



# Reducing high-temperature corrosion on high-alloyed stainless steel superheaters by co-combustion of municipal sewage sludge in a fluidised bed boiler



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## HIGHLIGHTS

- Effects of co-firing sewage sludge with biomass/waste in a CFB boiler are studied.
- Burning waste and biofuels results in a corrosive flue gas.
- The corrosivity is mainly due to the presence of alkali chlorides in the fuel gas.
- The addition of digestive sewage sludge decreases corrosion rate significantly.
- The corrosive alkali chlorides will transform to less corrosive alkali compounds.

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## ABSTRACT

One way of mitigating alkali chloride induced corrosion in biomass and waste-fired boilers is by using additives or by co-combustion and thereby decreasing the corrosiveness of the flue gas and deposits. The effect of co-firing digested sewage sludge with a mixture of biomass and waste (78% bark pellets + 22% Solid Recovered Fuel, denoted “SRF”) was investigated in a 12 MW circulating fluidised bed (CFB) boiler. The initial corrosion attack of the stainless steel 304L at 600 °C (material temperature) was investigated during 24 h exposures. The exposures were carried out in the flue gas environment from three fuel-mixes: SRF, MSS1-low (SRF with municipal sewage sludge, low dosage) and MSS2-high (SRF with municipal sewage sludge, high dosage). The results showed that the most severe corrosion attack on 304L occurred without sewage sludge in the SRF exposure. This attack was characterised by a corrosion product layer up to 100 µm in thickness and signs of internal corrosion of the steel. The deposit in the SRF case was dominated by alkali chlorides. The exposures with co-combustion of sewage sludge, MSS1-low and MSS2-high, showed a significant decrease in corrosion. The steel sample of 304L performed especially well in the latter case when it was protected by a thin oxide of less than 0.3 µm in thickness. This deposit was dominated by sulphate- and phosphate-containing compounds but traces of aluminium silicate compounds were also found. Furthermore, the concentration of alkali chlorides was low. Thus, the initial corrosion attack was greatly reduced by co-combustion of digested sewage sludge with SRF.

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## 1. Introduction

The production of electricity from renewable energy sources, such as waste and biofuels, is presently on the increase throughout the world. Being renewable, these fuels are not considered to make any net contribution of carbon dioxide (CO<sub>2</sub>) to the atmosphere when combusted. However, these fuels usually contain large

amounts of alkali chloride which result in a very corrosive flue gas. In contrast, the sulphur dioxide (SO<sub>2</sub>) content is typically low [1–4]. Hence, the deposits formed on the superheater tubes are often rich in alkali chlorides (potassium chloride (KCl) and sodium chloride (NaCl)) and it has been shown that high temperature corrosion of stainless steels is greatly enhanced by the presence of alkali chlorides [5–14]. The corrosion rates of the superheaters in a boiler can be reduced by keeping the steam temperature low. However, this results in poor electrical efficiency. The steam parameters can be maintained at high temperature

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and pressure if the high temperature corrosion is prevented. The strategies to prevent high temperature corrosion include co-combustion, additives and more advanced superheater materials or higher alloyed superheater materials.

One of the explanations for the corrosive behaviour of alkali chlorides towards stainless steels is the formation of alkali chromates. It has been shown that alkali chlorides react with chromium (Cr) in the initially formed protective oxide on stainless steel, forming alkali chromates [6,7,9,10,15–17]. This results in a chromium depleted oxide which is then converted into an iron-rich fast-growing oxide. This oxide has much poorer protective properties as it has higher diffusion rates compared to chromium rich oxides. This reaction scheme is also true for potassium carbonate ( $K_2CO_3$ ), which reacts with protective oxide forming potassium chromate ( $K_2CrO_4$ ) and  $CO_2(g)$  [16,18]. Thus, the chromate formation reaction is not limited solely to alkali chlorides. After the breakdown of the initially protective oxide, the iron-rich oxide formed after reaction with alkali compounds is susceptible to chlorine-induced corrosion by chlorine ions penetrating the oxide scale. This leads to the formation of transition metal chlorides (e.g. iron chloride ( $FeCl_2$ )) at the metal/oxide interface causing poor scale adherence.

Another explanation for the accelerated corrosion attack is the active oxidation mechanism, initially proposed by McNallan [19,20] and further developed by Grabke [5]. In this mechanism, it is suggested that chlorine ( $Cl_2(g)$ ) diffuses through micro cracks and pores in the oxide scale, forming volatile metal chlorides in the reducing environment at the oxide/metal interface. The gaseous metal chlorides then diffuse through the oxide, forming metal oxide in the outer part of the scale where the partial pressure of oxygen is higher, releasing  $Cl_2(g)$ . The molecular chlorine formed in this way has been suggested to diffuse inwards through the scale, to react with the metal again.

In order to mitigate the corrosion in waste and biomass-fired boilers, fuel additives can be used for altering the corrosive environment and thus restricting the corrosion attack. The fact that the flue gas chemistry can be altered by means of fuel additives or co-combustion has also been demonstrated in several papers [3,15,21–33] and the effect on the corrosion attack has also been evaluated [15,22,23,26–29]. In biomass and waste-fired boilers, the additives or co-combustion has mainly focused on increasing the availability of sulphur (in the form of  $SO_2$  and/or  $SO_3$ ) in the boiler. This includes sulphur-based additives such as elemental sulphur (S) [15,22,24,25,28] and ammonium sulphate ( $(NH_4)SO_4$ ) [24–26,29], sulphur recirculation [27] or by co-combustion of waste and biomass with coal, peat and municipal sewage sludge [21,23,26,30–33]. The main aim of using these additives (or co-combustion) was to sulphate alkali chlorides into their corresponding sulphates during the simultaneous release of hydrogen chloride (HCl) or  $Cl_2$ . Laboratory studies have shown that the presence of potassium sulphate ( $K_2SO_4$ ) induces no accelerated corrosion attack on stainless steels at 600 °C [18]. The non-corrosive nature of  $K_2SO_4$  at this temperature is explained by its reluctance to react with the protective, chromium-rich oxide form  $K_2CrO_4$ . Thus, the corrosion properties of the stainless steel remain intact.

In addition to decreasing the presence of alkali chlorides by sulphation, other measures have been taken [34]. By means of co-combustion of biomass/waste with sewage sludge, several reactions with alkali can occur. This includes, for instance, converting the alkali chlorides into alkali sulphates, alkali phosphates or by binding the alkali part of alkali chlorides to aluminium silicates. In contrast to alkali chlorides, they do not deplete the protective oxide in chromium by forming  $K_2CrO_4$ . In this study, two different municipal sewage sludges were tested as co-fuels at the 12 MW<sub>th</sub> CFB boiler on Chalmers campus. The focus lies on the initial corrosion attack of the stainless steel 304L and how these additives can mitigate the corrosive nature of the reference fuel (Solid Recovered

Fuel and Bark). Special attention is paid to the presence of S, phosphorus (P), calcium (Ca) and aluminium silicates in the deposits formed on the corrosion probe used and their ability to react with alkali chlorides in order to converting the alkali chlorides into less corrosive compounds.

## 2. Experimental

### 2.1. Research boiler, fuels and boiler operating conditions

The experiments were performed in the 12 MW<sub>th</sub> circulating fluidised bed (CFB) boiler, located at Chalmers University of Technology, shown in Fig. 1. The combustion chamber (1) has a cross section of 2.25 m<sup>2</sup> and a height of 13.6 m. The various fuels are fed to the bottom of the bed through a fuel feed chute (2). The circulating material is separated at a primary cyclone (5) and returned to the combustion chamber through the cyclone leg and loop seal. An external heat exchanger cools the circulating material before re-entering the combustion chamber when required. Primary air is introduced through air nozzles located at the bottom of the riser and secondary air 2.1 m above the bottom plate (4). The exhaust gas is cooled to 150 °C in the convection pass. Effective soot blowers (using steam blown probes) are installed along each section of the convection pass. These soot blowers are regularly used to keep the flue gas temperature below 180 °C (once or twice every 24 h). Fly ashes are separated in the secondary cyclone (8) and the textile filter (9). Silica sand ( $dp = 0.3$  mm) was used as bed material in all cases. The operating conditions presented in Table 1 are typical of a commercially operated CFB boiler. This means a fluidising velocity between 5 and 6 m/s in the top of the riser that leads to a proper circulation of bed material through the primary cyclone, good heat transfer of moving bed particles and an attrition of the fuel ash into fly ash, which is important in order to avoid accumulation of bottom bed ash. Other typical operating conditions are proper excess air ratio (20–25% excess air) and a bottom bed temperature of 850 °C.

Three combustion cases were investigated and their corresponding operating conditions are presented in Table 1. First, case *SRF* in which bark pellets were co-fired with waste (Solid Recovered Fuel) pellets produced by IcoPower in the Netherlands. The share of waste was 22% based on the total amount of dry fuel supplied to the boiler. The bark was crushed, dried and pressed into pellets. Secondly, case *MSS1-low* with additional combustion to the case *SRF* of municipal sewage sludge from a waste water treatment plant named Sjölundaverket with a mixture of 7.3%. Sjölundaverket takes care of sewage waste water from the city of Malmö in Sweden. Thirdly, case *MSS2-high* with additional combustion to the case *SRF* of municipal sewage sludge from a waste water treatment plant named Himmerfjärdsverket with a mixture of 13%. Himmerfjärdsverket takes care of sewage waste water from the city of Södertälje and the south-west part of Stockholm.

The element compositions of the separate fuels are given in Table 2. The main difference in composition is high chlorine content in the *SRF* case and the ashes from both *SRF* and bark have a high content of Ca. Moreover, the precipitating agent for P was iron-sulphate ( $Fe_2SO_4$ ) for both sewage sludges (*MSS1* and *MSS2*), which is reflected by the high iron (Fe) and P content. The digestion of the sludge during which methane ( $CH_4$ ) is produced leads to a higher ash concentration compared to undigested sludge. After digestion the sludge was mechanically dewatered using high speed centrifuges, lowering the moisture content from 92% to approximately 72–78% and it is difficult to decrease it further without the use of drying equipment. Moisture contents of 72–78% lead to low heating values in the range of 1–2 MJ/kg fuel as supplied to the boiler. These low heating values require a base

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