CHAPTER - 18
Boiler Chemical cleaning process & Erosion and corrosion control

Corrosion in Boilers:
Introduction:
Corrosion accounts for 50% of the forced outages in utility boilers. Corrosion problems are considered at the designing stage, but they are likely to become more severe than anticipated during service, and failure occurs. Corrosion means deterioration of metal by chemical or electro-chemical action within certain environments. In this section we will deal with the problems related with fire side and water side corrosion. We will discuss about other types of corrosion during the discussion of “Boiler Tube Failure”.
Most boiler tube failures are caused by problems on the waterside, but corrosion of boiler tubes from the fire side can also cause severe operational problems. The principal fire-side corrosion mechanisms are “hot-end” corrosion caused by sulfur and vanadium compounds and “cold-end” corrosion caused by acid-dew point sulfur. Fire-side and water side corrosion mechanisms can be identified by a combination of metallurgical and laboratory analysis.

Fire side Corrosion:
Fire-side corrosion is a potentially serious problem that can significantly compromise boiler operations. There are three major forms of fire-side corrosion in operating boilers: (1) “fuel-ash” or “hot-end” corrosion, (2) waterwall fire-side corrosion and (3) “cold-end” corrosion. A brief outline of these three principal types of corrosion damage follows.

Fuel-ash corrosion:
The presence of sodium and vanadium in the fuel is a major concern. In addition to vanadium pentoxide acting as a catalyst for the formation of sulfur trioxide, both vanadium and sodium compounds can cause fuel-ash corrosion. This form of corrosion occurs when sodium and vanadium oxides form a range of low melting-point hard scale deposits. These hard scale deposits penetrate the protective oxide scale and expose the underlying metal surface to rapid corrosion attack. Hard scales of Na2O and V2O5 have melting points as low as 995°F (535°C). These hard scales form corrosive slags and the subsequent wall thinning can rapidly result in failure of tubes due to creep rupture. Vulnerable locations where fuel-ash corrosion can occur are the high-temperature areas of the boiler, such as superheater and reheater sections, where the metal temperatures may sometimes exceed 1,100°F. Nowadays, the potential risk of fuel-ash corrosion has tended to limit maximum steam design temperatures to the 1,025-1,050°F (538-551°C) range. Fuel-ash corrosion may affect tube support and attachment equipment, which operates at higher temperatures than the tubes, as the latter are cooled.
Waterwall Fire-Side Corrosion:
Waterwalls fireside corrosion is associated with reducing conditions in the firebox. Incomplete combustion combined with sulfur from poor-quality fuels, results in the formation of Sodium and Potassium Pyrosulfates (Na$_2$S$_2$O$_7$ and K$_2$S$_2$O$_7$). When these compounds are present as molten slags, they can flux the protective magnetite, causing rapid oxidation and wall thinning of the tube metal. Since the Pyrosulfates are in a molten form at around 800°F (427°C) or less, this form of corrosion usually occurs only in the cooler boiler tubes, such as waterwall tubes.

Cold-end corrosion:
When high-sulfur-containing fuels are burned, the sulfur compounds are oxidized to form sulfur dioxide. Sulfur dioxide reacts with small amounts of atomic oxygen in the flame to form sulfur trioxide. Catalytic oxidation to sulfur trioxide also occurs in the presence of Vanadium penta-oxide (V$_2$O$_5$). Sulfur trioxide then reacts with any moisture present to form sulfuric acid. Once the temperature of metal in the boiler falls below the dew point for sulfuric acid, sulfuric acid mists deposit on the metal and cause severe corrosion. The dew point for sulfuric acid is dependent on the percentages of moisture and sulfur trioxide in the flue gas.

The following equations summarize the chemical reactions:

1. $\text{S} + \text{O}_2 \rightarrow \text{SO}_2$
2. $\text{SO}_2 + \text{O} \rightarrow \text{SO}_3$
3. $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$ ($\text{V}_2\text{O}_5$ catalyzes this reaction)
4. $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$

The deposit samples are dark gray/black in appearance. XRD and XRF provided the elemental and phase compositions of the solids. The primary constituents of the sample from the tube are mixture of complex hydrated iron sulfates.

The presence of sulfuric acid and iron sulfates is indicative of a type of corrosion termed cold-end corrosion. The most likely source of the sulfur is the fuel. When sulfur-containing fuels are burned, the sulfur compounds are oxidized to form sulfur dioxide and sulfur trioxide (equations 1-3 above). When the temperature drops below the sulfuric acid dew point, high rates of corrosion can occur, especially beneath tube deposits.

A solution for eliminating the sulfur compound is only to burn better-quality fuel. Since the fuel also contains sodium and vanadium, which could cause problems elsewhere in the boiler, this would be a particularly good way of mitigating the problem.

An alternative suggestion will be to make operational changes. Reducing the excess air to the burners to below 5% will minimize the conversion of sulfur to sulfur trioxide.

To keep the back-end temperature of the boiler always above the acid dew point temperature. Raising back-end temperatures will, however, decrease the
boiler efficiency, and any such measure should be carried out with judicious balancing act.

Another option is to add neutralizers to the combustion chamber in a finely powdered form with a compressed-air carrier. Usually, these additives are a proprietary mix of compounds such as magnesium oxide, magnesium carbonate, zinc copper oxide and carbon. Fuel additives can help neutralize cold-end deposits and also control slagging by producing deposits with higher melting points that are dry and removable by sootblowing.

Close-up view of tube pit
Fig. 1

Microsection of pit (original magnification 16X)
Fig. 2
Boiler water side corrosion:

pH and its relevance to water chemistry:

pH value influences the corrosion rate in a varied manner depending upon whether the metal is noble or whether its oxide is soluble in acids but insoluble in alkalis. In a power plant operation, we are concerned with corrosion of iron and alloys of copper. To combat corrosion a close pH control is important in addition to elimination of oxidants and oxide solvents. This further depends upon the temperature and pressure parameters the water/steam is subjected to. In order to control and restrain corrosion, different pH range would be necessary depending upon temperature, pressure and velocity of the water/steam and the metallurgical composition of the equipment.

In the pre boiler portions we have predominantly copper alloy components where temperature and pressure parameters are not very high. In the main boiler, the steam generating surfaces are mostly of carbon steel, while super heater and reheater elements are of alloy steel. Too low a pH will result in iron corrosion, while too high a pH will result in copper corrosion.

pH in pre boiler area:

Condenser and L.P. heater elements are made of brass / cupro-nickel alloy material with varying composition. Condenser tube composition is mostly based on cooling water characteristics. But composition of air cooling zone tubes might vary from main condenser tubes in order to provide corrosion resistance properties. In air cooling zone, concentration of gases like CO₂, O₂, N₂H₄ and NH₄OH will be more and such corrosion resistance property has to be in-built metallurgical. Normally the following alloys are employed for the construction of heat exchangers.

Brass, Aluminium brass, admiralty brass, cupro-nickel alloys of 70 - 30, 80 - 20, 90 - 10 composition , monal metal etc. Alloy and selection of material depend upon design concept and duty parameters. So, to avoid corrosion and pickup of copper and iron from condenser and carry over to Deaerator, we have to
maintain pH to a suitable level. In order to render brass surfaces less susceptible to corrosion, the surfaces have to be reduced to a passive state.

This is achieved by the formation of a thin and adherent copper oxide layer on the surface. If this oxide layer has to be maintained, feed water should be free from oxygen and carbon dioxide. It should possess adequate pH value; a pH between 8.5 to 8.8 is found to be adequate for return condensate. This is mostly maintained by hydrazine, ammonia and neutralizing amines. A pH value higher than the range recommended would result in an attack of the passive cuprous oxide and dissolve the layer opening the surface to further attack, more so in the presence of oxygen. It is therefore, essential to restrict the pH to 8.5 to 8.8 range for return condensate. If ammonia concentration increases, it results in copper attack and series of problems.

The corrosion resistance of copper is due to its being a relatively noble metal. The formation of cuprous oxide, the passive layer, is all that is important. However, if ammonia concentration increases, specially in the presence of oxygen, copper gets corroded rapidly with the formation of complex ions. Oxygen oxidizes cuprous oxide to cupric state, which is not adherent and passive. This results in the formation of highly soluble copper ammonium complex, thus exposing metal surface to attack. In other words, in the corrosion of Electro positive metals such as copper, the ease with which the anodic process can occur is all important. When the anodic process is possible as in the presence of complexing agents, a high rate of attack can occur, only when a strong cathodic de-polariser such as oxygen or rather an oxidant is present. Hence, where copper alloy heaters are provided in pre boiler system the pH of return condensate should be restricted within a limit of 8.5 to 8.8 which in turn will limit the level of ammonia. Even in a well maintained plant where condenser performance is good, oxygen to the tune of 0.02 ppm would be restricted to a maximum level of 1 ppm. In order to combat oxygen in pre Deaerator portions, hydrazine, is also introduced in the outlet of condensate extraction pump. This not only prevents oxidation of cuprous oxide layer but also maintains pH of the Deaerator feed water. In case tube material of high pressure heaters are of cupro-nickel alloy, feed pH should not to exceed 9.0. If the elements are of steel, to prevent iron going into solution pH should be closer to the upper limit. Deaerator performance should be maintained to control oxygen level in feed water. This is precisely why return condensate pH is towards lower limit and feed water after Deaerator is towards upper limit.

**pH and boiler water :**

So far as steel surfaces are concerned, more specifically on the steam generating tube surfaces in boiler, passive state is created by the formation of magnetite layer ($\text{Fe}_3\text{O}_4$). Our aim should be to preserve This passive and protective layer must be protected to remain intact.

The layer remains intact provided the following conditions are met:

a) Boiler water remains alkaline.
b) Boiler water pH value is kept within 9.5 - 10.5. (Finer values depend on pressure and temperature parameters)
c) No oxygen enters the system.
d) Unit is not subjected to much thermal shocks.
e) There is no deposit accumulation to encourage concentration mechanism.
f) Boiler water is free from chloride contamination.
g) There is no free hydroxide alkalinity.
h) Sufficient minimum OH ions present to promote magnetite formation and growth.
i) No accumulation of copper/nickel deposits due to pre boiler corrosion.

Magnetite layer is resistant to corrosion and remains intact without getting dissolved at a pH range between 9.5 - 10.5. When the pH value falls below 9.0 the layer is attacked. Formation and growth are then retarded opening the metal surface to attack. When the pH is high due to the presence of free hydroxide alkalinity, caustic soda gets concentrated converting magnetite to soluble ferrite. This exposes metal surface to attack, ultimately resulting in metal failure. It is therefore necessary to limit pH and avoid formation and concentration of sodium hydroxide to protect passive oxide layer.

Caustic Corrosion:
As pressures increase, film boiling and other causes of local overheating are most prevalent. This has led to the phenomenon known as caustic corrosion. Over concentration of sodium hydroxide destroys the protective magnetic iron oxide film (magnetite-Fe₃O₄), and the base metal is then attacked by the concentrated sodium hydroxide as shown in the following two equations:

\[
\begin{align*}
4\text{NaOH} + \text{Fe}_3\text{O}_4 & \rightarrow 2\text{Na}_2\text{FeO}_2 + 2\text{H}_2\text{O} \\
2\text{NaOH} + \text{Fe}^0 & \rightarrow \text{Na}_2\text{FeO}_2 + 2\text{H}^0
\end{align*}
\]

Caustic corrosion manifests itself as gouging and is fairly easy to identify. The tube does not lose ductility and, unless arrested, the gouging proceeds until thinning eventually causes tube failure.

It is generally accepted that caustic concentration in excess of 50,000 ppm or 5% is necessary for the above reactions to occur. While there is never caustic present to these levels in the bulk boiler water when using precision control, the concentrating mechanism at the tube surfaces that can occur above 900 psig limits its use to lower pressures.

The maintenance of clean boiler metal surfaces is a prerequisite for the prevention of caustic attack. Feedwater hardness, iron and copper should be kept at sufficiently low levels. Under ideal conditions, feedwater should contain no hardness, although this is not always possible as a result of inadequate performance of primary water treating equipment, condenser leakage, or other types of steam and condensate contamination.

Frequently, for boilers operating above 600 psig, the primary constituents in boiler deposits are metal oxides. Therefore, it is essential to maintain
adequate control over preboiler and after boiler corrosion. In addition, the use of condensate polishers may be desirable. Precommission cleaning of high pressure boilers is critical. It is essential that every tube and the associated feedwater and condensate systems be thoroughly cleaned. The presence of tramp iron, copper and silica can cause deposits and corrosion on startup.

**Erosion:**
Erosion is a term used when metal is attacked by the abrasive action of liquid, vapour or gas. Solid particles in flue gas which erode the boiler tubes is a well known factor. Tube surface deterioration by soot blowing action is also a common case of erosion. Tubes are externally eroded by soot blowing action when some gritty substance impinges on tube surface. When the blower nozzle is deranged, instead of discharging a diffuse spray, it is concentrated on an area of an individual tube. Once the outer skin is broken, the sand blast effect of the jet of the steam thins the tube wall and when it becomes too weak to support the pressure, raptures occurs. Hence periodic inspection of tubes in the way of soot blowing becomes essential and the corrective actions should be taken if the nozzles are found deranged.

Erosion is accelerated where the flow is restricted or when the direction of the flow is changed. Erosion is noticed at inlet or outlet nozzles fitted to vessels or elbows and valves, where flow is changed or reduced. Erosion by wet steam in the turbine blade where surface films break is a possibility. Steam containing particles may also cause the damage. Cavitation is also a form of erosion which is a form of vaporization in a rapid steam. Static pressure in a closed stream of fluid reaches an upper limit as soon as the absolute pressure becomes equal to the vapour pressure of the fluid. When this happens, the fluid vaporizes, forming pockets in the stream that disturbs the flow which by their subsequent collapse destroy the surrounding walls.

Weld spatters and icicles in the welded joints may also cause an erosion problem. Proper design and introducing materials resistant to wear may reduce erosion attack.

**Chemical Cleaning Of Boiler**

**Introduction:**
The interior surfaces of boilers are contaminated in course of erection with dust, sand particles and comprise mainly of silica, weld splash and mill scale etc. The steaming out of boilers will remove the loose surface deposits but not the bound mill scale. In order to avoid the possibility of damage of turbine blades due to these deposits in the steam generators the chemical cleaning of the boilers is reliable method prior to commissioning.

Water chemistry plays a significant role in boiler operations. However much clean is the water used for evaporation in the pressure parts, it is predictably seen that there is build up of scale on water side. If water quality is not given due care, the results are going to be worst. Deposits that form on the tube surfaces inhibit heat transfer and reduce boiler efficiency. The objective of a chemical cleaning is to safely remove all the deposits from the inside of the
boiler tubes. In low-pressure boilers, chemical cleaning typically removes calcium carbonate and other hard adherent scales. In higher-pressure boilers, the major deposit removed is magnetite and some copper. Chemical cleaning can improve the boiler heat rate and reduce the number of tube failures. It typically improves the stability of boiler chemistry. However, there also are down sides to chemical cleaning.

Online chemical cleaning programs are difficult to control and their results are unpredictable. Consequently, industry prefers offline chemical cleaning. The offline cleaning process is really expensive and oft late it has become too expensive with environmental restrictions stipulated in disposal of water with harmful chemical products. The frequency of cleaning will decline, if due care is taken to improve feed water quality.

Pre-Commissioning Cleaning:
The method of cleaning the boilers prior to commission consists of:
(1) Flushing with water to remove as much loose deposits as possible.
(2) Boiling out to remove traces of oil and grease.
(3) Main acid wash to remove mill scale and weld splash.
(4) Weak acid rinse to prevent iron from being thrown out of solution.
(5) Flushing with water to remove loose deposits.
(6) Passivation & Preservation.

Flushing with Water:
The boiler is first filled with water & then drained quickly to waste so that the water flush should remove as much loose material as possible.

Boiling Out:
Boiling out must be carried out as suggested by the manufacturer and under the supervision of an expert in the field. The boiler should be filled with D.M Water/soft water to some point below the bottom of the steam drum manhole. After the boiler is filled generally a weak solution of Tri-sodium phosphate or Soda should be added to the steam drum through the manhole. Or the regular chemical feed system may be used. After the addition of boiling out solution the boiler has to be prepared for firing as per normal start up procedures. The pressure of boiler should be brought to 21 Kg/cm² or to 1/5 of design pressure whichever is lower within 8 hours, thereafter the pressure be kept constant for 4hours. In order to assure that all part of the unit have been boiled out thoroughly the temperature of lower header should be observed. During the operation the feeding rate is maintained to keep normal level in the drum. Care must be taken to keep the furnace outlet flue gas temperature of superheater/reheater within limits.

The boiler is to be operated at least for 12 Hrs at this pressure continuously and blow down should be given after every two hours through all low point drains. After every blow down, drain samples are to be analyzed for phosphate, Ph, alkalinity, oil, conductivity and silica. Due to heavy blow down the Phosphate and alkalinity value may be depleting fast. To avoid phosphate
content to drop below half the initial value, further dosing of concentrated Phosphate should be resorted through phosphate dosing pumps. Boil out process is completed only when oil in blow down sample completely disappears. If two consecutive drain samples analysis are found to have no oil or only traces of oil content, the Boil Out operation may be declared over and terminated.

**Main Acid Wash:**
The main acid wash follows next and inhibited hydrochloric acid is normally used. At this stage no halogen chemicals are allowed in contact with austenitic steel parts, therefore only boiler is cleaned. In order to chemically clean the superheaters and/or reheaters etc. 3% solution of inhibited citric acid is used, an inhibited hydrochloric acid is undesirable for cleaning of austenitic steel parts because the residual chlorides gives rise to stress corrosion cracking. The main acid wash is based on using 5% solution (by weight) hydrochloric acid and 0.2% solution (by weight) approved inhibitor. Before admitting acid to the boiler, ensure that:
1) The superheater is full of condensate or demineralised water.
2) The furnace openings and dampers are closed.
3) All drum vent valves are open. Unless specifically mentioned, valves should be positioned as for boiling out.
4) All boiler blow down and chemical valves are closed.
5) The temporary boil out gauge is replaced or extended to permit observation of water level to the top of the steam drum.
6) Metal temperatures are observed & recorded. If hydrochloric acid is to be used, no metal temperature should exceed 80°C.

After attaining the metal temperature about 80°C fill the boiler up to the top of the drum with inhibited acid solution (5-6% hydrochloric acid). The temperature of the solvent is maintained between 80°C by blending the dilution water with steam. Test samples should be taken hourly and tested for acid strength & total iron concentration, approach equilibrium. Thereafter the acid should be drained from the boiler under a positive pressure of nitrogen (0.3Kg/cm²g).

Next the boiler should be filled to the top of steam drum with clear water at about 70°C. Simultaneously fill condensate of demineralised water to economizer and back flush superheater with condensate of demineralised water to discharge any acid which may have inadvertently entered the economizer or the superheater. The boiler shall be then drained under nitrogen as before.

**Weak Acid Rinse:**
The boiler is again filled with clear water at 70°C and about 0.1% to 0.2% by weight of citric acid is added to the water, to remove any ferrous chloride remaining on the metal surface and prevent iron hydroxide from being formed. Drain this under positive pressure of nitrogen.
After the weak acid wash has been drained, boiler is opened up for inspection and any debris lying in the drum and headers are removed before proceeding with remaining process.

**Flushing with Water:**
Fill the boiler to the top of steam drum with a neutralizing solution of water consisting of 1% by weight soda ash. Fire the boiler at low rate raising the pressure to 3Kg/cm$^2$ in two hours and held this pressure for two hour. At the end of 2 hours rinse period, the boiler should be allowed to cool gradually. During this period blow down the boiler intermittently to reduce turbidity. The solution level should be reestablished after each blow down. The drum vent should be opened when the pressure drops to 1.8 Kg/cm$^2$ and the boiler should be drained when the temperature fall to 90°C. The boiler should be refilled with condensate or demineralised water containing sodium sulphite 0.12 gms/litre, heated to 60°C upto the top of steam drum. After soaking for five minutes drain the water.

**Passivation & Preservation:**
After the acid cleaning, sodium nitrite should be injected into the system and circulated for 4.5 hours at 60°C. At the end of this period the system should be drained keeping all the vents & drains open. In the final step the boiler and superheater are filled with condensate or demineralised water containing 20 mgm/litre 100% hydrazine and the pH adjusted to 10 with ammonia. The unit should be pressurized (3-5 psig) with nitrogen.

**Precautions:**
Chemical cleaning should be done by experienced persons. The effectiveness of the inhibitor contained in the acid must be verified before admitting any acid into the boiler. A simple test would involve submerging an untarnished carbon steel specimen in a sample of the acid, which has been adjusted to the proper concentration and heated to 80°C. If one or more bubbles appear, rather than an occasional isolated bubble, the acid should not be used until adequate inhibitor is provided and the acid is proven safe by repeat test. Most of the inhibitors of hydrochloric acid are ineffective above 88°C and accelerated corrosion will occur if higher metal temperature is encountered. The temperature of at least 65°C recommended for effective cleaning and special care must be taken to established proper metal & solvent temperature. The warm up torches should be capable of delivering significant quantities of heat to the local areas of the boiler. Even with adequate circulation, this may result in locally high internal temperatures. For this reason, a boiler containing hydrochloric acid must never be fired.

**Post commissioning cleaning:**

**Standards for cleaning:**
Most standards use the deposit weight density from a tube sample to decide when a boiler should be cleaned chemically. Several methods can measure deposit weight density, and boiler users confirm that a consistent method is to be adopted. Some of the tools that can be used to determine the necessity for offline chemical cleaning include, boiler tubes / headers inspections, especially using a boroscope to view the generating bank tubes, deposit thickness and chemical analysis, boiler design and boiler operation history.

Before selecting a cleaning program, the deposit should be analyzed and matched with appropriate chemicals. Tables 1 and 2 are general guides to cleaning chemicals.

Table 1. General cleaning chemicals for boilers

<table>
<thead>
<tr>
<th>Cleaning chemical</th>
<th>Cleaning process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineral acids</td>
<td>Remove deposits by dissolution; must be inhibited to minimize base metal corrosion</td>
</tr>
<tr>
<td>Organic acids</td>
<td>Less aggressive but more expensive than mineral acids</td>
</tr>
<tr>
<td>Complexing agents</td>
<td>Form chelates and are safer than acids</td>
</tr>
<tr>
<td>Inorganic &amp; organic surfactants</td>
<td>Increase the solubilization of oils and greases; used primarily in pre-operational cleaning procedures.</td>
</tr>
</tbody>
</table>

Table 2. General boiler cleaning requirements and chemical options

<table>
<thead>
<tr>
<th>Cleaning requirement</th>
<th>Cleaning chemical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron oxide</td>
<td>Hydrochloric acid - lowest cost, must be controlled very carefully, with inhibitors.</td>
</tr>
<tr>
<td></td>
<td>Nitric acid - difficult to inhibit. Hence not used widely.</td>
</tr>
<tr>
<td></td>
<td>Citric acid - environmentally safe, but expensive and less aggressive than HCl</td>
</tr>
<tr>
<td></td>
<td>Formic / hydroxyacetic acid - Environmentally safe, less expensive and more effective than citric acid</td>
</tr>
<tr>
<td></td>
<td>Phosphoric acid - more expensive, less effective than hydrochloric acid</td>
</tr>
<tr>
<td></td>
<td>EDTA* - neutral to alkaline material, very effective method</td>
</tr>
<tr>
<td>Component</td>
<td>Cleaning Agents</td>
</tr>
<tr>
<td>-----------</td>
<td>-----------------</td>
</tr>
<tr>
<td>Hardness</td>
<td>Hydrochloric acid - lowest cost, must be controlled carefully</td>
</tr>
<tr>
<td></td>
<td>EDTA* - neutral to alkaline material, very effective</td>
</tr>
<tr>
<td></td>
<td>Sulfuric acid - difficult to inhibit, low cost, forms insoluble calcium sulfate scales</td>
</tr>
<tr>
<td></td>
<td>Sulfamic acid - slow acting, forms insoluble calcium sulfate scales</td>
</tr>
<tr>
<td>Copper</td>
<td>EDTA* - use ammonia salt instead of sodium salt.</td>
</tr>
<tr>
<td></td>
<td>Ammonium bromate - often used in a separate copper removal cleaning step</td>
</tr>
<tr>
<td></td>
<td>Thiourea, diethylthiourea - excellent for low concentrations of copper</td>
</tr>
<tr>
<td>Silica</td>
<td>Hydrofluoric acid - dangerous to handle</td>
</tr>
<tr>
<td></td>
<td>Ammonium bifluoride - excellent alternative to hydrofluoric acid</td>
</tr>
<tr>
<td>Pre-operational cleaning</td>
<td>Phosphate, di-sodium, tri-sodium - removes oils and greases</td>
</tr>
<tr>
<td></td>
<td>Potassium permanganate - removes oils and greases</td>
</tr>
<tr>
<td></td>
<td>Ammoniated citric acid - removes mill scale</td>
</tr>
<tr>
<td></td>
<td>Hydroxyacetic-formic acid - removes mill scale</td>
</tr>
</tbody>
</table>

* Ethylene diamine-tetraacetic acid (EDTA)

**Cleaning-process considerations.**

Most procedures use a combination of chemicals that address the primary constituents of the deposit. Mineral acids are almost always used with an inhibitor to minimize corrosion of the boiler base metal. However, if inhibited mineral acids are applied improperly, corrosion can occur.

Other considerations include the installation of temporary piping, valves, pumps, heaters and instrumentation (such as flow meters) to heat and circulate cleaning chemicals. The cleaning process should be carefully monitored to ensure that conditions conform to specifications and to document the amount of deposit removed via the spent cleaning chemicals. Once the cleaning is completed, the boiler must be flushed with a neutralizing solution and repassivated prior to returning it to service. Depending on the condition of the boiler tubes and the aggressiveness of the cleaning, tube repair may be required if thinned tubes leak on startup.

These procedures can also be applied to heat exchangers. Unfortunately, heat exchangers are seldom bypassed for offline cleaning, and the deposit is rarely sampled to properly select the cleaning solvent in most refineries and chemical plants. With proper preparation, heat exchangers and other jacketed vessels can be chemically cleaned offline.

**Process of Chemical Cleaning:**
The technological procedure for chemical cleaning is as follows.

**Water Washing:**
Before commencing alkali boil out, the Boiler is flushed with cold demineralised water as per the following procedure. The boiler is filled through economizer using boiler filling pump upto the top of the drum (care should be taken that the feed water does not enter superheaters). After filling, the water is drained in the shortest possible time by opening all the drain valves. This process is repeated two or three times till the water collected from drains are reasonably clear.

**Alkali Boil Out:**
This will be same as discussed above section.

**Rinsing After Alkali Boil Out:**
The rinsing after boil out is done after the boiler is considerably cooled, as described for water washing till the system is freed from alkali solution i.e. PH of the effluent should be equal to that of the water used for rinsing. Then the system is made ready for acid pickling, after water wall down comer orifice plate is fixed and nitrogen blanketing connection is made.

**Filling of Superheaters with Hydrazine Water:**
Hydrazine (200 ppm) and ammonia (to raise pH to 9.6) are added to DM water in dissolving tank and slowly pumped to superheaters. When the PH of water raises to 9.6 at connecting tubes from superheaters in drum, the connecting tubes are. The superheaters are kept under pressure (say 5 atm) throughout the cleaning process. Suitable arrangements have to be provided for pressuring superheaters during pickling if required.

**Acid Washing:**
The system is filled with DM water and circulation established. The temperature of DM water is raised and maintained at 65°C by admitted steam to dissolving tank. The charging procedure is as follows:
First, inhibitor is charged full and after few minutes the hydrochloric acid and ammonium bifluoride are charged simultaneously. The addition of chemicals should be completed within one hour to reach the required concentration of 4%.

Care should be taken to see that the hydrochloric acid concentration in the cleaning solution does not increase beyond 5% at pump suction.
During acid washing, the concentration of hydrochloric acid in the system is checked. Due to chemical reactions during washing process, the concentration of hydrochloric acid decreases rapidly at first and slowly afterwards and then it steadies at a constant value. Similarly iron value increase and attains a steady value. The constant values of hydrochloric acid and iron content denote the completion of acid washing. Then the system is drained under nitrogen blanketing and the drained acid is neutralized before disposal.
After draining the pickling solution completely, the boiler is filled with DM water. Circulation established, when uniform concentration of acid and iron is attained in the system, it is drained under nitrogen blanketing.

**Citric Acid Rinse:**
The system is again filled with water containing 0.2% by weight of citric acid. While filling the system with DM water and proportionate quantity of citric acid so as to give a uniform concentration of 0.2%. During this process steam can be admitted to raise the temperature to 55-60 °C. If required Ammonia can be added to bring up the pH of the circulating solution to 3.5-4.0. After attaining uniform concentration throughout the system, maintain circulation for one hour and drain the system under nitrogen blanketing.

**DM Rinses:**
Fill up the system with DM water. Establish circulation and maintain circulation for one hour. After one hour’s circulation drain the system under Nitrogen blanketing. During the rinsing operations check the drain samples for pH and Iron content. Repeat the rinsing operations till the Fe content of the solution drops down to less than 25 ppm and pH approaching to DM water pH.

**Soda Ash Washing:**
Fill up the system with DM water containing 1% weight of Sodium Carbonate. Proportionate amounts of Sodium Carbonate can be added while filling the system itself. After complete addition of chemicals and establishing circulation raise the temperature to 85 °C and maintain circulation for 4-6 hours at this temperature. Drain the system completely.

**Passivation:**
The object of passivation is to prevent corrosion since the cleaned surfaces are more susceptible for corrosion at a very fast rate. The corrosion is prevented by providing a thin layer of magnetite (I stage) which gets strengthened in the subsequent firing of the Boiler (II stage).

**First Stage Passivation:**
The system is filled with DM water and adjusted for circulation. The temperature of water is raised and maintained at 85 °C by external steam heating. pH of DM water is raised to 9.5 by adding ammonia and hydrazine is charged to get a concentration of 200 ppm. The solution is left to circulate for about 20 hours at a temperature of 95-90 °C. the hydrazine concentration is maintained at 200 ppm throughout the operation.

After 20 hours, the solution is drained hot from the system and left aerated by natural draft.

**Inspection of Preparatory Work for First Stage Passivation:**
The drum is inspected thoroughly and all loose debris cleaned manually. Ring header hand hole plate connections are removed and the header cleaned with water.
Reparatory Work For Second Stage Passivation:
The superheater plugs and Downcomer orifice plates are removed and the drum internals are refitted. All the provisional equipment are dismantled and original fittings and mountings are installed back. The boiler should be prepared for regular operations.

Second Stage - Passivation:
The chemicals viz., ammonia liquor, for raising the PH ppm are charged in the operating feed water tank. The boiler is filled with feed pump up to normal operating level in drum and lighted up with one or two oil burners. The steam pressure in drum is gradually raised to 40 atmospheres and maintained at that value. Water samples are taken from feed line to find out hydrazine concentration and PH value. The boiler is kept in service for 24 hours maintaining the hydrazine concentration not less than 20 ppm in feed water.

At the end of the process, the boiler is boxed up and allowed for natural cooling. At 1 or 2 atmospheres the superheater air vents are opened and at about 90°C (Drum temperature) the water in the system is drained & the system is left aerated by natural draft. The second stage passivation marks the end of the chemical cleaning process.

Risks involved in cleaning process:
When making the decision to clean a boiler with it should be remembered that chemical cleaning is:
- Very expensive process
- Potentially dangerous to personnel and equipment unless safety precautions are not taken properly
- An environmental and chemical spill risk
- A waste handling problem
- Time consuming, adding as much as a week to the end of an outage

A few years ago a power boiler was cleaned with ammoniated EDTA (ethylene diamine tetraacetic acid). The plant operators were unaware that chemical cleaning solution had found its way into the superheater and was not flushed out. When the unit went back on line, the chemical cleaning solution evaporated in the superheater and caused it to fail. Complete replacement of the superheater was required.

Disposal of the chemical cleaning solution also can be a problem. Recently during evaporation of the spent chemical cleaning solution in a utility boiler, the vendor allowed the solution to impinge on a riser tube, causing it to fail catastrophically. The resulting repair cost was mind blowing.

Another utility experienced a rash of catastrophic tube failures due to hydrogen Embrittlement. The failures followed an incomplete chemical cleaning with inhibited hydrochloric acid.
Considering these risks and costs, it is important to know when a boiler needs chemical cleaning. The only thing worse than not cleaning a boiler that requires it, after all, is the chemical cleaning of boiler that does not.
**Examples**

Q.1 Write short notes on any four of the following boiler problems, stating their reasons and remedial actions to be taken to prevent them;

External corrosion of boiler tubes

Ans. The sulfur compounds in fuel are oxidized to form sulfur dioxide and sulfur trioxide. When the temperature drops below the sulfuric acid dew point, high rates of corrosion can occur.

The presence of vanadium in the fuel is also a major concern. In addition to vanadium pentoxide acting as a catalyst for the formation of sulfur trioxide, both vanadium and sodium compounds can cause fuel-ash corrosion. Sodium and vanadium oxides form a range of low melting-point hard scale deposits which penetrate the protective oxide scale of the tube and expose the underlying metal surface to rapid corrosion attack.

A solution for eliminating the sulfur compound is only to burn better-quality fuel. Reducing the excess air to the burners to below 5% will also minimize the conversion of sulfur to sulfur trioxide.

It is also advised to keep the back-end temperature of the boiler always above the acid dew point temperature. Another option is to add neutralizers (additives) to the combustion chamber in a finely powdered form with a compressed-air carrier. Usually, these additives are a proprietary mix of compounds such as magnesium oxide, magnesium carbonate, zinc copper oxide and carbon. Fuel additives can help neutralize cold-end deposits and also control slagging by producing deposits with higher melting points that are dry and removable by sootblowing.

Q.2 Explain the phenomenon of ‘Caustic Embrittlement’. How can it be prevented?

Ans. It is a type of stress corrosion which occurs when hairline cracks appear in highly stressed areas due to high concentrations of alkaline salts that liberate hydrogen, which is then absorbed by the iron in steel, effectively changing its physical properties. This condition is caused largely by boiler water with pH values 11+ and manifests itself in high-temperature areas of the boiler. Boilers of riveted construction are prone to this type of failure, where the crack extends continuously from one hole to other.

Q.3 Erosion in FBC and PF fired boilers

Q.4 Differentiate between Corrosion and erosion

Q.5 What is chemical cleaning of boiler, why it is necessary and how it is carried out?
Q.6 State whether the following statement is TRUE or FALSE. If FALSE, correct and rewrite them.

The internal corrosion in water tube boiler drum is due to hardness in feed water.

Q.7 Write the correct answer against the statement

Formation of scale on a boiler tube
a) Protects it
b) Increases its life
c) Decreases its life
d) Life is unaffected
e) None of the above

Q.8 Write short notes on any four of the following boiler problems, stating their reasons and remedial actions to be taken to prevent them

i) Scaling in internal heating surface of boiler tubes
ii) Corrosion
iii) External corrosion of boiler tubes