Corrosion in biomass-fired installations

By Trine Nybo Lomholt, specialist & Søren Klinggaard, project manager

Straw and wood chips are attractive fuels, but firing with biomass rather than fossil fuels presents greater challenges in terms of corrosion.

Firing with biomass presents considerably greater corrosion-related challenges than firing with fossil fuels. This is due in part to the different chemical composition of biomass, especially its higher content of potassium and chlorine. The following is an introduction to the most common corrosion mechanisms.

Corrosion zones in biomass- and waste-fired boilers

Purely in terms of corrosion, biomass- and waste-fired boilers can be divided up into three zones:

- The fuel feed zone (funnels etc.)
- The high-temperature zone (combustion chamber, superheater etc.)
- The low-temperature zone (convection and economiser section etc.)
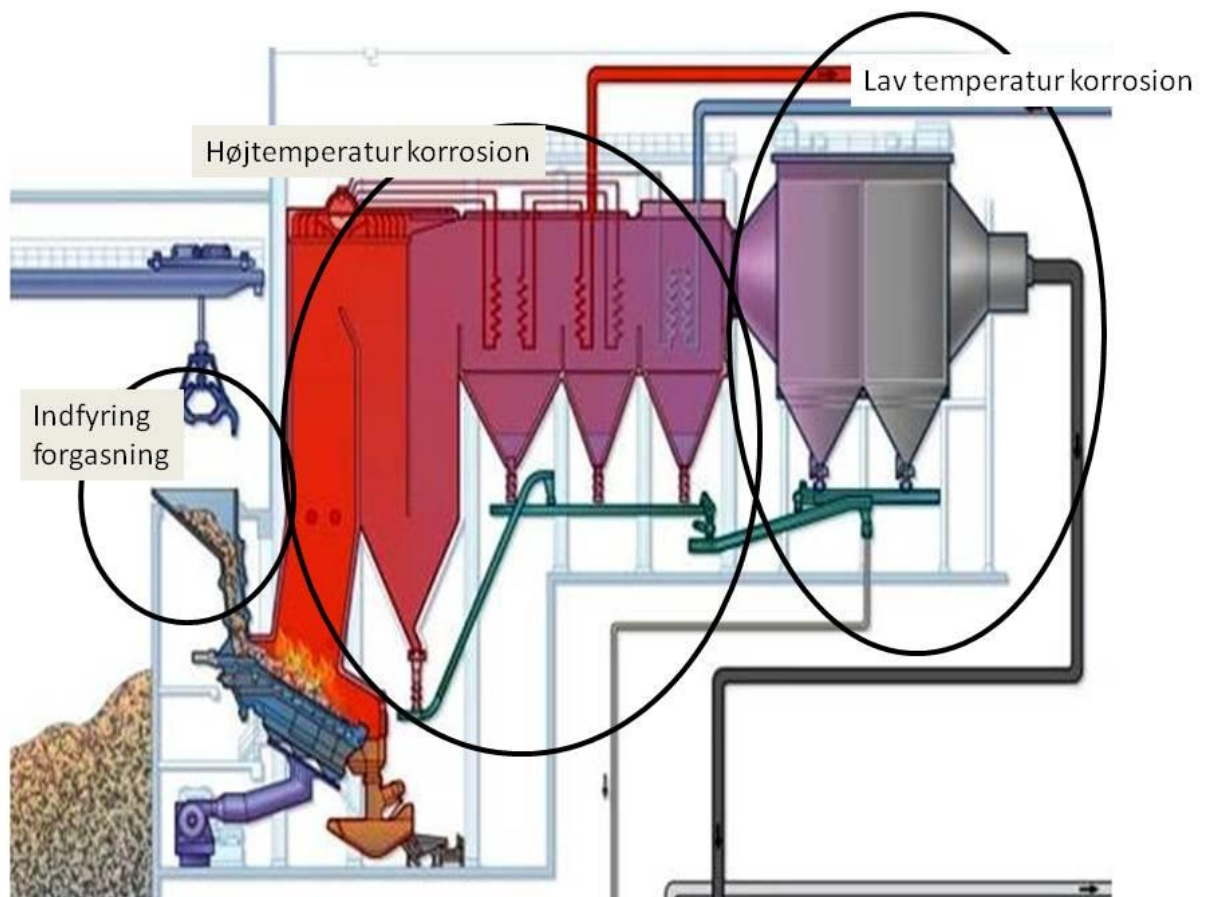

Figure 1: Corrosion zones in biomass-fired boilers

The fuel feed zone

In the fuel feed zone, partial gasification of the fuel can potentially result in the release of volatile hydrocarbon compounds and organic acids. These may be carried into the actual combustion zone, where they can re-evaporate, thus avoiding any increased corrosion risk. If, however, the gasified components diffuse back into the system and then come into contact with materials at low temperature, such as water-cooled walls, the situation is more critical.

In this case, the organic acids will condense out, giving rise to gradual corrosive attack, which ultimately could cause the boiler to leak. For instance, acetic acid and formic acid can begin to condense out at temperatures of just 110°C.

Corrosion damage caused by aggressive components condensing out of the combustion air can be mitigated/eliminated by cladding highly critical elements. This raises the surface temperature of these elements, preventing condensing out.

Grate corrosion

Corrosion is generally not observed in the area around the grate as often as in the hotter parts of the installation. However, there are two issues that can cause grate corrosion. The first is abrasion from biomass containing sand and soil. The second is uneven oxygen distribution across the grate, especially along the sides, where it can be difficult to maintain an oxygen surplus, rendering the atmosphere reductive. As a result, the metal surface cannot form a protective oxide layer.

An oxygen deficit will also mean a greater proportion of uncombusted particles and deposits in the flue gas, which will burn out on the metal surfaces and react with them. This can result in the oxide layer being partially dissolved and becoming porous, thus making it easier for aggressive substances to access the metal surface, potentially inducing increased corrosion.

Corrosion in the high-temperature zone

Most corrosion occurs in the high-temperature zone of the installation, including the superheaters. Superheaters are often made of alloy steel containing chromium, which forms a protective chromium oxide layer on the surface.

If chlorine and potassium are present in the flue gas, reactions can occur between the flue gas and the metal surfaces, as a result of which the protective oxide layer is broken down and the surface protection is lost. Three main corrosion mechanisms are common in the high-temperature zone:

- Chlorine corrosion
- Alkali corrosion
- Molten salt corrosion.

Chlorine corrosion

The mechanism behind chlorine corrosion is described in detail in the literature, so here a summary will suffice.

Chlorine in the flue gas is able to pass through small cracks and defects in the protective chromium oxide layer of the steel surface. The chlorine gas then comes into contact with the underlying metal surface and the subsequent reaction produces metal chlorides. At the high prevailing temperatures, the metal chlorides evaporate and pass back out through the oxide layer.

When the metal chlorides come into contact with the oxygen on the surface, they are converted into oxides, releasing more chlorine gas. This chlorine gas is free to penetrate the oxide layer, and the cycle begins again. This mechanism is illustrated in Figure 2, where iron (Fe) is used as an example.

$$Cl_2\,(g) \qquad 2FeCl_2(g) + 3/2\,O_2(g) = Fe_2O_3(s) + Cl_2(g)$$

oxidlag

$$Cl_2\,(g) \qquad\qquad FeCl_2(g)$$

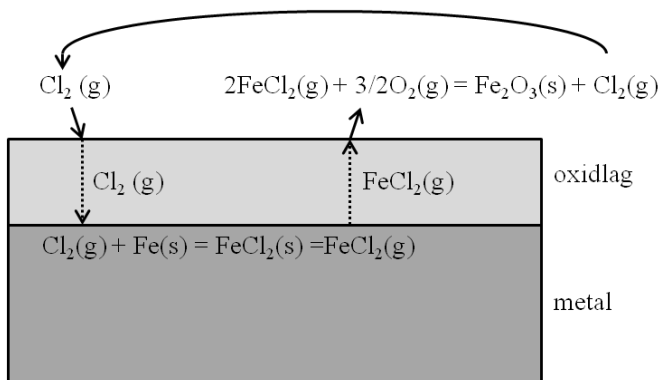$$Cl_2(g) + Fe(s) = FeCl_2(s) = FeCl_2(g)$$

metal

Figure 2: Illustration of chlorine corrosion, based on Asteman [1].

This type of corrosion effectively dissolves the metal beneath the oxide layer, inhibiting the growth of the protective chromium oxide layer. As a result of the chlorine corrosion, the oxide layer also becomes porous and peels off.

Alkali corrosion

In the past, chlorine was regarded as the biggest cause of corrosion in biomass-fired power stations. In recent years, however, there has been greater focus on the fact that alkali metals, chiefly potassium, also play a crucial role in the breakdown mechanism. When potassium is present in the flue gas, it will react with chromium oxide, forming potassium chromate. This means that chromium in the oxide layer is consumed, leaving behind an iron-rich oxide layer. Iron oxide is not as protective as chromium oxide in the atmosphere in question, which means the rate of corrosion is increased. This also leads to accelerated chlorine corrosion.

In some cases, sulphur can reduce alkali corrosion through the formation of potassium sulphate rather than potassium chromate – with potassium sulphate having a less corrosive effect on chromium oxide. It depends, however, on the specifics of the reaction, as it triggers the formation of chlorine gas. If potassium chloride is

converted to potassium sulphate in the flue gas, the chlorine gas will probably escape with the flue gas and not present any real risk. But if chlorine gas is formed beneath the coatings, it will cause chlorine corrosion.

Molten salt corrosion

In the case of chlorine corrosion, metal chlorides are formed, as described above. Many metal chlorides melt at the temperatures prevailing in the combustion chamber. Furthermore, many of the salts contained in the deposits from the fuel also melt at those temperatures. The metal chlorides and salts can also react and form so-called eutectic compounds, which melt at even lower temperatures. Molten chlorides, salts and eutectic compounds are extremely corrosive, dissolving the protective oxide layer of the metal surface. This mechanism is called molten salt corrosion.

Experiences from installations

The following general experiences have been acquired in the course of FORCE Technology's work as a consultant and through studies of damage observed in biomass-fired installations.

Temperature and flue gas flow

The steam temperature is not the only factor influencing corrosion in biomass-fired installations; the metal temperature, flue gas flow and heat flux also need to be taken into consideration. The metal temperature is dependent on the steam temperature, flue gas flow and heat flux.

It is important to optimise the interaction of these factors in order to reduce the rate of corrosion. Likewise, it is essential to avoid reductive gases in the installation, which can be done by ensuring that particles are burnt out before they come into contact with the metals.

Fuel type

Firing with straw causes the highest corrosion rates within biomass, primarily due to the relatively high contents of potassium and chlorine. However, although wood pellets and wood chips have a considerably lower content of these elements, they can still induce corrosion rates equivalent to those seen in straw-fired boilers, due to the lower content of other elements (aluminium, silicon, sulphur) with which the alkali metals normally react. Consequently, potassium chloride can be found in the gas phase after combustion, and this will condense on the surfaces and lead to the same type (and rate) of corrosion as with straw firing.

It should also be mentioned that it is essential to be extremely watchful with waste wood, as its chemical composition is different to that of untreated wood, and this has a major impact on corrosion. Waste wood may contain lead or similar chemical compounds, inducing the corrosion mechanisms evident in waste combustion.

Alloy type and chromium content

In coal-fired power stations, it is well known that a high content of chromium in the alloys gives low corrosion rates. But this is not necessarily the case in biomass-fired power stations, where the effect of the chromium content on the corrosion rate also depends on the type of alloy and the temperature.

The typical alloys used in superheaters can be divided into three categories:

- Ferritic/martensitic steel (Cr <12 wt%)
- Austenitic steel (Cr 15-18 wt%)
- High-alloy austenitic steel and nickel-based alloys (Cr 20-30 wt%).

Ferritic/martensitic steel alloys generally have an even outer-corrosion layer with no considerable grain boundary attack. Material loss is caused by peeling of the outer-corrosion layer. The corrosion rate decreases with an increase in chromium content. In austenitic steel, the corrosion layer is typically divided into a thin outer oxide layer and an underlying zone with grain boundary corrosion, which indicates the effect of chlorine. Austenitic steels can tolerate higher temperatures than ferritic/martensitic steels, so this modified appearance occurs mainly at higher temperatures. The corrosion is exacerbated by higher temperatures and a higher chromium content in the steel. In high-alloy austenitic steels and nickel-based alloys, a similar two-part corrosion layer is seen, but the internal zone suffers attacks inside the grains as well as at the boundaries. The depth of the internal corrosion zone increases with increased chromium content as an effect of chlorine corrosion.

Monitoring of corrosion conditions in biowaste-fired installations

As is evident from the above, there are many factors influencing corrosion conditions in the burning of biofuel. Some of these conditions make it difficult to predict the extent of corrosion in the boiler.

FORCE Technology is making a targeted effort to build up expertise in improving the predictability of corrosion conditions, and an important tool to this end is corrosion measuring performed with a newly developed corrosion probe. This probe is shown in Figure 3. It is air-cooled and designed so that the surface temperature can be precisely regulated, making it possible to test the effect of the flue gas at various temperatures. The corrosion probe has been used at the Danish Test Centre for Bioenergy to measure corrosion conditions in the burning of wood pellets. A number of other tests are being developed, which we hope to be able to present here at a later date.
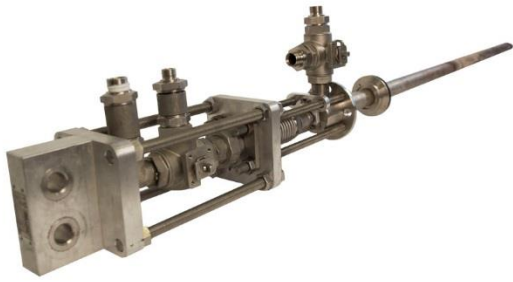
Figure 3: Corrosion probe

Figure 4: Close-up of the corrosion probe after approx. 1 month's exposure in a biomass-fired installation

References

[1] H. Asteman and M. Spiegel, *Corrosion Science*, 49 (2007) 3626–3637