TREATMENT OF COOLING WATERS

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Types of Cooling Water Systems

There are three major classifications or types of cooling water systems, each one being based on its condition of use. These are as follows:

- (a) once through;
- (b) open evaporative recirculating;
- (c) closed recirculating;

Once through cooling water systems are widely used where a plentiful supply of cheap water is available. This may be from deep wells or from a surface source such as a large river, lake, pond, reservoir, or sea water. Flexibility is a major advantage of these systems since substantial quantities of heat can be removed effectively by the relatively low water temperature which permits cooling with a minimum heat transfer surface. Since the water is used once and then returned to its source, chemical treatment, if required, of this type of system should be cheap and environmentally acceptable.

Open evaporative cooling water systems are used in applications where the use of once through systems would adversely affect the natural biological activity of the receiving water course. They consist of a cooling tower, cooling pond, or spray pond through which the water is recycled. Since cooling is accomplished by either natural or forced evaporation, these systems require blowdown to control their cycles of concentration as well as make-up to replace the evaporative and blowdown losses. Therefore, if treatment is required, only the make-up water, the amount of which is usually less than 10% of the recirculated water, is chemically treated. Consequently, higher treatment dosages can be more economically tolerated in these systems than in the once through systems. However, due to the blowdown requirement, the environmental considerations are just as applicable on these systems as the once through systems.

Cooling water systems are considered to be of the closed type if they do not employ open evaporation for cooling and have a water loss of less than 5% of the circulation rate. They consist of two inter-related systems, one being a completely sealed system for recirculating water and the other being a chiller or a once through system with a heat exchanger to remove heat from the former. Once these systems are charged with chemical, they normally remain charged. Therefore, higher treatment dosages can be more economically tolerated in these systems than both the once through and the open evaporative types. Environmental acceptability need only be considered if there is a possibility that the system will be drained.

Scale Formation

The principal scale forming material in cooling systems is calcium carbonate. Its formation is the result of the decomposition of calcium bicarbonate as illustrated by the following reaction:

$$Ca(HCO_3)_2 \qquad CaCO_3 + CO_2 + H_2O \qquad (1)$$

In water free of carbon dioxide, the solubility of calcium carbonate is very low - about 15 ppm at 32°F and about 13 ppm at 212°F. In water at atmospheric pressure and saturated with carbon dioxide at 32°F, 1620 ppm of $CaCO_3$ will dissolve to form $Ca(HCO_3)_2$. If this water were boiled, the $Ca(HCO_3)_2$ would decompose to $CaCO_3$ and CO_2. The CO_2 would be driven off, but 1607 ppm (ie., 1620 ppm - 13 ppm) of $CaCO_3$ would precipitate. However, cooling waters are not saturated with CO_2, nor do they contain 1620 ppm of calcium alkalinity, nor are they heated to the boiling point. But with any specific content of CO_2, there is an equilibrium at each temperature which establishes the maximum amount of $Ca(HCO_3)_2$ that can be held in solution. Raising this temperature decreases this maximum solubility, reaction (1) proceeding to the right until a new equilibrium for the new temperature is reached. Consequently, it is apparent that with waters high in $Ca(HCO_3)_2$ and low in CO_2, even a very slight elevation in temperature may be sufficient to form scale. The Ryznar index is used to predict the scale forming tendencies of a cooling water.

Forms of Corrosion

The dissolution of metals in water is essentially an electrochemical process. For example, iron dissolves at active points on the metal surface, called anodes, leaving electrons behind in the metal. In order to maintain neutrality, these electrons must flow through the metal to other points, called cathodes, where reactions which consume electrons can occur. The reaction sequence can be outlined as follows:

(a) Anode: $Fe^o \longrightarrow Fe^{++} + 2e^-$ (2)

$Fe^{++} + 2OH^- \longrightarrow Fe(OH)_2$ (3)

(b) Cathode: $1/2\ O_2 + H_2O + 2e^- \longrightarrow 2OH^-$ (4)

(c) Near Anode: $2\ Fe(OH)_2 + H_2O + 1/2\ O_2 \longrightarrow 2\ Fe(OH)_3$ (5)

The cathodic and anodic reactions each have an electrochemical potential relative to a standard electrode called the calomel cell. The difference in potential between these two reactions supplies the driving force for the net corrosion reaction, just as in a battery, the potential difference between the positive and negative poles provides the driving force for the battery current. The current that flows between the anodic and cathodic sites is called the corrosion current and the net potential of the corroding surface is the corrosion potential.

Galvanic corrosion occurs when two dissimilar metals are coupled together and exposed to the same environment. The intensity of corrosion will be determined by the potential differences between the metals and the ratio of cathode to anode areas. The further apart the metals are in the electromotive series (see table 1), the greater will be the accelerated corrosion of the least noble metal (anode).

TABLE 1: Electromotive or Galvanic Series

Potassium
Sodium
Calcium
Magnesium
Aluminum
Zinc
Iron
Tin
Lead
Hydrogen
Copper
Silver
Platinum
Gold

↑ increasingly more anodic

As the ratio of cathode to anode area increases, the current density at the anode increases and the cathode is more effectively depolarized. Thus, large cathode areas together with small anode areas should be avoided. When a bimetallic couple cannot be avoided, nor the metals insulated from one another, metals should be selected that are close to each other in the galvanic series. or the smaller of the two parts should be the one to be fabricated of the more noble metal.

Pitting corrosion results when small and specific areas become anodic with respect to the majority of the metal surface. Examples of this type of corrosion include "holidays" in corrosion inhibitive films, locally stressed and strained surfaces, discontinuities in rolling mill scales, etc. Because of the limited surface area of the anode, rapid metal oxidation accurs at these locations, resulting in the accumulation of corrosion products over the active corrosion site. Eventually, the deposited corrosion products become sufficiently thick and non-conducting that the pitting corrosion action is stifled.

Extraneous material settling on a metal surface can give rise to depletion of oxygen at the point of contact. In such cases, the site under the deposit becomes anodic with respect to the remainder of the metal. Localized "oxygen concentration cells" such as these result in severe underdeposit corrosion.

Erosion-corrosion is the wearing away of a metal by physical action. Turbulent water flow results in significant components of force acting at right angles to the direction of flow. This abrasive action is accentuated by entrained air and suspended solids.

Prediction of Scaling/Corrosion

By far the most commonly formed scale consists of calcium carbonate since its constituents, calcium and alkalinity, are present in most natural waters. For any given water composition and temperature, the tendency to form calcium carbonate scale can be calculated from the temperature, pH, and the concentrations of calcium, alkalinity, and total dissolved solids by the use of formulas or diagrams based on the work of Langelier.

For example, Figure 1 may be used to determine pHs (ie., the saturation pH or the pH at which water of a given composition is in equilibrium with calcium carbonate). The Langelier Saturation Index is then calculated as follows:

$$I_L = pH - pHs \qquad (6)$$

where I_L = Langelier Saturation Index

pH = actual pH

pHs = calculated saturation pH

If this index is positive, the water tends to form calcium carbonate scale; if negative, the water tends to dissolve calcium carbonate.

The disadvantages of the Langelier Saturation Index are as follows:

(a) It does not tell whether or not a scale will actually form, and if it does, how fast it will form;

(b) Within the range of +0.5 and -0.5, it is unreliable for predicting even the tendency to form scale;

(c) It does not indicate whether or not a water is corrosive.

Consequently, Ryznar combined the saturation pH and the actual pH in the following fashion to give the Ryznar Stability Index which was then correlated with field data to give a somewhat better picture of what may be expected of a given water:

$$I_R = 2\ pHs - pH \qquad 7)$$

where I_R = Ryznar Stability Index

As shown in Figure 2, a Ryznar Stability Index below 6.5 generally indicates a scale forming tendency which becomes more pronounced as this index decreases. Conversely, waters are usually increasingly corrosive to steel as this index rises above 6.5.

Other methods used to predict the calcium carbonate scaling/corrosive tendency of a water include The Momentary Excess, The Driving Force Index, the Marble Test, and Enslow's Stability Indicator. However, the Ryznar Stability Index is the method most often referred to when predicting the tendency to precipitate or dissolve calcium carbonate scale.

Measurement of Corrosion Rates

Corrosion rates are reported as IPY (ie., inches per year), MPY (ie., mils per year), or MDD (ie., milligrams per square decimeter per day). MPY is the most common designation and may be calculated from the field measured MDD by use of following equation:

$$\text{MPY} = \frac{\text{MDD} \times 1.44}{\text{Density of the metal, g/cm}^3} \qquad (8)$$

The severity of a measured corrosion rate is largely dependent on the size of the cooling water system. However, a corrosion rate of less than 2 MPY is generally considered to be acceptable, whereas a corrosion rate of greater than 50 MPY is totally unacceptable, both rates being referenced to continuous service conditions.

The procedures used to measure corrosion rates are most often non-destructive in nature, however, they are sub-divided into average and instantaneous rate determinations. A corrosion test coupon is used to determine an average corrosion rate, whereas an electrical resistance meter may be used to measure the instantaneous corrosion rate.

Corrosion coupons very in size and shape, however, they usually weigh from 10 - 50 grams and preferably have a large surface area to mass ratio. Their material is usually carbon steel or may be copper, admiralty, aluminum, or one of the many types of alloys. Smaller coupons are usually located in a by-pass line fitted with suitable holders, while others are suspended in basin water. A cleaned coupon is weighed prior to exposure, and again after exposure and recleaning, the loss in weight being used to calculate the average corrosion rate as per equation 8.

If a corrosion test sample is in the form of a thin wire or strip, its electrical resistance increases as corrosion reduces its cross section. Therefore, a periodic or continuous measurement of the resistance between the ends of the specimen can be used to monitor the instantaneous corrosion rate. This is the essence of an electrical resistance corrosion meter operation.

FIG. 1: LANGELIER SATURATION INDEX

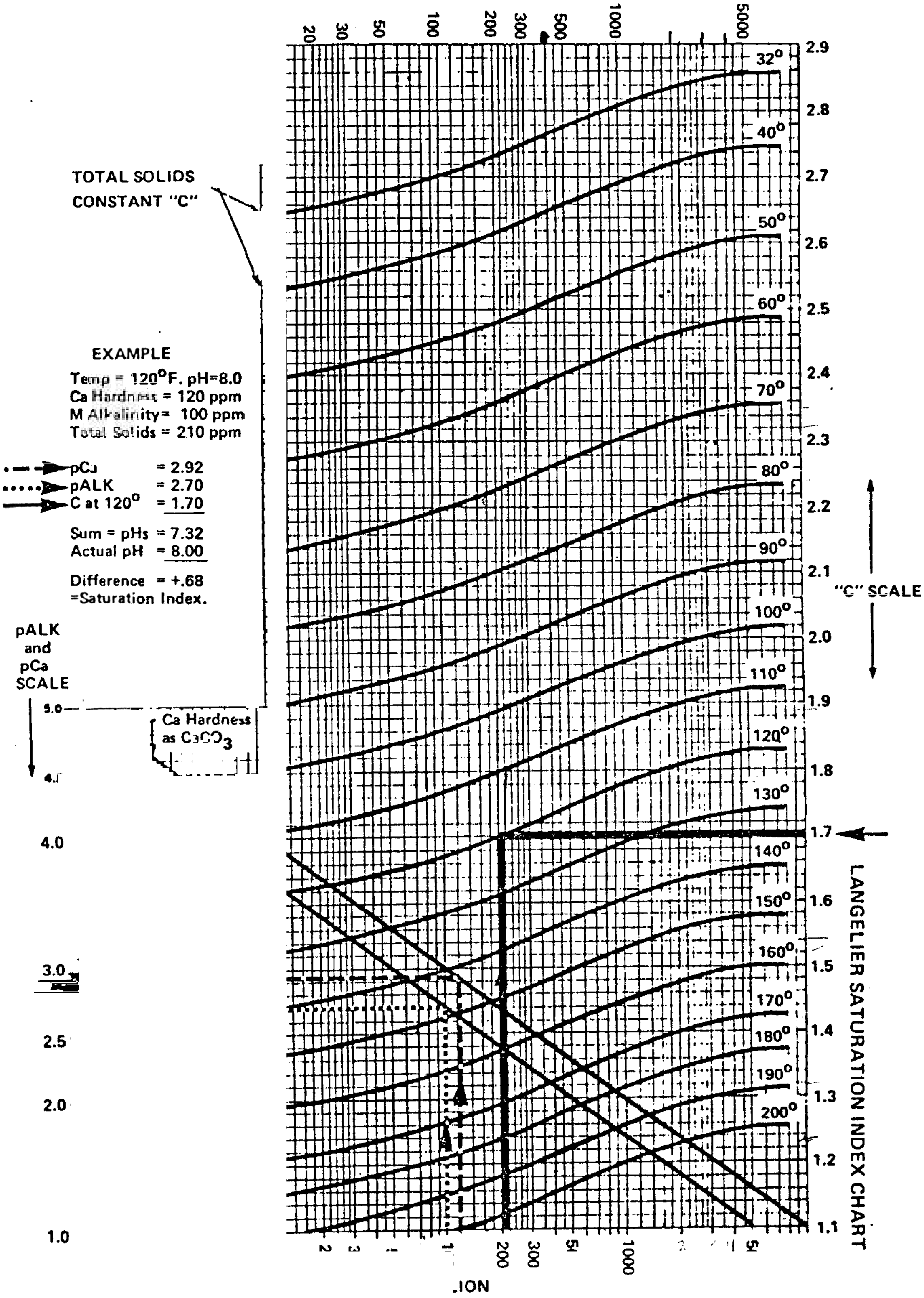
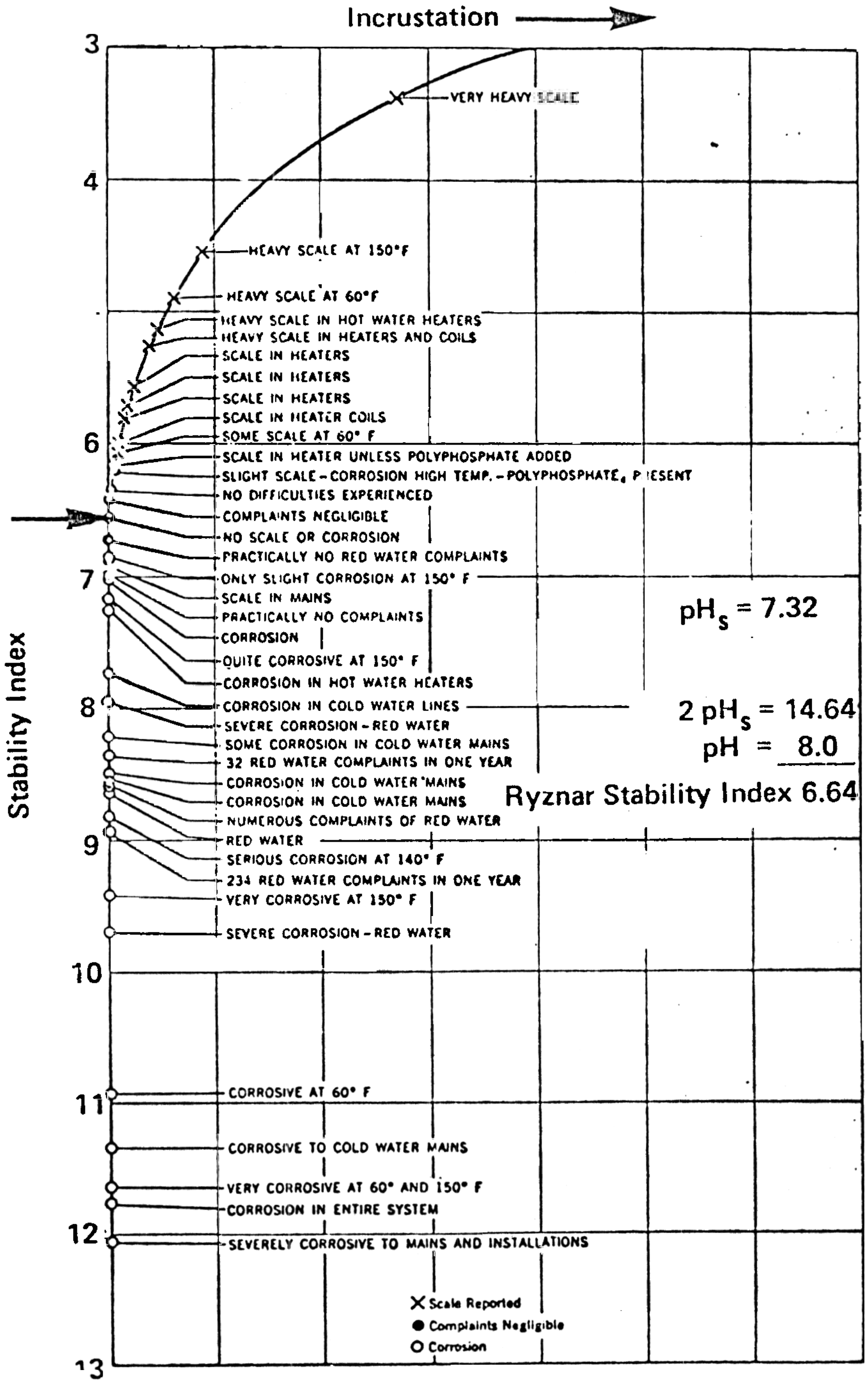


FIG. 2: RYZNAR STABILITY INDEX



$pH_s = 7.32$

$2\,pH_s = 14.64$

$pH = \underline{8.0}$

Ryznar Stability Index 6.64

Organic Growths

Fouling by microbiological slimes is a constant threat to the efficiency of a cooling system since the ambient conditions of sunlight, warmth, and moisture provide an ideal incubator for their growth.

The three principal types of micro-organisms are algae, fungi, and bacteria.

Algae produce their own food from air, sunlight, and water, and will not grow in the absence of any one of these. One or more of the three groups of algae may be found in open cooling water systems - the diatoms, the green, and the blue-green algae. The diatom algae, which contain brown pigment and silica in their cells walls grow best at 64 - 96°F and a pH of 5.5 - 8.9. The chlorophyll - tinted green algae grow at 86 - 95°F and a pH of 5.5 - 8.9. The blue-green algae grow best at 95 - 104°F and a pH of 6.0 - 8.9.

Although the term fungi includes all simple plants that do not contain chlorophyll, it is usually associated with only two groups - the molds and the yeasts. The black, brown, green, blue, grey, or tan coloured molds grow best at 32-100°F and a ph of 2 - 8, as do the leathery or rubber growths of pigmented yeasts. Both groups of fungi need moisture for growth, but they do not generally grow under water since they require atmospheric oxygen.

Bacteria, which do not contain chlorophyll, will grow in any water that contains nutrients in the form of organic matter or certain inorganic salts. The characteristics of some bacteria types are shown in Table 2 below. Those bacteria listed have a temperature tolerability of 68 - 104°F.

TABLE 2: Bacteria Common to Cooling Water Systems

Type	pH Range	Problems Created
Aerobic capsulated	4 - 8	Bacterial slimes
Aerobic spore-forming	5 - 8	Bacterial slimes
Aerobic sulfur	0.6 - 6	Oxidation of sulfur or sulfides to sulfuric acid
Anaerobic sulfate reducing	4 - 8	Grows under aerobic slime, causing corrosion
Iron	7.4 - 9.5	Precipitates iron as ferric hydroxide

Recently a strain of bacteria, which was found in certain cooling water systems, was also found to be detrimental to man. At the American Legionnaires' Convention of 1976, 182 persons fell ill and 29 died as a result of a pneumonia - like illness, later called Legionnaires' Disease. The bacteria, subsequently named Legionella pheumophila, responsible for this disease was present in the cooling water system and human contact was made via the air conditioning system.

External Treatment for Scale and Corrosion Control

As indicated earlier, the scaling tendency of a cooling water is reduced by increasing the Ryznar Stability Index above the 6.5 level. This may be done by any one or more of the following activities:

(a) reduce calcium hardness;

(b) reduce alkalinity;

(c) reduce temperature.

Calcium hardness may be reduced by cold/hot lime softening, sodium cation exchange, or demineralization. However, the capital cost of these units usually limits their application to closed cooling water systems.

For an open recirculating system, the first line of treatment consists of adjusting the Ryznar Index by controlling the cycles of concentration. As indicated in Table 3 overleaf, an increase in the cycles of concentration results in an increase in the potential for scale formation. Therefore, by limiting the cycles of concetration, scaling can be avoided. However, if very low cycles of concentration are required, the costs of make-up water, corrosion inhibitors, and treatment of blowdown water prior to discharge may be prohibitive. Therefore, the second line of treatment consists of the addition of acid, usually sulfuric acid, the primary purpose of which is to reduce the alkalinity, thus reducing the scaling tendency. However, pH control with acid is also useful in minimizing deposits due to calcium phosphate, iron and zinc. In any event, if sulphuric acid is used, the sum of calcium and sulfate concentrations, both as $CaCO_3$, must be kept below 1500 ppm in order to avoid the precipitation of calcium sulfate.

Table 3 also illustrates the effect of temperature on the scaling tendency of a cooling water. The system may be under control, as far as the Ryznar Index is concerned, at its average temperature, but a scaling tendency could be present at localized hot spots.

TABLE 3: Control of Ryznar Stability Index

		Make-up (60°F)	Cycles of Concentration		
			2*	2**	2***
Calcium	ppm $CaCO_3$	103	206	206	206
Magnesium	ppm $CaCO_3$	54	108	108	108
Total Hardness	ppm $CaCO_3$	157	314	314	314
Total Alkalinity	ppm $CaCO_3$	114	230	80	80
Chlorides	ppm $CaCO_3$	2	4	4	4
Sulfate	ppm $CaCO_3$	34	68	218	218
Silica, ppm SiO_2		3.7	7.4	7.4	7.4
pH		8.14	8.22	7.3	7.25
TDS, ppm		178	356	356	356
Ryznar Index		7.66	5.24	7.16	6.19

NOTE:

* Denotes 2 cycles of concentration at 120°F

** Denotes 2 cycles of concentration at 120°F with 75 ppm H_2SO_4 as $CaCO_3$.

*** Denotes 2 cycles of concentration at 180°F with 75 ppm H_2SO_4 as $CaCO_3$

Chemical Treatment for Scale Control

After the Ryznar Index has been adjusted to give an economically feasible mode of operation, the addition of scale or corrosion inhibitors may enhance system operation.

The first chemical scale inhibitor used was a polyphosphate, one of the most common of which is sodium hexametaphosphate. They have the ability to prevent calcium carbonate scaling through a phenomenon called threshold stabilization, the actual mechanism of which is not clearly understood, but only a few ppm (2 - 10) of polyphosphate is the standard dosage. Polyphosphates are very successfully used in once through cooling water systems, but their use in recirculating systems is limited due to their tendency to revert back to the orthophosphate through rehydration, thus reacting with calcium to form calcium phosphate sludge and creating a fouling problem. However, modern technology has overcome this problem by substituting the phosphate group onto an organic molecule which is hydrolically stable, thus maintaining the threshold stabilization properties of polyphosphates. Although a wide variety of different molecules are possible simply by varying the organic backbone used and the degree of substitution, they can be grouped into two general classes - phosphonates and phosphate esters, both of which are generally effective as scale inhibitors for calcium carbonate as well as calcium sulfate. Because phosphonates have a greater ability to prevent precipitation of iron, they are more commonly used in cooling water treatment. Both phosphonates and phosphate esters are proprietary in nature.

Chemical Treatment for Corrosion Control

Corrosion inhibitors work by interfering with the cathodic and/or the anodic corrosion reaction. In Table 4 below, some of the common corrosion inhibitors are classified as cathodic or anodic according to their effects on these reactions.

TABLE 4: Common Corrosion Inhibitors

Anodic	Cathodic
Sodium Chromate	Calcium Bicarbonate
Ortho-phosphates	Poly-phosphates
Sodium Ferrocyanide	Metal Cations (zinc)
Organics	Organics

Anodic corrosion inhibitors act by reducing the available anodic area on the metal surface. Since the corrosion in most cooling water systems is under cathodic control (ie., rate controlling reaction is at the cathode), large amounts of inhibitor must be used to protect the entire anode area.

For example, hexavalent chromium, the best known anodic corrosion inhibitor, injection must be at the 100 - 300 ppm level in order to avoid pitting. It is thought to work by reacting with the ferrous iron corrosion product to form a hard passive oxide film which is tightly bonded to the metal surface. The most probable half-cell reactions are as follows:

(a) Anode: $6\ Fe^{+2} \longrightarrow 6\ Fe^{+3} + 6e^{-}$ (9)

(b) Cathode: $Cr_2O_7^{-2} + 14\ H^{+} + 6e^{-} \longrightarrow 2\ Cr^{+3} + 2\ H_2O$ (10)

(c) Over-all: $Cr_2O_7^{-2} + 14\ H^{+} + 6\ Fe^{+2} \longrightarrow 2\ Cr^{+3} + 6\ Fe^{+3} + 7\ H_2O$ (11)

Ortho-phosphates form an adsorbed precipitate of iron phosphate at the anodic sites. However, this precipitate is loose and pH sensitive, so that it does not provide much protection.

Cathodic inhibitors work by reducing the cathodic area available for the corrosion reaction.

For example, polyphosphates - the best known cathodic corrosion inhibitor - react with iron or with particles of corrosion products to form positively charged colloids which collect at the cathode where they are neutralized by electrons from the metal surface. The resultant films are tightly bonded to the metal surface and provide good corrosion protection at neutral pH. At low pH levels, the protective film will dissolve and because of their sequestering action, polyphosphates become corrosive. At high pH level, calcium ortho-phospate becomes very insolvable and may cause fouling.

Metal ions, such as zinc, which form insoluable hydroxides are effective cathodic inhibitors. Since the liquid layer next to the cathode surface on the metal tends to have a high pH, zinc ions will precipitate there as zinc hydroxide which binds well to the metal and helps to make other inhibitor films more adherent.

Microbiological Control

Oxidizing and/or non-oxidizing biocides, both of which destroy cell protein, may be used to control biological fouling.

Included under the heading of oxidizing biocides are chlorine also chlorine dioxide, ozone, bromine, of which chlorine has the widest use because of its low cost and availability. However, hypochlorous acid, the most effective biocidal form of chlorine, dossociates in alkaline water to form the less active hypochlorite ion, the latter of which is much less effective as a disinfectant.

Non-oxidizing biocides are organic and proprietary in nature, and tend to be slower acting than chlorine, but are sometimes used in conjunction with oxidizing biocides for broader control. Typical examples include quaternary ammonium compounds, chlorinated phenols, organo sulphur compounds and brominated organics, all of which also hydrolyze at elevated pH levels.

Conclusions

As indicated in the foregoing, the treatment of cooling water is dependent on the type of cooling water system, the chemistry of the water within the cooling system, and the type and rate of corrosion, scaling and/or biological activity.

Once through cooling water systems, due to their environmental constraints, are usually treated with low level quantities of environmentally acceptable chemicals such as sodium hexa meta phosphate at 2 - 10 ppm if corrosion rates are unacceptable.

The water in closed recirculating cooling water systems often requires external treatment (ie., reduction of hardness and/or alkalinity) along with initially high levels of poly phosphate addition (ie., 60 ppm) with reduction to approximately 20 ppm after 1 - 2 weeks of operation in order to minimize scaling and corrosion. Biocide addition may also be required if plate counts indicate biological activity.

Because of the concentrative effects of open recirculating cooling water systems, their treatment is more involved and less forgiving to human error than the other two systems. The initial step in the treatment of these systems involves the collection and analyzing of historical data on make-up water chemistry. Based on this information, the Ryznar index is usually adjusted to give a corrosive tendency (ie., a Ryznar Index of approximately 8) by controlling the cycles of concentration and adding sulfuric acid. This eliminates the concern for scaling and allows concentration on corrosion inhibition. The apparent requirement to incorporate large dosages of anodic inhibitors (ie., sodium chromate at 100 - 300 ppm when injected by itself) into a corrosion control program may be alleviated by combining its addition with a cathodic inhibitor. For example, a chromate - polyphosphate combination gives both anodic and cathodic inhibition at much less reduced dosages than either one alone, thus reducing the environmental unacceptability of hexavalent chromium. Corrosion rates determine actual dosages, but the initial dosages of 50 ppm each followed by a reduction to 25 ppm each would be a good starting point. This presumes that the injection of oxidizing and/or non-oxidizing biocides keeps biological activity in check.