

COOLING WATER TREATMENT FOR HEAVY WATER PROJECT

H.N. VALSANGKAR - THERMAX LIMITED - CHEMICAL DIVN. PUNE

Introduction

With minor exceptions, water is the preferred industrial medium for the removal of unwanted heat from process systems. With the industrial revolution, one plant's effluent, with its chemical pollutants is the influent for another plant downstream. This problem is compounded by air-pollution, with various process gas leaks, absorbed in water and create alkaline or acidic conditions, thus encouraging scaling and corrosion.

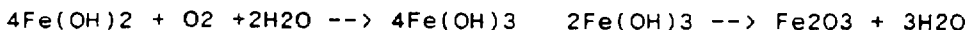
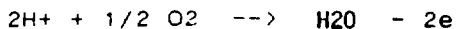
The open evaporative cooling system provide ample opportunity to recycle water. However, this is associated with a very important phenomena - the concentration of dissolved and suspended impurities in water. To offset this, a portion of the system water is "blow-down" to control such concentration. Even though blowdown helps control and reduce many potential problems. The application of various chemical treatments is required to protect the system from water related and process related problems of corrosion, scale and deposition and biofouling. The paper discuss the cooling water problems for heavy water industries alongwith the impact caused by associated fertiliser units.

All the above problems are inter-related and an overall approach is necessary to treat any one problem. The importance of selecting the treatment from a total stand-point cannot be overstressed.

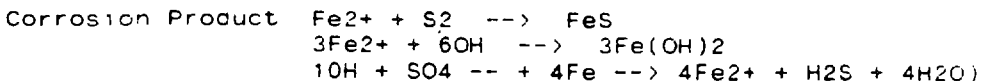
Corrosion:

Corrosion is identified as an electro chemical process in which a difference in electrical potential develops between two metals or between different regions of a single metal. This causes an electro chemical reaction at the anodic and cathodic sites. These sites contribute the corrosion cell as shown below:

Corrosion Reactions



H₂S Related corrosion



A number of factors influence corrosion, including the chemistry of the system, chlorides (stress corrosion), High TDS and Acid waters. The dividing line at moderate or slow corrosion to rapid destruction is at pH 4.55. Oxidising agents (eg. chromates) are both protective and also may act as anodic corrosion accelerators.

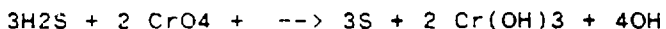
High temperature increases tendency for galvanic cell formation and thus corrosion. The process for NH₃/H₂S based exchange, with a catalyst would provide for heat exchange. When vacuum distillation of water is selected, to avoid product loss, a large amount of heat recovery apparatus is necessary to improve thermal efficiency. In all cases the right approach is necessary to protect heat exchangers from corrosion and scale due to the temperature effect.

Impurities like silt, mud, ash etc. coupled with high velocity of water flowing through heat exchangers, especially shell side exchangers found in heavy water plants erode the metal by abrasive action. Pitting is accelerated by the sulphate reducing bacteria.

CORROSION INHIBITORS

Inhibitors can be broadly classified as anodic or cathodic, according to the corrosion process controlled. Generally a mixed dose of both is given for optimal corrosion inhibition at both ends.

Chromate: It is one of the oldest known inhibitors, and is being used in many fertiliser plants alongwith zinc and polyphosphate. Its inhibitor function is dependent at alkaline pH control with Cr²⁺ ion predominating at alkaline pH and CrO₄ ion at acid pH. Chromate protects by forming oxide films over metal surfaces. In heavy water plants based on H₂S, H₂S reduces chromate to chromium hydroxide sludge by the following reaction.



The hydroxide is a gelatinous sludge that impedes heat transfer and aggravates underdeposit corrosion. Also chromate, in its hexavalent state is a known carcinogen and there are restrictions in its use.

Zinc: Zinc salts are the most common cathodic inhibitors in cooling water programmes. Zinc is usually blended with molybdates or phosphates to synergise corrosion protection. Zinc requires stabilisation when used in alkaline systems to prevent its hydroxide formation and reactions with phosphates.

Acrylic acid derivatives have, by far gained wide acceptance as scale and deposit control agents, where they are effective over a wide pH range and at very low doses. The performance of various co-polymers on phosphate, iron and silt dispersion are given in figures 3, 4 and 5 respectively.

It is possible, now, to operate cooling water system at a wide range of pH fluctuations and fouling conditions created because of system contamination. From the graphs, it is evident that the use of co-polymers like sulphonic acid acrylic acid copolymer will enable to run the system in a scale free conditions at 80 deg C temperature and upto pH 9.0. Sulphonic acid-Acrylic acid co-polymer has also shown good stabilisation of zinc in alkaline solution (figure 6)

MICROBIOLOGICAL FOULING AND CONTROL

A definition of biological fouling is the excessive growth and presence development of the members of Kingdom Prokaryote. Of special interest are the algae, fungi and bacteria. Algae are unique in a sense that they can manufacture their own food (autotrophs) and need sunlight for growth. Bacteria and fungi survive on organics scrubbed into the system, with some exceptions like the nitrifying bacteria and the sulfur oxidisers, which are autotrophic.

Algae: Algal growths are common in areas exposed to sunlight like cooling tower decks, louvers, etc. They cause mechanical plugging of pipes and pumps and pitting corrosion when washed into pipes due to local cell action.

Filamentous fungi, yeasts and molds occur over the water line in cooling towers and are responsible for decay of wood.

Slime forming Aerobic Bacteria of the general Pseudomonas, Aerobacter etc. grow in presence of oxygen and produce voluminous slime and cause choking due to growth and physical entrapment of dirt etc in slime.

Among the other aerobic bacteria, sulfur oxidisers and nitrifying bacteria generate acids from H_2S and NH_3 , increasing corrosion. surviving on system leaks and chemicals scrubbed into the water from air.

The anaerobic sulfate reducing bacteria predominantly the Sulfovibrio group grow in absence of oxygen and produce hydrogen sulfide. Normally, when oxygen is excluded, the microbiological system becomes polarised because hydrogen, which accumulates at the cathode, is not removed. The sulfate reducers depolarise the cell by removing hydrogen at the expense of sulfate, which is reduced to sulfide. The net result is a continuous loss of metal from anodic areas. Further, the metal reacts with H_2S forming sulfides. These organisms cause corrosion severe enough to perforate steel pipes.

Ortho/polyphosphates : Polyphosphates combine with calcium present in water to give durable films at the cathodic end. Generation of orthophosphate by hydrolysis polyphosphates or by direct addition affords anodic protection. The polyphosphate/orthophosphate system is applicable over a broad pH range with little sensitivity towards pH. It must be noted that phosphates combine with calcium, iron in recirculating water and generate scaling conditions. These conditions are aggravated by ammonia leaks from adjacent fertiliser units/from the plants themselves. Localised high pH zones cause deposits and under deposit corrosion and need a good phosphate dispersing polymer for good scale and corrosion protection in alkaline pH. A comparative graph is given in Figure 3.

SCALE AND DEPOSITS

The primary function of an open recirculatory system is to remove heat and any interfering factor has to be dealt with. Scales occur as water formed deposits and the causative agents usually are water borne salts, mud, iron, added corrosion inhibitors etc. The most common of the scales involve calcium salts. The primary characteristic with these salts is that they are inversely proportional with respect to solubility and temperature. This in effect means a heavy scaling potential in the heat exchangers put in the humidifier circuits, in which about half of the heat contained in the gas stream leaving the top of the hot tower is exchanged with a recirculating water stream that in turn heats and humidifies the gas entering the base of the hot tower. The common water borne scales are those of CaCO_3 , CaSO_4 complexes of Ca, Mg, Iron, Zinc etc with phosphates, silica and silicates and corrosion products.

In addition contaminants like H_2S cause the formation of sulphides of zinc, iron, reduce hexavalent chromate to hydroxides and cause scale formation. Formation of iron sulphide almost always is associated with under deposit corrosion.

Silt, mud, fly ash, microorganisms etc enter the cooling tower through the make up or from air and concentrate due to high cycles of concentration. Iron oxide corrosion products form due to high cycling of cooling water. Iron from one part of the system, such as distribution piping is transported and is deposited on heat transfer surface. Zinc salts can be either in form of hydroxides or phosphates or silicates in system with improper zinc stabilisation $\text{pH} > 7.5$

DEPOSIT & SCALE CONTROL

Carboxylic acid phosphate derivatives have found wide spread use in cooling water system and are used at 1-4 ppm level. The most common are Adenosine methylene phosphonic acid (ATMP) and 1 Hydroxy ethylidene-1, 1-diphosphonic acid (HEDP). HEDP is an excellent calcium carbonate scale inhibitor (Figure 2) with an effective dose level of 2 ppm. However it does not function well in high hardness water where it precipitates as a calcium salt.

CONTROL OF BIOFOULING

The most effective approach is a preventative programme which achieves and maintains control without the need for unplanned down time. A clean system alongwith the use of proper scale and corrosion inhibitors keeps the system from generating hideouts for bacterial proliferation. Use of biodispersants affords the operation of the system at higher bioloads by preventing attachment of bacteria to surfaces. Table 4 lists some major biocide classes in use today. Their proper selection is based after time-kill studies and system requirements. Effluent toxicity is another major factor in selecting biocides.

Table 1 : Biocides for cooling water treatment

A) OXIDISING

Chlorine, Hydantoins
Chlorine dioxide 2,2, Dibromonitrilopropion amide

B) NON OXIDISING

<u>Phenols</u>	<u>Quarternaries</u>	<u>Heavy metal containing</u>
Sodium Pentachloro-phenate Dichlorophene Na-2,4,5 - trichloro-phenoxide	Cetyltrimethyl ammonium chloride, dialkyl dimethyl ammonium chloride.	Mercurials, Arsenicals Organotins etc.
<u>Amines</u>	<u>Sulfur containing</u>	<u>Others</u>
N-coco trimethylene diamine	Methylene and Vinylene bis thiocyanates carbmates sulfones isothiazolines thiones	Acrolein Cyanurates dioxaborinanes

The current trend is to incorporate the use of biodispersants + chlorine enhancers like bromine which are effective at alkaline pH. Use of such programmes affords excellent biological control when systems are operated at pH ranges of 8-9 i.e. no acid dosing.

Operation of a clean system reduces dependency on biocides and also keeps the system scale and corrosion free. All three parameters being interlinked a properly designed programme should allow the operation of cooling water system at pH ranges of 7-9.0, with corrosion, scale and biofouling rates well under prescribed limits. In such cases, water hardness and alkalinity should not be a critical factor in effective treatment results.

FIGURE 2 — Relative CaCO₃ inhibition

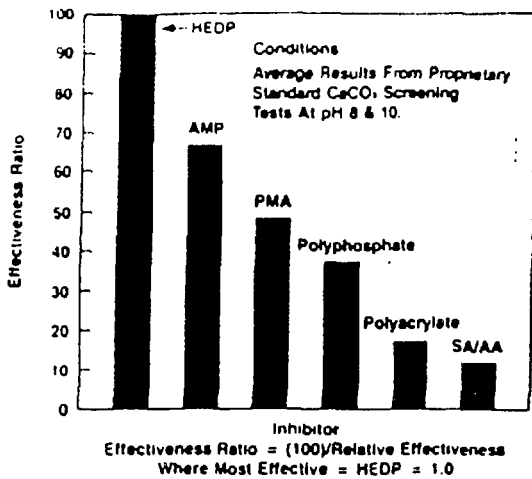


Figure 4 — Effectiveness of Various Organic Inhibitors for Metal Oxide Dispersion

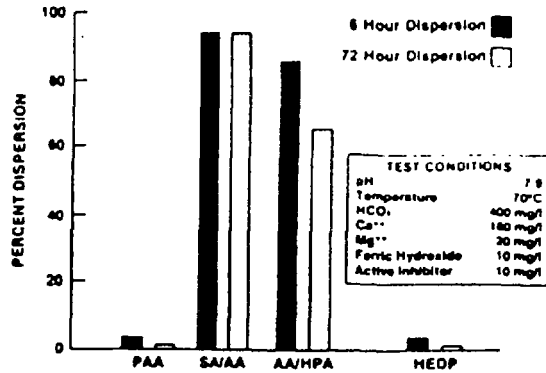


FIGURE 3 CALCIUM ORTHOPHOSPHATE SCALE INHIBITION

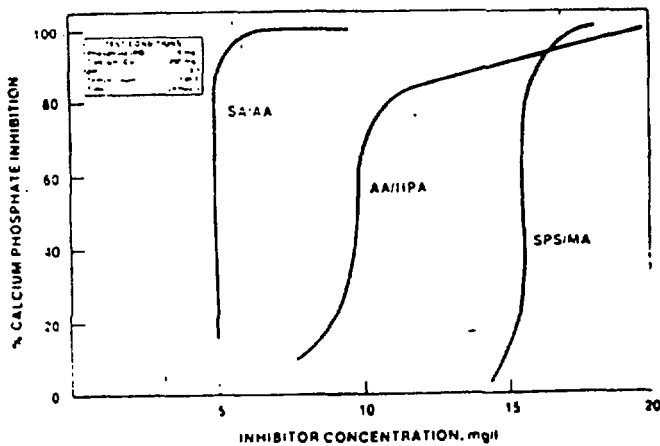


Figure 5 — Silt Dispersion vs Polymer Concentration

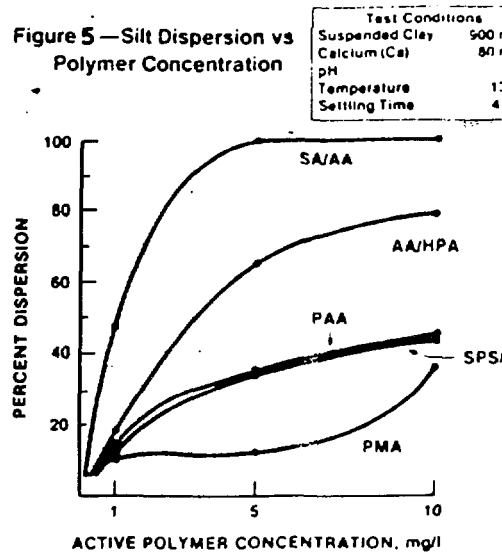


FIGURE 6: ZINC STABILITY

