



Short term online corrosion measurements in biomass fired boilers. Part 2: Investigation of the corrosion behavior of three selected superheater steels for two biomass fuels



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ABSTRACT

The high temperature corrosion behavior of the boiler steels 13CrMo4-5 (1.7335), P91 (1.4903) and 1.4541 has been investigated during short-term test runs (~500 h) at a biomass fired grate furnace combined with a drop tube. For the test runs performed with 13CrMo4-5 and P91 chemically untreated wood chips have been used as fuel, whereas waste wood has been used for test runs with P91 and 1.4541. Online corrosion probes and a mass loss probe have been used applying a methodology developed in a previous study to correct for a measurement error occurring during short-term measurements with online corrosion probes (mass loss correction). Furthermore, deposit probe measurements have been performed to evaluate the deposit build-up rate and the chemical composition of deposits. SEM/EDX analyses of the corrosion probes have been performed subsequently to the test runs to gain information regarding the chemical composition and structure of the deposits as well as the corrosion layers.

The furnace has been operated at constant load to ensure constant combustion conditions. The flue gas temperature at the probes has been varied between 740 and 900 °C and the probe surface temperature has been varied between 400 and 560 °C in order to determine their influence on the corrosion rate.

General trends determined by the variation of these temperatures were similar for all boiler steels: the corrosion rate increased with increasing flue gas temperature and also with increasing probe surface temperature. For chemically untreated wood chips combustion at low flue gas temperatures (740 °C) the corrosion rates were comparable for 13CrMo4-5 and P91 at all probe surface temperatures. However, at flue gas temperatures of 800 °C and higher P91 showed better corrosion resistance than 13CrMo4-5. For waste wood combustion 1.4541 generally showed a better corrosion resistance than P91.

The mass loss correction of the measurement error occurring in the initial phase resulted in different errors of 55% for 13CrMo4-5 and 32% for P91 for chemically untreated wood chips. For waste wood the mass loss correction resulted in errors of 55% for P91 and 77% for 1.4541. The results from the mass loss determination for the waste wood test runs scattered stronger compared to the wood chips test runs. Therefore, the fits were not that accurate and the error margin was higher. However, the results outline that the mass loss correction is relevant in order to achieve a meaningful comparison of different short-term test runs using online corrosion probes.

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1. Introduction and objectives

In a previous study [1] the application of online corrosion probes for the evaluation of high temperature corrosion in biomass-fired boilers based on short-term measurements has been investigated. It was shown that during the initial phase the measurement does not represent the actual corrosion rate, but the corrosion signal starts at zero and increases gradually until it is proportional to the corrosion rate.

This “start-up” effect results in an overestimation of corrosion rates. By the application of an additional mass loss probe a methodology was developed which allows for the correction of this error and results in a significant improvement of the accuracy of short-term corrosion probe measurements.

Several studies on high temperature corrosion of boiler steels report significant differences in the compositions and the structures of corrosion layers depending on the composition of the steel [2–7]. Corrosion layers of low-alloyed steels such as 13CrMo4-5 mainly consist of iron oxides [5,6] whereas for steels containing higher shares of chromium separate layers of iron oxides and chromium oxides were reported [7].

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These differences may also influence the “start-up” effect during online corrosion probe measurements. Therefore, the objective of the work presented was to demonstrate the performance of short-term test runs with online corrosion probes and mass loss probes using three boiler steels as well as an evaluation of the results based on the new methodology and a comparison between the different materials. Within the work presented the steels 13CrMo4-5, P91 and 1.4541 have been evaluated. The test runs have been performed using a 50 kW grate furnace combined with an electrically heated drop tube. For this purpose chemically untreated wood chips and waste wood have been used as fuels. Subsequently to the test runs, the corroded steels have been analyzed to determine the corrosion mechanisms prevailing.

2. Materials and methods

The test runs have been carried out in a biomass grate furnace combined with a drop tube using chemically untreated forest wood chips and waste wood as fuels. The chemically untreated forest wood chips fuel mainly consisted of logging residues but also contained bark as well as small fractions of fine particles and needles. The biomass originated from a local supplier close to Graz, Austria and was harvested within a radius of approximately 50 km around Graz. For the two test runs, two different batches of fuels were supplied. In the following, this fuel is referred to as “wood chips”. The waste wood was provided by a local supplier in the area of Graz and mainly consisted of demolition wood. For these test runs only one batch of fuel was used. The fuels used complied with the specifications according to EN 14961-1:2010 [8] as presented in Table 1.

The chemical compositions of the fuels can be found in Section 3.1, Table 4. Within the tests, the corrosion behavior of the superheater materials 13CrMo4-5, P91 and 1.4541 was investigated. The chemical compositions of the steels are shown in Table 2.

For the combustion of chemically untreated wood chips usually low and medium alloyed steels are applied for superheaters, therefore only 13CrMo4-5 and P91 have been investigated for this fuel. In case of waste wood combustion a higher risk for corrosion is assumed and therefore only the two higher alloyed steels P91 and 1.4541 have been investigated. The materials have been chosen, since these are materials which are typically used for superheaters in biomass CHP plants. The test run matrix is illustrated in Table 3.

2.1. Biomass test rig

The test rig (Fig. 1) consists of a biomass grate furnace equipped with air staging and flue gas recirculation coupled with an electrically heated vertical tube (the so-called drop tube). The drop tube has a length of 3 m and an inner diameter of 0.15 m. The grate furnace can be operated between 12–50 kW fuel input power (related to the net calorific value) and the drop tube has an electrical input power of up to 60 kW. At the exit of the drop tube the measurement ports for the online corrosion probe and the mass loss probe are located. A more detailed description of the experimental facility is given in [1,9].

2.2. Online corrosion probe

The online corrosion probes (Fig. 2a) applied within the test runs consist of a sensor (Fig. 2b) which is placed on the top of a carrier-lance. The sensor is temperature controlled and cooled by air allowing the simulation of heat exchanger tubes with different surface temperatures. It consists of 4 rings, which are made of a steel of choice, in this study 13CrMo4-5, P91 or 1.4541. When exposed to the flue gas, a layer of deposits and corrosion products forms on the surface of the sensor. This layer represents an electrolyte and allows the instantaneous determination of a corrosion signal with the three electrode rings which is proportional to the corrosion rate. The relation between the corrosion signal and the actual corrosion rate is determined with the mass loss of the mass loss ring. A more detailed description of the online corrosion probe can be found in [1,10–12].

Since the conductive layer starts to form as soon as the probe is exposed to the flue gas, the measured corrosion signal increases gradually from zero. As soon as a fully developed ionic layer has been formed on the surface, the corrosion signal is proportional to the corrosion rate. Therefore, in the initial phase of the measurement, which lasts about 300 h based on experiences with forest wood chips combustion, the actual corrosion rates cannot be correctly determined with the online corrosion probe. A detailed description of this measurement error is given in [1].

2.3. Mass loss probe

In order to gain data for correction of the measurement error from the online corrosion probe during the initial phase a special mass loss probe has been developed as described in [1]. The mass loss probe consists of an air-cooled carrier-lance with five test rings on top. The temperature of the test rings is controlled by cooling air which allows the simulation of a heat exchanger tube similar to the online corrosion probe. These rings have to consist of the same steel as the sensor of the online corrosion probe. For the measurement, the mass loss probe is exposed to the flue gas next to the online corrosion probe with a similar surface temperature set value. Individual test rings are removed from the probe after different times (24–340 h) to gain time-related mass losses. Hereby the trend of the corrosion rate during the initial phase of a test run can be determined. To determine the mass loss of the test rings, the rings are weighed before being exposed to the flue gas. After the test run, the corrosion products are removed according to ASTM G1-03 [13] and the mass loss is determined gravimetrically. Details regarding the mass loss probe are presented in [1].

2.4. Methodology for the evaluation of corrosion rates

At the start of the test run the online corrosion probe and the mass loss probe are exposed to the flue gas and are operated at similar surface temperatures throughout the whole test run. The test run is divided into two phases: the initial phase and the variation phase. During the initial phase the operating conditions of the plant and the probes are kept constant. In this phase the trend of the corrosion rate is determined with the mass loss probe. When a fully developed ionic layer has been formed on the surface of the online corrosion probe the variation

Table 1
Fuel specifications according to EN 14961-1:2010.

	Origin	Particle	Moisture	Ash	Bulk density
Wood chips	1.1.4.4	P45A ^c	M35 for 13CrMo4-5	A3.0	BD200
	1.1.4.5		M25 for P91		
Waste wood	1.3.1.1	P45A ^c	M25 for P91	A10.0 + (21.8) for P91	BD250
	1.3.2.1		M30 for 1.4541		

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