Cooling Water Problems and Solutions

Course No: M05-009
Credit: 5 PDH

A. Bhatia

Continuing Education and Development, Inc.

P: (877) 322-5800
info@cedengineering.com

COOLING WATER PROBLEMS AND SOLUTIONS

Water is used in cooling systems as a heat transfer medium and frequently also as the final point to reject heat into the atmosphere by evaporating inside cooling towers. Depending on the quality of available fresh water supply, waterside problems develop in cooling water systems from:

- Scaling
- Corrosion
- Dirt and dust accumulation
- Biological growth

Any of these problems – or more usually a combination of them – result in costly unscheduled downtime, reduced capacity, increased water usage, high operation and maintenance costs, expensive parts replacements, and acid cleaning operations which reduce the life of the cooling system.

There is no single method of treating cooling water. Selection of water treatment program for a specific system depends on:

1. System design, including system capacity, cooling tower type, basin depth, materials of construction, flow rates, heat transfer rates, temperature drop and associated accessories
2. Water, including make up water composition / quality, availability of pre-treatment and assumed cycle of concentration
3. Contaminants, including process leaks and airborne debris
4. Wastewater discharge restrictions
5. Surrounding environment and air quality

In this course, we will discuss the reasons and means for controlling scale, corrosion and biological fouling.

Critical Parameters

The critical parameters for cooling water are: conductivity, total dissolved solids (TDS), hardness, pH, alkalinity and saturation index.

Conductivity and Total Dissolved Solids (TDS)

Conductivity is a measure of the ability of water to conduct electrical current and it indicates the amount of the dissolved solids (TDS) in water. Pure distilled water will have a very low conductivity (low minerals) and sea water will have a high conductivity (high minerals). Dissolved solids present no problem with respect to the cooling capacity of water, since the evaporation rate of seawater, which has 30,000ppm total dissolved solids, is only 1% less than that of distilled water. The problem with dissolved solids is that many of the chemical compounds and elements in the water will combine to form highly insoluble mineral deposits on the heat transfer surfaces generally referred to as “scale”. The scale stubbornly sticks to the surfaces, gradually builds up and begins to interfere with pipe drainage, heat transfer and water pressure.

The primary maintenance objective in most circulating water systems is to minimize the formation of scale deposits and conductivity can be used as the controlling value after the TDS/conductivity relationship is determined.

pH

pH is a measure of how acidic/basic water is. The range goes from 0 - 14, with 7 being neutral. pHs of less than 7 indicate acidity, whereas a pH of greater than 7 indicates a base. pH is reported in "logarithmic units," like the Richter scale, which measures earthquakes. Each number represents a 10-fold change in the acidity/baseness of the water. Water with a pH of 5 is ten times more acidic than water having a pH of six.

Control of pH is critical for the majority of cooling water treatment programs. In general, when pH points to acidic environment, the chances for corrosion increase and when pH points to alkaline environment, the chances for scale formation increase.

Alkalinity

The pH values above 7 signify alkalinity. At pH values less than 8.3, most of the alkalinity in the water is in the bicarbonate form, and scale formation is normally not a problem. However, when the pH rises above 8.3, the alkalinity converts from the bicarbonate to the carbonate and the scale will start to form.

Hardness

The amount of dissolved calcium and magnesium in water determines its "hardness." The total hardness is then broken down into two categories

a. The carbonate or temporary hardness

b. The non-carbonate or permanent hardness

Hardness particularly the temporary hardness is the most common and is responsible for the deposition of calcium carbonate scale in pipes and equipment. Technically any bivalent metal ion such as iron, manganese or tin would constitute hardness, but calcium and magnesium are the two most prevalent forms.

Saturation Index

The saturation index of a water or Langlier Saturation Index (LSI) is a measure of the stability of the water with respect to scale formation. When LSI readings are positive they tend to be scale forming, and when they are negative they tend to be corrosive. Normally readings within 1.0 units from zero are considered stable.

SCALE INHIBITION

What is scale?

Scale is a hard deposit of predominantly inorganic material on heating transfer surfaces caused by the precipitation of mineral particles in water. As water evaporates in a cooling tower or an evaporative condenser, pure vapor is lost and the dissolved solids concentrate in the remaining water. If this concentration cycle is allowed to continue, the solubility of various solids will eventually be exceeded. The solids will then settle in pipelines or on heat exchange surfaces, where it frequently solidifies into a relatively soft, amorphous scale.

Problems

Scale, in addition to causing physical blockage of piping, equipment, and the cooling tower, also reduces heat transfer and increases the energy use. For example, the thermal conductivity BTU/ [hr (ft^2) (F/in)] of copper is 2674, while the common cooling water scale calcium carbonate has a thermal conductivity of 6.4 BTU/ [hr (ft^2) (F/in)]. A calcium carbonate scale of just 1.5 mil thickness is estimated to decrease thermal efficiency by 12.5 %. In compression refrigeration systems, scale translates into higher head pressures, hence an increase in power requirements and costs. For example, 1/8" of scale in a 100 ton refrigeration unit represents an increase of 22% in electrical energy compared to the same size unit free of scale.

Factors

The principle factors responsible for scale formation are:

1. As alkalinity increases, calcium carbonate- the most common scale constituent in cooling systems - decreases in solubility and deposits.

2. The second—more significant—mechanism for scale formation is the in-situ crystallization of sparingly soluble salts as the result of elevated temperatures and/or low flow velocity. Most salts become more soluble as temperature increases, however, some salts, such as calcium carbonate, become less soluble as temperature increases. Therefore they often cause deposits at higher temperatures.

3. High TDS water will have greater potential for scale formation.

Types

Typical scales that occur in cooling water systems are:

1. Calcium carbonate scale - Results primarily from localized heating of water containing calcium bicarbonate. Calcium carbonate scale formation can be controlled by pH adjustment and is frequently coupled with the judicious use of scale inhibiting chemicals.

2. Calcium sulfate scale - Usually forms as gypsum is more than 100 times as soluble as calcium carbonate at normal cooling water temperatures. It can usually be avoided by appropriate blowdown rates or chemical treatment.

3. Calcium and magnesium silicate scale - Both can form in cooling water systems. This scale formation can normally be avoided by limiting calcium, magnesium, and silica concentrations through chemical treatment or blowdown.

4. Calcium phosphate scale - Results from a reaction between calcium salts and orthophosphate, which may be introduced into the system via inadequately treated wastewater or inadvertent reversion of polyphosphate inhibitors present in recycled water.

The most common type of scaling is formed by carbonates and bicarbonates of calcium and magnesium, as well as iron salts in water. Calcium dominates in fresh water while magnesium dominates in seawater.

Control

Scale can be controlled or eliminated by application of one or more proven techniques:

1. Water softening equipment – Water softener, dealkalizer, ion exchange to remove scale forming minerals from make up water.

2. Adjusting pH to lower values - Scale forming potential is minimized in acidic environment i.e. lower pH.

3. Controlling cycles of concentration - Limit the concentration of scale forming minerals by controlling cycles of concentration. This is achieved by intermittent or continuous blowdown process, where a part of water is purposely drained off to prevent minerals built up.

4. Chemical dosage - Apply scale inhibitors and conditioners in circulating water.

5. Physical water treatment methods – Filtration, magnetic and de-scaling devices

Water Softening

The quality of the makeup water can be adjusted by a water softener, a dealkalizer, or an ion exchange unit. In areas where only hardness reduction is required, a water softener is used and where only alkalinity reduction is required, a dealkalizer is used. In areas where combined treatment is required, an ion exchange unit is used.

Water softeners replace unwanted magnesium and calcium ions with sodium ions, which have none of the negative effects of hard water. To do this, hard water runs through a bed of small plastic beads that have sodium ions attached to them. As the water flows through, the sodium ions—which also occur naturally in water—are released into the water, and are replaced with the magnesium and calcium ions on the resin beads. Eventually, the beads in a water softener contain nothing but calcium and magnesium ions and stop being effective. To refresh the system, water softeners periodically go through a process known as regeneration. In regeneration, a brine solution of sodium chloride—made from salt pellets or block salt—is flushed through the system, which replaces all calcium and magnesium in the system with sodium. The calcium and magnesium, along with the remaining brine, is then drained into the wastewater system. A water softener is easy to operate and maintain. These are also called single bed ion-exchange unit.

Dealkalizer units operate the same as water softeners, but use different resin bed materials and require strong caustic or acid regeneration. The makeup water is passed through a treated resin bed where the contaminants in the water are collected through a chemical exchange process. When the bed becomes saturated with contaminants, the bed is backwashed, treated with a concentrated electrolyte, rinsed, and placed back in service. For critical or continuous operations, treatment units may be dual-column units that allow switching from a saturated column to a regenerated standby column so that service is not interrupted for routine column regeneration.

The ion exchange process is to remove calcium and magnesium ions by replacing them with an equivalent amount of sodium ions. Unlike simple water softener, these are mixed bed ion-exchange unit consisting of cation and anion exchanger. The cation exchanger section removes metals, such as calcium and magnesium (hardness), and the anion exchanger section controls alkalinity and may remove bicarbonates (corrosion and embrittlement), sulfates (hard scale), chlorides (foaming), and soluble silica (hard scale).

pH Adjustment

Control of scale with pH adjustment by acid addition is a simple and cost effective way to reduce the scaling potential. It functions via chemical conversion of the scale forming materials to more soluble forms - calcium carbonate is converted to calcium sulfate (using sulfuric acid), a material several times more soluble.

Sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) are the most common additives used for controlling the formation of calcium carbonate scale. The acid is fed by variable stroke pumps that are controlled either by automatically adjusting the pump stroke based on circulating water pH, or by automatically starting and stopping manual stroke adjustment metering pumps based on circulating water pH. Sulfuric acid is normally used at a concentration of 93 to 98 percent (66° Bé). Hydrochloric acid is normally used at a concentration of 28 to 36 percent (18° Bé to 22° Bé).

The reaction of the acid with calcium bicarbonate is:

$H_2SO_4 + Ca\,(HCO_3)_2 = CaSO_4 + 2H_2O + 2CO_2$

$2HCl + Ca\,(HCO_3)_2 = CaCl_2 + 2H_2O + 2CO_2$

The Langlier Saturation Index (LSI) and the Ryznar Saturation Index (RSI) are utilized for system setup when pH adjustment by acid addition is used for scale control. Both indexes are merely convenient means of reducing the integrated parameters of calcium, alkalinity, pH, dissolved solids, and temperature to a single value, which indicates the tendency of water to form a calcium scale or promote corrosion. A positive LSI number (RSI less than 5.0) indicates a scale forming water while a negative LSI number (RSI greater than 7.0) indicates a scale dissolving, or corrosive, water. Normal practice is to maintain a slightly positive LSI number, +.2 to +.5, (RSI between 5.0 and 6.0) when utilizing pH adjustment by acid addition and add some chemical scale inhibitor to cope with the resultant slight tendency to scale.

Caution - Addition of excessive acid to the cooling water results in depressed pH values and extremely rapid corrosion of all system metals. Therefore, proper pH control is required to provide a suitable environment for both scale and corrosion inhibitors work effectively.

Chemicals

The list that follows includes generic or families of chemicals which may be used to condition cooling water stream. The specific name of the treatment product containing the listed chemical and the form of the chemical used will depend on the manufacturer. Most chemical treatment manufacturers have developed proprietary "brand names" which combine a number of the chemicals illustrated below and include other agents to enhance the performance of the product. Facilities should consult chemical suppliers to tailor the facilities’ chemical treatment needs to local conditions, and to establish procedures for safe chemical storage and handling.

1. Polymers (Polyacrylate, etc) - Disperse sludge and distort crystal structure of calcium deposits. Prevent fouling due to corrosion products. Commonly used, cost effective for calcium scale at 5 to 15 mg/l.

2. Polymethacrylate - Less common for calcium scale at 5 to 15 mg/l.

3. Polymaleic - Very effective for calcium scales at 10 to 25 mg/l, higher cost.

4. Phosphonates - Phosphonates are excellent calcium scale inhibitors at levels from 2 to 20 mg/l.

5. Sodium Phosphates (NaH_2PO_4, Na_2HPO_4, Na_3PO_4, $NaPO_3$) - Precipitates calcium as hydroxyapatite ($Ca_{10}(OH)_2(PO_4)_6$). Stream pH must be kept high for this reaction to occur.

6. Sodium Aluminates ($NaAl_2O_4$) - Precipitates calcium and magnesium.

7. Chelants (EDTA, NTA) - Control scaling by forming heat-stable soluble complexes with calcium and magnesium.

8. Coploymers - These products commonly incorporate two active groups, such as a sulfonate and acrylate, to provide superior performance to a single group compound at use levels at 5 to 20 mg/l, higher cost.

9. Terpolymers - Like the co-polymers, only incorporate three active groups to give yet better performance under severe conditions at use levels of 5 to 20 mg/l, costly.

10. Polyphosphates - Fairly good calcium scale control under mild conditions. Caution - Polyphosphates are of some value for scale control but must be applied cautiously, because hydrolysis of the polyphosphate results in the formation of orthophosphate ions. If this process is not properly controlled, calcium phosphate deposits may result.

11. Tannins, starches, glucose, and lignin derivatives - Prevent feed line deposits by coating scale crystals to produce sludge that will not readily adhere to heat exchanger surfaces.

As a general rule, common chemical scale inhibitors such as polyacrylate and phosphonate can be utilized if the Saturation Index (LSI) value of the cycled cooling water does not exceed 2.0. Cycled cooling water SI values up to 3.5 can be obtained by use of co- and terpolymers combined with surfactants. Multiple water treatment firms have reported operation of cooling systems with newer treatment chemistries scale free at cycled LSI values from 2.5 to 3.5 without pH adjustment.

Characteristics of some common scale inhibitors are tabulated in Annexure 1 at the end of the course.

Controlling Cycles of Concentration

To a great extent the quality of the inflow water determine the extent depositions on heat exchange surfaces. The higher the levels of hardness and alkalinity in the inflow water, the greater will be the potential for scale accumulation.

Two key relationships - “cycles of concentration” and “bleed off water” are important.

Cycles of Concentration

The cycle of concentration (also referred to as concentration ratio) is defined as the ratio of the concentration of a specific dissolved constituent in the recirculated cooling water to the concentration of the same constituent in the makeup water. This figure establishes the minimum blowdown rate that must be achieved.

The concentration ratio (C) is determined by the following equation:

$C = [E / (B + D)] + 1$………… (1)

Where:

E = Evaporation rate

B = Blowdown

D = Drift

Ignoring insignificant drift loss (D), the equation can be simply put as:

$C = M / B$…………….. (2)

Where:

M = Make up water equal to E + B.

The equation (2) tells us that as long as the amount of blowdown water is proportional to the amount of water entering the system, the concentration ratio will remain constant irrespective of variations in the inflow water chemistry.

Blowdown or Bleed-off

Evaporative loss from a cooling tower system leads to an increased concentration of dissolved or suspended solids within the system water as compared to the make up water. Over concentration of these impurities may lead to scale and corrosion formation, hence, fouling of the system. Therefore, concentration of impurities must be controlled by removing system water (bleed-off) and replacing with make up water. In order to control the total dissolved solids (TDS), bleed-off volume can be determined by the following formula:

$$B = \frac{E - [(C-1) \times D]}{(C-1)} \quad \text{……………………… (3)}$$

Where

- B – Blowdown rate (L/s)
- E – Design evaporative rate (L/s)
- C – Cycle of concentration
- D – Design drift loss rate (L/s)

The equation (3) tells us that it is practically impossible to ever achieve a concentration ratio of 1, because to do so would require an infinite amount of water. It also shows that as the concentration ratio increases the blowdown requirement decreases. As a rule of thumb, the minimum cycle of concentration shall be maintained at 5 to 6 for fresh water type cooling tower and 2 or less for seawater type cooling tower.

Increasing the blowdown is a simple way to reduce the levels of calcium and alkalinity in the water, but it is not in interests of water conservation.

Circulating Water System Design Data

Data affecting the circulating water cycles of concentration and the treatment equipment selection are:

1. Cooling tower evaporation rate - The evaporation rate is calculated based on the heat rejected by the cooling tower and site-specific conditions such as relative humidity and wet bulb temperature. As a “Rule of thumb”, the evaporation rate is approximately 1.0 percent of the cooling tower recirculation rate for each 10 °F temperature drop across the cooling tower. The percentage varies depending on the plant's geographic location. The evaporation rate used for final design should come from the cooling tower supplier.
2. Cooling tower drift rate - The drift rate is a function of the type of tower (induced, forced, or natural draft) and the internal mist eliminator design.
3. Circulating water recirculation rate - The recirculation rate is determined by the heat balance for the cooling system.
4. Cooling tower, piping, and heat transfer equipment construction materials and linings (if used) - The material selection determines the need for corrosion inhibitors or for modification of chemical operating parameters for equipment protection.

Physical Water Treatment Methods

A supplemental method limiting the concentration of water borne contaminants is through mechanical means such as in-line or side-stream filtration.

Filtration System

Filtration is a mechanical process to remove suspended matter such as mud, silt and microbial matter from water by collecting the solids on a porous medium. Removing suspended matter helps the overall water management program's success by eliminating deposit-causing substances, as well as chemical treatment products to work more effectively. There are two methods of filtration:

1. In-Line Filtration – In-line filtration allows all system circulating water to pass through a strainer or filter in order to remove impurities and suspended solids.
2. Side-stream filtration – Side-stream filtration means placing a filter in a bypass stream so that a portion of the total cooling water circulation rate (at least 5%) is filtered. Higher bypass

portion leads to better water quality but also increase the filtration equipment capacity. The advantage of side-stream filtration includes lower capital and space requirement than in-line filtration using the same filtration method. In addition, side-stream filtration has the advantage of being able to process the recirculation cooling system and remove debris, which has been drawn in by the cooling tower, as well as impurities precipitated in the bulk water.

Both in-line filtration and side-stream filtration processes help in reducing suspended solids to an acceptable level.

Filtration Equipment

A number of mechanical filtration devices commonly used in cooling tower systems are:

1. Strainers – A strainer is a closed vessel with a cleanable screen to remove and retain foreign particles down to 25µm diameter inside cooling water. It shall only be used as pre-filtration to remove large particles in the system. Routine inspection and cleaning is necessary to ensure strainers are in good condition and normal function.

2. Cartridge filters – Cartridge filters can be used as final filters to remove nearly all suspended particles from about 100µm down to 1µm or less. Cartridge filters are typically disposable, which shall be replaced if required. Frequency of replacement depends on the concentration of suspended solids in water, the size of the smallest particles to be removed and the removal efficiency of the cartridge filter selected.

3. Sand filters (Permanent media filters) – The degree of suspended solids removal in sand filters depends on the combinations and grades of the medium being used in the vessel. Typical sand filter can remove suspended contaminants down to 10µm. Specialized fine sand media filters are designed to remove suspended particles down to less than 1µm. Multimedia vessels with each layer containing medium of different size may also be used for low suspended solids application. When the vessel has retained enough suspended solids to develop a substantial pressure drop, the unit must be backwashed either manually or automatically by reversing the direction of flow.

4. Centrifugal-gravity separators – Cooling water is drawn through tangential slots and accelerated into the separation chamber. Centrifugal action tosses the particles heavier than the liquid to the perimeter of the separation chamber. Efficiency of centrifugal-gravity

separator depends on the gravitational mass of suspended solids; performance data indicate that separator efficiency is about 40% for particles in the range of 20µm to 40µm.

5. Bag type filters – Bag filters are composed of a bag of mesh or felt supported by a removable perforated metal basket, placed in a closed housing with an inlet and outlet. Filter bags can be made of many materials (cotton, nylon, polypropylene and polyester) with a range of ratings from 0.01mm to 0.85mm. Mesh bag are generally coarser, but are reusable. However, periodic replacement of filters is required to ensure the efficiency of filters.

Magnetic devices

This method involves the exposure of incoming make up water under the intense magnetic field. Magnetic field affects the suspended particles or the ions in solution and prevents the deposition of a hardened deposit. The particles will then form a mobile suspension or do not precipitate at all. Also, existing deposits of scale can be converted into solution. Some magnetic devices use permanent magnets and hence do not require electrical power input to the device.

Electronic De-Scaling technology

Electronic de-scaling technology makes use of induced oscillating electric fields using time-varying magnetic fields generated in the solenoid wrapped around a water pipe. Dissolved ions are then charged and collided with each other. Collisions between positive and negative ions facilitate precipitation of the ions in the pipe-work.

Electronic de-scaling technology can be used to enhance chemical-based water treatment program but caution: selection of chemicals used in corrosion inhibition and micro-biological control shall be compatible with the technology.

CORROSION INHIBITION

Next to scale, the next most important concern is the prevention of "corrosion".

Corrosion is defined as the destruction or loss of metal through chemical or electrochemical reaction with its surrounding environment. Mild steel is a commonly used metal in the cooling water system that is most susceptible to corrosion. Other metals in general, such as copper, stainless steel, aluminum alloys also do corrode but the process is slow. However in some waters and in presence of dissolved gases, such as H_2S or NH_3, the corrosion to these metals is more severe & destructive than to mild steel.

What causes corrosion?

Corrosion is a three step electrochemical reaction in which free oxygen in the water passes into a metal surface a one point (referred to as the cathode) and reacts with water and electrons, which have been liberated by the oxidation of metal at the anode portion of the reaction at another spot on the metal surface. The combination of free electrons, oxygen and water forms hydroxide ions. The hydroxide ions then combine with the metal ions, which were liberated at the anode as part of the oxidation reaction, to form an insoluble metal hydroxide. The result of this activity is the loss of metal and often the formation of a deposit.

Corrosion Problems

Common problems arising from corrosion are reduction in heat transfer and water flow resulting from a partial or complete blockage of pipes, valves, strainers, etc. Also, excessive wear of moving parts, such as pump, shaft, impeller and mechanical seal, etc. may resist the movement of the equipment. Hence, thermal and energy performance of heat exchange may degrade.

Factors

Many factors affect the corrosion rates in a given cooling water system. Few important factors are:

1. Dissolved Oxygen - Oxygen dissolved in water is essential for the cathodic reaction to take place.

2. Alkalinity & Acidity - Low alkalinity waters have little pH buffering capability. Consequently, this type of water can pick up acidic gases from the air and can dissolve metal and the protective oxide film on metal surfaces. More alkaline water favors the formation of the protective oxide layer.

3. Total Dissolved Solids - Water containing a high concentration of total dissolved solids has a high conductivity, which provides a considerable potential for galvanic attack. Dissolved chlorides and sulphates are particularly corrosive.

4. Microbial Growth - Deposition of matter, either organic or inorganic, can cause differential aeration pitting (particularly of austenitic stainless steel) and erosion/corrosion of some alloys because of increased local turbulence. Microbial growths promote the formation of corrosion cells in addition; the byproducts of some organisms, such as hydrogen sulphide from anaerobic corrosive bacteria are corrosive.

5. Water Velocity - High velocity water increases corrosion by transporting oxygen to the metal and carrying away the products of corrosion at a faster rate. When water velocity is low, deposition of suspended solids can establish localized corrosion cells, thereby increasing corrosion rates.

6. Temperature - Every 25-30°F increase in temperature causes corrosion rates to double. Above 160°F, additional temperature increases have relatively little effect on corrosion rates in cooling water system.

Some contaminants, such as hydrogen sulfide and ammonia, can produce corrosive waters even when total hardness and alkalinity are relatively high.

Corrosion Types

Many different type of corrosion exist, but the most common is often characterized as general, pitting and galvanic corrosion.

1. General attack: exists when the corrosion is uniformly distributed over the metal surface. The considerable amount of iron oxide produced contributes to fouling problems.

2. Pitting attack: exists when only small area of the metal corrodes. Pitting may perforate the metal in short time. The main source for pitting attack is dissolved oxygen.

3. Galvanic attack: can occur when two different metals are in contact. The more active metal corrodes rapidly. Common examples in water systems are steel & brass, aluminum & steel, Zinc & steel and zinc & brass. If galvanic attack occurs, the metal named first will corrode.

How to monitor Corrosion Rates?

Corrosion rates are most commonly tested using metal coupons. Mild steel and copper coupons are frequently used since these represent the metals that are most vulnerable to corrosion in the system. An acceptable cooling water treatment program should be able to reduce corrosion rates to the following average levels reported as mils/yr:

Corrosion Rate Standards

Rating	**Rate (Mils/yr)**
Poor	>5
Fair	3.5 – 5.0
Good	2.0 – 3.5
Excellent	0.0 – 2.0

Control Techniques

The principle methods to prevent or minimizing corrosion include:

1. Selecting suitable materials of construction to resist corrosion
2. Adding protective film- forming chemical inhibitors that the water can distribute to all wetted parts of the system.
3. Controlling scaling and micro-biological growth
4. Protect cathodically, using sacrificial metals
5. Apply protective coatings such as paints, metal plating, tar or plastics on external surfaces

Treatment Methods

Most corrosion control strategies involve coating the metal with thin films to prevent free oxygen and water from coming into close contact with the metal surface. This breaks the reaction cell, and reduces the corrosion rates. Several major chemical treatment methods can be used to minimize corrosion problems and to assure efficient and reliable operation of cooling water systems.

Types of Corrosion Inhibitors

In general, there are four types of inhibitors: 1) anodic, 2) cathodic, 3) mixed and 4) adsorption, commonly adopted in cooling water treatment. In addition passivation technique is used for galvanized components. Working principles of common corrosion inhibitors is described below.

Anodic inhibitor

Applying anodic inhibitor enables a protective oxide / inhibitor film to cover the anodic corrosion points inside the cooling water circulation system. This method is effective only if all points are filmed and isolated from corrosion initiator. Otherwise, severe localized corrosion may occur at the points without effective protection by protective film. Therefore, sufficient safety margin shall be applied and these shall generally be applied at high dosage levels (hundreds of mg/l). Common anodic inhibitors are chromates, nitrites, orthophosphates and silicates.

Cathodic inhibitor

Cathodic inhibitor is effective by the formation of protective inhibitor film at cathodic corrosion sites so as to prevent oxygen reduction. It is more effective than anodic inhibitor and lower dosage level is required. Therefore, it is commonly used in cooling water treatment. Common cathodic inhibitors are bicarbonates, metal cations and polyphosphates.

Mixed inhibitor

Mixed inhibitor composes of two or three types of inhibitor and majority of the proprietary corrosion inhibitor formula falls into this category. Since chemicals with different characteristics supplement their deficiency with each other, efficacy of the mixed inhibitor increases. Hence, dosage concentration can be significantly reduced, thus, lowering the operating cost and environmental impacts caused by chemicals.

Adsorption

Protective absorbed film is formed over the entire metal surface if adsorption inhibitor is used. The film helps to protect electrochemical reactions between metal and aqueous ions. Some of the organic compounds are suitable to act as adsorption inhibitors.

Passivation

In order to prevent corrosion on galvanized steel cooling towers and associated pipes, formation of a non-porous surface layer of zinc carbonate is one of the effective methods. The formation of zinc carbonate layer is called passivation, which is accomplished by controlling pH during initial operation of the cooling tower. Control of the cooling water pH in the range of 7 to 8 for 45 to 60 days usually allows passivation of galvanized surfaces to occur. In addition to pH control, operation and moderate hardness levels of 100 to 300ppm as $CaCO_3$ and alkalinity levels of 100 to 300ppm as $CaCO_3$ will promote passivation.

Common Chemicals

The following list notes some common inhibitors with pertinent comments.

1. Chromate **-** Excellent steel corrosion inhibitor, the standard against which all others are compared, banned by the USEPA for environmental reasons.

2. Zinc **-** Good supplemental inhibitor at 0.5 to 2 mg/l level, some environmental restrictions, can cause scale if improperly applied.

3. Molybdate **-** Non-toxic chromate replacement, often used as tracer, controls pitting corrosion control at 4 to 8 mg/l, primary inhibitor for steel at 8 to 12 mg/l, higher levels, 35 to 250 mg/l in closed loop and severe environments, very costly material.

4. Polysilicate **-** Excellent steel and aluminum inhibitor at 6 to 12 mg/l, not commonly used due to formulation difficulty.

5. Azoles **-** Three specific azole compounds, MBT, BZT, and TTZ, which are excellent yellow metal inhibitor compounds at the 2 to 8 mg/l level.

6. Polydiol **-** A proprietary organic steel corrosion inhibitor at 2 to 4 mg/l, also a dispersant.

7. Nitrate **-** Specific corrosion inhibitor for aluminum in closed loop treatments at 10 to 20 mg/l.

8. Ortho-phosphate **-** Good steel inhibitor at 4 to 12 mg/l, needs a minimum of 50 mg/l calcium present with a pH above 7.5 to be effective.

9. Polyphosphate **-** Good steel and yellow metal inhibitor at 4 to 12 mg/l, needs a minimum of 50 mg/l calcium present with a pH above 7.5 to be effective.

10. <u>Phosphonates</u> **-** Includes AMP, HEDP, and PBCT, which are commonly used as scale control compounds. Fair steel corrosion inhibitors when operated with pH values above 7.5 and more than 50 mg/l calcium present.

11. <u>Nitrite</u> **-** Excellent steel corrosion inhibitor at 500 to 700 mg/l, commonly used only in closed loops due to high level needed, attack by micro-organisms, and reaction with oxygen.

In general, high phosphate blends are the most economical, low phosphate blends are the next highest in cost, and no phosphate treatment is the most expensive. For facilities where the cooling water system is constructed of several materials, which would include almost all industrial facilities, a program using a blended corrosion inhibitor product is required to obtain satisfactory corrosion protection. For example, adding 2 mg/l of zinc to a phosphonate product at 10 mg/l reduced the corrosion rate on mild steel from 2.2 mils/yr to 0.9 mils/yr. Because of the increase in effectiveness it is common to see programs using mixtures such as molybdate-silicate-azole-polydiol, phosphonate-phosphate-azole, and molybdate-phosphonate-polydiol-azole.

Seawater application

For seawater application, nitrites and phosphates at appropriate concentrations can provide adequate protection. Organic inhibitors can also be used to provide protection where nitrites cannot be used.

Typical dosage concentration, pH range and characteristics of common corrosion inhibitors are tabulated in Annexure -2 at the end of the course.

Cathodic Protection

Cathodic protection (CP) is a method used to protect metal structures, pipes and equipments from corrosion. The cathodic protection can be obtained by connecting a noble metal to a less noble. In practice steel is protected by supply of electrons from less noble metal like Zinc, Aluminum and Magnesium alloys, often called sacrificial anode materials. The anode is sacrificed and eventually is used up, but the steel is protected.

In this method, a sufficient amount of electric direct current (DC) is continuously that corrodes a sacrificial anode. There are two methods for supplying DC to cathodically protect a structure. They are:

1. Galvanic Anode Cathodic Protection
2. Impressed Current Cathodic Protection

The galvanic anode cathodic protection system generates DC as a result of the natural electrical potential difference (electrochemical reaction) between the metal to be protected (cathode) and another metal to be sacrificed (anode). The sacrificing metals such as magnesium (Mg), zinc (Zn) or aluminum (Al) all have a lower more negative electrical potential. The amount of DC produced by this reaction is very small, and, in most cases, is less than 50 milliamperes. The current output of this system is affected by factors such as:

- Driving voltage difference between the anode and the cathode
- Resistivity of the Electrolyte (environment)
- pH factor
- Natural or man made environmental chemistry and/or contaminates

The impressed current CP system generates DC by using a CP rectifier. The CP rectifier can be powered by external power sources, such as alternating current (AC), solar power and thermoelectric generators. The CP rectifier converts the input power source into DC. DC is discharged from impressed current anodes made of metals such as steel, high silicon cast iron, graphite, platinum and titanium mixed metal oxide.

The potential current output of an impressed current CP system is limited by factors such as available AC power, rectifier size, anode material, anode size and anode backfill material. The current output of an impressed current cathodic protection system is far greater than the current output of a galvanic anode cathodic protection system. This type of system is primarily used on:

- very large cross-country pipelines
- bare or partially coated steel structures and pipelines

BACTERIAL & MICROBIOLOGICAL CONTROL

Elimination of “biological fouling” and prevention of the incubation of pathogens forms the third leg of the cooling water management triangle.

There are many species of microorganisms (algae, protozoa, and bacteria) that can thrive in cooling systems under certain circumstances; their growth is helped by favorable water temperature and pH, the oxygen picked up by the spray water, sunlight, and organics that provide food. Generally microbial organisms form colonies at points of low water velocity that leads to uncontrolled microbiological accumulations. The deposits are transferred throughout the piping system, which interfere with heat transfer surfaces and restrict flow through piping, strainers, spray nozzles, and control valves. The deposits are also concern for threatening infectious agents like the bacteria Legionella pneumophillus.

Possible types of micro-organisms that exist in cooling water

Micro-organisms	**Impact on cooling tower system**
Algae	• Provide a nutrient source for bacterial growth • Deposit on surface contributes to localized corrosion process • Loosened deposits can block and foul pipe work and other heat exchange surfaces
Fungi	• Proliferate to high number and foul heat exchanger surfaces
Bacteria	• Some types of pathogenic bacteria such as Legionella may cause health hazards • Sulphate reducing bacteria can reduce sulphate to corrosive hydrogen sulphide • Cathodic depolarization by removal of hydrogen from the cathodic portion of corrosion cell

Micro-organisms	Impact on cooling tower system
	• Acid producing bacteria produce organic acids, which cause localized corrosion of deposit laden distribution piping and also provide the potential for severe pitting corrosion of heat exchanger surface

In order to effectively control the growth of micro-organisms in cooling water, chemical and physical water treatment methods shall be adopted.

Treatment Methods

Chemical biocides are the most common products to control the growth of micro-organisms. Three general classes of chemicals are used in microbial control 1) Oxidizing biocides, 2) Non-oxidizing biocides and 3) Bio-dispersants.

Oxidizing Biocide

Oxidizing biocides are powerful chemical oxidants, which kill virtually all micro-organisms, including bacteria, algae, fungi and yeasts. Common oxidizers are chlorine, chlorine dioxide, and bromine, ozone, and organo-chlorine slow release compounds. Chlorine is one of the most widely used, cost effective biocides and is available in liquid, gaseous or solid form. Its effectiveness is increased when used with non-oxidizing biocides and biological dispersants. Bromine chloride or chlorine dioxide should be considered for use in circulating water treatment for systems with high ammonia concentrations. Ozone is now days widely used to curb microbial growth.

Chlorine

Chlorine is the most widely adopted biocide for large circulating water systems. It provides a residual biocide in the treated water and can be readily checked. It is cheap and readily available as a pure gas, as well as in the form of various liquid and solid compounds. Its effectiveness increases when it is used with other non-oxidizing biocides and biological dispersants.

Chlorination systems are normally quite effective, but must be carefully controlled and monitored due to effluent quality control guidelines. Chlorination has several limitations in application, including:

a. Loss of effectiveness in alkaline waters (i.e. pH of 8 and greater)

b. Loss of effectiveness in the presence of contaminants, such as ammonia, methanol and ethylene glycol, etc.;

c. Corrosive towards common materials utilized in cooling tower installations;

d. Potential formation of less environmentally acceptable products;

e. Rapid degradation under heat and light

Storage and handing of chlorine must comply with the Dangerous Goods Ordinance. In 1974, the Best Practical Control Technology Currently Available (BPT), Best Available Technology Economically Achievable (BAT), and New Source Performance Standards (NSPS) of the EPA limited free available chlorine (FAC) to mass limitations of 0.2 mg/l daily average concentration and 0.5 mg/l daily maximum concentration for plants with either once-through cooling systems or closed cycle cooling systems. In addition, neither FAC nor total residual chlorine (TRC) could be discharged from any single unit for more than 2 hours per day, and multi-unit chlorination was prohibited. In the 1980s, further restrictions were placed on chlorine discharges by the EPA and state agencies. With the movement to reduce chlorine discharges to the environment, two options are offered to plants that use chlorine: chlorine minimization or dechlorination.

- <u>Chlorine minimization</u> is a program designed to ensure the most efficient use of chlorine to reduce the amount of TRC discharged. Plant personnel conduct tests to determine the minimum amount of chlorine necessary to control biofouling. Chlorination practices are then adjusted in accordance with test results. The condensers are periodically monitored and inspected to ensure minimum chlorine use and proper operation. Many plants in the United States have found that their current chlorine usage can be reduced significantly to comply with effluent limitations without other means or technologies for chlorine removal.

- Dechlorination involves using chemical means to remove a significant amount of TRC. The most commonly used dechlorination processes use sulfur dioxide, sodium bi-sulfite, or sodium thiosulfate.

Sodium Hypochlorite

Chlorine can be dosed in the form of sodium hypochlorite. A mixture of hypochlorous acid (HOCl), hypochlorite ion (OCl), and chloride ion (Cl) is formed when hypochlorite is added to water. The pKa (dissociation constant) for hypochlorous acid is approximately 7.53 at 25 °C. At pH levels below 6.0, most of the free chlorine is present as hypochlorous acid.

- At pH levels above pH 9.0, most of the free chlorine is present as hypochlorite ion.

- In the pH range from 6.0–9.0, the ratio of hypochlorous acid to free chlorine residual decreases with increasing pH. Hypochlorous acid is a much more effective biocide than hypochlorite ion.

- The effectiveness of sodium hypochlorite as a biocide decreases rapidly as the pH rises above 8.0.

Caution - Chlorine and hypochlorites must be applied carefully, because excessive chlorine will increase corrosion and may contribute to deterioration of cooling tower wood and reduction of heat transfer efficiency.

Chlorine dioxide

Chlorine dioxide is another strong disinfecting agent that is effective in controlling microbiological growth at high pH values. It is similar to free chlorine but having certain advantages:

1. Chlorine dioxide does not react with ammonia this reduces the disinfectant dose relative to chlorine.

2. Chlorine dioxide does not react with organics to the extent that chlorine or bromine does; this reduces the cooling water demand for chlorine dioxide relative to chlorine or bromine.

3. It is more effective than free chlorine at high pH values. Also, chlorine dioxide is very effective against Legionella and its relatively long half life allows chlorine residual remains in cooling tower water circuit for a relatively long period.

Chlorine dioxide is an unstable chemical that must be generated on site. Chlorine dioxide is produced by mixing the chlorinated water from a normal chlorinator and sodium chlorite solution. The reaction takes place very quickly; however, the process is more costly than simple chlorination. Chlorine dioxide is also generated electrolytically from a variety of chemicals. For cooling tower applications, the acid/sodium chlorite and acid/sodium hypochlorite/sodium chlorite generation method are typically used.

Chlorine dioxide and some of the chemicals used to generate it are hazardous.

Bromine

Bromine is produced either by the reaction of sodium hypochlorite with sodium bromide on site, or from pellets. Bromine has certain advantages over chlorine, including:

1. Bromine is a more effective disinfectant than chlorine in applications where the pH range is 8.0–9.0.
2. Effective disinfectant at low dose rates
3. Effective in the presence of nitrogenous compounds and organics such as methanol and ethylene glycol
4. It kills micro-organisms more quickly
5. Reduced potential for systems corrosion
6. Lower environmental impact

Iodine

Similar to chlorine and bromine, iodine is a good oxidizing biocide. However, it is relatively expensive.

Ozone

Ozone is a powerful disinfectant agent and virus deactivant that is capable to oxidize many organic and inorganic compounds. Ozone kills bacteria by rupturing their cell walls, a process to which micro-organisms cannot develop immunity. Residual ozone concentrations greater than or equal to 0.4 mg/L have been shown to result in a 100% kill in 2 to 3 minutes for any type of micro-organisms. The effectiveness of ozone is about 100 to 300 times more than chorine and can be successfully employed at a low concentration.

Since ozone has a short half life (usually less than 10 minutes), it readily decomposes into oxygen after oxidization. However, ozone is corrosive to some materials, and the cooling system construction materials need to be resistant to ozone attack. Also, injection equipment for ozone shall be designed to provide adequate contact of the ozone with the circulating water and in larger system; multiple injection point may be required.

Application of ozone is not suitable under the following situations where excessive organic material in the water or high operating temperature has a high depletion of applied ozone:

1. High organic loading from air, water or industrial processes that would require a high chemical oxygen demand (COD) since ozone oxidizes the organics and insufficient residual may remain for the water treatment.

2. Water temperatures that exceed 43.3°C since high temperatures decrease ozone residence time and reduce overall effectiveness of the ozone treatment.

3. Make up water is hard (>500 mg/L as CaCO3) or dirty make up water. Softening and / or prefiltering of make up water is recommended.

4. Long piping systems which may require long residence time to get complete ozone coverage.

5. Installation in dusty and smoky environment, and hot places such as boilers, kitchen and their chimney and exhaust.

Hydrogen Peroxide

Hydrogen peroxide (H_2O_2) is a powerful oxidizer, with its power stronger than chlorine and chlorine dioxide, but weaker than ozone. However, it can be catalyzed into hydroxyl radicals (OH-), which is more powerful than ozone, for micro-organisms control. Catalysts, such as iron, copper or other transition metals compounds can be added to hydrogen peroxide to generate hydroxyl radicals for more rigorous oxidation. This is the most powerful method to destroy micro-organisms and trace organics in water.

Hydrogen peroxide decomposes into oxygen and water readily. It is a simple and effective treatment technology when comparing with conventional water treatment chemicals and does not cause any gaseous release or chemical residue problem.

However, hydrogen peroxide is totally soluble in water, which may cause safety problems if high concentration (>8% H2O2 by weight) is used. Safety precaution in storage, delivery, handling and disposal of hydrogen peroxide shall be considered, which shall be complied with related guidelines.

Application of oxidizing biocide

The most effective use of oxidizing biocides is to maintain a constant level of residual in the system. Oxidizing biocides are usually maintained at a continuous level in the system. Dosage may be adjusted in response to regular testing but fully automatic control of biocide level in using reliable and durable measuring systems is desirable since overdosing can lead to increased corrosion and adversely affect the water treatment performance. Shock dosing is also applicable, which can enhance the effectiveness by faster killing action.

Since oxidizing biocide may sometimes be corrosive, corrosion inhibitors shall be added and selected to ensure compatibility.

Non-Oxidizing Biocide

Non-oxidizing biocides are organic compounds, which kill micro-organism by targeting specific element of the cell structure or its metabolic or reproductive process. Non-oxidizing biocides are not consumed as fast as the oxidizing types and remain in the system for a significant period of time until they pass out with the blowdown. They often have the added advantage of breaking down into harmless, nontoxic chemicals after accomplishing their bacteria-killing purpose. They are effective where chlorine may not be adequate.

However, the non-oxidizing biocides are more costly and normally justified only in small systems, as a supplement to an oxidizing biocide in a large system, or when a particular problem exists in a large system and an alternative to the use of chlorine is required.

- Non-oxidizing biocides usually are organic compounds such as ammonium salts, Isothiazolinones, organo-metallics and organo-sulfur compounds.
- Quaternary ammonium salts or diamines are sometimes found to be toxic, but the low concentration application allows them to maintain in an acceptable limit for discharge.
- Isothiazolinones are biodegradable, which cause little adverse impacts to the environment.
- Glutaraldehyde is an effective and rapid-acting biocide and its reactivity prevents it from persisting to harm the environment.
- Non-oxidizing biocides such as organo-metallics, chlorophenols, organo-sulfur compounds and cationic biocides have not been adopted for use in large circulating water systems because of economics, degree of effectiveness, adverse side effects, or a combination of these reasons.

Generally accepted advantages to using non-oxidizing biocides are:

1. They are well suited to applications that are highly concentrated or fouled.
2. Contaminants such as ammonia, organic material, or nitrites cause a chlorine demand but do not affect a properly applied non-oxidizing biocide program.
3. They are active at low levels and are environmentally degradable, providing minimal discharge problems.
4. They will not attack organic scale inhibitors and are less corrosive than chlorine at normal dosages.

Disadvantages to using non-oxidizing biocides are:

1. The cost is considerably higher.
2. They are pH sensitive.
3. Some are specific to certain microbial organisms.
4. Some are not effective against algae.

5. In order to ensure the effectiveness of non-oxidizing biocides, monitoring of chemical concentration in cooling tower systems is required.

Non-oxidizing biocides shall be presented in sufficient concentration with adequate time for effective micro-biological control. System capacity, evaporation rate, bleed-off and make up rates shall be considered in calculating dosage concentration and frequency. Also, biocide hydrolysis (chemical degradation) rate affects the residual concentration of biocides containing in the cooling tower system.

Typically, except in air conditioning cooling systems, non-oxidizing biocides are used only as a supplement to chlorine. If, during operation, it is determined that a non-oxidizing biocide is required because of severe fouling problems, the chemical supplier should be consulted on the method of feed. Normally, the supplier will lease the storage and feed equipment for a minimal charge.

Bio-dispersants

Bio-dispersants do not kill organisms; they loosen microbial deposits, which can then be flushed away. They also expose new layers of microbial slime or algae to the attack of biocides. Bio-dispersants are an effective preventive measure because they make it difficult for micro-organisms to attach to equipment and / or pipe work surfaces to form deposits. Bio-dispersants can greatly enhance performance of biocides particularly oxidizing biocides. Possible bio-disperants include Acrylates, Ligonsulphonates, Methacrylates and Polycarboxylic acids, etc.

Biocide Dosage Rates

Biocide treatment is designed to either periodically shock the microorganisms with a relatively heavy dose of chemical, or maintain a continuous biocide residual in the circulating water. Below the lower threshold value of the biocide, the microorganisms will begin to multiply again. The recommended practices are:

1. Continuous chlorine residual systems typically maintain a residual of 0.5–1 mg/l as Cl_2.

2. Intermittent sodium hypochlorite feed systems typically dose at about 3 mg/l as Cl_2 for 1–2 hours per day to the circulating water flow. Shock chlorination is typically done 2–4 times per day, each with duration of 20–30 minutes.

3. Continuous bromine residual systems typically maintain a residual of 0.5–1 mg/l as Br.

4. Continuous chlorine dioxide residual systems typically maintain a residual of 0.2–0.5 mg/l as ClO_2.

5. Intermittent chlorine dioxide feed systems typically dose at about 1.5 mg/l as ClO_2 for 1–2 hours per day to the circulating water flow. Shock chlorine dioxide feed is typically done 2–4 times per day, with duration of 20–30 minutes.

6. Non-oxidizing biocide are generally slug-fed (such as once a week) at high concentrations. The concentration is specific to the biocide, but is typically in the 5–30 mg/l range as product.

To stay within the chlorine discharge limits, feed rates of 3ppm chlorine or less are required, depending on the circulating water system.

Ultraviolet Disinfection

Ultra-violet irradiation is commonly used to kill bacteria in drinking water, which can also be applied to cooling water systems. Specific wavelengths of electromagnetic radiation are used to inactivate micro-organisms through the denaturing of their DNA. Wavelengths ranging from 250 to 270 nanometres (nm) are effective in deactivating certain pathogens found in water.

Bacteria are vulnerable to UV light and can be killed, provided that light of the correct wavelength and intensity can penetrate individual cell walls. Effectiveness is compromised by the obstructing effect of particulate suspended matter or water turbidity, as well as deposition of solids on the light source. In order to maintain a wide coverage of UV light, it is necessary to install a filter located upstream of the UV lamp.

Ultra-violet irradiation systems can be controlled by UV source intensity and water flow rate. The dose of UV light is measured as the product of intensity and exposure time, as milliwatt-seconds per square centimeter ($mW/s \cdot cm^2$). The minimum UV dosage requirement is 20 $mW/s \cdot cm^2$. It is desirable to have integral monitoring instruments to ensure the lamp performance is not degraded. Also, regular cleaning of quartz sleeves surfaces and UV sensors are required to prevent particles from obstructing the UV light.

Copper and Silver Ionization

Ionization indicates the electrolytic generation of copper and silver ions in cooling tower water. If properly managed, copper and silver ion concentrations at 20 to 30 µg/L and 10 to 15 µg/L, respectively, can be effective to kill bacteria in the systems.

The ions assist in the control of bacterial populations in the presence of a free chlorine residual of at least 0.2 mg/kg.

It should be noted that in hard water systems, silver ion concentrations is difficult to maintain due to build-up of scale on the electrodes, and the high concentration of dissolved solids precipitating the silver ions out of solution. For both hard and soft water, the ionization process is pH sensitive and it is difficult to maintain silver ion concentrations above pH 7.6. It is not recommended to adopt ionization in systems having steel or aluminum heat exchanger since deposition of the copper ion and subsequent galvanic corrosion is significant.

WATER TREATMENT SYSTEM EQUIPMENT, CONTROLS AND MONITORING

Chemical Feed Equipment

The purpose of most chemical treatment control programs (other then certain biocides) is to maintain a constant concentration in the recirculating water at all times. The chemical feed pumps also referred to as metering pumps are used for this purpose.

The chemicals are fed from a bulk storage tank by variable stroke pumps, which can be either manually or automatically adjusted in proportion to circulating water blowdown. Because the pump has to inject a treatment chemical into what is frequently a high pressure stream, common chemical feed pumps are positive displacement units which use a reciprocating (piston) action to alternately fill a pumping chamber and discharge a fixed volume of solution. In many units, the piston acts through a flexible, non-corrosive diaphragm that isolates the mechanical elements of the pump from the chemical stream. Chemical metering pump discharge quantities can usually be varied by adjusting the stroke length of the pump by means of an external stroke length adjustment knob. The stroke adjustment of many electric motor-driven metering pumps alters a mechanical linkage that can be damaged if the pump is not operating when adjustments to stroke length are made.

<u>Recommended feed equipment parameters for acid dosing are:</u>

1. Storage tank - Minimum 14 days capacity. This may vary depending on site-specific requirements at the maximum chemical use rate. If the minimum capacity is less than one truck load, some customers may want the tank sized to allow full-truck-load delivery with a margin. The typical margin would be about 150 percent of the delivery volume. Sulfuric acid tanks need a desiccant breather and a method to prevent moist air from entering through the overflow. Hydrochloric acid tanks need a vent scrubber with a method of preventing hydrogen chloride fumes from venting through the overflow.
2. Pumps – 2 x 100-percent capacity (1 spare) variable stroke and acid-resistant internals.

The acid is introduced to the tower basin in a turbulent region. Before the acid is introduced, it is diluted, either internal to the piping, or in a mixing trough external to the piping. The method and point of introduction should be selected to prevent the partially diluted acid from contacting basin walls, cooling tower structures, and system metallurgy. Dilute sulfuric acid and all concentrations of hydrochloric acid are highly corrosive to carbon steel, and the acid will react with concrete.

There are two types of cooling water systems: 1) closed-loop systems and 2) open systems both requiring different approach.

Closed loop systems

In a closed system, there is very little or no loss of water into a known volume as system water remains in the piping. Little, if any, make-up water is required to maintain a filled system as little or none is lost through evaporation or steaming as in an open system where the water content of the system is open, at some point, to the atmosphere. In addition, the closed loop systems are pressurized at all times so that excess air can be eliminated through simple automatic air venting devices.

The water treatment in closed system is thus not very critical. Once the initial volume is chemically treated, the quality of the circulating fluid needs to be monitored on a regular basis and additional chemicals added as required to maintain recommended residual concentrations of treatment chemicals.

Examples of closed loop system include chilled water, recirculating cooling water, and hot water heating system.

- In cold service closed-loop systems, the system may only need to have chemical treatment when the system is filled initially and any time the system has been open for maintenance. <u>Cold service recirculating systems are usually treated to prevent corrosion from dissolved oxygen. Scale formation is usually not a problem in cold systems.</u>

- In warm or hot service closed-loop water circulating systems, regular monitoring and chemical additions may be required to prevent corrosion from dissolved oxygen and scale formation from precipitation of minerals in the water.

In closed systems, pot feeders are used to add chemicals to systems that do not require frequent chemical treatment. The chemical treatment can be accomplished as the system is filled or during normal operation of the system using a pot feeder in a bypass loop. Typical pot feeder installations are shown on figures below:

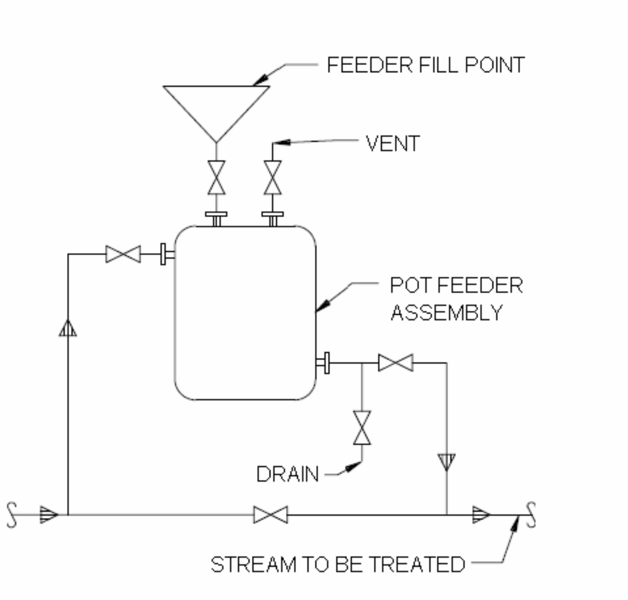


Fig (a)

TYPICAL FILL SYSTEM POT FEEDER INSTALLATION

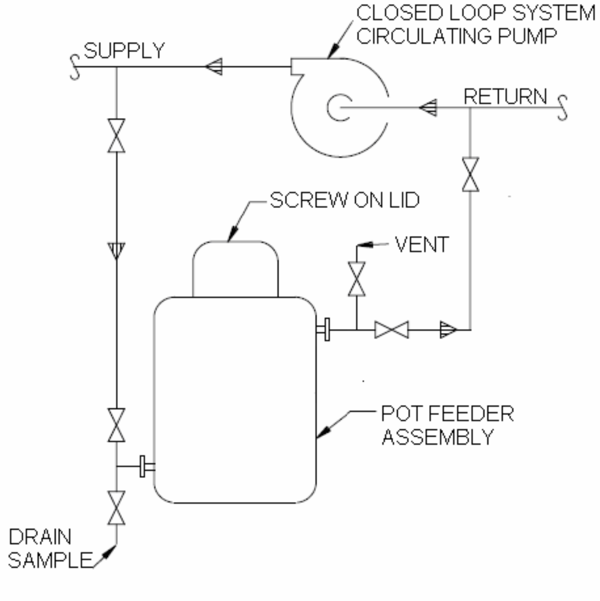


Fig (b)

TYPICAL POT FEEDER BYPASS INSTALLATION

Most closed-loop water systems use a sodium nitrite based inhibitor for corrosion control and a biocide to prevent biological contamination. These inhibitors will protect both the ferrous and non-ferrous materials in your piping system.

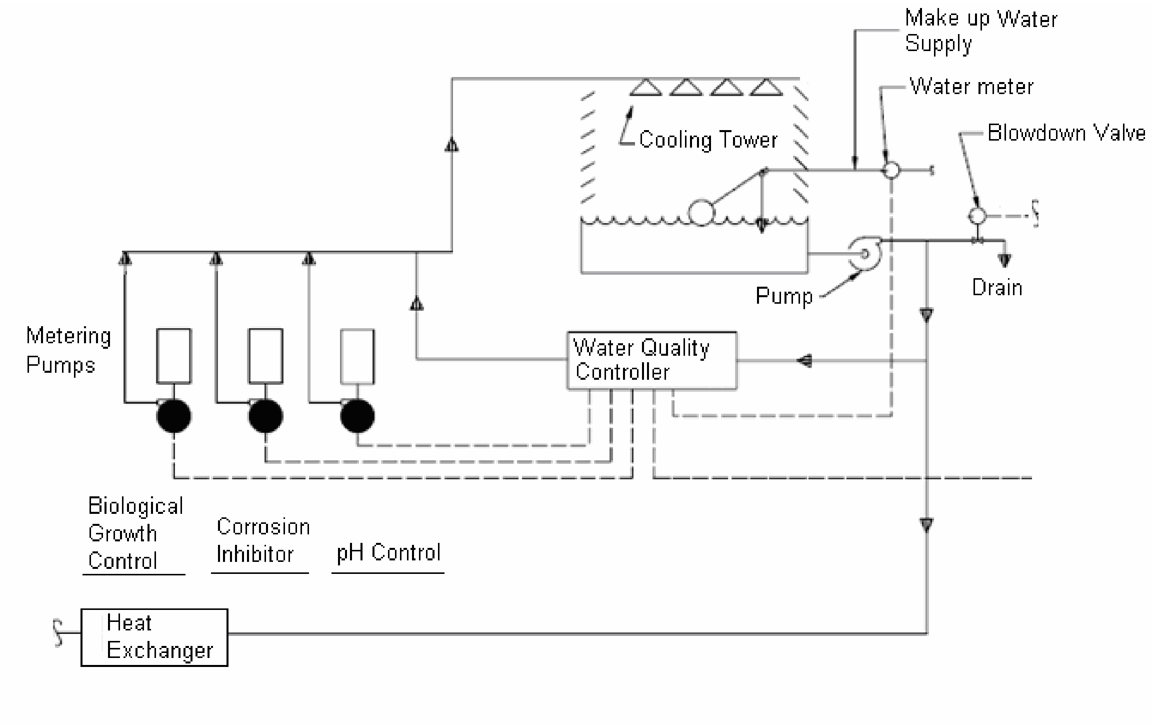
Open loop systems

In an open loop system such as cooling tower, there is constant loss of water due to evaporation and a constant addition of makeup water into the system which constantly changes the quality of the recirculating stream. This constant change in the system quality may require frequent water quality monitoring along with the frequent addition of chemicals to control corrosion, scale formation, and growth of biological agents. Some combinations of chemicals used may also change the pH of the system significantly which will require pH monitoring and adjustment.

Because evaporative towers scrub the air that passes through them, they are prone to absorbing oxygen and collecting debris from the air. The oxygenated water is primary cause of corrosion and the debris can accumulate and cause flow restrictions; as well as aggravate corrosion. Also, after the water evaporates, dissolved minerals are left behind and accumulate rapidly. For these reasons, the water quality in open systems must be regularly monitored and treated to control the following conditions:

1. Lime scale and other water mineral deposits
2. Corrosion of all types
3. Micro-biological growth, such as algae, bacteria, fungus and molds
4. Suspended solids accumulations, such as airborne dirt and debris that is washed into the cooling tower water

The water treatment options for open loop systems can be manual or automatic. In manual system, the operator periodically samples the water and makes slug additions of chemicals into the basin. In automatic operation, continuous water quality analyzer monitors the system parameters and then controls the operation of metering pumps which inject controlled doses of chemicals into the circulating stream to maintain a uniform water quality.



OPEN LOOP CHEMICAL TREATMENT SYSTEM

Water treatment chemicals shall be added to turbulent zones of cooling tower water system to achieve rapid mixing and well distribution of chemicals. Also, separate dosing point shall be used to ensure dilution of one potentially reactive chemical prior to adding the second chemical. The dosage concentration of chemicals, including inhibitors and biocides, shall be calculated based on the total quantity of water, make up water quality and bleed-off rate.

For biocide dosage, the pump operation frequency is usually timer controlled. The pump stroke is sometimes automatically controlled by a chlorine residual monitor that monitors a sample taken from the discharge of the condenser or heat exchanger.

Depending on the quantities of chemicals used and the chemical supplier, the tank and pumps may be leased for a nominal fee from the chemical supplier.

Piping and Fittings

Piping design, materials, fabrication, assembly, erection, inspection, and pressure tests for facility piping systems should be in accordance with American Society of Mechanical Engineers (ASME) B31.1, Power Piping. Major modifications of existing piping systems should include hydrostatic testing and radiographic or magnetic particle inspection of welds where applicable.

During testing, system components that have not been designed for the piping test pressure must be disconnected and protected against damage by overpressure.

Common piping materials used in chemical treatment systems are carbon steel pipe, and stainless steel pipe and tubing. Some low-pressure systems may use plastic pipe components. In general, when modifying or repairing a system, replace existing piping components or add to the system using piping components of the same materials of construction of the existing system, provided the service life has been good.

Common valve materials compatible with typical facility chemical treatment systems are carbon or stainless steel. Valve bodies from these materials should be cast or forged. In low-pressure systems, plastic valves from materials similar to polyvinyl chloride (PVC) may be used. In general, unless the valve has failed after only a short period of use, replace valves (and other piping components) with new valves constructed from the same materials. Typical types of valves that may be found in chemical treatment systems are as follows.

Gate valves may be specified with absolute bubble tight closure. Gate valves may be rising stem, outside stem and yoke (OS&Y), or double-disk type.

Ball or non-lubricated plug valves are generally used where quick or frequent opening or closing is required. Globe valves are used in systems at locations where manual control of the flow rate is required. General use of globe valves should be avoided, because of their high resistance to flow.

Check valves are used in chemical treatment systems to prevent backflow through pumps, branch lines, meters, or other locations where runback or reverse flow must be avoided.

Many piping systems will have one or more pipe test sections installed in the system. A test section is a short section of pipe that can be easily isolated and removed from the system to make a thorough visual inspection of the interior of the pipe system possible. Visual inspection confirms the need for or the effectiveness of a chemical treatment program.

Chemical Dosing Control and Monitoring

In order to maintain a stable chemical concentration in cooling water, a number of application methods can be adopted, including:

1. Shot / slug dosing
2. Continuous / intermittent dosing
3. Proportional dosing related to bleed-off volume
4. Proportional dosing related to make up water volume
5. Dosing controlled by sensor

Shot / slug dosing

Chemicals are added to the system manually on a routine basis. Shot / slug dosing is the most economic and effective application method, which may be adopted in small-scale cooling tower installation and particularly for biocide application. However, it is not recommended for large systems because chemical concentration cannot be controlled accurately and large fluctuations in chemical levels are always found.

Continuous / intermittent dosing

Continuous / intermittent dosing makes use of mechanical devices, such as timer and pump for chemical dosing. It is the simplest type of automatic dosing system. Since chemical dosing frequency and amount is regulated by the pre-set value, fluctuation of chemical concentration inside cooling tower water is always found.

Proportional dosing related to blowdown volume

System bleed-off can be controlled by simple timer, conductivity sensor or make up water flow. Signal from the device can also be used to initiate chemical dosing.

When the conductivity of the system water reaches a pre-determined value, a timer can be actuated which allows a dosage pump to run for a period to add the requisite amount of chemicals, in relation to the make up water entered the system.

A delay timer shall be installed to prevent wasteful chemical addition during blowdown.

Proportional dosing related to make up water volume

Proportional dosing maintains a nearly constant chemical level by dosing in proportion to a varying make up water rate. The treatment requirement is based on make up water quantity and injection rate varies as the water make up changes.

Impulse water meter installed in make-up line shall be used to activate a chemical dosing pump. Proportional dosing can be applied to all cooling tower systems continuously. Such dosing is particular benefit to systems which operate under conditions with great varieties.

Dosing controlled by sensor

Dosing controlled by sensor is ideal for controlling chemical concentration in a system. Correct amount of chemical is continuously presented to the system once the dosing rate and frequency are gauged by operational parameters. Therefore, concentration of chemicals inside cooling tower water can be maintained within a designated range. pH sensor, redox probes and oxidation reduction potential (ORP) probes are commonly used to control dosing of acids and oxidizing biocides, respectively.

Blowdown Control

For an accurate bleed-off control system, automatic control by conductivity sensor is recommended to regulate the amount of bleed-off required. Conductivity is a measure of total ionic concentration in water, hence, concentration of total dissolved solids (TDS). Blowdown control is a critical part to ensure scale prevention in cooling water systems.

Blowdown rate is related to the cycle of concentration, which shall be determined by water treatment methods being adopted. If a comprehensive water treatment program, including both chemical and physical methods, is implemented to control scale, corrosion and micro-biological growth effectively, blowdown rate can be significantly reduced.

There are a number of methods to control blowdown, including:

1. <u>Manual control</u>: a blowdown valve is opened in response to test measurements
2. <u>Timer / intermittent control</u>: a simple interval timer is set to open and close the blowdown valve intermittently
3. <u>Continuous bleed</u>: an orifice plate or pre-set valve is set to release water continuously

4. Proportional control: an impulse water meter on the make up line actuates the blowdown valve
5. Conductivity control: the cooling water conductivity is continuously monitored and the blowdown valve is opened at a pre-set conductivity.

A number of points shall be considered for a blowdown system.

1. To ensure the bleed assembly can be isolated from the system for maintenance purposes;
2. To ensure the head of the conductivity sensing probe is positioned in the main water flow, but not where air pockets can develop;
3. To place the conductivity sensing probe upstream of the blowdown system solenoid valve;
4. To clean the conductivity sensing probe regularly;
5. To regulate valve in the blowdown line so that the flow cannot exceed the make up water to the system;
6. To provide an alarm signal when solenoid valve and flow switch signals in the blowdown line do not correspond.

Central Monitoring and Control

Water treatment monitoring can be controlled through Building Management System (BMS). It co-ordinates the entire system operation and water treatment programme. This control strategy may have the following advantages:

1. Accurate dosing control is assured which optimizes chemical usages;
2. Blowdown and chemical dosage would not occur at the same time so that wastage of chemicals on drainage can be avoided;
3. Adjustment of water treatment programme in accordance with cooling tower system operation can be performed in the central control system;
4. Minimal chemical handling is required to reduce the risks of the operators' health and safe;

5. Water consumption, energy consumption, chemicals consumption are recorded accurately;
6. Any malfunction of water treatment equipment can be reported immediately.

Monitoring Devices

Sensors are generally used as monitoring devices in cooling water systems. Comparison between the measuring results and the set points for specific parameter are useful to determine the control action required for normal operation.

Different type of sensors to be selected is relied on the control strategy. Common types of sensors are described as follows.

Flow meter

Chemical feeding requirements are proportional to the make up water flow. Many chemical feeding systems are designed according this basis, which is the simplest automatic dosing method. Flow meters including orifices venturi, flow tubes and turbine meters can be used to suit the design.

Level sensor

Make up water supply to cooling tower sump depends on water level of cooling tower basin. Hence, chemical dosing can be controlled by monitoring of the water level. However, this dosing method is not accurate and cannot control the concentration of chemicals contained in the cooling system water precisely.

Conductivity sensor

Electrical conductivity of water relies on total ionic concentration of water, which indicates the concentration of total dissolved solids (TDS) in water. Both corrosion rate and scale formation potential for any specific systems are normally proportional to the conductivity of water. Conductivity sensor is frequently employed as chemical detection device. The sensor is usually used for operation of blowdown system for the control of cycles of concentration.

pH sensor

Carbon steel corrosion rate decreases with an increase in pH value, and the scale potential for most scale forming compounds increases with pH value. Also, water treatment chemicals work in specific range of pH value. Hence, pH value measurement is often the basic principle for acid dosing to maintain effective water treatment program.

ORP sensor

ORP stands for Oxidation-Reduction Potential and is a measure of the cleanliness of the water and its ability to break down contaminants". It has a range of –2,000 to + 2,000 and units are in "mV" (millivolts). ORP sensors work by measuring the dissolved oxygen. More contaminants in the water result in less dissolved oxygen because the organics are consuming the oxygen and therefore, the lower the ORP level. The higher the ORP level, the more ability the water has to destroy foreign contaminants such as microbes, or carbon based contaminants.

ORP sensors are used as real time monitoring and recording of oxidation reduction potential, which can be utilized to monitor chlorine residuals in cooling tower systems. It measures the inorganic and organic particles remaining in cooling water so as to facilitate chemical dosing. ORP sensor shall be used together with pH sensor since ORP values vary with pH value.

Chlorine residuals sensor

Chlorine is commonly employed biocide for water-cooled air conditioning system.

Continuously measuring chlorine residual analyzer is commercially available to measure either free or total chlorine residual.

Turbidity sensor

Turbidity measurement provides an indication of the amount of suspended matter in cooling water, which is useful in determining deposit potential. Therefore, it can be used for bleed-off control.

Corrosion rate sensors

Corrosion rate sensors are available in the market to provide continuous, instantaneous measurement of corrosion rates for any alloy. These sensors are normally based on linear polarization resistance between a pair of electrodes.

Corrosion coupon test method can also be used to determine corrosion rate.

Sensors for specific ions and Compounds

Sensors are commercially available to measure ion concentrations in water. Many analyzers are also available to measure either compounds or classes of compounds or classes of compounds dissolve in water.

The selection of proper location of sensors in the water-cooled air conditioning system is very important. Sensors measuring treatment chemicals shall be located at a point after the treatment is well mixed. Corrosion rate increases with increasing temperature. Therefore, corrosion monitoring device should be installed at the outlet of the heat exchanger where water with the highest temperature is passing through. Requirement of measurement and reliability of sensor shall also be considered in selecting an appropriate device.

Control Devices

In order to achieve maximum effectiveness of water treatment program, chemicals must be dosed into the system in an appropriate concentration periodically. Since handling of chemicals may be dangerous, it is always recommended to perform chemical dosing by means of automatic monitoring and control strategy. Chemical injection can be facilitated by different control devices.

Timer

It is a simple device allowing operator to set the operation of chemical dosing valve, hence, chemical dosing frequency, in a fix interval. Also, circulation of water during system intermittent down time can be achieved by using timer control.

Dosing pump

Dosing pump can be operated manually or automatically. For automatic control, dosing pump activates upon receiving signal from timer or sensors. It runs for a certain period to inject chemicals into the cooling tower water circuit.

Motorized valve

Motorized valve is an essential component for automatic controlled chemical dosing and bleed-off. It will switch to open / close position upon receipt of signal from monitoring devices, such as water meter and conductivity sensor.

Occupational Safety and Health

Sufficient personal protective equipment shall be provided to the personnel responsible to carry out pre-commissioning and commissioning work of a cooling tower system.

Training in safe work procedure, including the use and maintenance of protective equipment shall be provided to the personnel carrying out the cooling tower system commissioning.

Water treatment may involve application of relatively aggressive and toxic chemicals, which is the major concern. All personnel involved must be fully conversant with the safe handling of the products.

Material safety data sheet (MSDS) and relevant recognized data sheet for chemicals used in water treatment process shall be provided by water treatment services providers and included in the operation and maintenance manual. MSDS and relevant warning / safety label shall be provided on the surface of water treatment chemical bucket. The MSDS and labels shall be properly protected against water and chemical damage.

Eye wash bottles or washing basin with fresh water tap shall be provided adjacent to water treatment chemicals tanks or any appropriate location for emergency use. However, the water contained in the eye wash bottle shall be replaced periodically.

Water treatment chemical shall be stored at an appropriate location to facilitate chemical handling.

Mechanical / natural ventilation shall be provided to the room entirely / partially used for water treatment chemical storage.

Electrical fittings and luminaries serving water treatment chemical storage area shall be weather-proof and corrosion resistant type.

Warning signs shall be erected to alert for operation and maintenance personnel of the potential hazard caused by cooling tower.

Warning signs shall also be erected to restrict the unauthorized access to cooling towers.

Workers exposed to hazardous substances and engaged in processes of cleaning and disinfection and water treatment shall undergo regular health surveillance with a medical practitioner. In case any worker develops respiratory, cutaneous and other symptoms when exposed to hazardous chemicals, immediate medical attention shall be sought.

CONCLUSION

The choice of treatment is basically a mater of economics. In a once-through system, a very large volume of water passes through the system only once. Protection can be obtained with relatively few parts per million (ppm) of treatment because the water does not change in composition significantly while passing through the equipment.

In an open re-circulation system, more chemical may be present because the water composition changes significantly through the evaporation process. Corrosive and scaling constituents are concentrated. However, treatment chemicals also concentrate by evaporation, therefore, after the initial dosages only moderate dosages will maintain the higher level of treatment needed for these systems.

In a closed re-circulation system, water composition remains fairly constant. There is very little loss of either water or treatment chemical. The best form of treatment recommendation for closed water system includes the dosage of film forming inhibitors such as nitrites and molybdate.

Annexure – 1

Characteristics of some common scale inhibitors

Scale Inhibitors	Advantages	Limitations	Type / Dosage concentration/pH range
Polyphosphate [Inorganic]	Cost effective Highly soluble in water, thus low concentration is required Low order of toxicity	It has a tendency to hydrolyze and revert back to orthophosphate and forms insoluble calcium orthophosphate.	Type – Inorganic Dosage [mg/L] 1 - 5 Applicable pH range 6.8-7.5 Can be used for calcium carbonate and calcium sulphate inhibition
Organic polymer	No hydrolysis problem when compared with polyphosphate More hydrolytically stable in highly alkaline environment	Low calcium tolerance	Type - Organic Dosage [mg/L] 10 - 15 Applicable pH range Not specified It shall be used together with anionic or non-ionic type non-oxidizing biocide.
Sodium Polyacrylate	Applicable but no specific advantage.	No specific limitation.	Type - Organic Dosage [mg/L] 2 - 3

Scale Inhibitors	**Advantages**	**Limitations**	**Type / Dosage concentration/pH range**
			Applicable pH range Not specified Can be used for calcium carbonate and calcium phosphate inhibition
Aminotris[methylene phosphonic acid] (AMP)	No hydrolysis problem when compare with polyphosphate	Attack rapidly by oxidizing biocides Careful dosage is required to prevent precipitation	Type - Organic Dosage [mg/L] 10 - 20 Applicable pH range 7 - 9 Can be used for calcium carbonate inhibition
(1-hydroxyethylidene) diphosphonic acid (HEDP)	No hydrolysis problem when compare with polyphosphate	Careful dosage is required to prevent precipitation Attack slowly by oxidizing biocides	Type - Organic Dosage [mg/L] 5 - 40 Applicable pH range 7 - 9 Can be used for calcium carbonate inhibition
2-Phosophonobutane – 1,2,4-tricarboxylic acid	No hydrolysis problem when compare with polyphosphate	Careful dosage is required to prevent precipitation	Type - Organic Dosage [mg/L] 20 - 40

Scale Inhibitors	Advantages	Limitations	Type / Dosage concentration/pH range
(PBTC)	Stable to oxidizing biocides		Applicable pH range 7 - 9 Can be used for calcium carbonate inhibition

Caution - Use of these chemicals must be closely monitored because at low levels they can inhibit scale formation, but at higher levels they can create scale problems of their own.

Annexure – 2

Typical dosage rates, pH range and characteristics of common corrosion inhibitors

Corrosion Inhibitors	**Advantages**	**Limitations**	**Type / Dosage concentration/pH range**
Anodic Inhibitors			
Orthophosphates	Applicable but no specific advantage.	Well control of the system is required to control sufficient dissolved oxygen (DO) in water for oxide film formation. Deposits of iron phosphate can form anodes if corrosion starts and encourages under deposit corrosion. Formation of orthophosphate leads to precipitation of calcium phosphates.	Type – Anodic Dosage [mg/L] 5-20 (as PO4) Applicable pH range 6.5-8.5 Calcium phosphate scale inhibitors are always included in phosphate based corrosion inhibitor.
Molybdate	Less toxic compare with chromate. Can prevent pitting corrosion and under deposit corrosion crack.	Expensive Sensitive to chlorine and sulphate.	Type - Anodic Dosage [mg/L] 50-150 (as MoO4) Applicable pH range 7.0-8.5
Nitrite	Applicable but no specific advantage.	Subject to biological degradation - this leads to the loss of inhibitor and bio-fouling problems. Require careful control in open recirculating system as it can be easily oxidized	Type - Anodic Dosage [mg/L] 250-1000 Applicable pH range

Corrosion Inhibitors	**Advantages**	**Limitations**	**Type / Dosage concentration/pH range**
		to nitrate in open system.	9-9.5
Cathodic Inhibitors			
Polyphosphate (Molecular dehydrated, condensed polymeric, poly and metaphosphates)	Water quality insensitive.	Certain bacterial enzymes increase the reversion rate of polyphosphates. Formation of orthophosphate leads to precipitation of calcium	Type - Cathodic Dosage [mg/L] 10 - 20 Applicable pH range 6.5 – 8.5 Calcium phosphate scale inhibitors are always included in phosphate based corrosion inhibitor.
Organic Phosphorous Compounds (Phosphonates)	Water quality insensitive. Phosphonates do not revert to orthophosphate, thus no calcium orthophosphate deposition.	No specific limitation	Type - Cathodic Dosage [mg/L] 10 - 20 Applicable pH range 7 – 9 Require either calcium or metal ion, such as zinc, for effective corrosion inhibition.
Zinc Salts	Applicable but no specific advantage.	Above pH 7.5, zinc hydroxide precipitates from solution as hydroxides or as various organic zinc salts.	Type - Cathodic Dosage [mg/L] 0.5 -2 Applicable pH range 6.5 – 7.5

Corrosion Inhibitors	**Advantages**	**Limitations**	**Type / Dosage concentration/pH range**
			The pH range can be extended upward by including stabilizer to prevent zinc precipitation.
Mixed Inhibitors			
Zinc Phosphonate Dosage [mg/L] 1 – 5 (as Zn)	A more tenacious and protective film can be formed by adding zinc. Reduction in the dosage concentration when comparing with the usage of phosphonate only.	Hardness Sensitive Reduced rate of film formation	Type - Mixed Dosage [mg/L] 1 – 5 (as Zn) Applicable pH range 7 – 8.5
Zinc Phosphonate Dosage [mg/L] 7- 20 (as PO_4)	A more tenacious and protective film can be formed by adding zinc. Reduction in the dosage concentration when comparing with the usage of phosphonate only.	Biological nutrient Reduced rate of film formation	Type - Mixed Dosage [mg/L] 7- 20 (as PO_4) Applicable pH range 6 – 7.5
Molybdate / Phosphonate	Improved corrosion protection can be achieved at lower concentrations of molybdate when blended with organic inhibitors.	Film formation ability remains relatively weak, and the level of protection is marginal in corrosive environments.	Type - Mixed Dosage [mg/L] 5 –20 (MoO_4) Applicable pH range 7 – 8.5
Adsorption			
Benzotriazole (BTA)	Applicable but no	Toxic	Type - Adsorption

Corrosion Inhibitors	**Advantages**	**Limitations**	**Type / Dosage concentration/pH range**
	specific advantage		Dosage [mg/L] 1 – 5ppm Applicable pH range 6 – 9 Act as copper corrosion inhibitor
Tolytriazole (TTA)	Applicable but no specific advantage	No specific limitation	Type - Adsorption Dosage [mg/L] 1 – 5ppm Applicable pH range 6 – 9 Act as copper corrosion inhibitor

Annexure – 3

Typical dosage rates, pH range and characteristics of common biocides

Oxidizing Biocides	**Advantages**	**Limitations**	**Type / Dosage concentration/pH range**
Chlorine	Economic and readily available. Broad-spectrum activity. Simple monitoring for dosage and residuals.	Loss of effectiveness in alkaline water (pH - 8) Hydrochloric acid is by-product of the reaction which decreases system pH. Loss of effectiveness in the presence of contaminants: • Nitrogen compound • Ammonia • Hydrocarbon • Methanol • Ethylene glycol • Iron • Manganese • Sulphides Degrades rapidly under heat and UV light. Potential corrosion problem. Potential formation of environment formulation of environment unacceptable degradation	Type – Oxidizing Biocide Dosage [mg/L] 2-20 mg/L Applicable pH range 6 – 8 Free chlorine residuals: 0.2-1mg/L (continuous). 0.5-2mg/L (periodic slug-dose). Effectiveness increases with the usage of non-oxidizing biocides and biological dispersants.
Sodium hypochlorite Solution (Bleach)	Broad-spectrum activity. Simple monitoring for dosage and residuals. Compare with chorine	Loss of effectiveness in alkaline water (pH > 7.5) Potential scaling problem. Expensive. Sodium hydroxide is by-product of the reaction which increases system pH.	Type – Oxidizing Biocide Dosage [mg/L] 1-3 mg/L

Oxidizing Biocides	**Advantages**	**Limitations**	**Type / Dosage concentration/pH range**
	gas, it is easier to handle.	Loss of effectiveness in high pH since hypochlorous acid convert to hypochlorite ion. Loss of effectiveness in the presence of contaminants: • Nitrogen compound • Hydrocarbon • Iron • Manganese • Sulfides Degrades rapidly under heat and UV light.	Applicable pH range 6– 7.5 Free chlorine residuals: 0.2-1mg/L (continuous) 0.5-2mg/L (periodic slug-dose)
Ozone	Powerful oxidizing agent No residues produce and create no effluent problem. No re-growth of micro-organism Fast kill rate	Unstable, must be generated on-site before use. Leaving no residue in water and make it difficult to be detected. Very reactive and corrosive, not suitable to use in system constructed by low corrosion resistance materials. May cause unwanted precipitation of iron and manganese May destroy inhibitors and dispersants. Not suitable to be used in hard make up water (500 mg/L as $CaCO_3$).	Type – Oxidizing Biocide Dosage [mg/L] 1-5 mg/L Applicable pH range 7 – 9 Multi ingestion may require in large system to ensure full protection. Air pre-treatment and side-stream filtration of cooling tower water can enhance the performance of ozone.

Typical dosage rates, pH range and characteristics of common non- oxidizing biocides

Non - Oxidizing Biocides	**Advantages**	**Limitations**	**Type / Dosage concentration/pH range**
Carbamate e.g.: Sodium dimethyldithiocarbamate, Potassium dimethyldithiocarbamate	Practically effective at low pH or in the presence of heavy metal.	React with metal and cause potential corrosion problem.	Type – Non-oxidizing Biocide Dosage [mg/L] 12-18 mg/L Applicable pH range 7 – 8.5
Triazine group e.g.: 2-(tert-butylamino)-4-chloro -6-(ethylamino)-s-triazine	Excellent for killing algae Operates at full range of pH Non-foamer Not interfere by hardness	No specific limitation	Type – Oxidizing Biocide Dosage [mg/L] Not specified Applicable pH range 0 – 14
Glutaraldehyde	Fast acting biocide Effective to treat sulphur reducing bacteria and biofilms. Short half life and cause minimal environmental	Limited effectiveness for killing algae and fungi	Type – Non-oxidizing Biocide Dosage [mg/L] 45-56 mg/L Applicable pH range

Non - Oxidizing Biocides	**Advantages**	**Limitations**	**Type / Dosage concentration/pH range**
	impact.		6.5 – 9