

# Electrochemical Cooling Water Treatment: A New Strategy for Control of Hardness, Scale, Sludge and Reducing Water Usage

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## ABSTRACT

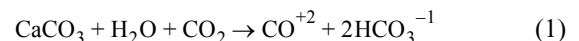
*Fouling due to calcium salts present in hard water has proven historically troublesome in metal plating, chlor-alkali production, and other electrolytic operations. It is perhaps ironic, this classical nuisance includes mechanisms for effective control of troublesome deposition throughout large, real-world recirculating water systems; effectively establishing a new water treatment strategy of environmental and economic benefit. An electrolytic process can be employed for evaporative cooling systems of all types to generate in-situ chemistry and physical activity totally controlling hard-water deposits and minimizing both corrosion and biofouling. This is accomplished without classical chemical treatment or water conditioning while also allowing substantial reduction in cooling system bleedoff.*

## INTRODUCTION

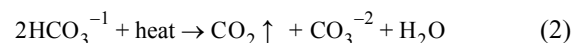
An evaporative cooling water system consists of a heat source, cooling tower, recirculating water pump, interconnecting piping, and water to transport heat from the heat source to the environment by evaporation taking place in the cooling tower. Water containing dissolved minerals (make-up water) is added to a cooling tower system to replace evaporative loss and maintain near constant water volume. As cooling tower water evaporates, dissolved minerals from the make-up concentrate and eventually become problematic. Dissolved mineral buildup is controlled through discharge of concentrated system water as bleedoff, subsequently replaced by relatively dilute make-up water. The volumetric ratio of make-up to bleedoff establishes an evaporative concentration factor of dissolved solids, termed cycles of concentration. Evaporation of water to dissipate heat is an ideal means of cooling because

each pound of water evaporated carries away almost 1,000 Btu's of heat. The more water can be concentrated without causing mineral deposition or other problems, the more cost and resource efficient the evaporative cooling system becomes.

Fresh water from almost all sources contains some level of dissolved minerals in the form of positively and negatively charged ions. Common positively charged ions include calcium ( $\text{Ca}^{+2}$ ), magnesium ( $\text{Mg}^{+2}$ ), sodium ( $\text{Na}^{+1}$ ), and potassium ( $\text{K}^{+1}$ ). Common negatively charged ions include chloride ( $\text{Cl}^{-1}$ ), sulfate ( $\text{SO}_4^{-2}$ ), and bicarbonate ( $\text{HCO}_3^{-1}$ ). These species dissolve in water as rain interacts with the Earth's surface and subsurface over long periods of time. Of these species, calcium and bicarbonate are of chief interest when combating mineral deposition in evaporative cooling water systems. Calcium bicarbonate is quite soluble in water and is the chief troublesome component of what is termed hard water. Its presence in fresh water is the result of slow, low temperature reaction of acidic rain water, containing carbonic acid or dissolved carbon dioxide ( $\text{CO}_2$ ), with limestone composed of calcium carbonate ( $\text{CaCO}_3$ ). This process may be summarized as follows:



Hard water becomes problematic in cooling water and other energy transfer systems because bicarbonate ion is thermally unstable and easily decomposes to carbon dioxide and carbonate ion according to the following reaction:



*Note: Upward pointing arrow (↑) indicates liberated gas as result of reaction.*

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Bicarbonate ion breakdown proceeds quickly under the conditions typically found with functioning cooling towers: modest water heating from tap water temperature to 95 °F, agitation that enhances surface release of carbon dioxide, and large air flow that readily accepts the release of CO<sub>2</sub>. The natural solubility of calcium carbonate in distilled water at room temperature to its constituent ions with sufficient time is approximately ten parts per million (ppm) as CaCO<sub>3</sub>, or 4 ppm as Ca<sup>+2</sup> and 6 ppm as CO<sub>3</sub><sup>-2</sup>. Cooling tower make-up may easily contain from 50 to 300 ppm or more of calcium bicarbonate and is then concentrated several times by evaporation. Of the bicarbonate present, approximately 20 to 40% undergoes thermal decomposition to carbonate ion. This sets the stage for the recirculating cooling tower water to become highly supersaturated with respect to calcium and carbonate ions, either typically reaching concentrations in excess of 100 ppm or more.

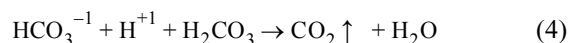
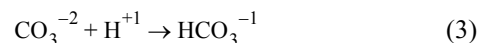
Calcium carbonate deposit formation in practical cooling water systems proceeds slowly even though both ions are present far in excess of their theoretical saturation level because the rate of formation of the smallest constituents of deposition, nucleated crystals, can be quite slow. The process of calcium and carbonate ions coming together to begin building calcium carbonate to the point of nucleation occurs throughout the entire volume of cooling water and is the primary rate limiting step. The entire reaction can take hours to several days to produce significant precipitation depending on the thermal and mechanical loading of the cooling tower system and the amount of time the water is held in the system, defined by the time required to discharge one full system volume by normal bleedoff. It then becomes essential to deal with potential calcium loss due to supersaturation, or risk deposit formation as scale on heat exchange surfaces, as sludge settling in the cooling tower basin or elsewhere, as mineralization and bulking of biofilm, or as increased residue at wet/dry boundaries of the cooling tower.

Traditional cooling tower treatment makes use of bleedoff to transport make-up water calcium through the system so it may be discharged to waste with bleedoff. Calcium loss prior to discharge is either prevented or minimized employing one of two basic strategies. In light of ever increasing demand for and cost of resources as well as concern over use of chemical used in water treatment, need exists for an alternate treatment methodology to lessen evaporative cooling resources and reduce or eliminate need to introduce chemical additives to water eventually discharged to sanitary or surface waters.

### TRADITIONAL DEPOSIT CONTROL STRATEGY

Two strategies of chemical water treatment have been employed for controlling calcium carbonate formation in cooling water systems. First, acid may be added to effectively reverse the formation of carbonate ion due to the thermal breakdown of bicarbonate and then remove bicarbonate by converting it to carbonic acid which in turn breaks down to carbon dioxide gas and water. Carbon dioxide then easily

escapes into cooling tower air flow. Acid introduction is used to change recirculating water chemistry so calcium carbonate cannot form by virtue of its carbonate formation potential being removed or significantly reduced. This is a very effective strategy for calcium carbonate control, but produces significant reduction in cooling water pH with an increase in corrosion potential and a need for corrosion inhibitors effective at the reduced pH established. Use of strong mineral acids such as sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) also represents a hazard issue of increasing safety and liability scrutiny. The reactions involved are:



The second primary strategy for controlling calcium carbonate formation relies on coordinated introduction of two types of deposit inhibiting additives, anti-precipitants (crystallization modifiers) and dispersives. Anti-precipitants act on the very smallest components of crystalline calcium carbonate as they enter the nucleation process throughout the recirculating cooling water. By interfering with nucleation and orderly crystal development, anti-precipitants dramatically slow or delay formation of calcium carbonate crystals of sufficient size to be significant in deposit formation. Retarding crystal development permits greater calcium transport via bleedoff. Dispersives are typically polymeric compounds used to impart uniform negative charge on very small calcium carbonate crystals at the nucleation point. Uniform like-charge on small particles tends to hold them apart and retard aggregation into larger composites that are more likely to interact with cooling system surfaces. Deposit inhibiting additives are not as effective in transporting calcium through a cooling water system as acid, but they have the advantage of not lowering pH or contributing significantly to corrosion.

In summary, make-up water containing soluble calcium bicarbonate is subject to bicarbonate breakdown, and quickly enters a meta-stable, supersaturated state with potential over time to produce substantial insoluble calcium carbonate. If traditional chemical treatment strategies are not used, the process leading to observable precipitation starts homogeneously throughout the mass of recirculating cooling water. Calcium carbonate formation starts with calcium and carbonate ions coming together to form ion clusters of immense number, but limited number of constituents. Under supersaturation, the average number of calcium and carbonate ion components of ion clusters tends to slowly increase with time as the average number of ion clusters slowly falls. Eventually as the point of nucleation is reached and true micro crystals of calcium carbonate begin to form throughout the volume of cooling water, evidence of the crystallization process becomes noticeable as water turbidity. As average crystal size continues to grow, individual crystals begin to aggregate into particulate matter able to settle where water velocity or turbulence is low.

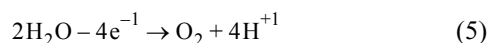
## A NEW DEPOSIT CONTROL STRATEGY

Recently, another type of treatment has been shown to reduce scaling in cooling water systems (Becker and Cohen 2007). The treatment is based on an electrochemical process, water electrolysis, which increases the pH in the vicinity of an electrode surface, causing precipitation of  $\text{CaCO}_3$  to occur at the electrode. It is well-known that calcium carbonate precipitation is a function of temperature; however it is also dependent on ion concentration, flow rate of the solution and the pH of the water (Devos et al 2003). Previously, electrochemical-based laboratory experiments have been used to study nucleation growth, crystallization, structure and morphology of calcareous deposits by exploiting the acceleration of the precipitation reaction by the electrochemical reactions occurring on the electrodes (Devos et al 2003, Pavez et al 2005, Xu et al 1999). In fact, the high pH ( $> 9.6$ ) needed to precipitate the calcium carbonate has experimentally been verified in these type of electrochemical experiments (Cachet, H. et al 2001).

In the case of the commercial water treatment method, the same principles apply in accelerating the calcium carbonate precipitation reaction. Mineral ions preferentially deposit on the cathodic surface of an electrolysis unit rather than at the other surfaces in the main cooling flow stream. The process, in essence, concentrates the scale-formation into the electrolysis unit such that scale is reduced in the functional part of the cooling water system. The electrolysis process operates by reducing water to hydrogen gas and hydroxide ions at an electrode surface (cathode), thereby creating a localized environment at the cathode that is highly insoluble to scale-forming mineral deposits.

Electrolysis of water containing an electrolyte produces two chemical reactions:

*Anodic Reaction (positive electrode), Oxidation of Water*

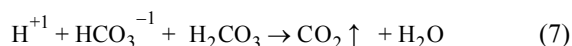


*Cathodic Reaction (negative electrode), Reduction of Water*



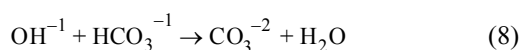
In hard water containing bicarbonate ion a secondary reaction occurs at the anode:

*Secondary Anodic Reaction*

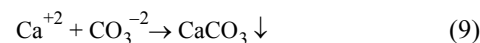


In hard water containing bicarbonate ion and calcium ion two secondary reactions occur at the cathode:

*Secondary Cathodic Reaction #1*



*Secondary Cathodic Reaction #2*



*Note: Downward pointing arrow indicates formation of solid precipitate as a result of reaction.*

The key phenomena governing the movement of the calcium ion/carbonate ion species towards the electrode and which influences the electrolysis precipitation reaction are ionic transport and the electrochemical charge transfer reactions occurring at the electrode/solution interface. Ionic mass transport in electrolyte solutions follows fundamental mass transfer laws (Fick's Law), but the mass flux equation now contains an additional force, called the migration term, that results from the electric field present between the electrodes (Newman 1973, Bockris). Migration of an ionic species is dependent on the electric field, the charge and ionic mobility of the ion, and its concentration. Migration can change the flux of a charged species in two ways. If the ionic species is positively charged, the migration flux is additive and enhances the overall flux. However, if the ions are negatively charged, migration works against the diffusional flux and decreases the overall flux. In addition, if solution flow and heat are also present, then a fluid convection and heat transfer term must also be taken into account to describe the ionic flux (Koryta and Dvorak 1987).

The charge transfer reactions occurring at the electrode also factor in to the transport and concentration distribution of the ionic species. The electrochemical reactions deplete the ionic reactants while causing an increase in the ionic products at the electrode surface. Hence, due to migration, diffusion, convection, and the charge-transfer reactions, concentration gradients of the various ionic species are formed near the electrode in a small thickness called the diffusion layer.

The established concentration gradients of the ionic species contribute towards the high pH at the cathode according to reaction 6 and also promote the formation of carbonate ion according to reaction 7. Hence, there is an abundance of negatively charged ions at the cathode that provides a driving force of positively charge calcium ions to migrate towards the cathode to maintain electro-neutrality in the solution. In actual cooling water systems, the ionic movement and transport phenomena becomes more complicated because of ion-clustering due to the supersaturated levels of calcium, bicarbonate and carbonate ions. However, the basic transport and charge-transfer principles still apply.

The net products from these reactions are three gasses ( $\text{H}_2$ ,  $\text{O}_2$  &  $\text{CO}_2$ ), which readily disengage from the anode and cathode, and one ionic species, hydroxyl ion that is of relatively limited mobility and at very high concentration the cathodic surface. Hydroxyl ion then reacts with bicarbonate ion to form carbonate ion at high concentration. Very high relative carbonate concentration induces rapid calcium carbonate precipitation directly on the cathode as in classical fouling of process electrolysis cathodes exposed to water containing calcium hardness.

This now signifies a new strategy for controlling calcium carbonate deposition that relies much less on bleedoff for calcium removal. This strategy relies on electrolysis to provide the chemistry and removal facility to capture calcium carbonate fast enough to effectively influence micro crystal development. Electrolysis can be used to establish a more intense calcium removal sink than found either in bulk phase precipitation or at heat exchange surfaces.

Water hardness deposits have historically been troublesome in electrochemical processes such as metal plating, chlor-alkali and bromine production requiring water conditioning and other measures to remove or control calcium. Recognizing that hydroxyl ion forms at the cathode of an aqueous electrolytic cell and that it freely acts to increase carbonate activity and cathodic scaling, a mechanism troublesome in one venue seemed to point to a means of capturing calcium potentially of value in other venues. Several years of experimentation and development showed that, indeed, calcium removal could be realized at a rate equal to or even greater than required for deposit free operation of evaporative cooling water and other water carrying systems.

Hydroxyl ion formation in the boundary layer of water in immediate contact with the cathode of an electrolysis cell can be projected to reach or exceed 10,000 ppm, or approximately 0.25 moles per liter. Given that bicarbonate and hydroxyl ions react very rapidly and quantitatively to produce carbonate ion, any bicarbonate very near a cathode will be rapidly converted to carbonate ion and cathodically localized carbonate concentration will rise and approach 10,000 ppm or more. Localized calcium ion saturation is therefore reduced proportionately as dictated by solubility product and common ion effect considerations.

Calcium carbonate saturation throughout a cooling water system is achieved theoretically with equal molar concentrations or about 4 ppm calcium and 6 ppm carbonate at 60 °F. Saturation requirements progressively decrease as water is warmed above 60 degrees. This is why scale tends to form on heat exchange surfaces where water is warmest throughout a cooling water loop.

In terms of solubility product and equal molar concentrations of  $\text{Ca}^{+2}$  and  $\text{CO}_3^{-2}$  (Dean 1999):

$$\begin{aligned} \text{At } 15^\circ\text{C}(59^\circ\text{F}) \quad & [\text{Ca}^{+2}] \times [\text{CO}_3^{-2}] = 0.99 \times 10^{-8} \\ [\text{Ca}^{+2}] = [\text{CO}_3^{-2}] & = 0.9949 \times 10^{-4} \quad (10) \\ \text{Ca}^{+2} = 4.0 \text{ ppm} \quad & \text{CO}_3^{-2} = 6.0 \text{ ppm} \end{aligned}$$

$$\begin{aligned} \text{At } 25^\circ\text{C}(77^\circ\text{F}) \quad & [\text{Ca}^{+2}] \times [\text{CO}_3^{-2}] = 0.87 \times 10^{-8} \\ [\text{Ca}^{+2}] = [\text{CO}_3^{-2}] & = 0.9327 \times 10^{-4} \quad (11) \\ \text{Ca}^{+2} = 3.7 \text{ ppm} \quad & \text{CO}_3^{-2} = 5.6 \text{ ppm} \end{aligned}$$

$$\begin{aligned} \text{At } 38^\circ\text{C}(100^\circ\text{F}) \quad & [\text{Ca}^{+2}] \times [\text{CO}_3^{-2}] = 0.55 \times 10^{-8} \\ [\text{Ca}^{+2}] = [\text{CO}_3^{-2}] & = 0.7416 \times 10^{-4} \quad (12) \end{aligned}$$

$$\text{Ca}^{+2} = 3.0 \text{ ppm} \quad \text{CO}_3^{-2} = 4.5 \text{ ppm}$$

*Note: Value based on four-fold estimated solubility decrease relative 15°C to 25°C change.*

Saturation at equal molar concentrations of calcium and carbonate ion limits calcium ion to 4.0 ppm at roughly 60 °F, falling to approximately 3.0 ppm at 100 °F. If either calcium or carbonate were to increase, the other species must fall to prevent supersaturation according to the solubility relationship for the waters' temperature.

$$\begin{aligned} \text{Cathodic } \text{Ca}^{+2} \text{ saturation at } 38^\circ\text{C} \\ \text{assuming localized cathodic } \text{CO}_3^{-2} = 10,000 \text{ ppm} \quad (13) \end{aligned}$$

$$\begin{aligned} \text{Ca}^{+2} \text{ saturation: } \quad & ([\text{Ca}^{+2}] = 0.55 \times 10^{-8} / [\text{CO}_3^{-2}]) \\ & = 0.55 \times 10^{-8} / 0.25 = 2.2 \times 10^{-8} \text{ moles/liter} \\ \text{Ca}^{+2} \text{ saturation} & = 0.0001 \text{ ppm} \end{aligned}$$

In comparison to calcium ion saturation at a heat transfer surface or in bulk phase water where  $\text{Ca}^{+2}$  &  $\text{CO}_3^{-2}$  ions are naturally found in roughly equal molar concentrations, calcium ion saturation at a cathodic surface is orders-of-magnitude less due to great molar excess of induced carbonate ion. The great difference between bulk phase calcium ion concentration and cathodic calcium saturation establishes by far the greatest precipitation driving force found anywhere in a cooling water loop, much greater than the relatively weak driving force created by reduction in solubility due to increased temperature.

With sufficient cathodic area and power, an excess amount of calcium carbonate above that theoretically anticipated to form on heat transfer surfaces or in the bulk phase per unit time can be captured electrolytically. Removing calcium at a rate exceeding the theoretical formation rate of ion clusters and subnucleated nanoparticles due to slow diffusion process draw upon subnucleated micro crystal resources and therefore starts a process retarding average crystal size development.

Initial ion clusters are equally apt to dissociate as they are to grow in size. As particle size increases, approaching nucleation, innate tendency to disassociate within a given cluster matrix diminishes. As ion clusters and sub-nucleated particles increase in size, there still remains some reverse equilibrium tendency that influences crystal development. If a force strong enough to influence equilibrium exists, the equilibrium governing precipitation may be reversed. High cathodic carbonate concentration lowers calcium tolerance to such an extent.

For any given cooling water system, characteristics governing natural precipitation tendencies are discreet and determined by water chemistry, heat transfer surfaces and

mechanical design. Therefore, the key to proper electrolytic prevention of scale precipitation will be governed by flow, current density and cathodic surface area of the electrolytic reaction cell. Electrolytic cells are incorporated into a cooling water loop in a side stream configuration. Figure 1 illustrates a typical installation of four electrolytic cells. The cathodic surface area required for any set of cooling system parameters is achieved by either varying the number of cells or the dimensions of the cells used. Variation of current is used to achieve precise control to match variation in cooling system load.

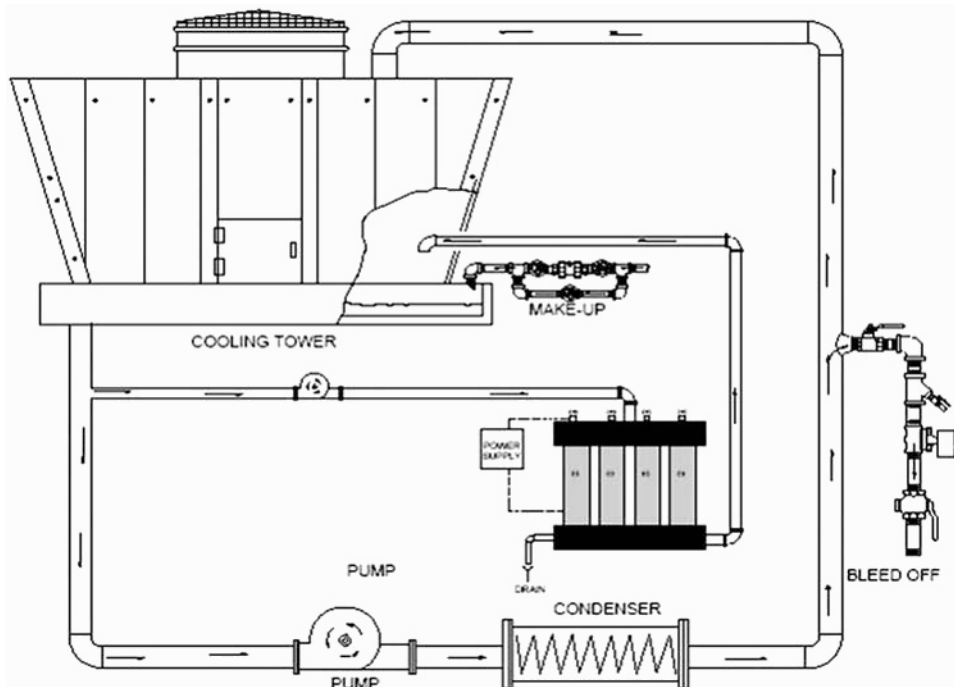
Current density, the amount of power supplied over the area of an electrolytic cell, is paramount when considering the reaction kinetics for electrochemical reactions. Caustic production at cathodic surfaces is determined by the hydrolysis reaction rate and thus, the amount of current supplied to the electrolytic cell. As mentioned earlier, electrolytic cells for cooling water treatment are designed to produce approximately 10,000 ppm hydroxyl ion at cathodic surfaces to achieve an appropriate reaction rate for carbonate ion production.

The effect of flow variation through side stream electrolytic process cells has been studied and field tested to maximize calcium carbonate capture. Flow optimization insures maximum presentation of ion clusters and time for positive fixed crystal growth to and on cathodic surfaces. Maximizing flow relative to capture also helps back mixing of ion clusters achieve homogeneous concentration throughout the cooling tower water and uniform net movement from tower water to the side stream capture process.

Cathodic collection of calcium carbonate effectively establishes calcium transport out of a cooling system apart from that provided by bleedoff. So long as sufficient cathodic area, driving force and residence time are available to limit microcrystal growth for a given set of cooling system operating conditions, there may be much less or no reliance on bleed-off to control residence time. Operating experience verifies this, indicating average water cycles of concentration to more than double without bulk phase precipitation or heat exchange deposition. Under some conditions zero discharge can be obtained.

In operation, a side stream electrolysis unit can accumulate a significant deposit and still function in a uniform manner. Eventually, though, accumulation must be removed to preserve operability. Deposition on cathodic surfaces can be seen in Figures 2 and 3. Deposit removal can be accomplished by various means, including electrolytic, mechanical and physical cleaning.

Along with calcium carbonate collection, there are additional benefits derived from continuous side stream electrolysis. The loosely packed crystals of calcium carbonate that form with rapid forced precipitation of calcium carbonate facilitate capture, co-precipitation and adsorption of organic contamination removed from air passing through a cooling tower. Organic contamination is troublesome due to its microbial nutrient potential. Since there is direct correlation between organic loading ('food') and biomass development, any removal of captured organics is beneficial in limiting biofilm and biomass.



**Figure 1** Typical cooling loop with side stream electrolysis capability.



**Figure 2** An 8" diameter cell with approximately 2" of  $\text{CaCO}_3$  after 3 months operation.



**Figure 3** 8 inch cells used to treat 450 ton industrial cooling tower under zero discharge mandate.

Electrolysis of halide containing water can, under certain conditions, lead to in-situ formation of chlorine or bromine; further aiding in controlling microbial growth. Controlling biofilm and organic filming of metals is generally beneficial in reducing corrosion of an active metal such as steel. Such metals are highly susceptible to microbiologically induced corrosion and under deposit corrosion.

## CONCLUSION

Clearly, introduction of hydroxyl ion (caustic) to recirculating cooling water results in conversion of bicarbonate to carbonate, fostering calcium carbonate precipitation. Electrolysis can provide the caustic to promote precipitation, capture, retention and removal mechanisms necessary to create a fully functional treatment strategy. While there are other means to produce similar partial water softening effects, such as traditional municipal and industrial cold lime soda softening, electrochemical methods do not require addition of chemicals, pH control, filtration or additional means of mechanical solids separation.

Electrolysis provides a vehicle for rapid, clean capture and fixation of calcium that is simple, easy to maintain and requires no chemical introduction or handling. This "old" technology is proving to be a valuable new tool, effectively allowing cooling water to be treated under a new strategy that not only improves performance, but also significantly saves water and eliminated need for chemical. It does this because it has the robust power to fundamentally affect the basic mechanisms behind evaporative cooling system hardness precipitation in a uniquely clean and direct manner.

## REFERENCES

Becker, H.A. and Cohen, J.J. Electrochemical Water Treatment: A New Strategy for Control of Hardness and

Sludge in Open Evaporative Cooling Water Systems. The Electrochemical Society Spring Meeting, May 2007, Chicago, Illinois, Paper #886.

Bockris, J. O'M. and Reddy, A.K.N. 1970. Modern Electrochemistry Volume 1. Chapter 4: Ion Transport in Solutions. New York: Plenum Publishing Corporation.

Cachet, H., El Moustafid, T., Herbert-Guillou, D., Festy, D., Touzain, S., Tribollet, B., 2001. Characterization of deposits by direct observation and by electrochemical methods on a conductive transparent electrode. Application to biofilm and scale deposit under cathodic protection. *Electrochimica Acta* 46 3851-3857.

Dean, J. A. 1999. *Lange's Handbook of Chemistry*, Fifteenth Edition, McGraw-Hill, ISBN: 0-07-016384-7.

Devos, O., Gabrielli, C., Tlili, M. and Tribollet, B. 2003. Nucleation-Growth Process of Scale Electrodeposition: Influence of Supersaturation. *Journal of the Electrochemical Society*, 150 (7) C494-C501.

Koryta, J. and Dvorak, J. 1987. *Principles of Electrochemistry*. Chapter 2: Transport Processes in Electrolyte Systems. Chichester, Great Britain: John Wiley & Sons.

Newman, J. 1973. *Electrochemical Systems Part C: Transport Processes in Electrolytic Solutions*. Englewood Cliffs, N.J.: Prentice-Hall, Inc.

Pavez, J., Silva, J.F., Melo, F., 2005. Homogeneous calcium carbonate coating obtained by electrodeposition: in situ atomic force microscope observations. *Electrochimica Acta* 50 3488-3494.

Xu, S., Melendres, C.A., Park, J.H., Kamrath, M.A., 1999. Structure and Morphology of Electrodeposited  $\text{CaCO}_3$ : X-Ray Diffraction and Microscopy Studies. *Journal of the Electrochemical Society* 146 (9) 3315-3323.