BOILER: FIRESIDE FOULING AND CORROSION

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Keywords : Fireside fouling, Coal ash, Final steam conditions, Sootblowers, Economizer, Air heater

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Summary

This article represents the author's experience gained over 30 years (1957-1987) whilst working as a power station chemist on some of the major stations within the Central Electricity Generating Board, UK. It reviews the various problems encountered and summarizes the many step that management can take to overcome them.

1. Introduction

Boiler fireside fouling and corrosion problems are mainly restricted to coal and oil fired installations. There are very few reported incidents of corrosion associated with gas fired units, the problem here being mainly confined to overheating due to incorrect operational firing arrangements.

Modern high pressure coal firing boilers are all designed to fire pulverized fuel. Coal is delivered to the power stations where it is crushed to a fine powder by passing it through crushing (milling) plants. The powdered coal from the mills is transported into the boiler by air where it is combusted in the furnace. Using the coal as a powder leads to higher efficiency because of the more intimate mixing of the fuel and air. A high percentage of the resulting ash passes over into the gas stream, through the super-heater and re-heater sections into the economizer, air heater and precipitators and can cause fouling in these sections. The corrosive environment in the furnace is brought about by the complex combination of the combustion gases, the elements released from the fuel and the type and nature of the ash being carried over in the gas stream together with the boiler materials of construction.

With oil fired units, there is no little or ash produced and the corrosive elements in the oil are quite different from those found in coal supplies.

The main coal impurities that take part in the corrosion process are sulfur, sodium, potassium and chlorine whilst sodium and vanadium together with sulfur are the major corrosive elements found in oil fired installations.

Generally, boiler corrosion problems can be classified into two groups:

(a) High temperature corrosion, which occurs in the high heat transfer areas such as the furnace wall tubes and the super-heater and re-heater sections of the boiler; and
(b) Low temperature corrosion, which is restricted to the cooler "backend" areas of the furnace such as the air heater sections.

2. High Temperature Corrosion

2.1. Coal Fired Installations

High temperature corrosion is a complicated issue and is dependent on many variables. The rate of corrosion is governed by certain gaseous, molten and solid components which are formed during the combustion process. As the gases cool, chemical reactions occur which result in the formation of highly complex mixtures normally containing sodium and potassium sulfates. These mixtures are highly corrosive.

The major coal impurities relevant to the encountered corrosion processes are sulfur, sodium, potassium and chlorine. In British coals these elements are present in the following concentrations: sulfur (1-3 per cent), sodium (0.05-0.4 per cent), potassium (0.3-0.6 per cent) and chlorine (0.02-0.75 per cent).

Operational experience gathered over many years shows that the chlorine content of the coal burnt in the boiler provides a useful guide to the corrosion rate, both for the furnace walls and for the superheater and reheater tubes (although the mechanism involved varies). Chlorine is rapidly released as HCl gas from the pulverized fuel during the initial stages of combustion. The HCl concentration is directly proportional to the chlorine content of the coal, but its role is complex and may be indirect. In the past it was assumed that the chlorine content of the coal was a good guide to the sodium content and the sodium content was important not just in itself but because it promoted the release of non-volatile potassium from the aluminosilicates during combustion. However, recent studies have shown that chlorine is not a useful guide to the sodium content nor does sodium always promote the release of potassium.

There is nearly always sufficient sulfur present in the coal (certainly British coals) to ensure that any sodium and potassium compounds released in the process form fusible sulfates. It is these products mixed with the ash particles which ultimately form the corrosive deposits on the heat exchanges surfaces. Variation in sulfur content does not appear to influence corrosion, providing excess sulfur is present. However variation in volatile sodium and potassium appears to have a marked effect. In addition, high ash content coals whilst initially concentrating the corrosive gases, finally result in less

corrosion as the ash helps to "soak up" potentially harmful alkali metal salts.

Whilst it is now accepted practice that fuel impurities are responsible for both furnace wall and superheater corrosion the mechanisms involved are quite different and therefore these areas are considered separately.

2.1.1. Furnace Wall Corrosion

Furnace wall corrosion deposits are usually a complex mixture of sulfides and oxides with ferrous chloride next to the metal. Severe corrosion is found to occur if:

(a) The high chlorine content of the fuel is in excess of 0.2 per cent.
(b) Impingement of incompletely combusted coal particles are present on the tubes.
(c) High carbon monoxide concentrations (in excess of 1 per cent) and very low oxygen concentrations (less than 0.1 per cent) are located close to the tube surfaces.
(d) There are areas of high heat flux zones in the boiler.

Generally, serious corrosion is almost always confined to the localized regions of the side and rear walls close to the burners. In these areas failure can occur between boiler overhauls, being totally unexpected. Severe corrosion occurs when reducing (sulfidizing) conditions, brought about by incomplete combustion, results in high levels of CO in the area of high metal temperatures. Initially it was considered that the primary effect of the HCl released was to cause metal loss by the formation of volatile $FeCl_2$ at the metal-oxide interface. However, it is now felt that under sulfidizing conditions the HCl reacts with the metal to form volatile chlorides which primarily increase the porosity of the sulfide containing scale. In consequence the scale weakens and spalls away when it is much thinner than scale formed in the absence of HCl. The process of scale build up followed by thin layer spalling is linear and continuous.

2.1.2. Superheater and Reheater Corrosion

Corrosion in these areas is associated with the deposition of alkali sulfates onto the metal surface, their concentration being increased at the metal surface by absorption onto the porous fly ash. The salts formed are usually molten and contain free sulfur trioxide which dissolves the protective oxide film to form iron and chromium based sulfates. Corrosion rates increase rapidly in the range 600-650°C. Plant and laboratory measurements indicate a strong relationship between corrosion rates and the chlorine content of the coal in the range 0.1-0.5 per cent. It was considered for many years that the only relationship between chlorine content and superheater corrosion was that measurement of chlorine indicated the amount of sodium in the fuel as sodium chloride. Sodium is found in the various sulfate deposits and it can also promote the release of non-volatile potassium in the fuel, which in turn can then take part in the overall reaction.

2.1.3. Gas Temperatures and Metal Composition

Furnace wall corrosion rates increase with increase metal temperatures above 380°C

and become very high at temperatures between 550 and 620°C. Final steam conditions in a modern coal fired boiler operating at 170 bar are generally 568°C/170 bar and 568°C/40 bar for the superheater and reheater sections. The external surface metal temperature will be some 60 to 70°C higher. This means that the final boiler outlet stages will be operating at approximately 640°C. In consequence these stages must be constructed of austenitic stainless steels to ensure adequate creep resistance (316, 321, and 374). Experience over many years shows that superheater corrosion is a function of metal and gas temperatures and chlorine contents of the coal. The tubes that directly face the combustion gases (leading tubes) are most vulnerable to attack.

There are typically several hundreds of tubes in each superheater bank and for a given set of operating conditions there will obviously be a distribution of gas and metal temperatures throughout each bank and hence there will be a variation of creep and corrosion characteristics. It is difficult for the boiler design engineers to ensure freedom from failure in these areas and an acceptable tube replacement programme is all that can be achieved. Normally the leading tubes are replaced every third planned overhaul. This planned approach overcomes the unexpected failures which can lead to load restrictions.

2.1.4. Operational Observations

If the necessary chemical elements known to be responsible for corrosion are present in the fuel and complete combustion cannot be achieved, then corrosion somewhere in the furnace is almost inevitable. One of the major contributing steps in combating corrosion is to train and motivate the boiler operators to be more vigilant and to apply corrective action as quickly as possible. Operators must always be on the lookout for signs of abnormalities. Visual observations of the state of combustion should be carried out as frequently as possible and corrective actions taken.

Corrosion will be most severe in the high temperature zones of the boiler and the parts at the greatest risk will be the leading tubes of the superheater and reheater elements, the radiant heat exchange surfaces, the burner components and the inadequately cooled hangers and wall tube supports in the path of the flue gas. Any tube out of alignment will obviously be vulnerable as it will then act as a leading tube.

Thermocouples and heat flux meters must be positioned throughout the furnace. Any abnormal reading should be investigated. If tests confirm that the thermocouple is reading correctly then the extent to which the temperature is above normal must be considered. A higher than normal temperature may indicate a problem with combustion or that fouling is occurring elsewhere in the plant causing excessive heat transfer in the high heat transfer area. High metal temperatures may also indicate lack of cooling in the tube due to water starvation from some form of blockage on the water side. Higher than normal flue gas temperatures at the air heater inlet coupled with the inability to achieve normal system temperatures may indicate serious fouling in the combustion chamber and in the superheater elements. Fouling in certain areas normally leads to high velocities and high metal temperatures elsewhere, with consequential erosion and erosion assisted corrosion problems. The fouling may be due to irregularities in combustion or to changes in chemical composition of the fuel. Alternatively

sootblowers may be ineffective or out of service. The reasons, whatever they are, should be investigated as quickly as possible.

2.1.5. Other Causes of Metal Loss

It is very important not to attribute fireside wastage of boiler components incorrectly to high temperature corrosion. Corrosion may be due to "off load" attack by acids or the metal loss may be simple corrosion in that particular area. Erosion due to passage of abrasive particles at high velocities can usually be found in the following locations:

(a) Close to the sootblowers.
(b) In regions of high flue gas velocities (greater than 25 m s^{-1}).

The appearance of eroded metal surfaces is quite obvious, being smooth with the metal loss profile being related to the direction of the gas flow.

2.1.6. Summary

The following factors give rise to unacceptable rates of high temperature corrosion:

(a) Flame impingement on the furnace walls or extended flames in the convection passes giving rise to hot fuel-rich (reducing) conditions.
(b) High temperature, resulting from gas laning causing locally high corrosion rates on the superheater and reheater tubes.
(c) Insufficient coolant flow through the tubes due to blockages in certain areas causing excessively high temperatures. This also leads to creep failures.
(d) Special factors in the composition of the fuel and pulverized ash.

Many of these problems may be overcome by improvements in maintenance of coal mills, classifiers and burners. In addition repairs should be carried out as quickly as possible to the tubes out of alignment.

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Bibliography and Suggestions for further study

Further information on the subject can be obtained by contacting the Power Production Authorities in the UK, namely:

(a) National Power Plc, Windmill Hill Business Park, Whitehill Way, Swindon, Wilts SN 5 6PB.

(b) Powergen, Plc. Westwood Way, Westwood Business Park, Coventry, CV4 8KG