

Corrosion Control in Industrial Water System

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Water used in chemical industry can be broadly classified as :

- (a) Process water—to be used in the actual processing of chemicals,
- (b) Cooling water—usually used in heat exchangers, condensers, etc., and
- (c) Boiler feed water.

PROCESS WATER

Water used in the actual processing of chemicals is obtained after treating the naturally available (hereafter called raw) water suiting the process requirement. In most of the processes, the treatment is to remove the hardness of water. This is done by the conventional softening plants. The usual objection to using hard water is that there is a likelihood of formation of calcium and magnesium salts which affect the reactions and also tend to form insoluble calcium and magnesium salts. Since process water remains inside a system only for a short time, one does not usually come across corrosion problem. However, if this water is to be stored for a long period in mild steel vessels, one adds sodium silicate and sodium carbonate to prevent the formation of iron hydroxide (a product of corrosion of iron surface through the intermediate iron oxide). Other inhibitors used are borax, sodium nitrite, sodium benzoate, etc., in the 500-1000 ppm range.

COOLING WATER

This is the type of water which is mostly used in industries, and which causes major corrosion problems. The cooling water system could be either a once-through or a recirculating system. In the once-through system, the cooling water is passed through the system (usually the jacket of reactors, tube side or shell side of heat exchangers, etc.) one time and is then discharged to waste. The water used is normally the raw water, which is untreated since treatment cost for such a huge quantum of water will be very high. In some of the western countries, the brackish sea water is usually used as an once-through cooling medium. This type of water is the most corrosive and the water, besides containing a high amount of dissolved solids, is usually saturated with oxygen and also contains suspended solids, silt, colloidal material, fungus, etc. ; these create a fouling effect on the surface. The biological growth of fungus and aqueous vegetation, if not checked properly, may even be so high in unseen parts of the equipment, that the entire flow of water may be stopped in due course. The usual treatment for checking this biological growth is to feed in sufficient amount of chlorine i.e., a residual free chlorine content of 0.1 to 0.2 ppm is always maintained. Chlorine treatment, if not properly controlled, may create a secondary corrosion problem. An excess of free chlorine results in free acidity leading to corrosion of mild steel surface. In such cases various other non-oxidising biocides like sodium chlorophenates, quaternary amines, acrolein, etc., are used to combat the biological growth. The silt or suspended matter fouling is usually controlled by adding 1-2 ppm of a polyelectrolyte which prevents the suspended matter from settling. To complete the task of corrosion control, 2-5 ppm of a molecularly dehydrated phosphate or silicate can be added.

Besides these chemical treatments, one could physically also try to reduce the corrosion rate. This is by increasing the velocity of water through the equipment such that the solid in suspension is always dragged off and is prevented from settling. In some of the refineries in Western Germany, the heat exchanger tubes through which salty and brackish-water is passed, are actually coated inside with a special resin which is hydrophobic, heat resistant up to 200°C and heat conducting as well. This is a silicon-carbon based furan resin, which is far cheaper than "Teflon" which is the other type of resin used in heat exchangers. Because of the hydrophobic nature, the suspended particles in the water are repelled from the surface along with the water. The resin coating also prevents corrosion of steel pipes due to the dissolved oxygen in the water.

The recirculating water system for cooling has also its own problems. The quantum of water required for recirculation system is only 5-10% of the amount required in an once-through system. This is the fresh make-up water used for the evaporation losses and for maintaining the level of total dissolved solids. The problems encountered in such recirculating cooling systems are discussed below.

(1) **Scaling** : Water containing calcium and magnesium salts when used as a cooling medium comes in contact with the hot surface and the inverse solubilities of the salts of calcium and magnesium favour the formation of precipitates which tend to form a scale on the surface. Similarly, silica may deposit if the evaporation rate or increase in silica content due to recirculation is such that the concentration exceeds its solubility. In some cases where some inhibitors like phosphates are used, aluminium salts usually deposit such scales. Scale formation prevents heat transfer besides reducing the area of flow. The usual method of preventing this is to use softened water for the recirculation system.

Another factor which increases the scale formation is the pH of the water. Higher the pH, higher is the scale formation in case of raw water. Usually the pH is controlled to about 7.0–7.5 for non-scaling purposes. Complete removal of scale or non-scaling will, however, create secondary problem, corrosion. Sometimes, the precipitation of some of the calcium and magnesium salts is prevented by the addition of chemicals to water called sequestering agents—examples of which are citric acid, glycolic acid, EDTA, Sodium tripolyphosphate (STPP). These chemicals are able to keep salts like calcium sulfate in solution in their presence and help in reducing the scale formation. It is because of this property that STPP is used as an additive in detergent powder so that the detergent has equal cleansing power in hard as well as in soft water.

(2) **Corrosion** : Recirculating cooling water is usually cooled in cooling towers where it comes in direct and intimate contact with oxygen. Thus, the water that leaves the cooling tower will be invariably saturated with oxygen. Hence, if this water passes through equipment, one can expect a lot of corrosion in the equipment. To prevent this, one could try to reduce the effect of free oxygen by adding reducing agents like sodium sulfite or hydrazin and maintain an overall positive content of the reducing agent in the recirculating water. However, this cannot completely remove the dissolved oxygen unless one expends in additional treating equipment for the completion of reaction.

In industry, it is usually the practice to safeguard against corrosion due to this residual oxygen, by interposing a barrier between water containing oxygen and the metallic surface. This barrier is usually the scale that forms due to the salts mentioned earlier. This, in effect, means a slightly reduced heat transfer in case of heat exchangers.

To an extent, corrosion of steel equipment due to water can be controlled by the addition of inhibitors. Treatment of water to contain 40 ppm polyphosphate and 20 ppm chromate and main-

taining a pH of 7.0 to 7.5 aids in corrosion inhibition—addition of either ferrocyanide, zinc molybdate to the polyphosphate—chromate system enhances the inhibition. The only trouble with these inhibitors is that the disposal of the blow down presents a problem. The other inhibitors used are organic chromates, silicates, etc.

Fouling in case of recirculating cooling system due to fungus growth, suspended water, etc., can be handled in the same way as in once-through system. Additional precaution needed in case of setting up of cooling towers is to see that the cooling towers are not open to the direction of sand storm, or located adjacent to the chimneys of chemical units. It is likely that if the wind direction is favourable, the exhaust from the chimney may pollute the water, more so if it contains acidic or reducing gases. Similarly, the wooden frame-work (grids) in the cooling tower are liable for decomposition and it is not an uncommon scene to see the growth of fungus and weeds on the wooden grids. This could be minimised by coating the wooden grids with some varnish which is water proof, or by replacing the wooden grids by plastic grids (polypropylene or PVC or PE). The latter step is expensive but worth the investment. The growth of fungus or settling of the dirt and colloidal matter in the equipment, can be somewhat reduced by keeping the operating velocity of water through the heat exchanger tubes or the jacket of a reactor at a fairly high rate of 6 to 8 ft./second—and by frequent and periodic cleansing. Dirt or silt once it settles in the surface of a tube in a heat exchanger at any point, actually occludes some oxygen between the dirt particle and the metal and starts oxygen corrosion. Result is pitting. This phenomenon goes on continuing and the metal is eaten away. At places where the cooling tower is exposed to atmospheric dust, one should install auxiliary filters to remove the dust and dirt from the cooling tower pump.

(3) Boiler feed water : Boiler feed water presents more problems than the circulating cooling water because of the two extremes in the physical parameters of pressure and temperature. Besides the formation of scale, the boiler water, if not treated properly, will create corrosion due to oxygen, carbon dioxide and cause caustic embrittlement.

Normally the boiler feed water is given the softening treatment either by lime soda or limesoda phosphate or Ion exchange process. Even the best process, i.e., Ion exchange, will not remove the entire hardness but will keep about 1 ppm hardness in the feed water. An idea about the amount of scale formed with such water containing 1 ppm hardness can be calculated. This will work out to about 80 lbs of scale per year for a boiler capacity of 10,000 lbs of steam per hour. The best way to maintain a good heat transfer will be to add some other chemical to loosen the scale and let it out of the system during the blow-downs.

One such chemical used was sodium carbonate. This no doubt prevented calcium sulfate scaling but presented other problems. For example, at pressures, above 200 psig. the sodium carbonate breaks down into sodium hydroxide and CO_2 . Sodium hydroxide was found to produce the caustic embrittlement on the rivetted construction of the boiler drums.

The second chemical was the phosphates, used in presence of organic compounds, such as, lignins and tannins. However, this also creates crater type corrosion in high pressure boilers (about 1500 psig.)

Oxygen, even if present at 0.05—0.1 ppm in feed water, is enough to create troubles in boilers due to corrosion. The corrosion is much evident at the water-steam interface as pits and on condensing surfaces and in condensate return pipes. The traces of oxygen in boiler feed water is usually removed

by oxygen scavengers or reducing agents (such as sodium sulfite or hydrazin) as in recirculating cooling water system. Excess of these scavengers may lead to other type of corrosion. For example, if residual sulfite is more than 50 ppm, it may decompose to hydrogen sulfide which is most corrosive. Besides, this will increase the total dissolved solid content necessitating in more frequent blow downs. An optimum should be struck.

Carbon dioxide is usually formed in boilers due to (1) decomposition of bicarbonates to carbonates and CO_2 ; (2) the decomposition of sodium carbonate to NaOH and CO_2 at higher pressures. The released CO_2 moves off with the steam and while condensing, forms the corrosive carbonic acid. The only way to avoid this is by careful control of the bicarbonate and carbonate content in the feed water.

The corrosion due to caustic embrittlement on rivetted joints of a drum of a boiler is overcome these days by having a welded drum. Besides this, one could also add inhibitors like sodium nitrate to check the caustic embrittlement.

Silica in feed water is likely to dissolve in high pressure steam and may cause troubles in the turbine blades by getting deposited while expanding. Thus silica in water is not really corrosive to the boiler but it is dangerous to use such steam or feeding to turbines, since it may imbalance the turbine shaft movement.

Thus it can be seen that water for industrial purposes need to be treated, depending on where it is to be used and if not properly treated will lead to corrosion in some form or other. In some cases, one may come across severe corrosion, even after taking all the precautions. In such cases, attention should be drawn to the other types of corrosion like stress corrosion. In practice, it was once observed on a medium pressure steam boiler (250 psig) that the M. S. seamless tubes (though they were of schedule 80) had started leaking after about six months service with deionised water in the tube side. To have a longer life of the tubes, it was thought that stainless tubes of equal thickness may be used. But surprisingly, these gave way earlier than the period for which M. S. tubes withstood. The corroded tubes were cut and inside it was observed that the tubes had actually given way because of stress corrosion. It may be that a residual chloride (though only in ppm) in the feed water, has actually caused this stress corrosion in stainless steel. Mild steel is a better material of construction in this case, since stress corrosion due to chloride is not evident in mild steel. A number of case histories like the above one could be cited. Precautions have to be taken to avoid recurrence of any such failure due to corrosion. Though water used in chemical industry is normally the safest chemical, still it is this water which creates a lot of trouble in critical equipment and one has to give equal importance to water as is being given to other corrosive chemicals such as acids, alkalies, etc.

DISCUSSION

DR. K. S. RAJAGOPALAN (CECRI, Karaikudi)

In any study of water corrosion the following factors play important role:

1. The effect of temperature.
2. The effect of concentration of corrosive salts.
3. The effect of pH.
4. The effect of rate of flow of liquid.
5. The form of corrosion.
6. The scale-forming tendency
7. Environmental factors including metal factors ; kind of equipment used, e.g., steel, brass, etc., in cooling systems.

Effect of temperature: The rate of corrosion increases upto 80°C in open system though in closed system the increase is maintained at temperature beyond 80°C also.

Effect of corrosive salts: In presence of chloride the corrosion rate increases upto 3% salt concentration and then goes down.

Effect of pH: The rate of corrosion falls with increasing pH reaching a steady value between pH 4 to 10 and then again increases.

Effect of rate of flow of liquid: Starting with 10 mdd in stationary condition, the corrosion rate goes on increasing with increase in flow rate reaching a figure as high as 200 mdd under certain conditions. In the absence of turbulence the corrosion rate, however, levels off after a certain flow rate. If the rate of corrosion is more than what can be tolerated, we have to take suitable preventive measures.

Prof. S. J. Arceivala has given a very lucid and excellent account of problem connected with cooling towers, but he has not considered the behaviour of water which is an important point. If we study in the laboratory or in the field, water corrosion of a particular metal and examine the kind of water that we have to use then we can consider the preventive measures to be taken. If we use copper alloys, stainless steel, etc., the rate of corrosion is very much lower than that of steel. So changing the material of construction is one solution. Other solution is use of chemicals added to bring down corrosion, scale formation, etc. My view is that the problem with regard to corrosion with cooling water is that of choosing a suitable inhibitor and combining it with suitable substances so that scale formation is controlled.

MR. A. G. NENE (Shriram Chemical Industries, Kota)

We have discussed the factors responsible for scaling and corrosion. We have also discussion on bicarbonates and Langlier Index, etc. Those of us who are in the industries generally feel that Langlier Index does not help much for controlling corrosion. There is one more factor which is important and that is velocity of water in condensers.

DR. A. K. LAHIRI (Corrosion Advisory Bureau, Jamshedpur)

Flow condition in the pipe is very important. At very high velocities turbulence created completely changes the nature of attack and increases corrosion rate. Even at lower velocities any fluid flowing through a pipe does not have the same rate all along the cross section. Due to the resistance at metal/fluid interface, the fluid near the wall has lower velocity than at the centre. Thus a thin layer of comparatively stagnant layer of water is formed on the pipe wall, the thickness of which is dependent on the flow rate. The temperature, inhibitor concentration, etc., is quite different in this layer from the bulk solution thus greatly affecting corrosion rate, inhibitor efficiency and scaling tendency.

MR. S. G. KRISHNAN (NOCIL, Thana)

In industrial uses of water we encounter two problems: (1) If we do not control our cooling water system, we get pitting types of corrosion leading to increase in maintenance cost. (2) With all the ideal conditions if you do create a scaling tendency, this means cutting down-time to about once or twice a year. Now what means we should adopt? From our experience we feel that the most important aspect is the initial surface condition of the equipment. In new installations you have tremendous amount of foreign material; grease and oil and other contaminants sticking to the surface. Any preventive measure taken will give better performance if the water comes in contact with a clean surface. This means surface conditioning is to be carried out before the installation is commissioned. The preparatory treatment no doubt appears prohibitive but if we work out economics for large plants this will be found paying. Once the cleaning is complete addition of 150-200 ppm of polyphosphate will be fruitful.

MR. K. R. BULUSU (CPHERI, Nagpur)

I think, I referred to two points about the use of polyelectrolytes and the effect of temperature on the Ryzner Index. We can see from the chart that the temperature effect will be quite less significant. At a temperature of 80°F we have a factor of about 2.3 or 2.2 and at a temperature of 200°F, we have a factor of about 1.2. When we see Ryzner Index, we see how insignificant is the change in temperature. The polyelectrolytes at a very low concentration of colloids are added with the objective of preventing settling. These polyelectrolytes are added for a definite purpose, i.e., when we introduce a polyelectrolyte the function that occurs is just to improve its settling characteristics and not preventing it. There is a possibility of very fine settling on the bed to filter out this colloidal suspended impurities. By virtue of the alkalinity, the water passing out will pick up some silica which will act as an inhibitor.