

CAUSES OF LOW-TEMPERATURE CORROSION IN COMBUSTION OF BITUMINOUS COAL

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Abstract – Maximizing energy recovery by keeping flue gas temperatures as low as possible is of great interest in the power business, as higher recovery leads to higher plant efficiency. However, minimum allowable temperature is often limited by the presence of sulfuric acid. Condensation of sulfuric acid on steel surfaces could lead to severe corrosion. Hygroscopic deposits may also cause severe corrosion by taking up water and thus leading to wet corrosion. In this study, the risk of sulfuric acid corrosion and corrosion caused by hygroscopic deposits was studied in a full-scale circulating fluidized bed (CFB) boiler. The boiler was run both with and without limestone addition to reveal the effect of limestone on sulfuric acid corrosion and the effect of limestone on wet deposit corrosion. Furthermore, the effect of load on corrosion was studied. The measurements were performed before and after the electrostatic precipitator (ESP). A KCl salt method, which has been developed to detect trace concentrations of gaseous sulfuric acid, was used to study the risk of sulfuric acid corrosion. Furthermore, an acid dew point meter was used to determine the dew point temperature in the flue gases. Additionally, an air-cooled short-term corrosion probe was used to measure the corrosion rate of carbon steel at various material temperatures. Windward, side, and leeward side deposits were collected from the probe and analyzed by means of scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX). Fuel and fly ash samples for the different test cases were collected and analyzed. The work revealed new interesting findings on the causes of low-temperature corrosion in combustion of bituminous coal. The different operational parameters of the boiler had a significant impact on deposit composition and on expected corrosion risk. In this paper, we discuss the risks of sulfuric acid corrosion as well as corrosion caused by hygroscopic deposits. Furthermore, the influence of boiler parameters on deposit composition and chemistry will be discussed.

Key words: Low-temperature corrosion, SO_3 , H_2SO_4 , hygroscopic deposits

INTRODUCTION

Efficient use of energy in boiler flue gases is of great importance in order to recover as much energy as possible. An effective way is to lower the boiler exit flue gas temperature. Every 10°C drop in the flue gas temperature could potentially increase the boiler thermal efficiency by 0.5%. However, lowering the temperature of the flue gases can lead to corrosion, here referred to as low-temperature corrosion, of pre-heaters and walls of the flue gas channel. One of the concerns with respect to lowering the flue gas temperature is the sulfuric acid dew point. If the temperature of metal surfaces is lower than the sulfuric acid dew point it may lead to severe corrosion (Mobin et al., 2008). In coal combustion, the ash plays an important role in the formation of SO_3 (Spörl et al., 2014). Sulfur trioxide can both be captured in the ash forming sulfates (Marier and Dibbs, 1974; Lisa et al., 1999; Kassman et al., 2010; Glarborg and Marshall, 2005) and the ash may also catalytically convert SO_2 to SO_3 at lower temperatures (Marier and Dibbs, 1974; Belo et al., 2014). The extent of SO_3 formation depends also on temperature and residence time (Fleig et al., 2013), sulfur content in the fuel, excess oxygen (Fleig et al., 2013; Bennett, 1976), additives, and SCR (Khan et al., 2013). When the flue gas temperature drops below some 500°C, SO_3 starts reacting with water vapor forming gaseous H_2SO_4 . At about 200°C all SO_3 is converted to $H_2SO_4(g)$. The dew point depends on the concentrations of $H_2SO_4(g)$ and H_2O and is normally 100-150°C.

Low-temperature corrosion can also be caused by hygroscopic deposits. It has recently been shown that sulfuric acid is not the cause of low-temperature corrosion in biomass boilers, while hygroscopic salts can absorb water, which subsequently may lead to corrosion (Vainio et al., 2016a and 2016b; Müller et al., 2012; Lindau and Goldschmidt, 2008).

In this work, the risks of sulfuric acid corrosion and corrosion by hygroscopic salts were studied in a full-scale CFB boiler burning bituminous coal. Different operational modes of the boiler were used. Tests were conducted at full and partial boiler load, with and without limestone feeding. Dew-point measurements and measurements of $H_2SO_4(g)$ were conducted before and after the Electro-Static Precipitator (ESP). Additionally, short-term corrosion probe measurements were done to determine the corrosion rate of carbon steel at different material temperatures.

EXPERIMENTAL

Boiler and fuel

The measurements were conducted in a full-scale CFB boiler burning bituminous coal at different operational conditions. Measurements of $H_2SO_4(g)$, dew point, and corrosion probe measurements were performed before and after the ESP (Fig. 1). The two first days were operated without limestone addition – the first day at full load and the second day at low load (55%) (Table 1). The sulfur and chlorine contents of the coal were 1.57 wt% and 0.64 wt%, respectively (Table 2).

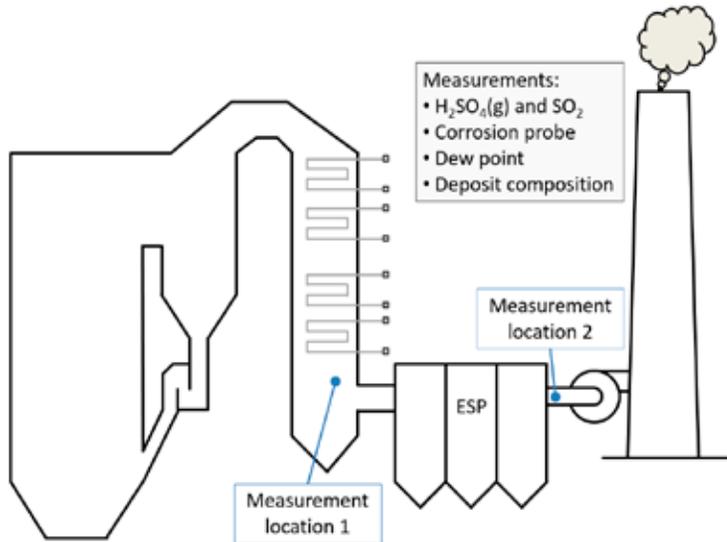


Fig. 1. Measurement locations and measurements in the CFB boiler.

Table 1. Measurement campaign matrix.

Day	Limestone feed	Load	Measurements
Day 1	Limestone off	Full	6x $H_2SO_4(g)$ + 3xcorrosion probe, flue gas temperature
Day 2	Limestone off	Low (~55%)	5x $H_2SO_4(g)$ + 2xcorrosion probe, flue gas temperature
Day 3	Limestone on	Full	5x $H_2SO_4(g)$ + 3xcorrosion probe, flue gas temperature

Table 2. Fuel properties. All numbers, except moisture, expressed on dry basis.

Total moisture	wt%	24.8
Ash content (815°C)	wt%	16.5
Volatile matter	wt%	31.7
Gross calorific value	MJ/kg	26.27
C	wt%	64.8
H	wt%	4.2
N	wt%	1.02
S	wt%	1.57
O (calculated)	wt%	11.3
Cl	wt%	0.64

Measurement techniques

H₂SO₄(g) measurements

A KCl salt method, which has been developed to detect trace concentrations of gaseous sulfuric acid, was used to study the risk of sulfuric acid corrosion. The method is described in detail in Vainio et al., 2016a. The detection limit for the method is 0.1 ppm_v.

Dew point measurements

An acid dew point meter (Lancom 200) was used to determine the dew point temperature in the flue gases. The probe has a sensor in the tip, which gives a signal when condensate forms on it. The probe tip is inserted into the flue gas channel, and the temperature is slowly decreased until the dew point is reached. The detection limit of the device is typically 5 ppm_v of SO₃ or 125°C – depends on application – and uncertainty ± 0.5°C.

Corrosion probe

An air-cooled short-term corrosion probe was used to quantify the corrosion rate of carbon steel at various material temperatures. The method is described in detail in Vainio et al., 2016a. Windward, side, and leeward side deposits were collected and analyzed by means of scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX).

RESULTS

H₂SO₄(g) and dew point measurements

The limestone feed was off during the first day, thus the SO₂ was relatively high, about 900 ppm_v (in dry gas). In spite of the relatively high SO₂, the concentrations of H₂SO₄(g) both before and after the ESP were below 0.1 ppm_v (Fig. 2). Additionally no sulfuric acid dew point was detected with the dew point meter. The measured dew point was between 50-62°C, which is well below the sulfuric acid dew point.

For Day 2 with low load and no limestone addition, the results were similar. No H₂SO₄(g) (<0.1 ppm_v) was detected before and after the ESP (Fig. 3). No acid dew point was detected with the dew point meter, and the measured dew point was 48-52°C. The reason for no H₂SO₄(g) before and after the ESP was probably the low temperature in the furnace of the fluidized bed, where the relatively low temperature lead to a low homogeneous conversion of SO₂ to SO₃. The SO₃ capturing potential of the fly ash may also be a possible explanation.

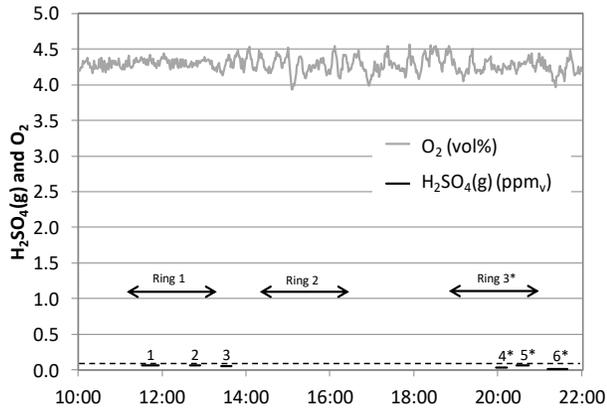


Fig. 2. H₂SO₄(g) measured before and after the ESP and SO₂ measured before the ESP during Day 1. The H₂SO₄(g) marked with * were measured after the ESP. O₂ was measured in the stack. SO₂ in the flue gas was about 900 ppm_v (dry gas). The times for the corrosion probe measurements are also depicted.

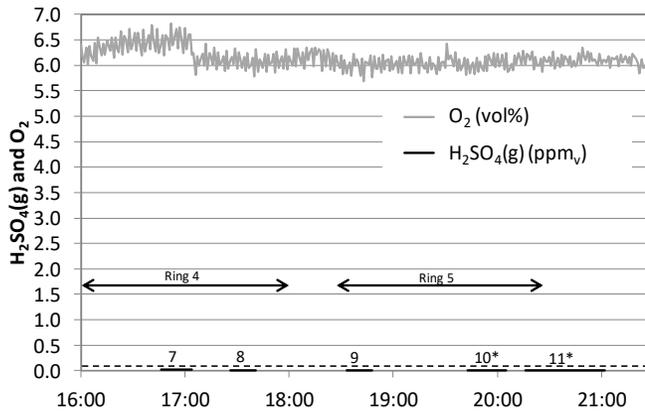


Fig. 3. H₂SO₄(g) measured before and after the ESP and O₂ was measured in the stack during Day 2. The H₂SO₄(g) marked with * were measured after the ESP. SO₂ in the flue gas was about 900 ppm_v (dry gas). The times for the corrosion probe measurements are also depicted.

When limestone was used during Day 3, SO₂ was on average 60 ppm_v, and again H₂SO₄(g) was below 0.1 ppm_v both before and after the ESP (Fig. 4). No acid dew point was detected with the dew point meter, and the measured dew point was about 55°C.

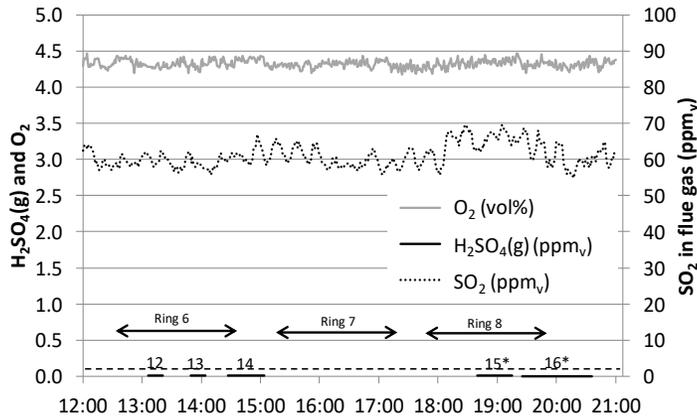


Fig. 4. H₂SO₄(g) measured before and after the ESP, and SO₂ and O₂ were measured in the stack during Day 3. The H₂SO₄(g) marked with * were measured after the ESP. The times for the corrosion probe measurements are also depicted.

Corrosion probe measurements and deposits

The estimated corrosion rates – linearly extrapolated as wall thickness losses per year – for the different cases are summarized in Fig. 5. As can be seen, the corrosion was mild with ring temperatures between 70-100°C, when limestone addition was off. The corrosion was more severe with limestone addition, confirming that corrosion risk is not associated to sulfuric acid condensation. Instead, the corrosion risk is related with the formation of hygroscopic deposits when limestone is used.

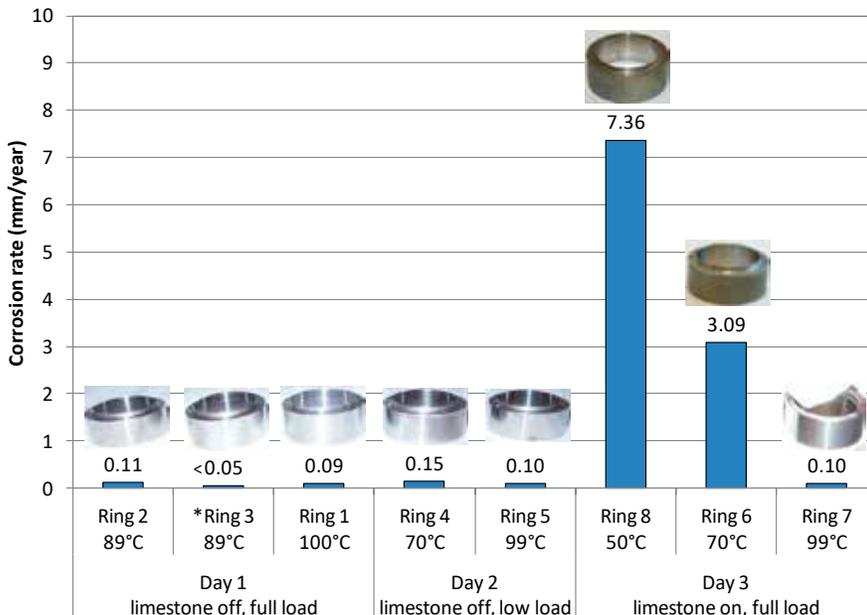


Fig. 5. Summary of the extrapolated corrosion rates and pictures of the side of the washed corrosion rings. The measurement marked with * is measured after the ESP.

Three corrosion probe measurements were conducted during Day 1 (full load and no limestone addition). Two measurements were done before the ESP and the ring temperatures were adjusted to 100°C and 89°C. The corrosion was mild, only ~0.1 mm/year. The rings had a very thin layer of deposit on the windward side and the side-side of the ring. Deposits could be collected only from the leeward side of rings 1 and 2. No corrosion was either observed in the corrosion probe measurement after the ESP (Ring 3), and no deposit samples could be collected due to the very low deposit build-up. The EDX analyses of the leeward deposits on Ring 1 and Ring 2 are given in Fig. 6. The deposits had a very similar composition, mainly aluminosilicates, while no chlorine was present.

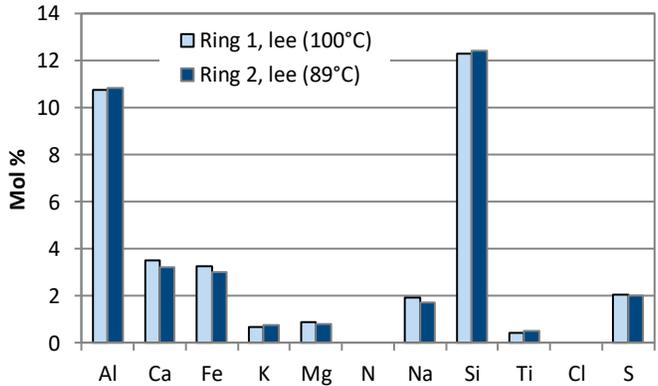


Fig. 6. EDX analyses of the leeward deposits on rings 1 and 2 (Day 1).

Two corrosion probe measurements were conducted during Day 2 (low load and no limestone addition). The measurements were done before the ESP and the ring temperatures were adjusted to 70°C and 99°C. The corrosion was mild in both tests, however with a ring temperature of 70°C a clear discoloration of the ring was observed on the side and leeward side. The corrosion was still very mild based on the weight loss and when extrapolated the corrosion rate was only 0.15 mm/year. It seems that the discoloration appeared on the same location as only some deposit was gathered on the ring. Interestingly, the wind and side deposits were high in chlorine and nitrogen, Fig. 7. The assumption is that the chlorine was present as NH₄Cl. The NH₄Cl in the deposit is likely to be formed from NH₃ and HCl present in the gas. There was no NH₃ injection during the test; however, NH₃ could originate from the fuel and remain unreacted throughout the boiler due to the low load. Ammonium chloride has previously been reported to cause low temperature corrosion, Müller et al., 2012. The darker color found on the leeward side of Ring 4 could possibly come from condensation of small amounts of acid gases or from the presence of hygroscopic salts that absorb moisture and cause wet corrosion.

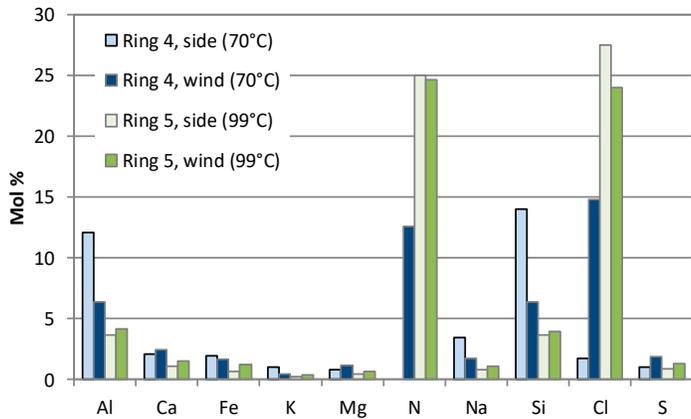


Fig. 7. EDX analyses of the side and windward deposits on rings 4 and 5 (Day 2)

Three corrosion probe measurements were conducted during Day 3 (full load and limestone addition). The measurements were done before the ESP and the ring temperatures were adjusted to 50°C, 70°C and 99°C. The corrosion was mild when the ring temperature was 99°C (0.1 mm/year), while severe corrosion was detected with a ring temperature of 70°C, which is clearly above the pure water dew point (~46°C). The corrosion rate at this ring temperature was 3.1 mm/year. This can be compared to the very mild corrosion (0.15 mm/year) during Day 2 with the same ring temperature but without limestone addition. The relative big difference could be due to the added limestone, which together with the chlorine from the fuel form hygroscopic chlorides, possibly CaCl₂. Calcium chloride has also been found to be the cause of low-temperature corrosion in biomass boilers (Vainio et al., 2016a; Lindau and Goldschmidt, 2008) and may be corrosive well above 100°C. The deposit compositions were high in both calcium and chlorine (Fig. 8). With a ring temperature of 50°C, clear wet corrosion occurred, and the corrosion was severe (7.3 mm/year).

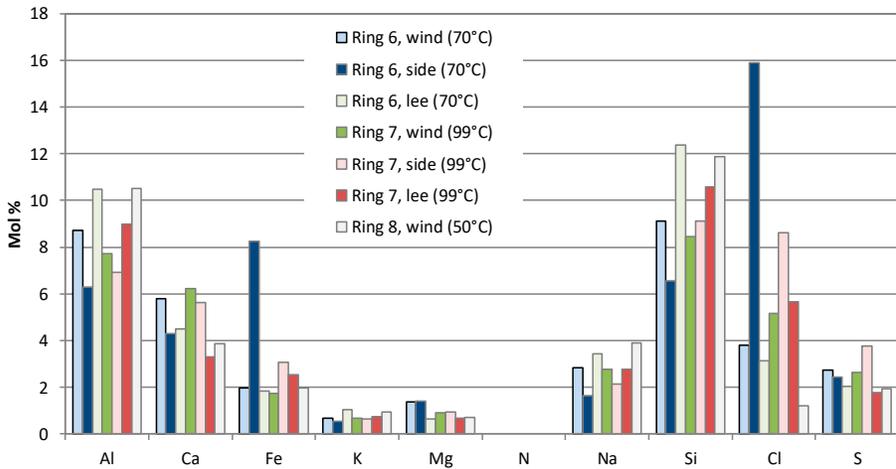


Fig. 8. Figure 1. EDX analyses of the deposits on rings 6, 7, and 8 (Day 3).

SUMMARY AND CONCLUSIONS

The causes of low-temperature corrosion were studied in a CFB boiler firing bituminous coal under different operational conditions. Measurements of H₂SO₄(g) and dew point measurements were conducted before and after the ESP. Additionally, a short-term temperature controlled corrosion probe was used to estimate the corrosion rate of carbon steel at various material temperatures. Deposits on the corrosion probe were collected and analyzed with SEM-EDX.

The H₂SO₄(g) concentration both before and after the ESP were below 0.1 ppm_v in all measurements, both with and without limestone addition. Additionally, no sulfuric acid dew point was detected with the dew point monitor. Without limestone addition, SO₂ was about 900 ppm_v and still H₂SO₄(g) was <0.1 ppm_v. This is probably due to the relatively low temperature in the furnace, which means that the homogeneous conversion of SO₂ to SO₃ is very low, together with the capturing potential of SO₃ to the fly ash.

In all cases, the corrosion was very mild with ring temperatures between 89°C and 100°C. In the case without limestone addition and lower load, the corrosion was also mild with a ring temperature of 70°C, which was the lowest temperature that was tested without limestone addition. At low load, the sampled deposits were rich in nitrogen and chlorine, most likely as ammonium chloride (NH₄Cl). Ammonium chloride is hygroscopic, but not as hygroscopic as e.g. CaCl₂.

Substantial corrosion was measured in the case with limestone addition and a ring temperature of 70°C. The corrosion rate was, through linear extrapolation, estimated to be about 3.1 mm/year. The whole

corrosion ring was covered in deposit, and the corrosion can be explained by the water uptake by a hygroscopic ash. The deposit was rich in calcium and chlorine, suggesting the presence of CaCl_2 . Calcium chloride is an extremely hygroscopic salt and forms a wet deposit at much higher temperatures than the pure water dew point. Hygroscopic iron chloride may have been also present.

In summary, this work showed that the $\text{H}_2\text{SO}_4(\text{g})$ in the flue gases was very low and that the corrosion rate of carbon steel was low at material temperatures between 89°C and 100°C . However, it was also shown that the corrosion was much more severe with a material temperature of 70°C when limestone was used (and full load). This was due to the formation of hygroscopic deposits, which increased the corrosion at temperatures much higher than the water dew point.

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