Research article

Investigating corrosion memory: The influence of previous boiler operation on current corrosion rate

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A B S T R A C T

The selection of fuel is crucial for a Combined Heat and Power (CHP) plant in terms of cost and corrosion and the fuel will vary over time. The corrosiveness of different fuels has been studied extensively, however, not how a current corrosion attack is influenced by corrosion history (i.e. previous deposit buildup and oxide scale formation) instead of the influence of the current flue gas composition (i.e. the current fuel mix being used). This influence of the corrosion history effect can be called "corrosion memory".

To investigate the corrosion memory effect on boilers, a novel setup was used. Air-cooled probe AISI304L samples were exposed in two different boilers to mimic different fuels. One boiler was a biomass-fired boiler representing a moderate corrosive fuel and the other was a waste-fired boiler representing a highly corrosive fuel. A three-step exposure program was performed in which a reference probe was exposed in the biomass-fired boiler for all three steps while another probe was exposed in the biomass-fired boiler for steps 1 + 3 and in the waste-fired boiler for the second step. All samples were investigated with material-loss measurements and SEM/EDX. The findings show that the deposit and oxide scales formed on the samples in the biomass-fired boiler had a mitigating effect on the corrosion attack. Consequently, corrosion history affects the future corrosion rate.

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1. Introduction

The selection of fuel for a Combined Heat and Power (CHP) plant will vary over time depending on cost and corrosiveness. By choosing less expensive fuels, operation costs are reduced, however, less expensive fuels are generally more corrosive, and the decrease in direct operation costs is offset by an increase in maintenance costs due to corrosion. The corrosion rate may, in addition, be affected by a former fuel mix, i.e. by the corrosion history of the boiler (i.e. previous deposit buildup and oxide scale formation). A fuel can, thereby, not only influence the present corrosion rate but can also leave a memory effect that influences the future corrosion rate. This can be illustrated with an example: If a boiler is first operated with non-corrosive fuels, relatively benign ash deposits will be formed on the surfaces of heat exchangers, and a corrosion attack can be expected to be mild. If a boiler is operated with a fuel mix that is more aggressive (e.g. has a high content of alkali chlorides), the formation of aggressive ash deposits may start to form. However, this deposit will form on top of the former, benign, deposit. Since the former deposit separates the material surface and this new, corrosive deposit, it can be regarded as exhibiting some corrosion resistance.

Due to the high net emission of CO_2 from fossil fuel combustion, the production of electricity from renewable fuels, such as biomass and waste, is on the rise. However, the combustion of these fuels often results in a flue gas rich in alkali chlorides and hydrogen chloride (HCl), while the sulphur dioxide (SO_2) content is typically low [1–4]. This generates deposits rich in alkali chlorides, which are well known to cause accelerated corrosion of the high temperature alloys used for heat-exchangers [5–13]. The increase in corrosion rate is often explained by "the active oxidation mechanism" [5,14,15] or by KCl-induced alkali chromate formation (K_2CrO_4) [5–13,16–20]. In the latter case, it is suggested that alkali reacts with chromium (Cr) in the initially formed protective oxide on stainless steel, forming alkali chromates. This reaction depletes the oxide in chromium and destroys its protective properties, resulting in a fast growing, iron-rich, and poorly protective oxide. This increase in corrosion may result in a failure of boiler operation or an unplanned shutdown of the boiler.

In order to decrease the corrosion rate in a boiler, it is possible to keep the steam and, thereby, the material temperatures moderate. However, these results in a boiler operated with poor electrical efficiency. In order to allow the boiler to be operated at high temperature and pressure, attempts have been made to mitigate such corrosion by changing the chemistry of the fireside environment. A successful way to minimize corrosive alkali chlorides is by sulphating them into less corrosive alkali sulphates [21–23]. This can be done by increasing the amount of available sulphur in a boiler by using sulphur-based additives or by co-combustion with a sulphur-rich fuel [17,24–31]. However, very little is known about how changes in the chemistry of the fireside

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environment will influence future corrosion rates, i.e. if there is a memory effect from the former fuel.

The main objective of this work is to investigate how the corrosion of heat exchange surfaces is affected by variations of the fuel mix in a boiler and corrosion history. This is done by introducing a novel scheme that utilizes probe exposures in two different boilers. The overall aim of this study is to generate generic knowledge about the dynamic corrosion processes in different environments and how these are affected by the history of boiler operation.

2. Materials and methods

The exposures were performed with air-cooled probes and sample rings made of a stainless steel (AISI 304 L, see the composition in Table 1). All sample rings were fabricated with a lathe and cleaned in acetone and ethanol using an ultrasonic bath prior to exposure. The outer diameter of the sample rings was 48 mm and the wall thickness was 2.7 mm. Each probe had three different temperature zones with three samples in each zone. The temperatures were 450 °C and 600 °C. Only the AISI 304 L samples at 600 °C will be included in this paper. The probes were exposed in two different boilers (a biomass- and a waste-fired boiler) at the EON plant in Norrköping, Sweden, in order to simulate changes in fuel. The flue gas temperatures at the probe positions were 700 °C and 850 °C, respectively, for the biomass-fired boiler and the waste-fired boiler.

2.1. Plant description

Two boilers were used for the exposures, one co-firing biomass-fired boiler and one waste-fired boiler. The biomass boiler was a Circulating Fluidized Bed (CFB) boiler with a thermal capacity of 131 MW. The waste-fired boiler was also a CFB boiler with a thermal capacity of 75 MW. Both boilers generate steam for electricity production, industrial processes, and heat for district heating. The co-firing biomass and waste fuel mix was composed of 30% tyre-derived fuel, 25–30% recycled wood, and 45–50% forest residues. The waste-fired boiler used a fuel mixture containing 50% household waste and 50% industrial waste. A more thorough description of the boilers and a table with the composition of the fuel mixes in each boiler can be found in [32].

2.2. Exposure strategy

A three-step exposure program was carried out using two identical probes in two different boilers with the temperature set at 600 °C. A schematic drawing of the exposure program is shown in Fig. 1. Both probes were first exposed for 313 h in the biomass-fired boiler (a moderately corrosive environment), resulting in a non-corrosive deposit, see Fig. 3. After the first step, the three samples in the outer temperature zone were changed on both probes, i.e. 3 out of 9 samples were replaced. During the second step, one of the probes (Probe 2) was exposed in the waste-fired boiler (a highly corrosive environment) while the other probe (Probe 1) was exposed in the biomass-fired boiler again. Both probes were exposed for 236 h in the second step. The third exposure (Step 3 in Fig. 1) was performed with both probes placed in the biomass-fired boiler for 162 h. Prior to each exposure, the three samples in the outer temperature zone were changed on both probes. After removing the probes from inside the boiler between exposures, they were

Table 1
Chemical composition of 304 L (w.%).

Cr	Ni	Mn	Si	Mo	Fe
19.5	9.6	1.4	1.1	0.3	67.0
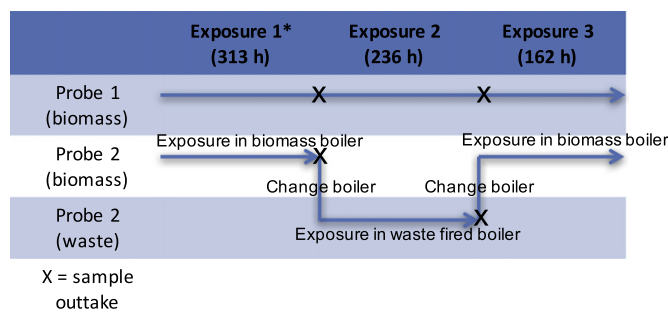
Fig. 1. A schematic drawing of the three-step exposure program. X marks the spot where the probes were removed from the boilers (change of samples) and re-installed (same boiler for Probe 1 and change of boiler for Probe 2 after each exposure).

cooled down to 30 °C in order to handle and store the samples. Then, three new samples were placed on each probe to replace the exposed ones, and both probes were inserted again and the next exposure was made. The whole process was carried out as fast as possible in order not to damage the samples. All the samples were placed in desiccators at dry conditions when removed to preserve them and to avoid altering the formed oxides.

2.3. Analytical techniques

2.3.1. Optical inspection
All samples were investigated with visual inspection after the exposure. The colour, thickness, and adherence of the deposit and/or the corrosion product layer provided general information about the overall condition of the exposed samples. All samples were stored in desiccators with the drying agent phosphorous pentoxide present while waiting for analysis.

2.3.2. Scanning electron microscopy/energy dispersive X-rays (SEM/EDX)
Scanning electron microscopy/energy dispersive X-Rays (SEM/EDX) were used to analyse the microstructure and the chemical composition of the deposit and corrosion products. The samples were cast in epoxy and then cut to make cross sections. The cross sections were polished dry and sputter-coated with platinum prior to SEM/EDX analysis. A FEI 200 Quanta FEG Environmental SEM equipped with an Oxford Inca Energy Dispersive X-ray analysis (EDX) system was operated in high vacuum mode and at an acceleration voltage of 20 kV.

2.3.3. Material loss measurements
The samples were evaluated by means of metal loss determination performed with a digital screw micrometer (0.001 mm resolution) and with SEM. Prior to exposure, the sample thickness was measured with a digital screw micrometer. Each sample was measured at 8 different locations by turning the sample ring 45° each time. After the exposure, the sample thickness was measured with SEM at sample cross sections. The edges of the ring and the deformed areas were avoided. The metal loss was determined by the difference between the sample thickness before and after exposure. The error in the measurements was estimated to be about 10 μm according to the micrometer specifications.

2.3.4. X-ray Diffraction (XRD)
Crystalline corrosion products and deposits were removed from the surface of each sample and analysed with Grazing-Incidence X-Ray Diffraction using a Siemens D5000 powder diffractometer equipped with a grazing incidence beam and Göbel mirrors. CuKα radiation was used, and the angle of incidence was 1–10°. The measurement range was 20° < 2θ < 70°.