

Fundamentals of Water Treatment

I. INTRODUCTION

Throughout history, the importance of different materials, utilized for the advancement of civilization, change as new technologies evolve.

From the Stone Age to the Computer Age only one material has remained the most precious and the most unique. Life, as we know it, cannot go on without it. The early Greek philosophers believed that it was the original substance of the universe, out of which everything had been made. It consists of two elements that are gases at ordinary temperatures. One will burn, while the other is necessary for combustion, yet combined it is used to put out fires. What is the precious, unique material? It is *ordinary water* and is the subject of our story.

The purpose of this paper is to explore and delineate the properties and processes through which water passes in commercial and industrial water treatment environments. Our primary focus will be those processes used in controlling scale formation experienced in the larger flow re-circulating water systems. The common chemical and the advancing physicochemical water conditioning methods available in the marketplace will be covered. The fundamental force associated with electric charges and their resulting fields that control *all chemical reaction* will be utilized in exploring these processes. This paper is not intended to be a rigorous scientific treatment of the subject, but rather aimed at gaining a conceptual understanding of possible phenomena.

As the human population increases and technology advances, more and more water is used. In ancient times, when the world population was a fraction of what it is now, the average person used from three to five gallons of water daily. In the nineteenth century, in the Western nations where technology was developing, the water consumption per capita

increased to approximately ten to fifteen gallons daily. Since 1900, both the population and the per capita consumption have made enormous leaps. In the U.S. according to one article, the per capita consumption of water has increased to 100 to 200 gal/day. This number represents our reliance not only from an industrial and commercial aspect but our personal demand as well, what with our automatic washers, dryers, dishwashers, air conditioning systems, garbage disposals, and so on. Overall it is estimated that America uses more than 400 billion gallons of water daily. In Europe, per capita water consumption is only 25 to 35% of that in the U.S., partially due to the higher cost of water and environmental pressures.

Some of this water can be used over and over again, but a significant portion of it cannot because it is lost as steam or polluted with waste materials or chemicals. Because of our demand, there is a steady lowering of the ground water tables, requiring deeper and deeper wells. The pollution of lakes and rivers by sewage and industrial wastes is becoming a more serious problem every year and one that is more expensive to solve.

On a global basis man has had the greatest impact on his environment, more than any other species, and this will increase as we continually develop technologies benefiting future generations. It is these modifications, which have produced increasingly acute water problems. At the present time our main line of attack upon this problem involves improvements in water economy, i.e., improvement in pollution prevention and/or its removal and the efficiency with which available supplies are used.

At this point we should reiterate that science is based on facts, and is the foundation from which we should review various water-related processes. From these, facts hypotheses are

formed. A successful hypothesis is not necessarily a permanent hypothesis, but it is one that stimulates additional research, opens up new fields, or explains and coordinates previously unrelated facts. This accumulated knowledge concerning physical facts is in effect the general truths and laws by which the facts are systematically related to one another. To this we must add that scientific truths or final answers are never achieved. We must continually search for better answers. So it is with our treatment of water.

II. ATOMIC FORCES

At the end of the nineteenth century, an English chemist named John Dalton did experiments that suggested that elements were composed of tiny particles called atoms. By the early part of the twentieth century, experiments had shown that atoms were made up of even smaller bits of matter called subatomic particles. Presently scientists are unlocking the secrets of subatomic particles and are finding still other layers of the subatomic building blocks.

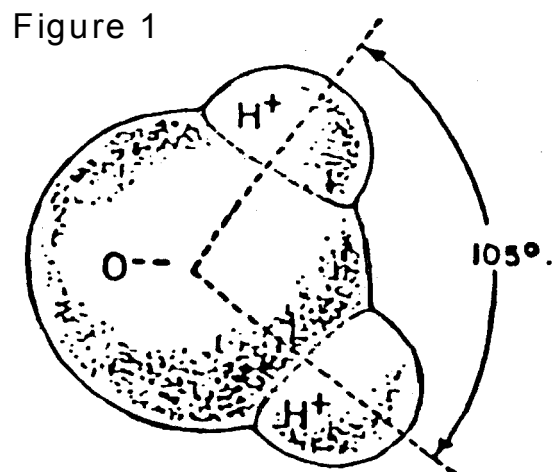
Atoms are made up of positively charged centers with negatively charged electrons circling about their centers. Atoms come in different sizes and form bonds of greater or lesser strengths and directionality with one another, resulting in great diversity in material properties. Atoms assemble themselves into different atomic structures depending on their relative size and the nature of the bond that engages them. Of primary importance in determining interatomic forces and the resulting atomic structure, is the arrangement of the atoms outer electrons, which strongly affects the nearest neighboring atoms in the structure.

There are four main types of bonds that play major roles in chemical reactions. In *ionic bonds*, the atoms have either lost or gained one or more electrons so that their outer electron shell is complete. Thus, they cannot share

electrons, but since they are electrically charged by virtue of having gained or lost an electron, they are attracted to atoms of the opposite charge. In *covalent bonds*, atoms share one or more pairs of outer electrons in filling their outer shells. In *metallic bonds* all the atoms share all the outer electrons. The *molecular bond*, also known as a van der Waals bond, arises from the displacement of the electrons within electrically neutral atoms that produce a weak attractive force between the atoms/molecules as they approach each other. Another molecular bond known as the hydrogen bond is the result of the fact that electrons can be easily displaced due to the atom's small size. All these bonds are idealized and all chemical interactions involve some combination of them. Note that all chemical reactions are based on the electronic characteristics of the various atoms.

III. WATER

Water is the only substance that commonly occurs in nature as solid, liquid, and vapors. Each of the elements combining to form water exists independently as molecules containing two atoms (H_2 , O_2) held together by covalent bonds. It is the covalent bond that also holds together the molecules of water (H_2O).



The distribution of the electrons in H₂ and O₂ determines the shape of the water molecule and its electronic structure. The resultant molecule of H₂O is what is called a polar molecule because its positive and negative charges are not spread evenly around a center but are instead distributed asymmetrically to form positive and negative poles. The two hydrogen atoms are arranged approximately 0.95Å or 0.95x10⁻¹⁰m from the oxygen nucleus and separated from one another by 104.5 degrees (see Figure 1).

Water molecules may be said to have a great deal of integrity in that they maintain their identity in circumstances that causes other kinds of molecules to split into ions. It has been calculated that a ton of pure water contains only about 0.1 milligrams of H⁺ and 1.7 milligrams of OH⁻ ions. This means that pure water is a very poor conductor of electricity, since it provides very few charged particles to constitute a current between two electrodes. However, this atomic arrangement gives it a strong tendency to orient itself (or to be oriented) in an electrical field with its negative end toward the positive plate and its positive end toward the negative plate. Water is therefore said to have an unusually large dipole moment whose behavior in an electric field may be illustrated as in Figure 2 & 3.

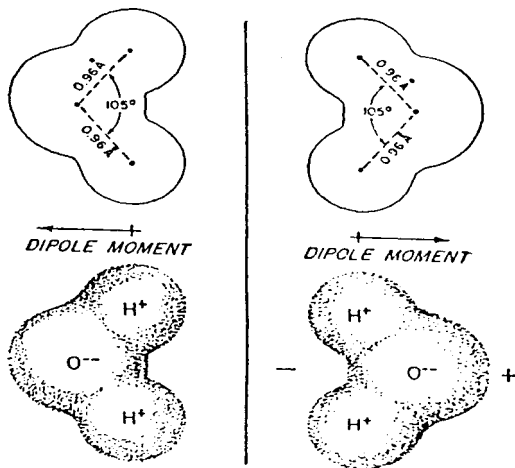


Figure 2 Dipole Moment

By orienting themselves in this way, water molecules tend to neutralize an electrical field--a fact expressed in technical language by saying that water's large dipole moment gives it an abnormally large dielectric constant. If we assume the dielectric constant of a vacuum to be one, then the dielectric constant of water is 80, which is to say that two electrically charged particles will attract or repel one another with only 1/80 as much strength in water as they would in a vacuum.

These structural and electrical characteristics account in part for water's remarkable ability to dissolve substances, and particularly those substances whose molecules are held together by ionic bonding. The negative ions of a substance are attracted to the partially positive hydrogen atoms of the water molecules. This weakens and overcomes the attraction of the negative ion for the positive ions in the substances (salts), and the negative ion is pulled into solution. Likewise, the positive ions are attracted to the partially negative oxygen atoms of the water molecules. As the ion moves into solution they are surrounded by more water molecules, a process called *hydration*, and thus an ionized solution is formed. Since, the attraction between the dissociated, oppositely charged ions is reduced by water's high dielectric constant to a fraction of what it would be in air, or to just 1/80 of its strength in a vacuum. The attraction is so slight that it can be completely nullified by mild thermal agitation and turbulence.

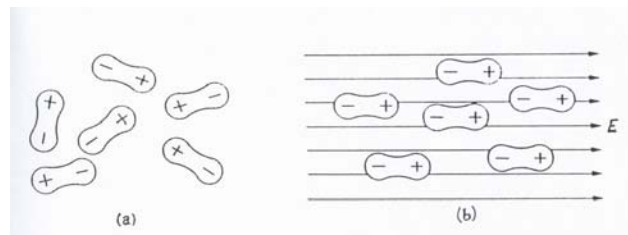


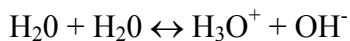
Figure 3 Water in an Electrical Field

The electrical charges of the polar water molecules cause water molecules to be attracted

to each other. In solid and liquid states, bonds form between water molecules. The oxygen of one water molecule is attracted to hydrogen of another water molecule. This interaction is called the *hydrogen bond* and is electrostatic in nature. It holds many water molecules together.

Although hydrogen bonds are not as strong as either ionic or covalent bonds, they do play a major role in the chemical and physical properties of water.

We usually consider pure water as non-electrolytic (no ions) that contains only molecules of water. However, if we were to measure very carefully, we would find that there are a few water molecules that do ionize. One water molecule in 10 million ionizes to produce a hydrogen ion (H^+) and a hydroxide ion (OH^-). Note that the hydrogen ion, which is just a proton, cannot exist by itself and is present as a hydronium ion (H_3O^+). The collision of two water molecules transfers a proton to form a hydronium ion (H_3O^+) and a hydroxide ion (OH^-):



or to simplify



In pure water at 25°C, the concentration of H^+ is 1×10^{-7} , which is equal to the concentration of the hydroxide ion, (OH^-). When the H^+ and the OH^- concentrations are the same (equal) and the solution shows no acidic or basic properties, we say that the water is *neutral* (pH = 7).

The product of the H^+ and OH^- concentrations gives a value called the *ion product* for water, which is 1×10^{-14} . The *ion product* is a constant, i.e., always 1×10^{-14} for pure water as well as for any other kind of aqueous solution, acidic or basic. In acids, the hydrogen ion concentration will be greater than the hydroxide ion concentration. When a base is added to water, the hydroxide ion becomes greater than the hydrogen ion concentration. The acidity or

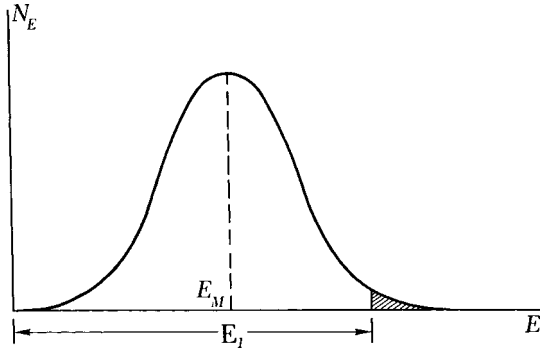
basicity of a solution is indicated by its pH. The value of pH is defined as $pH = -\log [H^+]$. Hence, the pH scale is a way of describing the H_3O^+ concentration, or $[H^+]$, by using the exponential of the concentration. This scale ranges from 0 to 14, where as a solution with a pH of zero is strongly acidic and a pH of 14 is a very strong basic solution.

IV. THERMAL ENERGY

Energy is defined as the ability to do work. This energy can take many forms. The energy available from the bonds of a chemical compound is chemical energy. The burning of wood converts chemical energy into thermal energy. The energy of electromagnetic radiation may take the form of light, while electrical energy in your home is yet another form of energy that can be converted into light or to thermal energy. Thermal energy, or heat, is an energy form with which you are probably most familiar and is associated with the motion of particles in a substance. This thermal energy is associated with the kinetic energy of the atom within the solid, liquid, or gas.

The English botanist Robert Brown observed the motion of pollen grains and other microscopic objects (such as colloidal particles) suspended in a liquid. This 'Brownian motion' constitutes a visual confirmation of the random kinetic motion of molecules, which is the direct result of thermal vibration. Two points to consider here are that all atoms do not have the same energy as they are constantly exchanging energy with one another. This distribution of energy is shown in Figure 4. The other consideration is that atoms / molecules in the bulk of a liquid or solid have fewer degrees of freedom (of movement) to break all their bonds, as do the atoms on the surface. There are many examples of atoms breaking their bonds and leaving the surface of the liquid, even though the average temperature is below the boiling point, e.g., steam rising from a cup of coffee.

However, the most germane example is the beloved cooling tower. In a cooling tower water enters at a temperature below the boiling point. The construction of the cooling tower is such that the surface area of the incoming water is increased tremendously affording the atoms that have obtained sufficient thermal energy the opportunity to break their liquid bonds and form



vapor. In doing so, these vapor atoms take with them the energy associated with their bonds, (latent heat) thereby decreasing the temperature of the remaining water.

Figure 4 – Boltzman Distribution of Energies

V. NUCLEATION AND GROWTH

Nucleation and growth are complex subjects and require understanding of Brownian motion and diffusion, surface energy and surface charge, as well as, solubility characteristics, and the rudiments of physical and colloidal chemistry. However, these subjects are easier to grasp by focusing on only the concepts required to understand them in relation to our primary subject, *water and scale formation*.

Since, this paper, is primarily concerned with the solid (crystalline or scale) to liquid (water solution) interface, we will focus on that interface. Note that in this discussion the atoms and molecules in solution (minerals) are considered to be ionic.

It is assumed, for this discussion, that the crystal, (in our case scale or colloidal particles) is undistorted right up to its surface, and that all the atomic bonds have the same energy

distribution as the bonds within the crystal. The atoms at the surface, however, will naturally have fewer, nearest neighbors, therefore, fewer crystalline bonds. The energies of these surface atoms are higher than that of atoms in the interior of the crystal, in proportion to the number of missing bonds. One can easily visualize that on a smooth crystalline surface it would require more energy to remove an atom from that surface than for removing an atom that rests on top of this surface (one not surrounded by other atoms). A detailed discussion of this case would not be appropriate for this paper. However, the basis of the argument is as follows: an ion (a single atom or molecule) from solution arriving at the solid crystal surface (scale) may 'stick' in the sense that it loses part of its latent heat of solution by forming one or more atomic bonds. It is then able to move about on the surface, through the aid of thermal energy, until one of three events occurs: 1) It acquires sufficient thermal energy to go back into solution, 2) It finds a site, on the edge of an existing crystalline step where the number of neighbors is sufficient to 'trap' the atom / ion by lowering its energy, (by forming additional bonds), Or, 3) it encounters sufficient other adsorbed mobile atoms / ions to stabilize each other by the formation of an 'island' of a new layer. Theory shows that the last can occur only if the concentration of ions / atoms at the surface is high. This requires high supersaturation, or driving force, otherwise the rate of arrival of ions / atoms would be too low. Event #2 above is the method most likely and easily visualized since crystalline defects, such as, dislocations, and grain boundaries can lower the energy required to 'trap' incoming ions or atoms.

It can be shown that the crystal growth process is primarily the result of single atoms / ions arriving at and departing from the surface of the solid. The probability that a small crystal (floating) would be 'in register' with the surface of a growing crystal (e.g., at a pipe wall) is extremely small. In addition, the driving force

or attraction of a small colloid particle to a like crystalline substrate would not be favorable (to be discussed in further detail later). The growth of a crystal in this single ion or atomistic approach can take place, only when the rate of arrival is much higher than it would be for equilibrium, such that there is a high probability of a number of neighboring sites being filled simultaneously and thereby stabilizing each other. This departure from equilibrium is the degree of supersaturation, i.e., driving force that is required for precipitation or scale build-up. Note that *equilibrium* conditions exist if the diffusion or flux of the arriving and leaving ions from a crystal surface is equal.

It is logical that the incoming ions that obtain the largest number of nearest neighbor bonds are more likely to remain on the solid side of the interface, whereas, atoms more exposed, ones that have only one or two nearest neighbor bonds, are more likely to go back into solution. One must always remember that the distribution of thermal energy can cause variations in ionic concentration in the liquid and allow for the movement of atoms/molecules across the crystal (scale) liquid (water) interface. This phenomenon continually allows crystal like 'clusters' to form in the liquid with various numbers of atoms and then they dissociate, going back into solution. The average number of atoms in these crystal 'clusters' will increase as the degree of saturation increases for a given solution, i.e., larger driving force, therefore larger probability of ions forming crystal like clusters. Hence, if the variation in the degree of supersaturation is large enough the 'critical radius' or volume of one of these 'clusters' will become large enough to be stable and continue to grow. This condition is known as 'Homogeneous Nucleation'. Therefore, for a given degree of supersaturation a critical size crystal must be reached before a crystal will continue to grow. If the crystal is smaller than this critical radius, they will go back into solution. However,

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homogeneous nucleation does not normally occur in industry settings.

We find that it is not necessary for the initial crystal to be a complete sphere; any part of its surface that is in contact with the liquid and has a sufficiently large radius of curvature will have a better chance of growing. Therefore a 'cluster' containing a given number of atoms can form a spherical cap on a substrate that has a much larger radius of curvature than a sphere of equal volume as shown in Figure 5. From this it can be readily seen that a nucleus of critical size can be catalyzed by a suitable surface in contact with the liquid (water solution). The process is called 'Heterogeneous Nucleation.' The 'nucleation catalyst' or 'nucleant' may be either a solid particle (dust / dirt) suspended in the liquid, or the surface of a container (pipe / chiller).

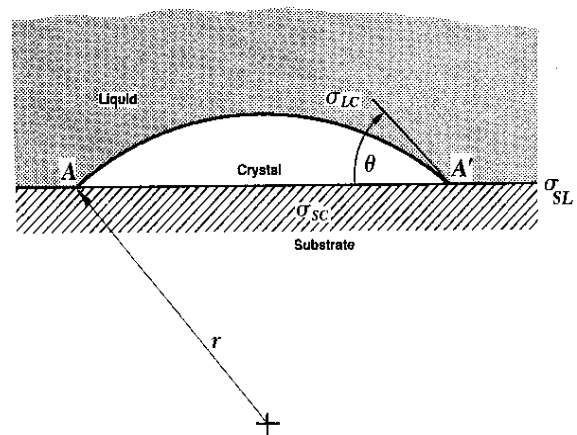


Figure 5 Embryo on Substrate

The point here is that heterogeneous nucleation can take place on a surface to which these small (less than the critical radius) clusters wet or stick. The stability of the nuclei on a substrate depends upon the radius of curvature facing the liquid. However, at a surface, the atoms or molecules are pulled inward, drawing the surface atoms or molecules tighter together to form a 'skin' on the surface. This physical property at the surface is called *surface tension*.

Also, since the surface atoms are not surrounded by other atoms there are unsatisfied bonds. These unsatisfied or incomplete bonds are sometime referred to as *dangling bonds*. These incomplete or dangling bonds can give rise to a surface charge, whereas metals normally have a positive surface charge and materials made up of molecules with oxygen will generally have a negative surface charge.

The departure from equilibrium, i.e., solubility or saturation limit, in either direction is the *driving force* for dissolving a material (concentration below the saturation limit) or precipitation (nucleation and growth if above the solubility limit, i.e., supersaturated). The degree of departure from equilibrium controls in part the kinetic or speeds of the scaling or crystallization process. Note that *heterogeneous nucleation* requires a much lower degree of supersaturation or driving force. There are, however, other factors that come into play: viscosity, temperature, nucleation site availability and characteristics, pressure, size and charge of the molecules in solution, surface charge, etc. We will consider some of these factors affecting nucleation enhancement and crystal growth control as we continue, but let's discuss some of the parameters affecting water-formed scale deposits.

VI. SCALE FORMATION

Water is always in the process of dissolving or depositing solids. We will call these deposited solids *scale*. *Scale*, the term generally used in industry, refers to any deposit on equipment surfaces. The general usage of the term scale denotes hard, adherent deposits of inorganic mineral constituents of water that formed in place. Sludges, sediments, foulants, etc. all describe less adherent deposits that may be formed in place or may be transported from some other source and redeposit. The word *descaling* is normally used to describe the removal of a previously formed scale. The important thing to remember is that many

substances will dissolve to some extent in water. Therefore, we have a constant flow of atoms or ions across the solid / liquid interface.

The impact that mineral scale and other deposits have on industrial operations, range from: the reduction in pipe carrying capacity, the impedance of heat transfer capability, the increase in operational safety hazards, the localization of corrosion attack, the increase in operating costs due to inefficiencies, in addition to increased downtime and maintenance, among others.

Scale is formed by precipitation of primarily, calcium carbonate that becomes insoluble at higher temperature decreasing the efficiency of both boilers and chillers. This scale has been shown to be a very effective thermal insulator. The following are examples of how much additional energy consumption is required for a given scale thickness:

Thickness of Scale	Boiler	Chiller
1/64"	~5%	~11%
1/32"	~9%	~26%
1/16"	~15%	>50%
1/8"	~30%	--N/A---
1/4"	~50%	--N/A---

This data was taken from several sources, averaged and rounded off, to demonstrate the trend of scale build-up. Generally, in most industrial cases, mineral scale deposits are a problem. Prevention, control, and treatment of mineral scale are the objectives of water treatment.

As mentioned earlier, the mineral that remain in the water may be controlled by dividing these minerals into three groups; materials that are in solution (ionic), precipitate out as small suspended colloidal particles, or deposits as scale on surfaces.

Practically speaking, no chemical is pure, whether naturally occurring or artificial. Most

industrial chemicals have a level of impurity usual measured in percentage, or parts per million (ppm). Anything in water that is not H₂O, (plus H⁺ & OH⁻) is a contaminant or impurity, and all water is impure. Generally a contaminant is considered a pollutant when its concentration reaches a level that may be harmful to aquatic life or to the public health.

The amount of water man has been able to use is limited; and throughout the past few centuries we have not been able to add significantly to the amount of available fresh water. Since the world has experienced an increase in population and technological growth, the available water is insufficient for future needs and is becoming increasingly polluted. The causes are by and large due to dissolved solids. As we have discussed, water is almost designed to become contaminated.

The ability to dissolve, transport, and deposit solids are the primary roles that water plays in the scaling process. Because of its dissolving power, water can leach significant concentrations of mineral matter as well as other material, with which it comes in contact.

In some cases the dissolving power is enhanced by the nature of the constituents. The solubility of a given material in water is controlled by variations of temperature, pressure, pH, redox potential, and the relative concentrations of other substances in solution. These variables are related in such a complex manner that exact solubilities cannot always be predicted, but in some cases these estimates are helpful in understanding the relationship and behavior of certain minerals.

Generally, the solubility of most minerals increases as the pH of the water is lowered irrespective of how the acidity occurs. The main natural cause for acidification is the bonding of carbon dioxide from the air with rainwater. Carbonic acid (H₂CO₃) then forms.

Similar processes can occur with sulfur dioxide

and nitric oxides. Both oxides are dissolved in rainwater and sulfuric, and nitric acids are formed. As the acidic water passes through lime deposits, larger amounts of lime are taken into solution. If lime is absent, the water remains acidic and may absorb other material such as heavy metals. Most metallic elements are soluble as cations (positive ions) in acidic ground water but will precipitate as hydroxides or basic salts with an increase of pH.

We have listed some of the chemical reactions between water, carbonic acid and calcium and magnesium, the so-called water hardeners, as shown here:

1. H₂O ↔ H⁺ + OH⁻ plus
 2. CO₂ + H₂O ↔ H₂CO₃ then
 3. H₂CO₃ ↔ HCO₃⁻ + H⁺ or
 4. HCO₃⁻ ↔ CO₃²⁻ + H⁺ and
 5. CaHCO₃⁺ ↔ Ca²⁺ + HCO₃⁻ and
 6. CaCO₃ ↔ Ca²⁺ + CO₃²⁻ or
 7. H₂CO₃⁻ + OH⁻ ↔ HCO₃⁻ + H₂O or
reverse #3, or with heat
 8. Ca(HCO₃)₂ + heat ↔ CO₂ ↑ + CaCO₃ ↓
+ H₂O
 9. CaSO₄ ↔ Ca²⁺ + SO₄⁻ and, etc.,
 10. MgHCO₃⁺ ↔ Mg²⁺ + HCO₃⁻,
 11. MgCO₃ ↔ Mg²⁺ + CO₃²⁻,
 12. MgSO₄ ↔ Mg²⁺ + SO₄⁻
- and so on. (Note that reaction 3 & 4 make up the carbonic acid - bicarbonate buffer system.)

These reactions are all reversible equilibrium reactions and are interrelated to each other. Carbonic acid (H₂CO₃) is formed by the dissolution of carbon dioxide (CO₂) in water. Carbonic acid dissociates into hydrogen ions (H⁺, the actual acid ion) and hydrogen carbonate ions HCO₃⁻. Hydrogen carbonate ions, in turn, can release another H⁺, forming carbonate ions, CO₃²⁻. It is the concentration of H⁺ ions, (the pH value), that mainly determines in which direction the reaction actually takes place. A

lowering of the pH value, that is, an increase of the H^+ concentration, will shift the reactions 3 and 4 towards the left of the equations. A lowering of the H^+ concentration (increase of the pH value) will push the reactions towards the right, which would result in an increased concentration of CO_3^{2-} pushing reaction 6 to the left, i.e., precipitating $CaCO_3$. Generally, if you increase the concentration of one of the components on the right the reaction will move to the left.

Calcium may be present in water as Ca^{2+} , or it may exist as $Ca(HCO_3)^+$, or $Ca(OH)^+$. Moreover, remember that the water molecule itself can take part in these reactions, as we have noted, by surrounding the ions and is usually associating with metal cations in a ratio of 4:1 or 6:1 to form hydrates. For example, several hydrate forms of $CaCO_3$ are found with hexahydrate being the most common. Hydrates are thought to be associated with initial crystallization process.

As calcium carbonate is formed from ions in solution we find three distinct crystalline forms: *calcite*, (the most stable) *aragonite* and *vaterite* (metastable forms) all of which have different solubilities. The conditions affecting precipitation of calcite, aragonite and vaterite depends primarily upon temperature, pH, pressure and impurities present. It has been reported that when $CaCO_3$ precipitates, a gel can form (a hydrate?) and its lifetime depends on temperature and pH. Generally, $CaCO_3$ is negatively charged, however, under varying conditions of formation, $CaCO_3$ may have a different charge. One of the major controlling factors for calcium carbonate precipitation and the resulting predominant crystalline form is temperature. Generally, calcite forms at temperatures below $30^\circ C$ and aragonite is predominant above $50^\circ C$. The crystal structure of the aragonite is dendritic, dense, and is reported to be more adherent than calcite. The crystalline structure, the conditions under which they form and the surface charge of small

colloidal particles will come into play during scale deposit prevention and control.

VII. CHEMICAL TREATMENT

As one can readily see, the reactions affecting the solubility of minerals such as calcium carbonate in water is complicated and more difficult to predict than the solubility data suggests. There are numerous equilibrium reactions occurring in the water that affects the interpretation of simple chemical data. One must rely on empirical data based on plant experiences to estimate the scaling characteristics of a water system.

Minerals can be kept in solution using acids; lower the pH, or they must be removed or controlled as a precipitate (usually in a higher pH environment). In a low pH environment, the emphasis shifts from controlling scale to corrosion and biological control considerations. If we move toward an alkaline system (higher pH) we must focus on: a) removal of ions or suspended solids before water is used; or b) leaving the *dissolved and suspended* solids in the water and treating the water chemically or physically in order to control scale buildup. The removal of both suspended and/or dissolved solids from waters can be accomplished by water softening, ion exchange, filtration, sedimentation, coagulation, flocculation, reverse osmosis, etc. We will discuss the increased solubility and removal techniques to help in understanding the overall 'water / scale' system. However, in this paper, our main emphasis will be placed on techniques that inhibit suspended and dissolved solids from forming scale.

Acid (solubility)

In the 'good old days', acid was added to the cooling system in sufficient quantity to depress the re-circulating water's pH to the point where scale would not readily form. In turn the corrosion was controlled, in the early days (1920 - 1945), by adding inorganic

polyphosphates. Chromates were used in conjunction with phosphate-based programs at pH values below 6.5 - 7.0. The chromate inhibited microbiological growth due to the toxicity of the chromates. This toxicity would later be the cause of legislation against the continued discharge of chromate to public waterways and wastewater treatment plants. Over the years a wide variety of anti-scaling control compounds have evolved. Some systems use acid, but control the pH such that a balanced system is obtained, inhibiting scaling and minimizing corrosion and bio fouling by additional chemical agents.

Acid or special chemicals (polyphosphate, etc.) can be added to increase the water solubility of scale forming constituents. Sulfuric acid is most often used since it is the least expensive, but hydrochloric, citric or other acids are also suitable. Acid systems can reduce the bicarbonate, forming calcium and magnesium sulfate or phosphate that is more soluble than the carbonates. Acid salts are more applicable to smaller cooling systems for improved pH control but in all acid systems fluctuations in feed rates can produce widely varying pH levels and corrosion inhibitors are needed.

Polymeric organic phosphorus compounds, e.g., phosphonates, polyacrylates, polynaleics, etc., are commonly used to prevent calcium-based scales. Polyacrylate in the cooling water can keep calcium carbonate and calcium phosphate scale from forming, by keeping it in solution.

Alkalinity (solubility)

As discussed, scale deposits result from the ions in the water consisting of positive charged metallic ions such as calcium, magnesium and iron in combination with negative charged ions such as sulfate, carbonate, silica and oxygen. A technology being offered by Terlyn Industries Inc. consists of adding chemicals with an extremely strong negative nucleus to attract

ocations from the solution. The chemical additive attracts positive metallic ions with a significantly strong bond such that the negative ions remain as free radicals (ions). This chemical (thought to be a polymer) can attract several thousand calcium or positive metal ions per molecule.

With this *advanced chemical technology*, corrosion is controlled as a result of a reduced bleed (zero blowdown claimed) allowing the pH to rise above 8.3 so a natural passivating film will develop. In addition, biological fouling needs metallic ions to grow. With the new chemical a complex metallic ion is formed with strong bonds removing them from the food chain, hence growth is hindered. Their field experience supports these claims.

Briefly, let us again turn our attention from minerals in solution (ionic) to suspended solids and colloidal particles. Those solids that are large and heavy will settle out. The concentration of the intermediate suspended solids can be determined by filtration, and weighting the collected solids if the particles are of sufficient size to allow filtration. The remaining solids are very fine and result in turbidity. Turbidity in water is measured by the effect of the fine suspended particles on a light beam. The very fine suspended minerals or colloidal particles causing turbidity usually carry a negative charge, as discussed earlier. These surface charges result in a repulsion force between the particles preventing them from coagulating into larger particles and are kept in suspension by thermal energy (Brownian motion). We will discuss this phenomenon in more detail later when 'zeta potential' is explored.

The crux of the scale problem is that there has been neither a simple nor a sophisticated chemical process that has totally eliminated scale formation without some side effects. Increasingly stringent ecological requirements

have complicated the once simple decisions regarding water management problems; particularly those concerned with deposits. Projects that once were merely return-on-investment decisions have become necessities by legislation, and management is frequently confronted with major economic decisions as to where and how to best handle potential deposit problems. Thus, the more one understands the significance and costs of deposit-causing solids, the more likely that sound economic judgments can be made. Therefore, a discussion of the current practices employed to minimize or prevent scale deposition must include the relevant interdisciplinary theories on the mechanism of scale inhibition, for only through a coalition of disciplines can the best solutions for preventing scale formation be selected.

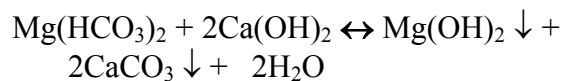
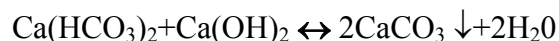
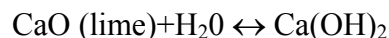
The use of trace amounts of certain types of chemical additives has long been known to have a profound effect on the solubility as well as the growth rate of crystals formed in aqueous media. The exact mechanisms of all these additives are not completely understood. There is, however, general agreement that adsorption of the additives must take place. Scale control agents generally work by interfering with the growing face(s) of a crystal. Therefore, the interest will be on the effect these additives have on the nucleation, precipitation, and the growth of adherent scale.

Crystal Modifiers (suspension and removal)

Chemical additives can be used to distort the crystal structure, changing scale to a non-adherent sludge. It is also effective at higher temperatures. Two different types of chemicals are effective as crystal modifiers; they are the polymaleic acids and sulfonated polystyrenes. These synthetically produced polymers are classified as water-soluble. The resulting sludge can be allowed to settle out, removed by blowdown or by side-stream filtration. Treated cooling water will appear turbid, indicating that the crystal modifiers are working.

Lime (removal)

One of the oldest methods in the softening of water is with lime. The following reactions are expected:



Removing most of both calcium and magnesium from solution.

Coagulation and Flocculation (removal)

For coagulation to take place the energy barrier of growth should be lowered or removed. Compressing the double layer or reducing the surface charge can do this. *See information under Zeta Potential for details on these characteristics.* Double layer compression involves adding salts to the system. As the ionic concentration increases, the double layer and the repulsion energy curves are compressed sufficiently so that the van der Waals forces (attractive) predominate and coagulation takes place. Salting out compresses the colloid's sphere of influence and does not necessarily reduce its charge.

Charge neutralization results when a positively charged coagulant, such as alum or a cationic polymer, is adsorbed on the surface of the colloidal particle. These coagulant additions will lower the surface charge and the repulsive energy curve. More coagulants can be added to completely eliminate the energy barrier. Coagulation destabilizes these colloids by neutralizing the forces that keep them apart. Generally, collision between particles is accomplished by applying mixing energy, i.e., supplying the opportunity and the kinetic energy for collision to overcome the energy barrier.

Ion Exchange (removal)

Another solution to the problem is to get rid of the calcium and magnesium in solution. One process is through the use of ion exchange. Ion exchange is the process of removing unwanted ions from a solution in an equivalent exchange for preferred ions supplied by a solid having a special structure to do this.

The solids consist of small polystyrene beads, also known as resin or zeolite. These beads carry a negative charge. In normal operation, hard water moves into the tank that contains the resin beads and the calcium and magnesium ions, both possessing positive charges, move to the beads, replacing sodium ions. The sodium ions now replace the calcium and magnesium ions to 'soften' the water. Once the resin beads are saturated with calcium and magnesium, the unit enters a regenerating cycle. Sodium ions also have positive charges, albeit not as strong as the charge on the calcium and magnesium. When a very strong brine solution (NaCl) is flushed through the tank that has resin beads already saturated with calcium and magnesium, the sheer volume of the sodium ions is enough to drive the calcium and magnesium ions off the beads, which in turn goes down the drain. The ion exchange is now ready to remove more calcium and magnesium from solution. Because of the sheer volume of sodium ions required for regeneration, a portion of them are flushed with the calcium and magnesium ions. This increases the salinity of the back wash and is the primary environmental concern with the use of 'softeners.'

Reverse Osmosis or Membrane Separation (removal)

Reverse osmosis, called hyperfiltration, indicating its relationship to a high-pressure filtration process. Where as ultrafiltration,

which uses lower applied pressures and different membranes removes only solutes of intermediate molecular weight. Reverse osmosis can remove low molecular weight ionic species. RO uses a membrane that is semipermeable, allowing the fluid that is being purified to pass through it, while rejecting the contaminants. Reverse osmosis is capable of rejecting bacteria, salts, sugars, proteins, particles, dyes, and other constituents. It is interesting to note that the separation of ions with reverse osmosis is aided by charged particles. This means that dissolved ions that carry a charge, such as salts, are more likely to be rejected by the membrane than those that are not charged, such as some organic'. The larger the charge and the larger the particle, the more likely it will be rejected

Precipitate / colloidal particles (suspension)

More than forty years ago it was discovered that some types of phosphates would prevent precipitation of certain scale-forming materials. In low concentrations, the basic theory regarding the mechanism of scale inhibition by phosphate addition is that the phosphate served to hold large concentrations of calcium carbonate in suspension. The phosphates do not stop the initial formation of scale (crystal nuclei), but keep them in the submicroscopic range (colloidal) by inhibiting their growth.

To understand, from the atomistic side of things, we need to look at how colloids interact with each other. Turbidity particles range in size from about 0.01 to 100 microns. The larger size particles tend to settle out or can be filtered out easily. The smaller sizes, (colloidal particles in the .01 to 5 microns), have settling times that are very slow and are not readily filtered. *A 0.01 micron size particle will contain almost 7 million CaCO₃ molecules, a 1 micron particle will contain just under 10 billion.*

Colloidal particles in water, as discussed earlier, carry an electrical charge that is normally negative. We know that like charges repel each other and it follows that this would prevent effective agglomeration and flocculation. Therefore, charged colloidal particles tend not to grow in size and remain in suspension or dispersed throughout the liquid.

Zeta Potential (suspension)

To visualize the environment surrounding a charged colloidal particle and demonstrate how the repulsive forces, as well as, the ionic concentration varies with distance, a double layer model is normally used. At the surface of the negative colloidal particle a layer of positive ions will form. This layer of positive ions is known as the *Stern layer*. More positive ions will be attracted by the negative colloid but they are partially repelled by the positive Stern layer.

Conversely to the distribution of positive ions is the distribution of negative ions, i.e., very few at the colloid surface and increasing with distance until equilibrium is reached. See Figure 6, (Courtesy of, Zeta-Meter, Inc.).

The region in which the positive ions are decreasing and the negative ions are increasing, hereby reaching the bulk equilibrium concentration, is called the *diffuse layer*. The *Stern layer* and the charged *diffuse layer* are referred to as the *double layer*. The thickness of the double layer depends upon the concentration of the ions in solution. A higher level of ions means more positive ions are available to neutralize the negative charge of the colloidal particle, and in turn a thinner double layer leading to an increased probability of intimate contact or collision between collide particles and hence coagulation or colloidal particle growth. On the other hand, a decrease in the ionic concentration reduces the number of positive ions resulting in a thicker double layer leading to increased dispersion

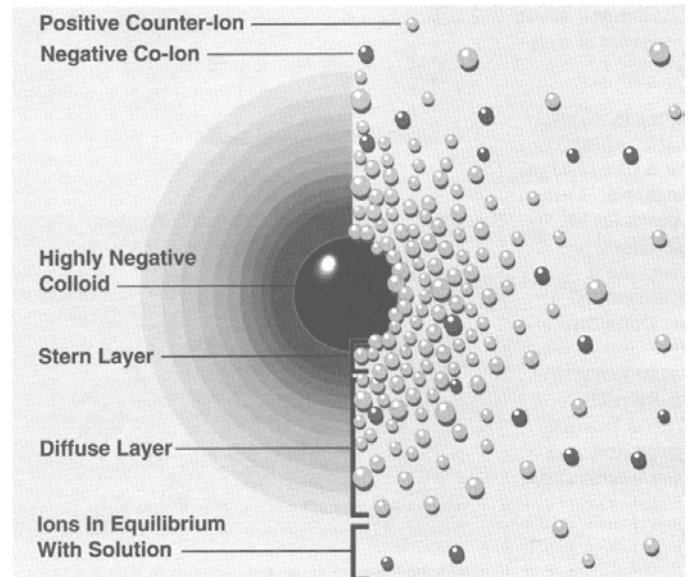


Figure 6. The Double Layer

Also, the valence of the positive ion addition has an impact on the double layer thickness. The concentration of aluminum (Al^{3+}) ions will be more effective in decreasing the colloidal charge and its double layer thickness than would sodium (Na^+). The electrical potential is at its maximum at the surface of the colloid and drops toward zero as the distance increases across the Stern layer and the diffuse layer, i.e., with increasing distance from the surface of the particle. The potential curve indicates the strength of the repulsive force and the distance at which these forces come into play.

The potential at the junction of the Stern layer and the diffuse layer is known as the *Zeta potential*. Zeta potential is a tool used for coagulation control because changes in Zeta potential indicate changes in the repulsive force between colloids. If one looks at the balance of forces between two colloid particles, one finds an electrostatic repulsion and a van der Waals attraction. The electrostatic repulsion becomes significant when two particle approach each other and their electrical double layers begin to overlap. Energy is required to overcome this repulsion and force the particles together. This is the energy barrier that must be overcome. The height of the energy barrier indicates how resistant the system is to effective coagulation. For agglomeration to take place two particles

must collide with sufficient kinetic energy to jump over this barrier.

VIII. PHYSIOCHEMICAL TREATMENT

Catalytic Processing

In 1836, J. Berzelius defined a catalyst as a compound, which increases the rate of a chemical reaction, but which is not consumed by the reaction. The catalyst affects only the rate of the reaction; it changes neither the thermodynamics of the reaction nor the equilibrium composition.

The study of catalysis is fascinating in that it is largely an empirical science. The application of catalysis has been a necessity for the chemical industry for at least 150 years. However, until about 25 years ago, the experimental techniques for investigating the process of catalysis at the atomic level were not readily available. For this reason vast amounts of empirical knowledge exist and await systematic investigation.

A catalyst provides an alternate path with a lower activation energy by which the reactants can proceed to form the products. The lower activation energy means a much higher proportion of the total reactants (ions) will have sufficient energy to react effectively along the catalyzed path than could have reacted along the uncatalyzed path. Hence, the kinetics, or rate of the reaction can be greatly increased by the presence of the catalyst. However, there is no change in the free energy of the reaction since the catalyst does not affect the energies of the products and reactants.

Many processes in nature are influenced by enzyme catalysis. Therefore the use of the catalysis principle in ways that resemble those used in bio-mineralization should not be too surprising. Honeywell's *kaltecpro*TM is such a technology and is based on a natural process in which crystallization takes place as a result of a

surface process, utilizing this catalytic principle, which generates a large number of seed crystals (colloid particles) or nuclei.

To examine this process let's back track a little and reiterate what we have already discussed, but this time with a slight twist. Hydration is an important property of dissolved calcium carbonate, which must be understood to appreciate how scale forms, based on this natural principle works. Calcium carbonate dissolved in water mostly takes the 'hydrated' form. This means the calcium (or magnesium) and the carbonate ions are entirely surrounded by loosely attached water molecules. Even if the solution is saturated, the driving force may not be sufficient to allow the combination of the cations and anions in quantities necessary to form critical radius nuclei (stable via homogeneous nucleation). However, they can precipitate out on solid metal pipe walls (or dirt particles etc.) if the supersaturation, i.e., driving force, is sufficient. In doing so they lose their hydrate envelopes, i.e., the barrier separating them from the opposite ions and scale deposits start forming.

Using a container filled with the activated *kaltecpro*TM material, as a catalyst to overcome the hydrate envelopes, which usually prevent the forming of crystals in water, bio-mineralization takes place. This induces the growth of crystals on the *kaltecpro*TM material surface. Friction forces then shear off the newly formed crystals from the *kaltecpro*TM beads. These crystals are of sufficient size to be stable and serve as 'seed crystals' for further precipitation, e.g., heterogeneous nucleation, of the dissolved calcium carbonate. Once this process has started, it continues in the hot water container system. The total surface area of the colloidal size seed crystals is many times greater than that of the system containment walls and serves as site for heterogeneous nucleation and scale growth. Hence the deposition of scale preferentially takes place on

the colloid size seed crystals rather than forming scale on the system components. Due to the natural principle of catalysis, the process of crystallization needs no energy input and the maintenance of the *kaltepro*TM unit requires the catalytic material be changed approximately every three years. This technology has passed stringent European water quality standards, which include the German DVGW - W512. The products derived from this technology are primarily focused toward the residential market for potable hot water systems.

Magnetic

Magnetic technology used in the treatment of water has been cited in the literature and investigated since the turn of the 19th century, when lodestones and naturally occurring magnetic mineral formations were used to decrease the formation of scale in cooking and laundry applications. 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. The use of magnets may be one of the oldest methods for the prevention of scaling in heat transfer components and the transportation of hard water. It is believed that permanent magnets work by precipitation of the ions, similar to that found in the chemical arenas.

Hard water contains ions, both positive and negatively charged, cations and anions. The general operating principle for the magnetic technology is a result of a moving ionized fluid (an electric current) through a magnetic field. When ions pass through the magnetic field, a force is exerted on each ion (Lorentz Force). This force is perpendicular to both the magnetic field and to the direction of motion and is proportional to the velocity. Since the force is at right angles to the velocity, it will not affect the magnitude of the velocity nor its kinetic energy but will merely alter its direction. The forces on ions of opposite charges are in opposite directions. The opposing redirection

of the ions tends to increase the frequency with which ions of opposite charge collide and combine to form a mineral precipitate, (a colloidal particle) similar to affect of thermal agitation discussed earlier. Since this reaction takes place in a low-temperature region of a heat exchange re-circulating system, the precipitation formed is non-adherent (heterogeneous nucleation) and similar to the effect of chemical additions as discussed above. Since the removal of calcium carbonate changes the ionic equilibrium balance in the solution, the water is now able to reabsorb some existing scale.

Commercialization of the technology began after World War II, with the largest advances coming in the last 20 years with the development of high-power, rare-earth element magnets advancing the technology to the point where it is more reliable. There are records of installation of the technology in the United States from about 1950. Manufacturers claim to have installations operating satisfactorily for as long as 30 years. It has been estimated that approximately 1,000,000 units have been sold. It appears that most of the presently available units, based on manufactures' specifications, are designed to be used in smaller flow applications.

Electronic / Induced Electric Field

Electronic descaling (ED) technology, developed by Dr. Cho of Drexel University and first offered by York Industries, uses a time varying electronic current in a solenoid wrapped around a pipe to create an induced electromagnetic field inside the pipe. We know from physics that moving magnets or changing magnetic fields can produce electrical current as in the generation of electricity. Also moving electric charges can produce magnetic fields, as in a solenoid. To help quantify this one can refer to *Faraday's law of induction*. Faraday's 'law of induction' states that the electromotive force induced in a circuit is directly proportional to

the rate of change of the magnetic flux through it. Note that this is merely the principle on which a transformer operates, i.e., the primary a-c current, sets up the (changing) magnetic flux (the magnetizing current) inducing an a-c current in the secondary winding.

An applied current flowing in a clockwise direction in a solenoid wrapped around a pipe creates a magnetic field, which will induce an electric field inside the pipe. The induced electric field is in the counterclockwise direction and is proportional to the radius. The direction of the electric field E changes when the direction of current changes. When the current flows in the counterclockwise direction, the induced electric field points to the clockwise direction.

The distribution of E , the induced electric field, decreases to zero at the center of a solenoid. However, the velocity of the fluid flow is at a maximum at the pipe center and decreases to zero at the pipe wall. To improve the efficiency of the induced electric field an offset coil is used resulting in an induced electric field E that is larger than that of a solenoid centered on the pipe diameter. In addition, to the increases strength of the induced E , a square-wave current input, is used to increase the rate of change of the magnetic flux, and therefore the induced electric field.

When charged ions such as calcium and carbonate ions pass through the ED coil, they experience an induced pulsing electrical field.

The induced electric field provides necessary molecular (ion) opposing redirection of the charged mineral ions, increasing the number of collisions such that, nucleation and precipitation occurs. The ions are converted to insoluble calcite crystals at room temperature. The particles are powdery and fluffy, easily removed by turbulence and routine blow down. The level of saturation of the water significantly

decreases; thus, new scale deposits on the heat transfer surface are prevented.

Electrolysis / Electrostatic

A unique design concept by BWT has evolved out of Europe and is based on electrostatic forces resulting from a low voltage applied across a set of electrodes (low current, <1 amp).

To maximize the surface area and enhance the electrostatic field (by minimizing the distance between anodes and cathodes) a specialized conductive cartridge is filled with non-conductive and conductive spheres in an alternating pattern. As voltage is applied to the primary electrodes, the spheres in turn have a bipolar charge induced (one side positive and the other side negative) on their surfaces. The calcium and magnesium ions migrate to the negative surface. The carbonates and sulfates migrate toward the positive surface. This electrostatic field induced diffusion results in a localized concentration gradient around the conductive spheres. As we have discussed earlier, an increase in the concentration of one reactant will cause the reaction to progress in the direction that tends to minimize the increase (increased probability of precipitation).

In addition to the unique electrode cartridge design, BWT, ('AQA Total' in the USA), further innovations take the form of voltage control. By monitoring flow rates and electrical impedance, the control system reverses the polarity of the electrodes to prevent the crystal nuclei (*nanocrystals* as called by the manufacturer) from growing too large to prevent colloid suspension, i.e., no settling. This reversal of the polarity causes a movement reversal of the ions in solution resulting in increased probability of collision and additional colloidal particles.

The need for an environmentally sound answer to water treatment plus the higher cost of water forced a greater demand for this technology in

Europe than in North America. The European residential and commercial market purchased 45,000 units in a three-year period. This BWT technology has passed stringent European water quality standards, which include the German DVGW-W512 guidelines as well as independent laboratory testing in the United States.

Electrostatic

Electrostatic water treatment technology got its start in North America in 1957 when Roy C. McMahon started his company, Electrostatic Equipment Company. The major North American suppliers of electrostatic water treatment technology can trace their roots to McMahon's basic technology. ElectroStatic Technologies, Inc. is a direct descendent of the Electrostatic Equipment Company while Zeta Corporation (1994) and York Energy Conservation (1978) were founded later.

Electrostatic water treatment technology is based on the formation of a strong electrostatic field between an electrode (an anode in most cases) and ground (second electrode) similar to that found in a capacitor. The capacitance of a system is equal to the charge on the electrode divided by the applied voltage (primary field). The original (McMahon) applied voltage started at 3kV and has evolved upward through 5kV to, as high as, 30kV. Various dielectric-insulating materials isolate the anode (positively charged) from the fluid (water in our case). The dielectric material, the electrode design, and its placement in the re-circulating hot water system all play a role in its effectiveness.

The hypothesis explaining the operating principles of an electrostatic water treatment system must follow the same physical and chemical fundamental concepts used for other treatment systems. Industrial water, as we have discussed, has not only the hydronium (H_3O^+) and hydroxide (OH^-) ions, but also concentrations of the calcium, magnesium,

carbonate, and sulfate ions. In the presence of an electric field an attractive or repulsive force will be imposed on these charged ions. Therefore, the positive ions will be attracted toward the negative electrode and repelled by the positive. Conversely, the negative ions will be attracted to the positive surfaces and repelled by the negative. This electrostatic force field causes movement or diffusion of the ions toward their respective electrodes. This diffusion will cause localized concentration gradients within the moving water, changing the localized chemical equilibrium. In parallel with the build up of a localized concentration, the opposing movement of ions increases their respective kinetic energy and the frequency of collision between cations and anions. These two phenomena create a condition favorable for nucleation and the formation of colloidal particles. Furthermore, an electrostatic treatment system uses a directly applied electric field as opposed to an induced electric field and can be stronger using less energy and is more focused, increasing its effectiveness.

It has been noted, both in the literature and in the development of this technology, that an electrostatic field can increase the surface charge of the colloidal particles therefore increasing the zeta potential. As discussed earlier the zeta potential provides a measure of the repulsive force between colloids. This secondary effect, the enhanced zeta potential, retards the growth of the suspended colloidal particles, preventing agglomeration and sedimentation. However, if the colloidal particles are formed in the cooler portion of the re-circulating system, the decreased solubility in the warmer section will give the necessary driving force for possible additional precipitation. Due to the much larger surface area of the now existing colloidal particles compared to the walls of the heat exchanger the scale growth on these surfaces will be minimized. Conversely, if the degree of saturation is small or negative, descaling can take place. In a cooling tower environment this

enhanced nucleation and subsequent growth control allows for a slightly elevated pH normally between 8.2 and 9.5, leading to an improved corrosion and bio-fouling environment.

Field experience has shown that corrosion and biological consideration are usually minimal when accompanied by electrostatic treatment.

This is thought to be the result of the fact that the free metallic ions are significantly reduced in concentration. This reduces the food available for the microscopic cells that cause fouling such that growth is impeded. Corrosion is minimized due to the positive pH levels and the tendency for the formation of a pacification layer on metal component

Electrostatic treatment systems by their design are capable of handling a wide variation of water qualities and fluid flows. This allows the application of these products across the spectrum to include commercial and heavy industrial installations.

IX. SUMMATION

We have viewed water treatment from the primary factors that affect the scaling process.

The interconnectivity of the various chemical, electrical, and magnetic phenomena have been discussed. As noted, chemical reactions are controlled by the electrical charges contained within atoms and how these electrical characteristics affect the behavior of water and the minerals in solution or suspension. That the initiation of nucleation and resulting stable colloidal particles go through various transitions due to the interplay of surface tension and surface charge. We have also pointed out that an intimate relationships exist between magnetic and electrical fields and that an electrical field, induce or applied directly, can create stable changes in a water / mineral solution through the formation of small colloidal particles. Finally, these interrelated

phenomena affect the scaling processes in water recirculating heat transfer systems.

In all cases, monitoring of the system is necessary to ensure that both its mechanical and chemical components are operating within desired limits. Mineral scales consisting of calcium sulfate, barium sulfate and high silica content may create special local problems and may or may not have to be treated as a special case depending on characteristics of the process environment and the water / mineral solution.

The road to truly understanding, the overall scaling process is complex and fraught with many twists and turns (variables). We have opened the door to some of the secondary or supporting phenomena. For instance, the bipolar nature of water leading to its high dielectric constant, its surface tension, its hydration effect, its electrical conductivity, the impact of pressure and secondary ions, etc., has been relegated a secondary or supporting role in the overall chemical and physical water treatment arena. These supporting phenomena are of interest but will be addressed, as more information becomes available.

<p>This paper was written by David McLachlan. Dr. McLachlan holds his PhD from Iowa State University in Metallurgical Engineering. He currently holds the position of V.P. Technical Development for Fluid Treatment Solutions, Inc. If you have further questions you may contact Dr. McLachlan at dml@estatusa.com.</p>
