THEORY

of

Evaporative Cooling Tower Hard Scale Prevention using ReDOXPro3 Media Recirculating Water Treatment Systems

As with all the various water treatment phenomena produced by *ReDOXPro3* KDF redox alloy, the first effect is the 1.1 volts of energy created by the standard electrode differential between the copper (+0.3402 volts) atoms and zinc (-0.7829) atoms, which are the main constituents of the *DeDOXPro3* KDF reticulated foam media. This spontaneous energy release is the primary cause for the three significant and measurable changes in recirculating cooling water characteristics upon surface contact with ReDOXPro3 KDF redox media......

1. E_h values, measured with an ORP (oxidation/reduction potential) meter in millivolts (mV), typically are lowered from an ambient value of -0200 mV (barely oxidizing) for influent surface water, down to -300mV (reducing environment). Cooling water tends to remain in the negative mV ORP (E_h) range when continuously recalculated through *ReDOXPro3* KDF redox alloy.

 $pH = -log [H+]:pE = log[e]:=nF/2.3RT = E_h$

 E_h = redox potential = energy gained in the transfer of 1 mol of electrons from an oxidant to H₂. E symbolizes the electromotive force, and _h indicates the potential on the hydrogen scale. E_h is measured in volts (millivolts or mV).

F = the Faraday constant (9.65 x 10⁴ coulombs x mole⁴)

R =the gas constant

T = absolute temperature

n = number of electrons (e) in the $\frac{1}{2}$ reaction

2. PH values, almost without exception, increase from typical make up water measurements of slightly below 7.0 to a recalculated cooling water pH of 8.0.

3. Complex catalytic reactions are not well understood, but appear to be more or less pronounced depending on the temperature and ion concentration of the recirculating cooling water.

The primary cause of cooling tower scale is the precipitation of calcium carbonate crystals $(CaCO_2 \text{ as calcite})$ out of solution and onto the cooling tower and heat exchanger surfaces as a limestone type formation. Extensive scanning electron microscopy and X-Ray crystallography studies demonstrate that hardness scale from raw untreated water is formed by relatively large

and irregularly shaped acicular crystals of calcium and magnesium minerals. These ionic salts form a hard, insoluble and interlocking network of vitreous limestone or dolomitic limestone scale. Water treated through *ReDOXPro3* KDF redox media radically alter the morphology of the insoluble calcium/magnesium carbonate crystals to relatively small, evenly shaped rounded grains and rods that from an unconsolidated powdery compound (CaCO₃ as aragonite) that refuses to adhere to metallic, plastic and ceramic surfaces: a majority of which is simply removed by physical filtration. The theory is lower ORP water prevents formation of calcite crystals caused by the "extra" electrons available in the reducing environment. Increased electron activity seems to prohibit calcite crystal lattice growth, thereby permitting the formation of cryptocrystalline aragonite. The corresponding rise in both pH and ion concentration in the recirculating cooling water will , of course, increase precipitation of aragonite out of solution. Calcium carbonate solubility is inversely proportional to increased water temperature, i.e. the warmer the water, the more calcium carbonate precipitates from solution. ORP (E_h) is a measure of the readiness or relative ease to part with (or exchange) electrons; with values in mV related to the pH of water.

Calcium and magnesium are both considered light metals and their associated soluble cations behave in *ReDOXPro3* KDF redox media treated water, to a degree, like their heavy metal cation counterparts. Therefore, the typical heavy metal reduction reaction is weakly or partially translated to the calcium and magnesium cations. Anecdotal reports from a wide range of end users have indicated small reductions of mineral hardness using *ReDOXPro3* KDF media; always by physical filtration of the precipitated calcium/magnesium oxides and hydroxides, since both Ca and Mg are relatively reactive in an aqueous solution.

From the scanning electron microscopy photographs we can see structural change in the calcium carbonate (calcite for raw untreated water and aragonite for water filtered through KDF). Since cooling towers hard scale is, in the main, a crystalline structure, it has been observed in virtually all cases that the KDF redox media has changed the electro-mechanical structure of hard scale. This change in water character allows the remaining mineral hardness to form a more rounded crystal which is observed in cooling towers as a soft scale that can be hosed from the surfaces of the tower. The absence of the dendrite-like shapes of hard scale result in a scale that does not cling to surfaces. When this theory is proved conclusively, the potential for maintaining cooling tower efficiency in the presence of hard water will be fully realized. In fact, some cooling water treatment end users are running their towers at TDS levels exceeding 12,000 ppm. Using traditional methods of tower maintenance, TDS levels such as this would lead to scaling of an unprecedented nature followed by the failure of the equipment that the tower is attempting to cool. At least one industrial cooling tower has been running at this level for more that two years with clear water and no discernible scale.

One would expect relative high readings of dissolved oxygen in recirculating cooling water due to the fact that an evaporate cooling tower acts as a large air scour system. Therefore, air gases (oxygen) and particulates are continually being introduced into the cooling water at the air/water interface. But on cooling towers treated with KDF redox media, the dissolved oxygen reading are relatively low. It is sell accepted that dissolved oxygen promotes corrosion within a cooling

towers, but corrosion coupons in KDF redox treated cooling water indicate well below the expected levels of corrosion. Where is all this dissolved oxygen going. We have two theories, with the first one stating the O_2 is electrochemically reduced by KDF media to form water molecules. This theory is substantiated by the fact of the Electrochemical Series, Zinc at -0.7628 volts and Oxygen at +a.2290 volts fives an extremely large standard electrode difference of 1.9918 volts. The reaction stated in the Handbook of Chemistry and Physics is described as $O_2 - 4H^2 - 4e > 2H_2O$. At lease one electrochemist suggests that KDF redox media treated water favors the formation of calcium bicarbonate, which takes up twice the amount of dissolved oxygen as calcium carbonate. Or maybe both reactions are occurring simultaneously! Significantly less corrosion is also due, in part, to less hydrogen sulfide from decomposing bacteria because KDF redox media treatment inhibits the growth of microorganisms in recirculated cooling water.

This sums up the theory of preventing the formation of hard scale using **ReDOXPro3** KDF redox media water treatment systems. Now let's theorize and briefly describe a related but slightly different subject — the removal of existing hard scale. This phenomenon has been manifested by virtually every previously scaled cooling tower that has been converted from traditional chemical additives to KDF redox media treatment. Existing cooling tower scale is generally a mixture of precipitated calcium and magnesium minerals plus limited amounts of suspended solids held together by biological growth, i.e. algae, bacteria, etc../. A normal function of these biological growths is that they develop a stickiness that allows them to adhere to points in the flow of cooling tower water. This method of attachment allows the growth to sit in the flow and let their food source come to them, which is why we sometimes describe algae and bacteria as slimly. The "glue" that these organisms produce also attracts small particles to their sites and over a period of time, as the organisms go through their life/growth/death/life cycle, a scale forms at these sites. We theorize the KDF treated water, with its altered ORP, causes the dead cells to extrude contained water (by altering osmotic pressure about the cell membranes/) causing the cells to contract or break apart. KDF redox media treated cooling water actually removes existing bard scale by the synergy of its anti-microbial action couple with the "breakdown" of the calcite to unconsolidated aragonite. If it is, indeed, the sessile bacteria colonies that cause the interlocking scale to adhere to surfaces, then, by killing these sessile bacteria, KDF redox media treatment will interfere with the adhesive effect and cause the scale to slough off the cooling tower components.