Boiler Water Problems and Its Causes

Water is the essential medium for steam generation. Conditioning it properly can increase the efficiency of boiler and as well as extend the boiler’s life. Treating boiler water also insures safe and reliable operation: without proper treatment, severe problems can develop, some so severe that boiler itself can be destroyed. Boiler water problem generally falls into classes: deposit related and corrosion related. Because the two often interact, it is very common to find a boiler experiencing both simultaneously. There are many instances where deposit causes corrosion and corrosion causes deposits. The other problem is of steam purity.

Therefore the aim of the boiler water treatment is
1) To prevent the formation of scales and deposits on heating surface
2) To prevent corrosion in the boiler and steam system.
3) To maintain high level of steam purity.

The pressure and design of boiler determines the quality of water it requires for steam generation. The sequence of treatment depends on the type and concentration of the contaminants found in water supply and the desired quality of finished water to avoid three major problems in boiler systems – Deposits, Corrosion and Carryover.

1. Scaling

One of the aims of boiler water treatment is to prevent the formation of scales and deposits in the boiler systems. Scale can be prevented by external method or by conditioning with internal treatment. At times combination of both external and internal treatment is done.

Water gets evaporated due to high heat transfer rate. This concentrates the water and scale precipitates. The type of scale will depend upon the chemical composition of the concentrated water.

Scales formed in boiler systems can be divided into four groups:

a) Scale due to calcium & magnesium
b) Scale due to iron oxide
c) Scale due to copper
d) Scale due to silica

The combination in which they exist will not be same. It will vary from boiler to boiler. In some boiler the scale can be due to Calcium and in some due to Iron.

Scale forms as the solubilities of the scale forming salts in water decreases and the temperature and concentration increases. When feed water temperature is elevated to boiler water temperature, the solubility of scale forming salt is decreased, and solid scale begins to form on the boiler system. Thus we can say that Scale formation is a function of two criteria

a) The concentration and solubility limits of the dissolved salts.
b) The retrograde solubility (inversely proportional to temperature) characteristics of some salt.
Causes of deposit formation
Boiler deposits result from the impurities carried in with feed water. Their source is either make up water containing mineral salt, condensate containing process contaminants, corrosion products or in the case of condensers – in leaking cooling water. Deposits can also be formed due to the internal chemicals used.

2. Corrosion
Corrosion is the destructive attack of metal by chemical or electrochemical reaction. Corrosion is always because of chemical reaction. Physical deterioration is termed as erosion, wear or galling. Deterioration can be due to both chemical and physical attack.

Water corrosiveness is determined by the impurities present in it. Oxygen, dissolved solids, and dissolved acids in water attack the common construction material. Alkali can also be corrosive, at high temperature, as in boiler.

Problems due to corrosion
1. Thinning of metal
2. Development of crack
3. Pitting of metal
4. Metal perforation
5. Interference with heat transfer
6. Contamination of water

Corrosion is a complex problem and many factors influence corrosion. The factors to be considered are physical, chemical and biological.

Factors influencing corrosion

Physical Factors
1. System construction
2. System Pressure
3. Temperature
4. Flow Velocity
5. Water Chemistry

Chemical factors
Chemistry plays a very important role in corrosion. We have already explained earlier that corrosion is electrochemical reaction and is influenced by chemical factors like pH, alkalinity, dissolved salts and others.

a) Alkalinity

Alkalinity in water is due to presence of Bicarbonates, carbonates and hydroxyl ions. In raw water alkalinity is mainly due to bicarbonates. Some times carbonates ions may also be present.
Carbonates and particularly hydroxyl ions are rarely encountered in untreated waters. Hydroxyl ions normally get introduced during treatment of water. Alkalinity is determined by using standard acid solution using methyl or phenolphthalein indicator. Alkalinity determined by using methyl orange indicator is termed as M-Alkalinity or Total Alkalinity. P-Alkalinity is determined by using phenolphthalein as indicator. The different type of alkalinity present in water supplies can be calculated from M and P-Alkalinity value determined by titration. Alkalinity is the ability of natural water to neutralize acid. This happens because of buffering mechanism. Alkalinity in raw water is primarily composed of bicarbonates and carbonates. Acid compounds having free h+ ions react with CO3 and HCO3 ions and conversely Oh ions also reacts with CO3 and HCO3 ions.

\[
\text{CO}_3^{2-} + \text{H}^+ \rightarrow \text{HCO}_3^- \\
\text{HCO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{CO}_3 \\
\text{HCO}_3^- + \text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}
\]

In either case acid or base is neutralized by the carbonate or bicarbonate. Thus it can be seen that when Acid (or caustic) is added to water having high concentration of bicarbonate or carbonate the pH of water does not change much compared to when the same amount of acid (or caustic) is added to pure water. This is known as buffering capacity.

b) pH

When pure water dissociates, the number of hydrogen ions is equal to number of hydroxyl ions. Such a solution is called neutral solution. pH is defined as negative logarithm of H+ ions. Solution having pH less than 7 are acidic and those greater than 7 are basic. Low pH is Corrosive and high pH is protective to pipe. Very high can cause scaling and deposits.

c) Dissolved Oxygen

Oxygen is considered has one of the most corrosive components in water chemistry. Dissolved O2 with traces of chlorides or solids can cause pitting corrosion of metallic surface. The resulting condition may be severe, even at low pressure.

d) Dissolved Solids

Dissolved solids or salt content of water present as ion increases electrical conductivity of water. Higher the conductivity, greater the potential for corrosion. Some salts like CaCO3 are involved in scale forming and thereby reducing corrosion.

e) Hardness

Hardness is generally associated with scale forming. Hardness is composed primarily of Ca & Mg ions but may also include other metallic ions like iron and manganese. All hardness ions have the property of forming scales. One of the methods for corrosion control is by planned deposition of CaCO3.
f) Chloride & Sulphate
Chloride and sulphate ions inhibit the formation of scale by keeping hardness ions in solution. Trace amount of Chlorides even with dissolved oxygen can cause corrosion in boiler.

Type Of Corrosion

The type of corrosion classified with respect to outward appearance or altered physical properties are

Uniform attack
Pitting
Cavitation erosion
Dezincification & parting
Intergranular corrosion
Cracking

Oxygen Corrosion

Water coming out of deaerators has residual oxygen. As explained earlier even a trace amount of oxygen can cause corrosion. This last trace of oxygen is removed chemically. Sodium sulphite and hydrazine or one of its product is used for removal of residual oxygen. Sodium sulphite is used for low pressure boiler. Amine is preferred in high pressure boiler because it does not add to TDS, unlike Sodium sulphite.

Effect of pH

Both high and low pH can cause corrosion in boiler. In acidic range the protective layer of magnetite is not able to form and it cause corrosion. In very high pH range the protective layer of magnetite breaks down and this leads to caustic corrosion. For corrosion prevention maintaining proper pH and alkalinity is very important.

Acid Corrosion

Excess acid cause damage at more rapid rate than excess base. Simply because this happens, it should not be taken as an operating guideline. Magnetite film forms due to corrosion but once formed adhere tightly and acts as a barrier between boiler water and steel. Acids are capable of destroying this film and hence water chemistry must be so maintained that the protective film is not disrupted. This can be done by keeping the water in alkaline range.
Caustic Corrosion.
Feed water is maintained at alkaline pH. Alkali is added to provide optimum pH in the feed water to prevent corrosion of piping and equipment. Caustic soda (sodium hydroxide) is generally added for this purpose. Sometimes sodium carbonate is also added. Even though caustic soda is added with control, there are occasions when pH increases and cause corrosion as shown by the equation below. The damaged caused by excess alkali is because it dissolves the magnetite film forming sodium hypo ferrite and sodium ferrite both of which are soluble in hot concentrated caustic soda. In addition concentrated reacts directly and more rapidly with iron to form hydrogen and sodium ferrate.

\[
\text{Fe}_3\text{O}_4 + 4\text{NaOH} \rightarrow 2\text{NaFeO}_2 + \text{Na}_2\text{FeO}_2 + \text{H}_2\text{O}
\]

\[
\text{Fe} + 2\text{NaOH} \rightarrow \text{Na}_2\text{FeO}_2
\]

Caustic attack on boiler can two forms - Gouging or cracking. Caustic cracking is also known as caustic embrittlement.

Caustic gouging causes deep elliptical depression in boiler metal surface. This occur in areas of high heat flux or under heavy porous deposits. Underneath these deposits, boiler water can concentrate to the point where high concentrate of caustic can accumulate causing a localized corrosion. This action can be rapid.

Boiler water chemistry if properly maintained will prevent caustic gouging.

Caustic embrittlement or cracking is a form of stress corrosion. Cracks occur rapidly and are often undetectable leading to sudden failure of boiler –at times causing a violent failure. All parts of boiler are subjected to this type of corrosion. The only way to stop this type of corrosion is to prevent high concentration from forming.

Caustic corrosion is generally confined to
a) Water cooled tubes in region of high heat flux.
b) Slanted and horizontal tubes.
c) Location beneath heavy deposits.
d) Heat transfer region at or adjacent to packing rings.

Caustic corrosion is prevented by coordinate caustic program. Phosphate ions act as a buffer ion. It does not allow pH to increase in water, no matter how concentrated OH ions become. Buffer ions are also useful in avoiding similar high OH concentration which leads to stress corrosion cracking (caustic embrittlement). In low pressure boiler sodium nitrate is added in a definite ratio to caustic alkalinity to prevent caustic embrittlement.

Galvanic corrosion
We have already explained what galvanic corrosion is. A metal or alloy if it is electrically coupled, galvanic corrosion occurs. Corrosion by copper is the most common form of galvanic corrosion in boiler system. Copper can be carried from pre boiler section. Water deposits copper as decomposition of bicarbonates or as ammonia complexes. Pitting of boiler tubes has been reported due to copper deposit.
Iron Oxide deposits

In boiler the steel reacts with water in absence of oxygen to form a magnetite film. This film than acts as a protective layer for further corrosion. Iron oxide also enters with feed water into boiler as corrosion product. This layer is very porous and can be easily penetrated. This allows boiler water to seep through and flash into steam leaving behind dissolved solids which concentrates in localized areas. This excessive concentration can lead to metal dissolution and metal failure.

Condensate corrosion
Steam generated in boiler is transported to point of use through pipes. Steam condensate is also returned to boiler feed water. Corrosion of steam lines and condensate return line occurs because of the low pH. The chief source of acid in steam is carbon di oxide. High temperature and pressure decomposes alkalinity to carbon di oxide, some of which dissolves in steam making it acidic. This lowers the condensate pH and leads to corrosion of return lines. Oxygen can enter a condensate system from other sources even if the deaerator is functioning properly. Oxygen causes a deep pitting of condensate lines.

High Velocity and low pH can result in extremely severe corrosion conditions. The best way to minimize this is by keeping the pH above 9.0 Other gases which can be corrosive in the condensate system are Ammonia, Hydrogen sulphide and sulphur di oxide.

Impure steam can create problems of carryover, priming and foaming in boiler. Steam gets contaminated because of the boiler water it carries with it or because of salt and silica which are, soluble in steam at high pressure. Solids carried over with steam can get deposited on super heater and turbine. Carryover can also effect the product quality.

3. Carryover
Carryover is defined as contamination of steam with droplets of boiler water. Carry over can be due to entrainment of water drops in steam or due to property of certain salt like silica in boiler water to get vaporized and get into steam.

The factors responsible for carry over are
a) Amount of dissolved solids in boiler water.
b) Chemical nature of dissolve solids.
c) Suspended solids in boiler water
d) Boiler design
e) Boiler operating condition

Many factors, both mechanical and chemical contribute to carryover.

Mechanical Causes
Boiler design & operating conditions plays an important role in carryover. Without going into details we can say that major design & operating factors responsible for carryover are :

a) Design pressure
b) Steam drum size
c) Design generating rate
d) Circulation rate.
e) Arrangement of down comers and risers
f) Type of mechanical separating equipment.
For example even when the TDS is within the limit, carryover can still occur because of change in operating condition. For example sudden increase in steam demand may lower the steam header pressure. This reduces drum pressure and water in the drum gets mixed with steam bubbles and the level rises. The rise in the drum level can cause carryover.

**Chemical Causes**

*Priming* and *foaming* are two terms used with carryover. Priming is the surging of water in the steam outlet and is caused by factors like high water level in boiler, steaming rate, load fluctuations and boiler design. Priming is thus due to mechanical factors.

Foaming is formation of stable bubbles. The bubbles don’t break because of high surface tension. Causes of foaming are:

1. High Alkalinity: Caustic soda (NaOH) or sodium carbonate (Na2CO3) have greater influence on foaming than neutral salts.

2. High TDS: High TDS causes carryover. For a given boiler design and a given set of operating condition, there is a limiting dissolved solid content above which a serious steam contamination occurs. Reducing blow down by small amounts every few days and measuring steam purity this limiting TDS value can be found out. This value is found by keeping boiler operating conditions and other operating variables such as feed water composition and treatment constant. If a graph is plotted between conductivity of condensed steam & boiler water TDS the limiting figure is that corresponding to slightly less than where steam quality deteriorates.

3. Suspended solids also cause foaming

4. Oil is not present in boiler water. It can enter boiler system through leaks in condenser or other heat exchanger. Oil can also system because of lubrication of steam driven reciprocating equipment. Oil is undesirable in boiler for two reasons
   a) It acts as binder to form scale
   b) It also causes foaming. Even a very small amount can cause severe foaming and hence immediate action should be taken for complete removal of oil.
   c) Silica is another chemical which causes carryover. This is dealt separately.

### 4. Silica Deposition

All natural water contains silica. Like calcium and magnesium silica also forms scale. Removing silica from water is more difficult than removing Hardness (calcium and magnesium). At high temperature Silica volatizes and gets carried into steam and forms hard coating on turbine blades. Silica can form various kind of scale such as amorphous silica or magnesium Silicate. Amorphous silica scale forms like a glassy deposit which is very difficult to remove. Hydrofluoric acid is used to remove such scales. Silica scale is generally found in low pressure boiler because only softener is used and softener does not remove silica. Silica is not considered to be a big problem in low pressure boiler.