

INHIBITORS FOR BOILER-WATER CORROSION

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Thermal power generation based on boiler/turbine system and using fossil fuel for the generation of steam provides vast world's supply of electricity. In India, power generation is also based on the same system. Water tube boilers have evolved as the only practical means of producing steam in sufficient quantities and at the appropriate pressure for running the steam turbines to generate electricity. The corrosion problems being faced by the system are not in common with hydroelectric plants or atomic power station. Basically, the thermal power plants consists of boiler, boiler drums, superheater, heater, steam pipes, rotors, bladings, erosion shields, turbine casings, condensers, return systems, etc. Each item has its own problem and, therefore, requires proper attention to achieve better performance. The corrosion of boiler is divided into internal corrosion (water side) and external corrosion (Fire side). There are also a number of locations in a boiler system where various types and amounts of corrosion occur. In order to obtain the maximum return from a modern high pressure high efficiency boiler, the unit has to have a very high degree of reliability. Corrosion has the effect of bringing down the reliability of a power plant with a concomitant need for

stand-by equipment. The corrosion may be caused by the solids and gases dissolved in the water and by decomposition of steam. It, therefore, warrants the efficient control of feed water quality. In this paper, the boiler system will be discussed in three generalised locations pre-boiler, boiler and post-boiler with respect to corrosion inhibition.

Pre-Boiler

It is defined as the feed water pumps and the line entering the system. Both corrosion and deposit problems are encountered in the system. The corrosion may be general corrosion, pitting or erosion corrosion. General corrosion or pitting may occur due to dissolved oxygen, low pH, presence of deposits, stagnant areas, stresses in metals, defects in metal composition and surface conditions. Dissolved oxygen often causes pitting attack low pH leads to general corrosion. Other factors are also responsible for localised attack. Cavitation erosion is also observed in pumps or other locations where turbulence at high velocity flow occurs.

Sources of deposits in the pre-boiler system are from (1) improper

clarification of the water before it enters the system and (2) dissolved calcium, magnesium and poly-phosphate salts. High alkalinity and temperature contriutes to the formation of the carbonate, magnesium hydroxide and orthposphate.

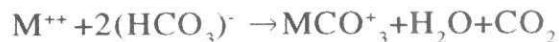
Boiler

In boiler also, deposits and carry-over lead to corrosion. Deposits in boiler are of two categories, namely sludge and scale. Sludge is a loose/dispersible product whereas scale is gnerally tightly adherent product on the surface of metal. Scales commonly consist of calcium carbonate, sulphate or silicate, magnesium hydroxide or sodium alumino-silicate. The carry-over water present in the steam accumulates solids (NaCl, Na₂SO₄, NaOH), resulting on deposits in the turbine blades. Saturated steam under high pressure conditions is not safe for turbine blades unless it contains less than 0.010 to 0.015 mg SiO₃/Kg. Also, pitting, concentration corrosion, caustic embrittlement, nitrate cracking, stress corrosion cracking and erosion corrosion are observed in boilers.

Water Chemistry

The most important corrosive agent in steam plant is water. Natural waters contain corrosive ionic species like Co⁺⁺, Mg⁺⁺, Na⁺, K⁺, Cu⁺⁺, Cl⁻, H⁺, SO₄⁻², HCO₃⁻, OH⁻ and SiO₄⁻⁴, dissolved gases O₂, CO₂ and H₂S, organic matters and suspended maters. All need careful treatment before water is fed in the boiler.

The bicarbonate of Ca & Mg, conferring temporary hardness to water, forms scale according to the equation



Permanent hardness due to chloride and sulphate of Ca and Mg is liable to leave scales at the metal water interface. The thermal conductivity of adherent sacle deposit is of the order of 1.5 Btu/ft²x ft/h°F which is about the same as that of insulating fire brick. At heat transfer rate of 100,000 Btu/ft²/ft/h/°F achieved in the highly irradiated section of a high pressure boiler, a scale thickness as low as 10 mm may lead to metal failure by overheating.

In general, the higher the boiler pressure, the more stringent the requirement of purity of feed water. Table - 1 shows typical specifications for boiler feed water and Table - 2 the desirable boiler water composition.⁽¹⁾

It appears from the tables that maintenance of boiler water composition is more important than the feed water requirements of boilers which may very depending on the operating parameters.

Post-Boiler

It consists of superheater and the condensation and return system. The following three factors are responsible for attack on super heater.

1. Reaction between steam and metal at high temperature

2. Carr-over by steam of salts
3. Condensation

The last two items are dealt with here. Item -1 does not find scope here to deal with since it is not controlled by the use of inhibitor.

The salts which are carried over by steam are NaCl , CaCl_2 , SiO_2 , Na_2SO_4 and CaSO_4 . NaCl and CaCl_2 are decomposed by steam at 400°C with the formation by hydroxid of Na^+ and Ca^{++} . Other salts are hydrolysed by superheater steam at temperature as low as $288\text{--}316^\circ\text{C}$.

Condensation of steam in superheater tubes takes place when the boiler is shutdown. The condensed water having dissolved oxygen and carbon dioxide creates condition for the corrosion to take place. Oxygen leads to pitting corrosion and CO_2 the general corrosion. The mechanism for O_2 attack involved is depolarization of the cathodic areas on the metal surface. Collins and Henderson⁽²⁾ have arrived at the following conclusions about the O_2 attack.

1. O_2 concentration below 0.5 ppm causes negligible corrosion when the temperature is less than 70°C and the pH-6 or higher.
2. In the pH range of 6 to 8 and at oxygen concentrations of 0.5 to 4 ppm, the rate of attack for general corrosion is given by the equation

$$R = 24(C-0.4)^{0.9}$$

where R is the average rate of penetration in mdd and C is the oxygen concentration in ppm. Oxygen from air dissolves in water to the extent of 10.2 ml STP/L at 0°C and 4.5 ml at STP/L 40°C . Attack by oxygen is aggravated at comparatively lower pH values, prevailing in condensate lines and in boiler where adequate alkalinity is not maintained. The presence of carbon dioxide in the system would, then, accelerate the corrosion by oxygen.

Carbon dioxide attack is manifested by thinning and grooving the metal walls. The equation developed by Collins⁽³⁾ indicates the corrosion rate of CO_2 attack.

$$R = 5.7 W^{0.6}$$

where R is the rate in mdd and W is the concentration of CO_2 in condensate in ppm multiplied by the weight of condensate flowing in lb/hr multiplied by 0.1. An increase in temperature from $60\text{--}90^\circ\text{C}$ raises the rate of attack of carbonic acid on steel by a factor of 2.6. Carbon dioxide from the atmosphere dissolves to the extent of 1 ppm at 0°C and 0.3 ppm at 40°C . Other sources of CO_2 are the oxidation of traces of organic matter present in the water and also the high temperature partial hydrolysis of sodium carbonate sometimes added to boilers to control alkalinity.

Inhibitor

In order to combat corrosive attack of feed water, pre-treatment of the water is a must and designed

Table - 1
Feed Water requirements of Boilers

Boiler pressure lb/in ²	pH	Dissolved oxygen ppm	Hardness CaCO ₃ ppm	Chloride as NaCl ppm	Phosphate as Na ₃ PO ₄ ppm	Sulphite as Na ₂ SO ₃ ppm	Hydra- zine ppm	Cu and Fe ppm	Total dissolv- ed solids ppm
200 (Softened water make up)	8.5	0.05	2	3	3	0.5	--	--	8
200 (Distilled water make up)	8.5	0.05	nil	nil	1	0.5	--	--	2
400 (Softened water make up)	8.5	0.03	2	3	3	0.3	--	--	8
400 (Distilled water make up)	8.5	0.03	nil	nil	1	0.3	--	--	1.5
600 (Distilled water make up)	8.5	0.02	nil	nil	--	0.2	0.04	--	1.0
900 (Distilled water make up)	8.5-9.0	0.01	nil	nil	--	Not recom- mended	0.02	0.02	0.2
1,500 (Distilled water make up)	8.5-9.0	0.007	nil	nil	--	-do-	0.015	0.02	0.05
2,500 and above	8.5-9.0	0.005	nil	nil	--	-do-	0.01	0.02	0.02

Values given in columns 3 to 10 should not be exceeded.

Table - 2
Requirements of Boiler Water Composition

Boiler pressure lb/in ²	pH	Total alkalinity as CaCO ₃ ppm	Hydroxide alkalinity as CaCO ₃ ppm	Phosphate ppm	Sulphate ppm	Chloride ppm	Sulphite ppm	Hydrazine ppm	Silica ppm	Total dissolved solids ppm
200	11	400	200	100	--	100	30	--	--	2,000
400	8.5	200	100	60	--	50	20	--	--	1,000
600	10.5-11.5	120	60	50*	--	20	5	--	--	250
900	10.5-11.0	70	40	30	20	20 Not recommended	Trace	Trace	1.0	150
1,500	10.5-11.0	50	20	30	10	10	-do-	Trace	0.5	100
2,500 and above	10.5	20	10	10	5	5	-do-	Trace	0.1	50

Values given in columns 3 to 10 should not be exceeded.

to render it as non-corrosive or non-scale forming as far as possible both in pre-boiler and boiler systems. In high pressure steam boiler, it is desirable to remove from a raw water the ions of calcium and magnesium using ion-exchange resins, which are known to play part in scale formation even at low heat transfer rates.

Recently, it is reported that sedimentation or scale formation in hot water reservoir (e.g., a boiler or kettle) can be reduced by the application of stainless steel sponge. It is made of stainless steel wire having a rectangular cross section with thickness which lies between 0.03-0.05 mm and width of 5-20 times the thickness.

Prevention of general corrosion is most frequently practiced by the maintenance of pH at 9.0 by the addition of NaOH. As the $(OH)^-$ activity is raised, the solubility of all oxides and hydroxides is reduced and the degree of super saturation set-up in the liquid close to the metal increases. This situation leads to the formation of a protective film, consisting of closely packed nuclei of ferrous hydroxide, iron oxides or magnetite. In high concentration of NaOH, the protective film is destroyed and the iron becomes active again and dissolves with evolution of hydrogen and formation of sodium ferroate (Na_2FeO_4). The hydrogen, so generated, results in caustic cracking (hydrogen embrittlement). To avoid caustic cracking, a more recent and quite popular approach to pH control in pre-boiler system is the use of ammonia,

morpholine or cyclohexylamine. These amines are very effective provided oxygen content in the system is maintained at very low value. It is reported that morpholine is superior to ammonia and cyclohexylamine. For any neutralising compound to be effective the following requirements are to be met by the compound:

1. Should have adequate concentration in the vapour and liquid phases
2. volatility should match with high pressure steam
3. should react with CO_2 and form stable water/steam soluble compounds
4. should be effective at extremely low treatment level
5. should not decompose or change its chemical properties at high temperatures and pressures
6. should not boil at low temperature
7. should not react with feed water treatment chemicals.

Only morpholine satisfies the above prerequisites. Because of favourable distribution ratio to morpholine, very little is lost in blow down whereas losses in case of cyclohexylamine is on higher side. The following table shows the merits and demerits of neutralizing amines.

	Ammonia	Cyclohexyl-amine	Benzyl-amine	Morpholine
Distribution Ratio parts in steam to parts in condensate	7-10:1	2-4:1	3-4:1 ^d	0.4:1
Dosage to adjust pH of pure water to 9.0				
ppm in water	0.2-0.5	2.0	2.2	4.0
ppm in steam	1.4-5.0	4-8	6.6-8.8	1.6
Dosage to adjust pH of condensate to 7.4	-	2.0	2.21	1.95
ppm/ppm of CO ₂				

The superior distribution ratio of morpholine is obvious from the table. It is the only one in which the concentration in the condensate is greater than that in the steam. It is relatively stable upto 2500 psi and 649°C. It is very effective in controlling metal pick-up.

Another approach to the prevention of corrosion of steam condensate and return line is to use film forming inhibitor. The use of long chain nitrogenous compounds as film formers for condensate and return lines has been found to be very successful. Amongst film forming inhibitors, octadecylamine (C₁₈H₃₇NH₂) and its salts are very frequently used. octadecylamine does not function by neutralizing CO₂ in the system. It adheres to the metal surface and forms a protective film. Water condenses on such a surface in the form of droplets rather than as

a uniform film. The surface wetting is kept to a minimum since the protective hydrophobic organic film which is already present repels the water and acts as a barrier between metal and the corrosive condensate, thus protecting it from oxygen and CO₂ attack. The adsorbed film on the metal surface is believed to be substantially of monomolecular thickness. It is generally used as the acetate salt. Its wetting characteristics are improved by blending it with a suitable wetting agent and cyclohexylamine in the ratio of 90 to 9 to 1.

The use of film forming inhibitors becomes economical when the CO₂ content of the steam is very high so that the cost of sufficient neutralizing amine becomes excessive. The dosage of film forming inhibitor is independent of dissolved gas concentration. Typical dosages

of film forming inhibitors are recommended to be 5 to 20 ppm. Prior to the use of the inhibitor, it is better to clean the lines. This cleaning action is to improve heat transfer as well as impart corrosion inhibition.

Other film forming inhibitors which have been patented include the followings:

1. Reaction product of an organic carboxylic acid and a polyamine e.g., oleic acid, tall oil and diethylene-triamine⁽⁸⁾
2. Mixture of octadecyl alcohol and stearamide
3. Imridazolines.⁽⁹⁾

Control of Dissolved Oxygen

It is accomplished chemically by the use of either sodium sulfite or hydrazine. Catalysed sulfite is also used. Catalysts employed are very small amount of salts of copper or cobalt. Speller⁽⁴⁾ states that about 8 lb of Na_2SO_3 are required to remove 1lb of oxygen. 20 to 40 ppm of Na_2SO_3 are recommended for scavenging oxygen completely, but still some oxygen is left dissolved in water. For high pressure boilers, 100-140 ppm of Na_2SO_3 are recommended. Also, for high pressure boiler, both vacuum and pressure de-aeration followed by addition of O_2 scavenger to reduce the dissolved oxygen of the feed water to 0.005 ppm are practiced. The disadvantage of using Na_2SO_3 is that it decomposes to form SO_2 or H_2S in high pressure equipment, thus

appreciable increasing the corrosion rates in the steam fed water cycle. It also loads the systems with dissolved solids (Na_2SO_4), thereby requiring frequent blowdown. The catalysts used along with Na_2SO_3 plate out in boiler tube, thereby promoting pitting. In view of these drawbacks of Na_2SO_3 , hydrazine hydrate has been considered alternative to Na_2SO_3 . The reaction between hydrazine and oxygen has been stated to be the following:



It is reported that hydrazine decomposes thermally or at pH 8.0 with the liberation of ammonia which affects non-ferrous metals. However, hydrazine has edge over the Na_2SO_3 . It does not increase the solids in the feed water and does control the alkalinity by use of proper excess of hydrazine. Finally, the cost is relatively low, the removal of oxygen is more efficient than by the use of Na_2SO_3 , much small dosage levels are required, and it is used in wide spectrum of pressures ranging from 400 to 2500 lb/in². But, it is toxic in nature.

In recent years, alternatives to hydrazine for oxygen removal in boiler system have been introduced. Diethyl hydroxylamine, a new technology, has been shown to be an effective oxygen scavenger for both feed water and condensate systems within the boiler cycle.^(5,6) It has also been shown to be a strong metal passivator. Another recent oxygen scavenger is based upon NNN'N' tetramethyl-1, 4-phenylenediamines.⁽⁷⁾

Table - 3

Corrosion Inhibition

Condition : Cl - 300 ppm; Exposure - 4 days; Temp. : 80°C

Conce. of Inhibitor	Corrosion Rate (mpy)	%I.E.
0	26.10	-
30	1.20	95.4
40	0.52	98.0
Proprietary Inhibitor		
40	1.41	94.59

Inhibition of Scale Formation

Condition : T.H - 1230 (CaCO₃); pH - 6.4-8.5; Temp. : 90°C; Time : 15 days

Conce. of Inhibitor	% Scale Inhibition
30	96.0
40	98.8
Proprietary Inhibitor	
40	90.0

Consumption of Treatment Chemical is Less

It provides oxygen scavenging capabilities, metal passivating capabilities and volatility such that condensate system in an operating boiler are protected.

The oxygen scavenger developed at NML is very fast in removing dissolved oxygen. It is based on Pyrazolidone. The details are shown in Table - 3.

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