Investigation of the corrosion behaviour of 13CrMo4–5 for biomass fired boilers with coupled online corrosion and deposit probe measurements

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HIGHLIGHTS

• Online corrosion probe measurements were applied.
• Deposit probe measurements were applied.
• A fixed bed/drop tube reactor was used for the measurements.
• An empirical corrosion model was developed.
• Possible corrosion mechanisms are discussed.

ABSTRACT

High-temperature corrosion in biomass fired boilers is still an insufficiently explored phenomenon which causes unscheduled plant shutdowns and hence, economical problems. To investigate the high-temperature corrosion and deposit formation behaviour of superheater tube bundles, online corrosion probe as well as deposit probe measurements have been carried out in a specially designed fixed bed/drop tube reactor in order to simulate a superheater boiler tube under well-controlled conditions. The investigated boiler steel 13CrMo4–5 is commonly used as steel for superheater tube bundles in biomass fired boilers. Forest wood chips and quality sorted waste wood (A1–A2 according to German standards) as relevant fuels have been selected to investigate the influence on the deposit formation and corrosion behaviour. The following influencing parameter variations have been performed during the test campaigns: flue gas temperature between 650 and 880 °C, steel temperature between 450 and 550 °C and flue gas velocity between 2 and 8 m/s. One focus of the work presented is the detailed investigation of the structure and the chemical composition of the deposits formed as well as of the corrosion products. A further goal of the work presented was the development of an empirical model which can be used within CFD simulations of flow and heat transfer to calculate and evaluate the local corrosion potential of biomass fired plants already at the planning stage. The corrosion probe measurements show a clear dependency on the parameters investigated and the empirical function developed reproduces the measured corrosion behaviour sufficiently accurate. Since the additional calculation time within the CFD simulation is negligible the model represents a helpful tool for plant designers to estimate whether high-temperature corrosion is of relevance for a certain plant or not, when using fuels with similar compositions and the steel 13CrMo4–5.

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1. Introduction

Ash related problems have a strong influence on the operation of biomass combustion plants, resulting in unscheduled outages and reduced economic efficiencies. Among these problems, material corrosion of steel surfaces in the hot furnace, of radiative boiler walls and of convective heat exchanger tube bundles (superheaters) is of major importance. This is especially of interest when firing biomass fuels with high contents of chlorine and alkali metals (e.g. waste wood as well as agricultural and herbaceous fuels like straw and Miscanthus). Also corrosion is of relevance for conventional wood fuels (e.g. forest wood chips and bark) in more
efficient future biomass combined heat and power (CHP) plants with increased steam parameters. Therefore, a lot of research has been done in the last decades to identify and quantify the most influencing parameters on high-temperature corrosion occurring in biomass fired boilers (an overview is given by [1,2]).

High-temperature corrosion has already been extensively investigated in plants firing biomass rich in chlorine such as straw (e.g. [3–6]) and, furthermore, in municipal solid waste incinerators (an overview is given by [3,7–9]). Also the corrosion processes occurring in plants firing fuels with low to moderate chlorine contents, such as forest wood chips and bark as well as quality sorted waste wood have already been investigated (e.g. [10,11]). However, in measurements in real-scale biomass plants it is often not possible to vary just one parameter of interest to determine its effect on the high-temperature corrosion.

In addition, a wide range of experimental data exists, where the effect of deposits of certain species (e.g. KCl or NaCl) are investigated and possible corrosion reaction mechanisms are proposed (e.g. [12–15]). Nevertheless, these experiments are also not sufficient to predict the high-temperature corrosion behaviour of real-scale plants accurately, due to the interaction and the high complexity of the processes involved.

2. Objectives

The aim of the work presented was the detailed investigation of the high-temperature corrosion processes occurring in the superheater section of biomass fired CHP plants. Therefore, online corrosion probe measurements (see Section 3.2) as well as deposit probe measurements (see Section 3.3) were performed to investigate the corrosion behaviour of the steel 13CrMo4–5 in a specially designed packed bed reactor. To study the effect of different biomass fuels fired on deposit formation and on high-temperature corrosion, two test campaigns were carried out. In the first one, forest wood chips and in the second one quality sorted waste wood (A1–A2) were applied to determine the effects on high-temperature corrosion. Here, the methodology differs for the two test campaigns. For forest wood chips, the parameter variations were all done starting from pre-defined reference conditions, which mean a flue gas temperature of 710 ± 10 °C, a steel temperature of 480 ± 1 °C and a flue gas velocity of 2.8 ± 0.5 m/s, which were also used to build up the ionic layer. After the parameter variations, this reference state was re-established before the furnace was shut down. In doing so, the reproducibility of the reference signal was ensured on a daily basis with the drawback, that the majority of the data points are located within relatively narrow spaces of the parameter variation range. To achieve a better distributed data set the procedure was changed for waste wood. Here, only one steel temperature was investigated per day, and the flue gas temperature was slowly but steadily increased and after reaching the maximum flue gas temperature of approximately 880 °C decreased again to a temperature of around 710 °C. Meanwhile the flue gas velocity was kept constant to 3.6 ± 0.5 m/s. To ensure the reproducibility, all steel temperature variations were repeated at least two times. Flue gas velocity variations were performed subsequent to the temperature variations. To determine the combustion conditions during the corrosion probe test campaigns, balance test runs were performed. The characteristic data of the combustion conditions can be found in Table 3.

3. Methodology

The corrosion probe test campaign took place at the specially designed packed bed/drop tube reactor of BIOENERGY 2020+ GmbH (see Section 3.1). The boiler steel investigated was 13CrMo4–5. The composition of this heat resistant ferritic steel can be found in Table 1. To investigate the effect of different fuel compositions, especially regarding increased chlorine and heavy metal contents, two test campaigns with typical treated and untreated woody biomass fuels were carried out. Forest wood chips, with a rather low chlorine and heavy metal content, and quality sorted waste wood (A1–A2), which shows significantly higher chlorine and heavy metal contents, were used as fuels. The compositions of the fuels are presented in Table 2. The molar S/Cl ratios calculated based on the fuel analyses for the fuel wood chips is 6.9, whereas the ratio of the waste wood used is 1.4, which indicates a higher corrosion potential according to [21].

The following parameter variations were performed during the test campaigns: flue gas temperature variation between 650 and 880 °C, steel temperature variations between 450 and 550 °C and flue gas velocity variations between 2 and 8 m/s. The flue gas temperature variations were achieved by a variation of the electrical heating power of the drop tube (see Section 3.1), the variations of the steels temperature were established by variable air cooling of the probe (see Section 3.2) and the flue gas velocity was varied by an increase of the furnace load.

The duration of the corrosion probe test campaign of forest wood chips was 1070 h in which the biomass furnace was 325 h in operation. The test campaign of waste wood lasted 1512 h with a furnace operation time of 329 h. Due to safety reasons the furnace had to be shut down in the evenings and at weekends. To prevent chipping of the corrosion layer caused by thermal stress the drop tube was heated overnight at a constant temperature of 850 °C of the heating elements, with air streaming through the drop tube, which led to a constant probe steel temperature of about 440 °C.

The corrosion probe applied needs a fully developed ionic layer at the corrosion front to achieve a stable corrosion signal. Horn et al. [22] reported that it took around 10 days to achieve a stable layer structure in similar measurements, performed in municipal solid waste CHP plants. Therefore, both test campaigns were split in two parts in which the first ≈130 operating hours were used to develop an ionic layer. During that time the parameter settings were not changed. After gaining a reproducible signal from the online corrosion probe over several days, parameter variations were applied to determine the effects on high-temperature corrosion. Here, the methodology differs for the two test campaigns. For forest wood chips, the parameter variations were all done starting from pre-defined reference conditions, which mean a flue gas temperature of 710 ± 10 °C, a steel temperature of 480 ± 1 °C and a flue gas velocity of 2.8 ± 0.5 m/s, which were also used to build up the ionic layer. After the parameter variations, this reference state was re-established before the furnace was shut down. In doing so, the reproducibility of the reference signal was ensured on a daily basis with the drawback, that the majority of the data points are located within relatively narrow spaces of the parameter variation range. To achieve a better distributed data set the procedure was changed for waste wood. Here, only one steel temperature was investigated per day, and the flue gas temperature was slowly but steadily increased and after reaching the maximum flue gas temperature of approximately 880 °C decreased again to a temperature of around 710 °C. Meanwhile the flue gas velocity was kept constant to 3.6 ± 0.5 m/s. To ensure the reproducibility, all steel temperature variations were repeated at least two times. Flue gas velocity variations were performed subsequent to the temperature variations. To determine the combustion conditions during the corrosion probe test campaigns, balance test runs were performed. The characteristic data of the combustion conditions can be found in Table 3.
3.1. Biomass reactor

The corrosion probe test campaigns were carried out using a combined packed bed/drop tube reactor (Fig. 1), with which conditions regarding flue gas temperature, composition and velocity as well as temperatures at the steel surface, typically prevailing in biomass combustion plants can be achieved. The used setup consists of a packed bed reactor (biomass grate furnace equipped with air staging and flue gas recirculation), which is connected via an upper transition part to a heated vertical tube with isothermal conditions (the so-called drop tube) which is followed by the measurement port. With the heating elements of the drop tube (60 kW electrical input power) flue gas temperatures of 900 °C can be achieved at the measurement port at the reference load operation mode of the reactor. An additional water cooled pipe is installed to bypass the measurement unit during the startup and shutdown of the reactor. The drop tube has a length, which is sufficient to achieve a fully developed flow at the entrance of the measurement port.

### Table 1
Chemical composition of the steel 13CrMo4–5.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>N</th>
<th>Cu</th>
<th>Cr</th>
<th>Mo</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min [weight-%]</td>
<td>0.08</td>
<td>–</td>
<td>0.40</td>
<td>–</td>
<td>0.03</td>
<td>–</td>
<td>–</td>
<td>0.70</td>
<td>0.40</td>
<td>Remaining</td>
</tr>
<tr>
<td>Max [weight-%]</td>
<td>0.18</td>
<td>0.35</td>
<td>1.00</td>
<td>0.01</td>
<td>0.01</td>
<td>0.30</td>
<td>1.15</td>
<td>0.60</td>
<td>Remaining</td>
<td></td>
</tr>
</tbody>
</table>

### Table 2
Chemical composition of the fuels investigated. Explanations: mv ... mean value, std ... standard deviation, w.b. ... wet basis, d.b. ... dry basis; wt.% ... weight percent; number of samples: forest wood chips = 3; waste wood = 8; for forest wood chips the concentrations of the elements C, H and N have only been determined from one representative sample.

<table>
<thead>
<tr>
<th>Unit</th>
<th>Forest wood chips</th>
<th>Waste wood A1–A2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content</td>
<td>wt.% w.b.</td>
<td>24.1</td>
</tr>
<tr>
<td>Ash content</td>
<td>wt.% d.b.</td>
<td>2.4</td>
</tr>
<tr>
<td>C</td>
<td>wt.% d.b.</td>
<td>1.9</td>
</tr>
<tr>
<td>H</td>
<td>wt.% d.b.</td>
<td>48.1</td>
</tr>
<tr>
<td>N</td>
<td>wt.% d.b.</td>
<td>5.9</td>
</tr>
<tr>
<td>S</td>
<td>mg/kg d.b.</td>
<td>0.3</td>
</tr>
<tr>
<td>Cl</td>
<td>mg/kg d.b.</td>
<td>280</td>
</tr>
<tr>
<td>Si</td>
<td>mg/kg d.b.</td>
<td>90</td>
</tr>
<tr>
<td>Ca</td>
<td>mg/kg d.b.</td>
<td>2122</td>
</tr>
<tr>
<td>Mg</td>
<td>mg/kg d.b.</td>
<td>6045</td>
</tr>
<tr>
<td>K</td>
<td>mg/kg d.b.</td>
<td>1.96</td>
</tr>
<tr>
<td>Na</td>
<td>mg/kg d.b.</td>
<td>63</td>
</tr>
<tr>
<td>P</td>
<td>mg/kg d.b.</td>
<td>204</td>
</tr>
<tr>
<td>Al</td>
<td>mg/kg d.b.</td>
<td>446</td>
</tr>
<tr>
<td>Fe</td>
<td>mg/kg d.b.</td>
<td>265</td>
</tr>
<tr>
<td>Mn</td>
<td>mg/kg d.b.</td>
<td>108</td>
</tr>
<tr>
<td>Zn</td>
<td>mg/kg d.b.</td>
<td>19</td>
</tr>
<tr>
<td>Pb</td>
<td>mg/kg d.b.</td>
<td>1</td>
</tr>
<tr>
<td>Molar S/Cl ratio</td>
<td>mol/mol</td>
<td>6.9</td>
</tr>
</tbody>
</table>

### Table 3
Combustion conditions during the corrosion probe measurements. Explanations: mv ... mean value, std ... standard deviation, w.b. ... wet basis, d.b. ... dry basis, NCV ... net calorific value, Nm³ ... m³ at 0 °C and 101325 Pa.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Forest wood chips</th>
<th>Waste wood A1–A2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel power input related to NCV</td>
<td>23.4</td>
<td>25.7</td>
</tr>
<tr>
<td>Fuel flow rate</td>
<td>6.3</td>
<td>6.7</td>
</tr>
<tr>
<td>Temperature primary combustion zone</td>
<td>818</td>
<td>15</td>
</tr>
<tr>
<td>Temperature secondary combustion zone</td>
<td>896</td>
<td>29</td>
</tr>
<tr>
<td>CO₂</td>
<td>11.1</td>
<td>0.9</td>
</tr>
<tr>
<td>CO</td>
<td>13.8</td>
<td>0.7</td>
</tr>
<tr>
<td>O₂</td>
<td>9.5</td>
<td>0.9</td>
</tr>
<tr>
<td>SO₂</td>
<td>8.6</td>
<td>2.8</td>
</tr>
<tr>
<td>HCl</td>
<td>6.6</td>
<td>3.8</td>
</tr>
<tr>
<td>Primary air flux</td>
<td>15.4</td>
<td>14.5</td>
</tr>
<tr>
<td>Secondary air flux</td>
<td>16.1</td>
<td>16.3</td>
</tr>
<tr>
<td>Total air flux</td>
<td>31.5</td>
<td>30.9</td>
</tr>
<tr>
<td>Flue gas recirculation volume flux</td>
<td>–</td>
<td>5.8</td>
</tr>
<tr>
<td>Air ratio primary combustion zone</td>
<td>0.86</td>
<td>0.98</td>
</tr>
<tr>
<td>Total air ratio (Including flue gas recirculation)</td>
<td>1.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>
port, which is equipped with a corrosion and/or a deposit probe. Therefore, the reactor enables corrosion measurements under defined flow and temperature conditions with a flue gas typical for fixed bed combustion systems. Finally, the flue gas is transferred via a lower transitional part to a water cooled heat exchanger before it enters the chimney. An additional port is installed before the entrance to the chimney to allow flue gas analysis.

3.2. Online high-temperature corrosion probe measurements

The corrosion probe provided by the company CORRMORAN GmbH (Augsburg, Germany) is based on a system which was developed at the Institute of Physics, University of Augsburg in Germany. The system is especially designed to simulate high-temperature corrosion occurring on superheater tubes. The probe design consists of an air cooled support lance made from a heat resistant nickel based super alloy (Fig. 2 left) with an air-cooled probe head (Fig. 2 right). The probe head itself is composed of four sample rings that are separated by ceramic rings. These sample rings, made of 13CrMo4–5, are held at a constant temperature which can be arbitrarily changed by the air cooling. When exposed to the flue gas, an ionic layer is formed which allows the measurement of a linear polarization resistance between the steel surface and the ionic layer. This resistance is directly proportional to the current corrosion attack [24]. The measured signal can be related to a corrosion rate, which describes the steel loss over time, subsequent to the test campaign by quantifying the actual loss of weight of an additional ring, the so-called mass loss ring, over the whole test campaign. A detailed description of the probe can be found in [8,17].

It should be mentioned that the corrosion rates measured within this work give only qualitative information about the corrosion potential in dependence of relevant operating parameters. High-temperature corrosion is a strongly time-dependent process which often follows a paralinear trend [24]. Therefore, the corrosion rates gained within short-term measurements generally differ from those found within long-term measurements. Nevertheless, the short-term online corrosion measurements still allow the investigation of the dependence on a certain parameter. The steel temperatures investigated were 450, 480, 500, 520 and 550 °C.

3.3. Deposit probe measurements

To gain more information about the chemical composition, the build-up rate (RBU) and the structure of the deposit layer, deposit probe measurements were performed. These measurements were...
carried out subsequent to the corrosion probe test campaigns to avoid an interaction of the corrosion and the deposit probe. The deposit probe consists of a carrier lance with a test ring on top, which is cooled by air and is inserted into the flue gas at the position of the corrosion probe (see Fig. 1). The air cooling of the probe allows the investigation of arbitrary constant ring temperatures to simulate different steam temperatures. Deposit probe measurements at different probe temperatures give an indication regarding the condensation temperature of gaseous flue gas components such as KCl or NaCl. The mass gain of the test ring is determined by gravimetric measurements of the test ring before and after the exposure to the flue gas. A more detailed description of the deposit probe measurement can be found in [17]. Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analyses were performed to analyse the deposits subsequently to the measurements on three different locations (windward, windward + 50° and the leeward side) of each deposit probe ring. For each fuel two deposit probe measurements were performed. In case of forest wood chips the temperatures investigated were 480°C and 550°C. For waste wood, the temperatures 450°C and 550°C were investigated, representing the highest and lowest steel temperature investigated during the test campaign. All deposit samples were taken at a flue gas temperature of around 700°C and a superficial flue gas velocity of 2.8 m/s for forest wood chips and 3.6 m/s for waste wood, respectively. The sampling time was two hours in each case and the measurements were conducted with clean probe rings made of the steel 1.4841.

3.4. SEM/EDX- analyses and sample preparation

To investigate the chemical composition of the deposit layer by means of SEM/EDX- analyses, the deposit probe rings were first coated with a thin carbon layer to avoid an electrical charging of the sample. The samples were analyzed using a ZEISS Gemini 982 field emission scanning electron microscope equipped with a Noran Voyager X-ray analysis system (Si(Li) detector, ultra-thin window). The oxygen content was determined by stoichiometric calculations. The compositions of the deposit layers were determined by area scans using magnifications of 100 at representative spots of the ring sections: windward, windward + 50° and leeward. Because of the interaction volume of the electron beam with the sample not only the deposit layer becomes analyzed, but also the underlying steel of the probe ring. Especially for thin deposit layers, as formed during short-term deposit measurements, this is an essential problem. Due to the fact that the amount of Ni and Cr is negligible in both fuels and the release rate of Fe from the fuel is typically low, these elements were excluded from the analyses. The measured quantities of these elements are most likely components of the probe steel ring.

To gain more information regarding the corrosion mechanism, SEM/EDX analyses of the corrosion probe rings were performed subsequently to the test runs. To investigate the elemental distribution through the tube crosscut, first the ring was embedded in epoxy resin, afterwards the profile was grinded using sand papers with decreasing grain sizes until a smooth, plane surface was achieved. The cross sections were prepared under dry conditions without the use of a lubricant. Afterwards, the ring was coated with a thin carbon layer. Between the various steps the probe rings were stored in a desiccator. Elemental mappings were performed at a magnification of 400 to analyse the chemical composition of the corrosion layer. The systems used for the mappings are a Zeiss Ultra 55 field emission scanning electron microscope equipped with an EDAX Pegasus X-ray analysis system. These elemental mappings show the distribution of each element over the area investigated (bright colours mean a high concentration, weak colours a low concentration). Within these mappings the oxygen content was measured and not stoichiometrically calculated to detect oxides and to achieve a clear separation between the corrosion layer and the original steel surface. Since alkali chlorides are quite sensitive to heat it was ensured that the probe ring did not become too hot during the grinding process. Therefore, a reference sample with well-defined KCl content was prepared and analysed in the same way as the corrosion probe ring. The pre-defined KCl content of this sample could be confirmed with EDX analyses. In doing so, it is assured that KCl is not removed from the corrosion probe rings during sample preparation.

3.5. Fuel and ash analyses

To investigate the fuel composition, representative samples of the fuels were prepared. The moisture content of the fuel sample is determined according to CEN/TS 14774. Fuel sample preparation is carried out according to CEN/TS 14780. The ash content is determined according to CEN/TS 14775. Additionally, the corrected ash content were calculated by a reduction of the ash content by the amounts of carbonates in the ash. These carbonates are formed during the ashing process, which occurs at a constant temperature of 550°C. In fixed bed biomass furnaces carbonates do typically not occur due to the high temperatures prevailing. The determination of C, H and N is carried out according to CEN/TS 15104. The chlorine content is determined according to CEN/TS 15289. Major and minor ash forming elements are determined by multi-step pressurized digestion of the fuel with HNO3 (65%)/HF (40%)/H3BO3 followed by inductively coupled plasma optical emission spectroscopy (ICP-OES) or inductively coupled plasma mass spectrometry (ICP-MS) depending on detection limits.

3.6. HCl/SOx measurements

The determination is carried out according to VDI 3480, Sheet 1. Flue gas is sucked from an extraction point over several successively connected washing flasks with distilled water and diluted sodium hydroxide solution (enriched with H2BO3). The dissolved anions are measured by ion-chromatography (IC). HCl/SOx measurements were performed three times during the test run (conditions can be found in Table 3) at the position of the corrosion probe (see Fig. 1).

4. Results and discussion

4.1. Deposit formation

4.1.1. Deposit probe measurements

The chemical composition of the deposits has been determined by means of SEM/EDX analyses (see Section 3.4). The findings are presented in Fig. 3. The deposit layer of the fuel forest wood chips (see Fig. 3 left) mainly consists of potassium and sulphur which indicates the presence of potassium sulphate based on the molar ratios measured. Chlorine can only be found in very small amounts in the case of 480°C steel temperature, with a slightly higher concentration on the leeward side of the probe ring. This indicates that the condensation temperature of the gaseous chlorides lies somewhere between 480°C and 550°C. Furthermore, the amounts of Si, Ca and Mg, which are typical elements in the course fly ash, are rather low.

The composition of the waste wood deposits differs strongly from the results obtained for forest wood chips (see Fig. 3 right). Here, chlorine can be found in both deposits, although the amount of chlorine is a little bit higher for 480°C, indicating a higher condensation rate of chlorine containing salts for this temperature. One can also see, that the amount of the typical elements of the
coarse fly ash is increased compared to forest wood chips. Furthermore, in contrast to the forest wood chips deposits the waste wood deposits contain a considerable amount of Zn and Na.

For forest wood chips the RBU’s measured are $2.8 \text{ g/m}^2 \text{ h}$ for $480 \degree \text{C}$ and $1.4 \text{ g/m}^2 \text{ h}$ for $550 \degree \text{C}$. For waste wood values of $6.9 \text{ g/m}^2 \text{ h}$ for $450 \degree \text{C}$ and $7.0 \text{ g/m}^2 \text{ h}$ for $550 \degree \text{C}$ have been found. Therefore, a faster deposit build-up has to be expected in the case of waste wood in the initial state of the test campaign.

4.1.2. Deposits formed on the corrosion probes

One has to keep in mind that the long-term deposition behaviour can vary from the findings obtained from short-term deposit probe measurements due to increased surface temperatures. Therefore, the final deposit layers formed on the corrosion probes of both test campaigns have also been investigated. Fig. 4 shows the deposits on the corrosion probe formed during the test campaign with forest wood chips, whereas Fig. 5 shows the waste wood deposits. The deposit formation on the deposit probe is much faster in the case of waste wood. This result has already been indicated by the short time RBU’s measured. Furthermore, the two deposits differ regarding their structure. The deposits of forest wood chips are powdery and loosely bound to the corrosion probe and no sintering occurred. On the contrary, the waste wood deposits are sintered to single columns where the binding within the particles is quite strong but the sintered deposit layer has only a weak binding to the corroded probe surface and therefore, can be easily removed.

To investigate time dependent changes in the composition between the short-term deposit probe measurements and the deposits on the corrosion probes, the deposits of the corrosion probes have been analysed according to Section 3.5. The results of the chemical analyses can be found in Fig. 6. In contrast to the deposit probe measurements no chlorine could be found in the deposits of the corrosion probes. This result and its effect on the corrosion mechanism will be discussed in detail in Section 4.4. Furthermore, in the case of forest wood chips, the relative amount of coarse fly ash on the windward side significantly increased compared to the short-term deposit probe measurements. A plausible explanation can be given by the growing deposit layer, which results in increased surface temperatures. Hence, condensation of aerosols becomes limited and impaction of coarse fly ash particles becomes the dominating process. This effect is not distinctive in the case of waste wood due to the higher amount of coarse fly ash particles in the flue gas. In contrast to the short-term deposit probe measurements traces of Pb can be found in the deposits of the corrosion probe. An explanation could be
given by the strong deviations of the heavy metal content in the case of waste wood (see Table 2) and the rather short measurement time of the deposit probe measurements. A further difference in the chemical composition between the deposits of the deposit probe and the corrosion probe is the missing of chlorine in the deposits of the corrosion probe.

4.2. SEM/EDX analyses of the corrosion probe rings

To determine the chemical structure over the ring profile of the corrosion products and the deposit layer, SEM/EDX element mappings have been carried out on the windward, windward + 50 and leeward side of a corrosion probe ring. The findings of these analyses are presented in Fig. 7. Since the general information obtained for the various ring sides is the same, only the mappings of the windward side are presented. The composition of the deposit layer has already been determined with chemical analyses (see Section 4.1.2). The findings of the EDX analyses presented confirm the results of the chemical analyses. At the corrosion front two aspects are of special interest. The first one is the absence of chlorine for all EDX mappings. Therefore, one can only see the equally distributed background noise of the EDX analyses in the Cl mappings (see Fig. 7). The second one is the enrichment of sulphur at the corrosion front. This layer is stronger developed in the case of forest wood chips but one can also find this layer in the case of waste wood. Quantitative EDX analyses of this layer showed that it consists of Fe, O and S, with strong variations regarding the sulphur concentration. Highly resolved spot analyses show areas where the layer consists solely of Fe and S indicating the presence of FeS or FeS2. Therefore, it is concluded that the layer consists of a mixture of the two phases iron sulphide and iron oxide rather than iron sulphate. Due to the low Cr content of the steel (see Table 1) no protecting Cr2O3 layer is formed at the corrosion front (see Cr element mapping in Fig. 7).

The results for forest wood chips are in good agreement with comparable measurements carried out in a wood chips fired CHP plant [17]. Within that work also an enrichment of sulphur at the corrosion front was reported as well as the absence of chlorine.

4.3. Corrosion probe measurements

The corrosion signal measured during the combustion of forest wood chips (see Section 3.2) shows an exponential dependence on the flue gas temperature (see Fig. 8, left) as well as on the steel temperature. The empirical model in comparison to measurement values for forest wood chips [25] (left) and for waste wood (right) as a function of flue gas temperature. Explanation: flue gas velocity has been kept constant to 2.8 ± 0.5 m/s in the case of forest wood chips and to 3.6 ± 0.5 m/s in the case of waste wood; TS ... steel temperature, TFG ... flue gas temperature.

![Fig. 7. SEM/EDX element mappings through the cross section of a corrosion probe ring on the windward side. Results for forest wood chips are shown left and for waste wood right.](image)

![Fig. 8. Empirical model in comparison to measurement values for forest wood chips [25] (left) and for waste wood (right) as a function of flue gas temperature. Explanation: flue gas velocity has been kept constant to 2.8 ± 0.5 m/s in the case of forest wood chips and to 3.6 ± 0.5 m/s in the case of waste wood; TS ... steel temperature, TFG ... flue gas temperature.](image)
The trend of an increased corrosion attack with an increased flue gas velocity is shown in Fig. 10 on the left hand side. An exponential dependence on the flue gas temperature could also be found in the case of the waste wood test campaign (see Fig. 8, right). But instead of an exponential increase with increasing steel temperatures the measured signal stagnates and even slightly decreases when reaching temperatures above 500 °C (see Fig. 9, right). The steel temperature variations have been performed at least two times and the trend shown could be reproduced. However, the measured signal is more scattered than those found within the forest wood chips test campaign. A plausible explanation for that could be given by the strong deviations of the waste wood composition during the test campaign (see Table 2). Therefore, only mean values and standard deviations over ±5 °C are shown in Fig. 8 (right) and Fig. 9 (right). Also in this case a dependence on the flue gas velocity could be found. The trend is shown in Fig. 10 on the right hand side.

The dependence on the flue gas velocity is moderate for both fuels. A precise determination of this dependence is difficult, since the scattering of the measured corrosion rate for constant flue gas and steel temperatures over the whole test campaign is of similar order. Nevertheless, the dependence on the flue gas velocity can be seen on the time curve of the measured data. An example of such a time curve for waste wood is shown in Fig. 11.

Based on the experimental data, an empirical function has been derived. The empirical model developed is a combination of an Arrhenius function which describes the dependence on the steel surface and the flue gas temperature and an additional linear factor which describes the dependence on the flue gas velocity. The coefficients of the empirical model (see Eq. 1) have been determined within a stepwise approach using a least square method. First the coefficients $E_{\text{act}}$ and $A$ for each steel temperature and constant flue gas velocities have been optimized. Then the functional dependencies of these optimized parameters on the steel temperature (see Fig. 9, left). The trend of an increased corrosion attack with an increased flue gas velocity is shown in Fig. 10 on the left hand side.
have been determined for constant flue gas velocities. In a last step, the dependence on the flue gas velocity is assumed to be a linear correction of the empirical function. Due to the moderate influence and the scattered data the linear dependence is a first but sufficient assumption.

The optimized coefficients are shown in Table 4. In Figs. 8–10 the calculated corrosion potential using Eq. (1) is plotted as solid lines. One can see that the optimized function correlates adequately with the measured data.

\[
k = A(T_S) \cdot \exp\left(\frac{E_{acti}(T_S)}{R \cdot T_{FG}}\right) \cdot C(v_{FG}) \cdot 1000
\]

\[A(T_S) = \exp\left(a_1 \cdot T_S^2 + a_2 \cdot T_S + a_3\right)
\]

\[E_{acti}(T_S) = b_1 \cdot T_S^2 + b_2 \cdot T_S + b_3\]

\[C(v_{FG}) = c_1 \cdot v_{FG} + c_2\]

with: \(k\) ...corrosion rate (mm/h), \(A(T_S)\) ...pre-exponential factor (mm/h), \(R\) ...gas constant (J/mol K), \(E_{acti}(T_S)\) ...activation energy (J/mol), \(T_{FG}\) ...flue gas temperature (K), \(T_S\) ...steel temperature (K), \(v_{FG}\) ...flue gas velocity (m/s), \(C(v_{FG})\) linear correction factor and \(a_1, a_2, a_3, b_1, b_2, c_1, c_2\) ...coefficients.

The dependencies measured for forest wood chips are in good agreement with those found in real-scale CHP plants [17].

### 4.4. Corrosion mechanism

Many authors [e.g. [2,26]] reported a compact inner corrosion layer, consisting of FeCl₂ in the case of Cl-induced oxidation (detailed mechanism can be found for example in [26]). In some cases an additional FeS or FeS₂ layer subsequent to the inner FeCl₂ layer is reported [e.g. [9,26]]. In this work the EDX analyses confirm the presence of an iron sulphide layer, but due to the absence of chlorine in the deposition as well as in the corrosion layer, it is concluded that the condensed chlorine species in the initial state of the measurement campaigns (see Section 4.1.1) get sulphated and that the supply of chlorine species cannot be maintained due to increasing surface temperatures over time. Therefore, chlorine might be involved in the initial stage of the corrosion process, but no evidence for active Cl-induced oxidation can be found after ≈300 operating hours. Since the measured corrosion signal gained during the parameter variations was reproducible, it is concluded that chlorine has no or only a negligible effect on the corrosion rate throughout the time parameter variations have been performed.

In the case of the forest wood chips test campaign solid potassium sulphate is the main component of the deposit. Usually solid potassium sulphate has only a minor effect on the corrosion behaviour [1]. The only known mechanism involving sulphates is hot corrosion [1,2,27] which can be excluded as corrosion mechanism due to a missing molten sulphate layer. Since the chromium content of the steel 13CrMo4–5 is too low to form a protective chromium oxide layer (see Section 4.2), a corrosion mechanism involving the dissolution of such a layer (as proposed in e.g. [28]) can also be excluded. Therefore, it is suggested that the main corrosion mechanism in this case is the oxidation of the steel by oxygen in the flue gas. The formation of the iron sulphide layer can most likely be explained by the reaction of gaseous SO₂ with the steel or oxide layer [29].

The measured corrosion signals in the case of waste wood differ strongly from those of forest wood chips. For low temperatures (\(T_F < 480\) °C, \(T_{FG} < 700\) °C) the measured corrosive attack is much higher. This is in good agreement with the lower molar 2S/Cl ratio and the higher concentration of heavy metals (see Section 3) in the case of waste wood. This behaviour changes with increasing temperatures since the corrosion potential of waste wood does not show the exponential dependence on the steel temperature. Therefore, it is most likely that an additional or another mechanism is responsible for the corrosion behaviour found. A stagnating or even decreasing corrosion rate as a function of an increasing temperature is typically found in the case of hot corrosion type II (e.g. [30–32]). Thereby, depending on the temperature prevailing, the corrosion occurs by basic or acidic fluxing in a thin molten layer of alkali and heavy metal sulphates and/or chlorides. In general, the melting temperatures of Na₂SO₄, K₂SO₄ as well as mixtures of these sulphates are too high for melts to occur. Nevertheless, according to [33] eutectic mixtures with very low melting temperatures can be formed in the presence of heavy metal rich sulphates. Since the amount of Zn found in the deposits is considerable, the formation of a partly molten sulphate layer could be possible. This layer could be responsible for the corrosion behaviour found. This is also in agreement with lab-scale work of van Lith [34] in which the corrosion behaviour under conditions typically prevailing in waste wood fired boilers has been investigated. Within this work molten deposit layers were found at 500 °C.

### 5. Summary and conclusions

To investigate the high-temperature corrosion and deposit formation behaviour of superheater tube bundles, online corrosion probe and deposit probe measurements have been carried out in a specially designed fixed bed/drop tube reactor. The investigated boiler steel 13CrMo4–5 is commonly used as steel for superheater tubes in biomass fired heat and power plants. Forest wood chips and quality sorted waste wood (A1–A2 according to German standards) have been used as fuels to investigate the influence of different fuels on the deposit formation and corrosion behaviour. The reactor used allows an independent variation of a single parameter of interest. Therefore, the quality of the measured correlations between the corrosion probe signal and the influencing parameters exceeds those already published. The corrosion probe measurements show a clear dependence on the parameters flue gas temperature and velocity as well as steel temperature. Following, variations have been carried out to investigate the influence on the corrosion behaviour: flue gas temperature between 650 and 880 °C, steel temperature from 450 to 550 °C and flue gas velocity from 2 to 8 m/s. Based on the experimental data gained, an empirical function has been developed which is a combination of an Arrhenius function which describes the dependence on the flue gas and the steel temperature and a linear dependence on the flue gas velocity. This empirical function is able to reproduce the corrosion potential measured sufficiently accurately.

Therefore, the empirical model developed allows plant designers and operators a quick estimation if high-temperature corrosion is of relevance for a certain parameter setup or not, when using the
The corrosion probe signals obtained for waste wood show a different behaviour. Here, the measured corrosive attack does not increase exponentially with the increasing steel temperature. Also in this case no chlorine could be found in the deposit layer or at the corrosion front. The temperature behaviour found is typical for hot corrosion type II. Since the content of Zn in the deposit is clearly enriched compared to forest wood chips, the formation of a low melting eutectic is possible. This is also in agreement with the findings of Misch and Warnecke [18]. Analyses of the deposits formed on the probe as well as subsequent SEM/EDX investigations of the corrosion probe rings show that the deposit layer mainly consists of potassium sulphate. Furthermore, no chlorine could be found neither in the deposit layer nor at the corrosion front. Therefore, it is suggested that the main corrosion mechanism prevailing is the oxidation of the steel by oxygen in the flue gas.

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References