electrostatic/Ultrasonic Water Conditioners

The ELECTRA-A-SONIC system is manufactured and marketed by Allen Industries Inc., Erie, Pennsylvania, and claimed to eliminate scale, corrosion and biological fouling in cooling towers, after-coolers, boilers and air conditioners. Similar units are marketed by other companies under different trade names. The manufacturer claims that this device combines an electrostatic force field and sonic energy to prevent scale and remove old deposits through cavitation effects. Destruction of microbiological growth by atomic oxygen and ultrasonic forces also is claimed. Claims added or modified by some ELECTRA-A-SONIC distributors claim ability to generate ozone which serves to disinfect water passed through the unit. All these effects are claimed in spite of the fact that total power consumption is said to be less than 7.5 watts! These units also are claimed to prevent corrosion.

Distributors' literature specifies "Allen Industries have developed a portable ozonator called ELECTRA-A-SONIC.....can be used wherever there are chemical and bacteriological problems..." In the ELECTRA-A-SONIC unit, as in other electrostatic devices, the force field is imposed across a water-filled annulus - the water having appreciable conductivity and dissolved solids content. Ozone generation required passage of very dry air or oxygen through a very high voltage electrostatic field (5,000 - 50,000 V), and power consumption in the process is high. By very dry air is meant drying to a dewpoint of -60°F. Power requirements for ozone generation by electrostatic means are very high - typically 7 to 10 kW-hr per pound of ozone produced. Contrast these power requirements with the typical power input of 7 to 100 watts for electrostatic water treaters. Private communications with representatives of the International Ozone Institute have shown that ozone formation in an electrostatic field is not a spontaneous reaction, but requires great energy input. They state that in the absence of an actual gas phase (air or oxygen bubbles) in

the water flowing through an insulated electrostatic column, possibility of ozone generation at the low power inputs claimed would be remote to non-existent.

The basis for the ultrasound energy claim is unclear. Sales literature states that 60 Hz power is converted to high frequency current, which is then transformed to mechanical energy in a transducer. The literature also suggests that microorganisms are disintegrated by sonic wave intensity and 'highly accelerated particulate energy of generating free electrons.' Medical references confirm potential utility of high intensity ultrasound energy for disintegration of bacteria and viral cultures, but indicate that lengthy contact time is required on very small amounts of solution, plus substantial power demand to operate the specialized equipment. Even small laboratory ultrasonic generators used for glassware cleaning, emulsification, etc., require power consumption approaching 500 watts, to produce ultrasound outputs of 1 to 400 watts. Both crystals and magnetostriction oscillators are used as generators and transducers. Both require substantial cooling and sound baffling. For a flow rate of 250 gph, a commercial Raytheon sonic oscillator requires a power input of 5 kilowatts. This raises serious questions as to validity of the claimed microorganism control method utilizing ultrasound, in view of the low power input of 7.5 watts, (regardless of water treating capacity).

Magnetic Water Conditioning Devices

A wide variety of systems employing magnetic fields for water conditioning have been marketed in the past for industrial and commercial applications. Some of the newer units employ permanent magnets mounted externally around a water pipe. Others (such as CEPI - COMAV) have permanent magnets mounted inside a cylinder through which water flows, and in direct contact. Others use a water-conveying magnetic cylinder containing a separate magnetic rod, with water flowing through the annular space between rod and cylinder. A variety of electromagnetic units also have been used, including the ELECTRO-MAG device (Turbomag Corporation) earlier described by Dr. George Kvajic.

In 1958 Eliassen and co-workers evaluated performance of several water conditioners (5) with respect to deterioration of complexing properties of scale-forming compounds; effect on ionic structure; formation and removal of scale; and corrosion of iron surfaces. Also studied was claimed effect of magnetic fields on scale formation, and on influencing particles within atoms. Physicists have shown that intense magnetic fields of the order of magnitude of 1 million gauss (an energy density of about 5000 joules/ml) are needed to dominate motions of charged particles within atoms. Such an electromagnet would require a 10 megawatt power generator and a substantial cooling supply. Contrast this with energy density of only 0.5 joules/ml in magnetic water conditions tested by Eliassen et al!

An investigation of magnetic water treatment devices was the basis of a Doctoral dissertation by Edward A. Duffy at Clemson University in 1977.⁽¹¹⁾ This useful study includes an extensive

bibliography (145 references) of pertinent literature, both U. S. and foreign. Research included evaluation of commercial magnetic antiscale devices (HAKO and CETP-COMAV), to determine effect of magnetic fields on water, water solutions, and CaCO_3 scale formation. Also investigated was effect of magnetization on corrosion of steel, and effect of iron compounds on precipitation of CaCO_3 .

A few of the conclusions in Dr. Duffy's research are significant to our specific areas of concern:

1. Commercial magnetic devices evaluated did not affect rate of precipitation of calcium carbonate, nor the formation of CaCO_3 scale at 85°C .
2. Neither dynamic nor static magnetic treatment affected the structure of water.
3. Magnetization of a 1018 steel rod caused an 18.6% increase in the rate of corrosion at 25°C in a 3% NaCl solution.
4. Addition of $\text{Fe}(\text{OH})_3$ to feedwater decreased the amount of scale formed in a laboratory heat exchanger, the effect varying directly with concentration of ferric hydroxide added, and inversely with temperature of scale formation.
5. Ferric hydroxide retarded the rate of calcium carbonate precipitation in the pH range 6 to 11, the effect being directly related to concentration of ferric hydroxide in solution; it also retarded formation of calcium carbonate in the allotropic crystalline form of calcite, at low temperatures.

These results suggest a possible mechanism by which commercial magnetic antiscale devices could indirectly retard calcium carbonate scale formation. If use of the devices increases corrosion rate of system metals by magnetic or galvanic effects, this would increase concentration of iron ions in solution, eventually providing ferric hydroxide which can retard calcium carbonate scale growth under certain conditions.

It should be noted that the electromagnetic unit discussed earlier by Dr. Kvajic (ELECTRO-MAG or TURBOMAG) is recommended to prevent scale formation and iron oxide deposits in systems using the magnetic-treated water. However, the unit as shipped includes a wire brush to clean out the water passages which are the core of the device; that is, the magnetized iron tube in which is inserted a freely rotating iron impeller. It seems strange that a device marketed to prevent formation of iron oxide deposits and scale should experience such deposits within the area of most intense magnetic fields.

SGA Water Treatment System (for cooling systems)

This relatively new and unique 2-component system comprises an ozone generator ('Bacteria Controller') and a 'Colloid Generator',

plus sacrificial anodes. Ozone generated in a small conventional electrostatic unit supplied with air dried through a small desiccant column, is introduced into the suction side of an external pump, which continuously recirculates water from the cooling tower or basin. Ozone is dispersed and dissolved in the recirculating water. The 'Colloid Neutralizer' (a cylindrical chamber with an enclosed electrode and an external power supply) is installed in a bypass on the cooling tower makeup water line. Sacrificial anode blocks (magnesium) are submerged in the tower basin and electrically connected to the metallic structure. Small zinc anodes are provided for installation in the condenser heat exchanger heads. Both the sacrificial anodes and blocks are described as ". . . insurance against electrolysis. . ." Their value for this purpose is doubtful, since no attempt is made to locate them to provide uniform current directly on surfaces to be protected, and their zone of effectiveness would therefore be limited.

The manufacturer claims that the SGA system (Source Gas Analyzers, Inc.) functions by the following mechanisms:

1. Removing the colloidal nuclei to which dissolved solids ions attach, before they enter the tower in makeup water.
2. Oxidizing the bacteria present in the condensers, thus removing the 'sticking mechanism' for calcium carbonate and other scale-forming media, which cause scale adherence in low temperature heat exchangers.

Mechanism 1 ignores the known phenomena of 'in situ' scale deposition previously discussed, and like electrostatic water treater proponents, assumes that scale can deposit only via a colloid nucleation process. In any event, the periodic exposure of makeup water to electric pulses of alternating charge has not been proven to affect colloid content of water passed through the neutralizer, nor to alter the scaling properties of the water once it has concentrated in the evaporative cooling tower, and exceeds the solubility products of scaling species, at heat transfer surfaces. However, the sacrificial anodes added to the system may play a major role in scale control, by addition of magnesium and/or zinc ions to the recirculating coolant flow. So, regardless of utility in corrosion control, the anodes may provide other benefits. To the extent that corrosion of ferrous metals in the system is stimulated by continuous ozonation, the resulting ferrous hydroxide particles also may become involved in suppression of calcium carbonate scaling. The SGA system is restricted to relatively low temperature cooling circuits.

Concerning Mechanism 2, manufacturers' representatives disclaim knowledge of precise processes by which the SGA system functions to prevent scale deposition and corrosion. However, they are convinced that scale-forming elements are bonded to biological growths, and that if such deposits (microbial slimes)

are removed or prevented, no scale will be deposited. The manufacturer also indicates that tower bleed-off can be eliminated or substantially reduced.

Without question ozonation is effective for control of microbiological growths in cooling towers and associated heat exchangers, providing the load of incoming oxidizable organic matter, process contaminants, corrosion products, reducing agents and microorganisms in makeup water or scrubbed from the air is not excessive. In two case histories available, the SGA approach failed to prevent heat exchanger scaling and microbiological growths in a refinery cooling system; in this case the cooling tower was located in an industrial complex where heavy contaminant loads should be expected. In another 'clean' location where the cooling tower utilized a high-silica makeup water, microbiological growth was fully controlled, and no scale deposited in heat exchangers, even though the cooling tower was operated without voluntary blowdown, and allowed to reach concentration limits regulated only by involuntary water losses, such as tower windage and leaks. Validity of this field test with respect to scale control is open to question, since the system load was only 40% of rating, the compressor was idling, and ΔT on the cooling tower was only 20°F. Condenser pressure was very low, showing absence of load and minimum heat dissipation requirements through heat exchangers. In addition, the makeup water had a negative Langelier Saturation Index (SI=1.75), indicating a corrosive water with minimal scaling tendencies. (Even after being heavily concentrated in the absence of voluntary bleedoff, the Saturation Index was only +1.1.)

Although voluntary bleedoff was zero in this latter test, tower concentrations were partly controlled by windage and other involuntary losses. High solubility ions in makeup water (Cl, NO₃, SO₄, Na and K) showed concentrations anticipated from involuntary bleedoff of about 1.5% (about 60-65 concentrations average); but very high losses of Ca, Mg SiO₂ and HCO₃/CO₃ alkalinity were observed in concentrated cooling water. Silica concentration was only 2.24 times makeup water silica. For Ca, Mg and CO₃/HCO₃, concentration factors were 18.75, 11.3 and 8.15 respectively. Even though no scaling was reported in condensers, substantial dropout of silica, hardness and alkalinity had to be occurring somewhere. Part of the CaCO₃ loss can be explained by heavy deposition on exterior surfaces of slats at the side of cooling tower basin, indicating water carryout by windage, spray and splashing. A water sample from the cooling water circulation line contained a moderate quantity of fluid, gelatinous sludge which was identified as serpentine.

This raises interesting questions as to the effect of magnesium sacrificial anode blocks in the cooling tower basin, in providing magnesium ions to supplement those already available in the makeup water, providing sufficient magnesium to react the silica out of solution in favorable Serpentine form. Since raw water silica content is 67 mg/liter, and raw water magnesium only 41 mg/l

(as CaCO_3), a very large supplement of Mg would be required for Serpentine formation. Cooling water pH leveled off at 8.8, not entirely favorable for magnesium silicate precipitation.

It must be emphasized that under full load, heat exchanger scaling certainly must be anticipated under these unfavorable conditions of pH, alkalinity, calcium and silica concentrations. The ability of the silica gel desiccant in the ozone generator to provide bone-dry air at all times also is doubtful, which suggests the probability that some nitrogen oxides or nitric acid also would be generated along with ozone. This could also suppress anticipated calcium carbonate scaling tendencies, under full load conditions.

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