



Full Length Article

The influence of flue gas temperature on lead chloride induced high temperature corrosion



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HIGHLIGHTS

- Lead forms a compound together with alkali metals and chlorine.
- The first melting temperature of the detected K-Na-Pb-Cl mixture is about 368 °C.
- This mixture was found to be corrosive in hot and cooler flue gas temperatures.
- Higher corrosion rate was detected in the hot flue gas sample.
- Molten deposit causes corrosion at high flue gas temperatures.

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ABSTRACT

Firing of waste-based fuels increases the risk for heavy metal-induced corrosion in the furnace walls and in other low-temperature heat transfer surfaces, such as primary superheaters. Lead-containing compounds, especially alkali lead chlorides, have been detected in the boiler water walls, causing severe corrosion. Corrosion rate of chlorine-induced corrosion is known to be dependent on the material temperature and the objective of this work was to study the influence of the flue gas temperature on lead chloride-induced corrosion.

The experiments were carried out with full-scale corrosion probe and deposit probe measurements in a recycled wood firing CFB boiler. The material used in the corrosion probe measurements was low alloy steel EN10216-2 16Mo3 and the material temperature was adjusted to 360 °C. Two corrosion and deposit probes were used in different locations in order to expose the probes towards hot, 800 °C, and cooler, 490 °C, flue gas temperatures. Changes of the wall thicknesses were measured and the samples were analysed with SEM/EDS and XRD for more detailed deposit characterisation.

Corrosion was detected in both the hot and the cooler flue gas samples. A low melting ($T_0 = 368$ °C) alkali-lead-chloride mixture was identified. Findings from these measurements strongly indicate this mixture to be the corrosion-causing compound at both flue gas temperatures. However, the corrosion rate was higher in the hot flue gas sample compared to the cooler flue gas sample. A much steeper deposit temperature gradient was calculated for the hot flue gas sample, suggesting that the alkali-lead-chloride mixture is in the molten form. These findings, together with the higher proportion of the present alkali-lead-chloride mixture, are the potential factors for the higher corrosion rate in the hot flue gas sample compared to the cooler flue gas sample.

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1. Introduction

Waste-based fuels are becoming more and more conventional in power boilers. The reasons for the increased use are many:

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low price, good availability and renewable energy benefits. Waste-based fuels are usually heterogeneous and can consist of different fuel fractions, such as organic waste, household waste, industrial waste and waste wood. Waste wood may include, for example, demolition wood, which means that plastics, paints and even metallic components can be present. Waste fuel typically includes troublesome elements such as heavy metals (lead and zinc), chlorine, potassium, sodium and sulphur. It is known that

this kind of fuel is more problematic due to its high corrosivity than other, less heterogeneous, fuel types [1–3].

Fuel composition is a determining factor from corrosion and fouling points of view. Recovered wood, solid recovered fuel (SRF) and municipal solid waste (MSW) are the fuel types with increased amounts of heavy metals and chlorine. Boilers combusting these types of fuels experience increased fouling on furnace walls, superheaters and economizers as well as failures due to corrosion. Alkali chloride-containing deposits are well-known to cause corrosion in biomass and waste-fired boilers [4,5]. Typically, alkali chloride-induced corrosion is a problem in the hottest areas of the superheaters, in material temperatures over 450 °C [6,7], while the heavy metal-induced corrosion moves corrosion towards colder surfaces, such as furnace walls, and other low-temperature heat transfer surfaces, meaning material temperatures below 450 °C [8,9]. The presence of lead and zinc together with chlorine and sulphur can dramatically lower the first melting point of the deposits forming on heating surfaces. This can lead to unexpected corrosion failures at relatively low temperatures (350 °C and below) [10,11].

Zinc has been a research topic in many studies involving heavy metal-induced corrosion [11,12]. Zinc-containing compounds, for example zinc chloride and a mixture of zinc chloride and potassium chloride, have already been shown to cause corrosion at material temperatures as low as 350 °C for low alloyed steels [13–16]. During combustion, zinc is mainly vaporised as gaseous zinc in the reducing part (lower part) of the furnace. Due to its low melting point (420 °C), it can be present also as molten zinc at the lowest part of the furnace [8]. The most problematic part of the furnace when considering corrosion [17] is located between the secondary and tertiary air levels, where the amounts of gaseous zinc chloride are low and zinc is expected to be present mainly as gaseous zinc oxide [8]. Zinc oxide has proven less corrosive than zinc chloride [14]. Some traces of zinc can be found from deposit samples collected from the furnace walls and other low-temperature heat transfer surfaces [17,18]. However, the concentrations of zinc are small and are not considered to have as great an influence on corrosion as does lead.

Lead, especially gaseous lead chloride, has proven to be more prevalent than zinc after the secondary air level all the way up to the superheater and economizer areas. While zinc chloride oxidises as low as 300 °C, lead chloride oxidises above 400 °C [19]. The presence of lead chlorides throughout the entire boiler has been confirmed by several authors using different research methods, such as gas and fine particle measurements [8,20,21].

Lead chloride was also suggested to exist by studies utilising thermodynamic calculations [8,20]. The condensation temperature of lead chloride is between 290 °C and 440 °C for the concentrations expected in waste combustion [2,22]. The condensation temperature depends on the concentration of lead chloride and may vary from announced. Alipour indicated that water wall corrosion is caused by hydrogen chloride if using low alloy material [23]. In a case of nickel-based alloy, the reason for corrosion was shown to be potassium-lead mixture. He found this mixture to be present in the corroded furnace walls when firing waste wood [23]. Potassium-lead-chloride mixture was also noticed in laboratory combustion tests with synthetic used wood containing different amounts of lead [18].

The dependence of the temperature on corrosion rate has been investigated by many authors [24–26]. They noticed that the superheater tube and flue gas temperature had crucial effects on corrosion. An increase of material or flue gas temperature, also increased the corrosion rate. The studies showed the temperature dependence of not only alkali chloride-induced corrosion, but also lead chloride-induced corrosion [27]. Temperature dependence has also been studied in laboratory measurements [28,29]. Pure lead chloride and a mixture of lead chloride and potassium chloride

were reported to cause significant corrosion at material temperatures of 400 °C. The mixture of lead chloride and potassium sulphate caused corrosion on low alloyed steels at material temperatures as low as 325–350 °C. The higher the material temperature, the higher the oxidation rate.

As mentioned, the corrosion rate of lead chloride-induced corrosion is dependent on the material and flue gas temperatures. Thus, the objective of this work was to study the influence of the flue gas temperature on lead chloride-induced corrosion with full-scale measurements in a recycled wood-fired boiler. Another purpose was to examine whether the same corrosive species are present in hot and cooler flue gas temperature areas and to study corrosion rates while keeping the material temperature constant. Finally, deposit temperature gradients were estimated for both flue gas temperature samples, which is a novel tool in corrosion research.

2. Experimental

Full-scale corrosion and deposit probe measurements were carried out in a 120 MW_{th} circulating fluidised bed boiler firing recycled wood. Short- and long-term probe tests were carried out in two different parts of the boiler with two different flue gas temperatures. The hotter flue gas area was located in the upper part of the back pass and the cooler flue gas area was in the lower part of the back pass, after the boiler bank. The boiler bank is located after the superheaters. The locations are illustrated in Fig. 1. In the upper back pass, the flue gas temperature was around 800 °C and roughly 490 °C in the lower part. The material temperature in both cases was adjusted to 360 °C. More detailed descriptions of the probe measurements are presented in the following chapters.

2.1. Short-term deposit probe tests

The short-term experiments were performed in order to collect and analyse the initial deposit. The measurements were carried out with the air-cooled deposit probe presented in Fig. 2. The duration of one measurement was two hours. The short-term measurements were carried out in between the long-term corrosion probe measurements. One austenitic stainless steel probe ring was used at a time and the ring was replaced after each measurement. Austenitic stainless steel was used in order to avoid major corrosion reactions between the ring and the deposit. The ring temperature was adjusted with cooling air to 360 °C and monitored with a thermocouple drilled into the material ring and connected to a regulator unit. The thermocouple measuring the flue gas temperature was placed outside of the ring as presented in Fig. 3. Fuel sampling

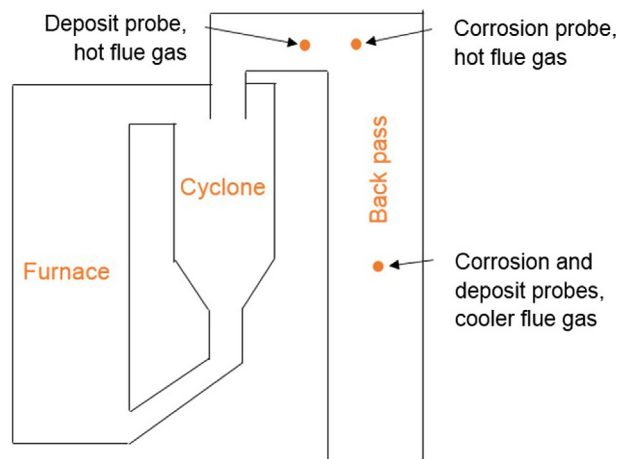


Fig. 1. Locations of the probes.

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