

LOW-TEMPERATURE CORROSION IN BIOMASS-FIRED COMBUSTION PLANTS – ONLINE MEASUREMENT OF CORROSION RATES, ACID DEW POINTS AND DELIQUESCENT CORROSION

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ABSTRACT: Low temperature corrosion affecting the surface of heat exchanger tubes is a main issue when it comes to efficient heat recovery technologies in flue gas flows from biomass combustion plants. Acid dew point corrosion as well as deliquescence corrosion caused by hygroscopic salts are supposed to be the main activators. In this paper the results from test runs performed in two grate combustion units in Austria firing chemically untreated wood fuels applying a newly developed low temperature corrosion probe shall be presented. Furthermore, a new methodology regarding the determination of SO₃ has been applied enabling the quantification of low SO₃ contents in the flue gas in biomass combustion plants. The test runs with the corrosion probe indicated, that corrosion due to acid dew points plays a minor role at these applications. Measurements of dust emissions and ash deposits on the sampling probes showed considerable amounts of KCl and K₂CO₃ present which are both hygroscopic salts. The deliquescence characteristics of these salts are most likely responsible for the elevated temperatures (considerably above the water dew point) at which corrosion signals started to occur.

Keywords: corrosion, low temperature, combustion, biomass, acid dew point, deliquescence, SO₃

1 INTRODUCTION AND OBJECTIVES

Modern biomass heating and CHP plants usually feature some kind of heat recovery unit downstream the boiler to improve the energy efficiency of the plant. Currently heat recovery units applied are combustion air pre-heaters, flue gas heat exchangers with a mixing valve to raise the return temperature, which feature a relatively low energy efficiency, as well as flue gas condensation units, which have a limited area of application, due to the low return temperatures required (45°C or below). The combination of a flue gas condensation unit with an integrated heat pump features elevated efficiencies but also high investment and operating costs. A common problem for all these systems is, that depending on the operating conditions, corrosion related damages at the heat exchangers may occur. Within a currently ongoing Austrian R&D project a simple and efficient heat recovery technology relying on the direct heat exchange between the return of the district heating network and the flue gas in a heat exchanger independent of varying operation conditions (dry or wet = condensing operation) shall be developed ("simple heat" technology). An increase of the plant efficiency by 2 to 5% (absolute, based on the net calorific value) and thus a better economic feasibility is expected in comparison to conventional economisers which operate with elevated return temperatures in order to inhibit low temperature corrosion. An optimal material selection is a key issue for the realisation of the new heat recovery technology requiring a fundamental understanding regarding low temperature corrosion mechanisms. In course of the R&D project appropriate experimental heat exchangers with different tube materials have been developed, designed, constructed and tested in long-term test runs. Furthermore, the application of a newly developed low temperature corrosion probe in two different biomass combustion plants as well as a new method for SO₃ detection provided significant knowledge about acid dew points and critical parameters for

deliquescence based corrosion for various biomass fuels and process conditions. The results gathered shall form the basis to develop a methodology regarding suitable process control, design concepts and material selection for such heat exchangers.

The objective of this paper is to present the results of test runs with the low temperature corrosion probe and the knowledge gained concerning low temperature corrosion caused by acid dew points and deliquescence of hygroscopic salts in biomass combustion plants using chemically untreated wood fuels.

2 METHODOLOGY

A better understanding regarding low temperature corrosion mechanisms is a key issue for the development of an advanced heat recovery technology. Especially the influencing parameters on corrosion in biomass-fired heating plants are of great interest. The main known activators for low temperature corrosion are corrosion due to acid dew points [1,2,3] and the deliquescence of salts [3,4,5]. In every case the presence of a liquid phase is of importance.

It is well known, that sulfur trioxide, sulfur dioxide, hydrochloric acid or nitrogen oxides present in the flue gas will condense at a given condensing temperature mainly dependent on the amount of the compounds and the water content forming corrosive liquid acids [2,3,4]. According to [3] within the typical range of SO₂, HCl and NO_x contents of flue gases from the combustion of chemically untreated industrial or forest wood chips of different qualities, the acid dew points of named compounds are lower or in the range of the flue gas' water dew point and can therefore not be detected by the low temperature corrosion probe. The sulfuric acid dew point, however, is significantly higher and may explain corrosion effects which often occur at temperatures considerably above the water dew point of the flue gas. For this reason only the

SO₃ dew point of the flue gas has been further investigated within this work.

Based on experimental data usually gained from the combustion of fossil fuels like coal or oil several empirical equations for the mathematical determination of acid dew points have been developed in the recent years. The relation according to Verhoff and Banchero [6] for the estimation of the sulfuric acid dew point can be found most commonly in literature and coincides well with most other empirical models. It has therefore been chosen for sulfuric acid dew point calculations within the present work. For comparison also correlations proposed by Pierce [7] and Okkes [8] have been used. The application of the named equations for biomass-fired heating plants, however, has to be handled with care because the equations are based on data gained from coal-fired combustion plants which feature considerably higher amounts of SO₃. The range of validity of these models could not be determined wherefore the equations might not be applicable for the low SO₃ contents in biomass-fired combustion plants.

During the combustion of biomass, coarse and fine ash particles are present in the flue gas. Furthermore, volatile and low-volatile elements like S, Cl, K, Na and Zn are released from the fuel bed to the flue gas forming aerosols (salt particles) as well as SO_x and HCl. The dust emissions arising downstream the boiler are mainly precipitated by adequate flue gas cleaning devices. A small amount, especially fine particles, however, remain in the flue gas and form deposits on surfaces of heat exchanger tubes located downstream the flue gas cleaning devices. The composition of these deposits varies depending on different parameters and may contain certain amounts of hygroscopic salts. In a dry environment these hygroscopic salts are crystalline. However, due to their property to humidify themselves they absorb water when the humidity of air/flue gas reaches a value characteristic for every salt at a given temperature [4,9]. A saturated salt solution is generated, which is in equilibrium with the partial pressure of water vapour in the air/flue gas [3,9]. The relative humidity of air, at which this process starts is called "relative humidity of deliquescence" and is dependent on the kind of salt used as well as the temperature. The electrolyte deriving from the deliquescence of the salt has a corrosive impact on the material's surface.

In order to study the appearance as well as influencing parameters on low temperature corrosion in more detail, a newly developed low temperature corrosion probe has been applied. The head of the probe can be seen in Figure 1. It is equipped with five metal rings, which are separated by teflon isolators. Two of these rings (1 and 5) can be used to detect the mass loss of the material for the calibration of the probe. The other rings (2, 3 and 4) are used for corrosion measurements. The potential difference between the work electrode (2) and the reference electrode (3) should usually be zero. As an electrolyte is forming at the surface of the probe, the equilibrium will be disturbed and the voltage can be measured as an indicator for a dew point. By applying a voltage between the work electrode (2) and the counter electrode (4) a current can be detected, which is proportional to the corrosion rate, the so-called corrosion signal. The air-cooling of the corrosion probe enables the simulation of different heat exchanger surface temperatures. By defining a temperature slope with specified intermediate stops it is possible to determine the temperature dependence of corrosion at given operating conditions. A possible corrosive attack can be distinguished by a sudden rise of the corrosion signal.

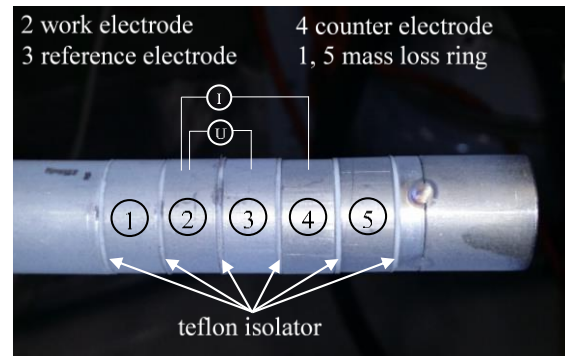


Figure 1: Low temperature corrosion probe

A number of test runs with the new online low temperature corrosion probe has been performed to identify the most important influencing parameters on low temperature corrosion. Beside lab-tests on a small pellet stove to determine the correct settings of the corrosion probe, field tests in two biomass combustion plants in Austria have been executed. In the biomass-fired heating plant in Lienz the influence of two different biomass fuels with also different moisture contents (industrial wood chips from softwood without bark (30 wt% w.b.) and forest wood chips from softwood with bark (55 wt% w.b.)) and in the CHP plant in Kufstein two different operation conditions (with and without urea injection of the SNCR unit) have been investigated. In Kufstein the test runs have been performed using forest wood chips of low quality containing little branches and needles (medium moisture content 43 wt% w.b.). In both biomass combustion plants 2–3 days of measurements have been executed during normal operation of the plants. Moreover, in Kufstein also a long-term measurement period with the corrosion probe took place over about 2 months.

The measurements with the corrosion probe have been accompanied by various other analyses to gather an overall survey on the frame conditions and the plant's operation. The measurement setup can be seen in Figure 2. Every biomass fuel used has been analysed to determine the water content, the ash content and its elemental composition regarding S, Cl, Si, Ca, Mg, K, Na, P, Al, Fe, Cu, Mn, and Zn. Furthermore, a continuous FTIR (Fourier transform infrared spectrometer) analysis of the flue gas concerning O₂, (CO₂), CO, H₂O, HCl, SO₂ as well as NO, NO₂ and NH₃ has been performed. The most important gaseous emissions have been additionally analysed by discontinuous measurements. HCl and SO₂ have been determined according to VDI 3480 sheet 1 by passing the flue gas through cascaded bottles filled with distilled water and H₂O₂ diluted caustic soda and quantifying the ions of HCl and SO₂ by high performance liquid chromatography. A discontinuous flue gas sampling according to VDI 3496 passing two cascaded bottles with 0.05 m H₂SO₄ has been used for NH₃ quantification. A Berner-type low-pressure impactor (BLPI) has been used for dust measurements. All measurements have been performed downstream the electrostatic precipitator units (ESP) installed in the heating plants upstream the position, where heat recovery units (ECO) are installed. The flue gas flow occurred from the top to the bottom.

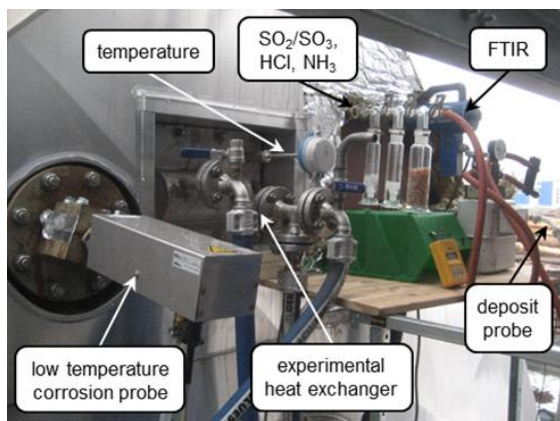
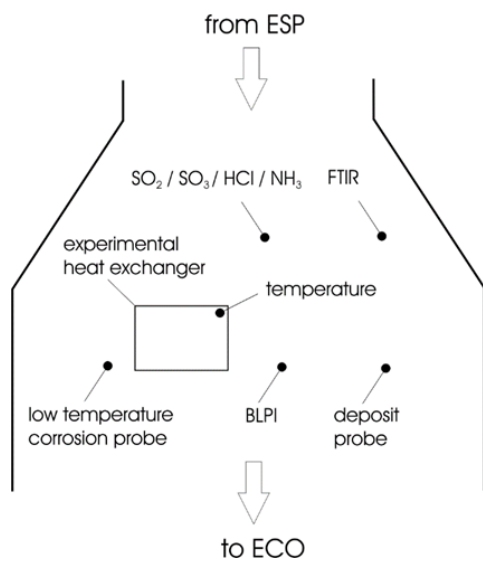


Figure 2: Measurement setup at the biomass combustion plant in Lienz

The SO_3 content of the flue gas is of major relevance to calculate the sulfuric acid dew point. Its experimental determination is difficult, however. For this reason usually the SO_x content of the flue gas determined as SO_2 has been used taking a SO_x to SO_3 conversion rate (referred to the volume) into account [3]. According to [10] this conversion rate is in a range of 1 – 5 vol% in combustion plants fired with coal and oil, but it is unknown for biomass-fired plants. In [11,12] a new method for the experimental determination of SO_3 in flue gases has been presented. It is based on a probe filled with a chlorine salt like NaCl or KCl, which is passed through by the flue gas. At temperatures below 500°C , SO_3 and water are forming H_2SO_4 . When the flue gas passes the salt, the sulfuric acid reacts with the chlorine salt changing the SO_4^- ion with the Cl^- of the salt forming hydrochloric acid. The SO_4^- however is bound to the salt and can be quantified by titration or chromatography. The method described has been adapted by the authors in order to fit to the framework conditions (low SO_3 concentrations) and used during the test runs performed to be able to determine the conversion rate of SO_x to SO_3 (referred to the volume) in biomass combustion plants. Ultrapure KCl is therefore packed in a small tube and fixed with quartz wool at both ends. The tube is positioned in the flue gas flow until the probe and the salt inside have reached flue gas temperature. Then a vacuum pump is started sucking flue gas through the

probe, where K_2SO_4 is formed. A gas meter is used to determine the flue gas flow. The SO_3 contents of the flue gas are quantified by dissolving the salt and analysing it by ICP-OES (inductively coupled plasma optical emission spectrometry).

To determine the particle size distribution of aerosols as well as the total dust concentration in the flue gas Berner-type low-pressure impactors have been used. The dust samples gained have additionally been analysed regarding their chemical composition. Furthermore, a deposit probe with a regulated surface temperature of 100°C was supposed to deliver information about ash deposit formation. To gather data regarding the presence of hygroscopic salts which may cause deliquescence corrosion, selected samples of ash deposits as well as of impactors have been further analysed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX).

3 RESULTS AND DISCUSSION

3.1 Results of test runs at the biomass-fired heating plant in Lienz (East Tyrol, Austria)

The biomass-fired heating plant in Lienz (East Tyrol, Austria) consists of two grate fired furnaces with warm water boilers with nominal heat capacities of 7 and 8 MW and is equipped with a multi-cyclone and an electrostatic precipitator for flue gas cleaning. To evaluate the influence of the biomass fuel used on the temperature at which the corrosion signal starts to rise, test runs with the low temperature corrosion probe have been performed with two different biomass fuels. The first one chosen was industrial wood chips from softwood (mainly spruce) without bark at a mean water content of 55 wt% w.b.. Subsequently the same measurements have been performed during the plant operation with forest wood chips from softwood (mainly spruce) with bark at a mean water content of 30 wt% w.b.. The chemical composition of the wood chips used during the test runs can be seen in Table 1. All values are in a representative range compared to biomass data base values available.

Table 1: Element analysis of wood chips used in the biomass combustion plants in Lienz and Kufstein

	Lienz		Kufstein
	Industrial wood chips	Forest wood chips	Forest wood chips
Moisture content [wt% w.b.]	55.6	29.7	43.3
Ash content [wt% d.b.]	0.7	0.6	5.8
S [mg/kg d.b.]	76	63	341
Cl [mg/kg d.b.]	298	184	205
Si [mg/kg d.b.]	343	100	8,210
Ca [mg/kg d.b.]	1,500	1,310	8,350
Mg [mg/kg d.b.]	200	218	1,970
K [mg/kg d.b.]	669	830	2,750
Na [mg/kg d.b.]	27	31	381
P [mg/kg d.b.]	89	42	390
Al [mg/kg d.b.]	99	43	2,340
Fe [mg/kg d.b.]	63	30	1,360
Zn [mg/kg d.b.]	11	13	36

d.b. ... dry basis; w.b. ... wet basis

During the test runs with wet industrial wood chips, the water content of the flue gas was in a range of 20 to

24 vol% at an oxygen content of about 9 vol% d.b. as can be seen in Figure 3. The corresponding water dew points of the flue gas are in a range of about 58 – 63°C. A rise of the corrosion signal is the indication that the corrosion probe has reached a temperature, where low temperature corrosion may start to occur. In the case of wet industrial wood chips, this initial temperature was in the range of 73 – 81°C, which is significantly higher than the related water dew point of the flue gas. Three repetitions of the corrosion probe measurements have been performed within each test run. The set and actual temperature indicated in Figure 3 correspond to the surface temperature of the corrosion probe.

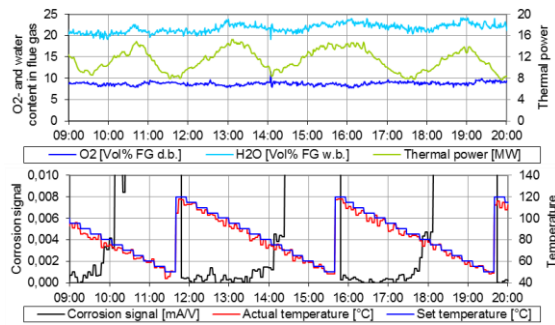


Figure 3: Results of corrosion measurements at the biomass-fired heating plant in Lienz with industrial wood chips (moisture content of the biomass fuel: 55.6 wt% w.b.)

Figure 4 shows the results for the test runs with dry forest wood chips with bark. Corresponding to the lower moisture content of the fuel, the water content of the flue gas was reduced to a range of 8 to 16 vol% at a varying oxygen content of 8 to 15 vol% d.b. The water dew points of the flue gas at these conditions varies between 46 – 53°C. It can be seen, that during these test runs, the corrosion signal started to rise at temperatures in a range of 50 – 61°C and therefore at a significantly lower level than determined while using wet wood chips but again at higher temperatures than the corresponding water dew point.

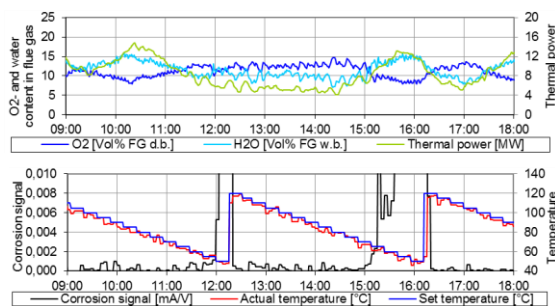


Figure 4: Results of corrosion measurements at the biomass-fired plant in Lienz with forest wood chips (moisture content of the biomass fuel: 29.7 wt% w.b.)

The test runs with the low temperature corrosion probe have been accompanied by discontinuous sulfur and chlorine measurements. The HCl contents detected during the test runs with industrial wood chips and forest wood chips with bark have been low (in a range of 0.4 – 0.45 mg/Nm³ and 0.29 – 0.48 mg/Nm³ respectively; values related to dry flue gas and 13% O₂). The detection

limits for SO₂ and SO₃ contents are determined by the analysis device and the sampled flue gas flow. During the test runs in Lienz the limit varied between 0.0681 – 0.111 mg/Nm³ for SO₃ and 0.5691 – 1.017 mg/Nm³ for SO₂ (related to dry flue gas and 13% O₂). All results gained during the test runs in Lienz have been under the corresponding detection limit wherefore the SO₂ and SO₃ contents could not be determined. Due to the low concentrations of SO₃ and HCl the rise of the corrosion signal occurs most likely due to the presence of hygroscopic salts. The results of fine dust measurements were in the range of 1.1 – 4.2 mg/Nm³ (industrial wood chips) and 0.9 – 1.8 mg/Nm³ (forest wood chips).

The results of the discontinuous measurements performed in Lienz and the corresponding calculations are summarised in Table 2.

Table 2: Results Lienz – discontinuous measurements and corresponding calculations

		Industrial wood chips (M55)	Forest wood chips (M30)
HCl	m s mg/Nm ³	0.44 0.03	0.38 0.09
SO ₂	m s mg/Nm ³	below detection limit <0.57 – <1.02	
SO ₃	m s mg/Nm ³	below detection limit <0.07 – <0.11	
NH ₃	m s mg/Nm ³	n.d.	n.d.
PM ₁	m s mg/Nm ³	2.6 2.2	1.4 0.6
Water dew point (calculated)	°C	58 – 63	46 - 53
Increase of corrosion signal at	°C	73 - 81	50 - 61
H ₂ SO ₄ dew point (Verhoff)	°C	n.d.	n.d.

All emission data related to dry flue gas and 13 vol% O₂; n.d. ... not determined; m ... mean value; s ... standard deviation

Elemental analyses of the dust in the flue gas and of the ash deposits were supposed to supply relevant information concerning the presence of hygroscopic salts which may cause deliquescence corrosion. The results are shown in section 4 and discussed in comparison to the results of the CHP plant in Kufstein.

3.2 Results of test runs at the biomass-fired CHP plant in Kufstein (Tyrol, Austria)

The biomass-fired CHP plant in Kufstein (Tyrol, Austria) consists of a grate fired steam boiler with a nominal steam power of 30 t/h and a steam turbine. For flue gas cleaning a multi-cyclone, an electrostatic precipitator as well as a flue gas condensation unit are used, whereby the measurements described in this paper have been performed downstream the electrostatic precipitator but upstream the condensation unit. To keep the NO_x emission limits a SNCR (selective non catalytic reduction) unit with urea injection is installed.

According to [4] ammonium chloride originating from excess ammonia from the SNCR unit may be an important activator for low temperature corrosion. To evaluate the impact, test runs with and without operation of the SNCR unit have been performed in Kufstein. During these measurements low quality forest wood chips with bark (mainly spruce) with a mean water content of 43.3 wt% w.b. have been used. The chemical composition can be seen in Table 1.

In Figure 5 the results of the test run without operation of the SNCR unit are shown. It can be seen, that the initial temperature, at which a rise of the corrosion signal could be detected, is in a range of 64 – 70°C. The mean water content of the flue gas was about 21,5 vol% and the oxygen content was comparably low with 5 vol% d.b.. The water dew point has been estimated with 61°C. The regular peaks of the flue gas water content shown in Figure 5 originate from the soot blowers.

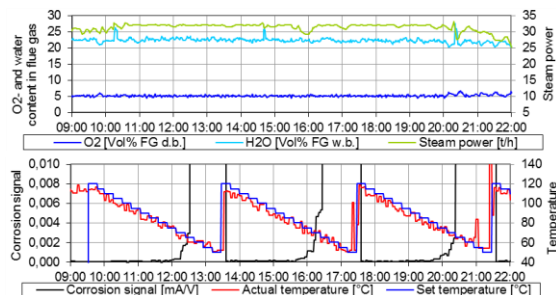


Figure 5: Results of corrosion measurements at the biomass-fired CHP plant in Kufstein without operation of the SNCR unit (biomass fuel: low quality forest wood chips with bark and a moisture content of 43.3 wt% w.b)

With operation of the SNCR unit the mean water content of the flue gas increased to about 24.3 vol%. The rise of the corrosion signal could be detected at temperatures in a range of 70 – 76°C and therefore at elevated temperatures compared to the test runs without urea injection. The results can be seen in Figure 6.

The results of discontinuous measurements performed in Kufstein and the corresponding calculations are summarised in Table 3. Due to the newly developed measurement method for SO₃ emissions, it was possible to determine the SO₂ (2.7 – 6.9 mg/Nm³) and SO₃ (0.04 – 0.07 mg/Nm³) contents in Kufstein. These have been higher than those in Lienz, which were too low to be quantified. The resulting share of SO₃ in SO_x in Kufstein is in a range of 0.2 – 2.1 vol%. The HCl contents were in a range of 2.1 to 5.2 mg/Nm³, also clearly higher than in Lienz (0.29 – 0.48 mg/Nm³).

Table 3: Results Kufstein – discontinuous measurements and corresponding calculations

			Forest wood chips (M43) with SNCR	Forest wood chips (M43) w/o SNCR
HCl	m	mg/Nm ³	2.11	5.20
	s		0.52	2.22
SO ₂	m	mg/Nm ³	2.69	6.93
	s		0.69	3.53
SO ₃	m	mg/Nm ³	0.06	0.07
	s		0.01	0.04
NH ₃	m	mg/Nm ³	45.5	n.d.
	s		20.5	
PM ₁	m	mg/Nm ³	3.8	6.8
	s		0.7	1.4
Water dew point (calculated)	°C		~61	~63
Increase of corrosion signal at	°C		70 – 76	64 – 70
H ₂ SO ₄ dew point (Verhoff)	°C		97 - 104	

All emission data related to dry flue gas and 13 vol% O₂; n.d. ... not determined; m ... mean value; s ... standard deviation

For a mean O₂ content of 5 vol% d.b., a water content of 22 vol% and 0.07 mg/Nm³ SO₃, the sulfuric acid dew point is supposed to be in a range of 97 – 104°C (acc. to [6,7,8]). In any case the acid dew point calculated could not be identified by the corrosion probe. One probable explanation could be the buffering effect of the dust deposits on the surface of the corrosion probe. The dust content of the flue gas in the biomass-fired heating plant in Kufstein has been determined in a range of 3 – 8 mg/Nm³ (related to dry flue gas, 13% O₂). These values are about a factor of 50 – 100 higher than the SO₃ contents detected. It is hence likely, that arising droplets of sulfuric acid are immediately bound by the deposits and thus hindered from causing corrosion.

3.3 Analysis of fly ash and deposit samples as well as evaluation of results

The results of the corrosion probe measurements of the test runs performed in Lienz and Kufstein are displayed in Figure 6 in dependence of the moisture content of the flue gas. It is obvious, that in all cases the initial temperatures, at which a rise of the corrosion signal could be detected, are higher than the water dew point of the flue gas. The rise of the corrosion signal measured has probably been induced by acid dew point or deliquescence corrosion mechanisms. The comparison of the results shows, that the water content of the flue gas is a relevant influencing parameter on low temperature corrosion mechanisms. The higher the water content, the higher is the initial temperature at which the corrosion signal started to rise. Comparing the initial temperatures of the corrosion measurements at which the corrosion signal started to rise for the CHP plant in Kufstein with and without operation of the SNCR unit, it can be stated that the measurements with urea injection show a certain temperature increase. The water contents in the flue gases during the test runs in Kufstein using low quality forest wood chips (43.3 wt% w.b.) and the test runs in Lienz using industrial wood chips are in a similar range. The initial temperatures at which the corrosion signal started to rise, however, differ. Due to the very low SO₃ contents in Lienz it is most likely, that the rise of the corrosion signal has been induced by the presence of hygroscopic salts. In Kufstein the SO₂ and SO₃ concentrations could be detected in the flue gas but no rise of the corrosion signal could be seen in the temperature range where the acid dew point is expected (97 to 104°C).

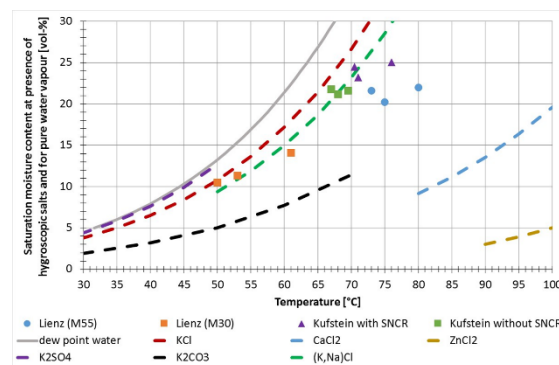


Figure 6: Comparison of corrosion signal measurements performed in Lienz and Kufstein

In Figure 6 the dew point line of water vapour as well as moisture saturation lines for relevant hygroscopic salts

are displayed. It can be seen that several initial temperatures, at which a rise of the corrosion signal could be detected are in the range of the saturation line of KCl or (K,Na)Cl. But there are also signals appearing at higher temperatures.

Table 4 shows the results of the element analyses of dust and ash deposits from Lienz and Kufstein. All impactor samples (impactor < 1 µm ... dust with an aerodynamic diameter of < 1 µm measured with a Berner-type low-pressure impactor; impactor > 1 µm ... dust with an aerodynamic diameter of > 1 µm measured with a Berner-type low-pressure impactor) as well as the ash deposits of the deposit probe and the corrosion probe from Lienz are dominated by potassium. The higher potassium content of the fine particles in all cases is typical because potassium salts occur essentially in the form of fine aerosols. Taking also the sulfur and chlorine concentrations detected in the aerosols into account, KCl, K₂SO₄ and K₂CO₃ may be the most relevant salts present.

Table 4: Element analysis of dust and ash deposits from the biomass combustion plants in Lienz and Kufstein (n.a. ... not analysed)

Element [mmol/kg d.b.]	Test runs performed in Lienz					
	Industrial wood chips			Forest wood chips		Ash deposits on the corrosion probe (24 days)
	impactor < 1 µm	impactor > 1 µm	Ash deposits (11,4 h)	impactor < 1 µm	Ash deposits (24 h)	
S	2,252	1,597	1,884	1,566	1,634	1,715
Cl	5,557	2,547	1,283	3,643	973	1,261
Si	36	80	278	113	119	156
Ca	235	1,819	1,248	61	1,332	1,130
Mg	52	420	337	14	357	310
K	11,484	8,031	9,944	11,024	11,382	9,208
Na	552	574	642	592	594	705
P	21	140	103	11	115	99
Al	-	-	54	-	33	21
Fe	13	112	73	8	25	193
Mn	12	59	46	26	68	45
Cu	-	-	-	-	-	6
Zn	151	109	143	148	153	106
NH4-N	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Element [mmol/kg d.b.]	Test runs performed in Kufstein					
	Forest wood chips without SNCR			Forest wood chips with SNCR		Ash deposits on the corrosion probe
	impactor < 1 µm	impactor > 1 µm	Ash deposits (7,3 h)	impactor < 1 µm	impactor > 1 µm	
S	2,383	1,590	2,183	2,514	2,146	
Cl	5,190	2,680	2,787	2,539	931	
Si	178	712	947	202	655	
Ca	1,302	5,514	3,917	1,098	4,990	
Mg	473	1,790	1,173	461	1,646	
K	8,108	2,839	4,322	8,261	3,172	
Na	696	319	478	1,013	439	
P	223	713	523	276	752	
Al	-	-	-	-	-	
Fe	110	374	244	105	304	
Mn	37	129	74	36	104	
Cu	-	-	6	-	-	
Zn	197	148	126	191	124	
NH4-N	36	n.a.	n.a.	221	n.a.	

The amount of potassium detected in the samples from the test runs in Kufstein are a little bit lower compared to those in Lienz. In contrast Ca and Mg are elevated, corresponding to the higher dust content measured in Kufstein. These elements are usually mainly bound as coarse fly ash particles and removed by the electrostatic

precipitator. The high amounts of Ca and Mg especially in the coarse impactor samples and in the ash deposits are most likely induced by the regular cleaning of the electrostatic precipitator or the soot blowers entraining small amounts of already precipitated particles. The low amounts of ammonium salts detected in the fine impactor samples with operation of the SNCR unit suggest, that the formation of the hygroscopic salt ammonium chloride seems to be of minor importance regarding deliquescence corrosion.

Selected impactor samples and ash deposits have additionally been analysed by X-ray diffraction (XRD) to gain further information concerning the hygroscopic salts present in the flue gas. The results of these measurements are shown in Table 5.

The evaluations confirm the results of the elemental analyses showing that KCl, K₂SO₄ and K₂CO₃ are the most important salts present in the dust of the biomass-fired heating plant in Lienz. The KHCO₃ which was found by the XRD analysis is most probably formed from K₂CO₃ during sample manipulation and transport because KHCO₃ is not stable at temperatures above 50°C. The higher amounts of Ca detected in Kufstein are also confirmed by the results of the XRD measurements. The fine dust particles and deposits in Kufstein are dominated by KCl, CaSO₄ and CaCO₃. A difference between a plant operation with and without operation of the SNCR unit, however, could not be detected, the XRD results are in principle the same for both operation conditions thus only the XRD results without SNCR are shown in Table 5. Ammonium salts could not be detected by XRD.

Table 5: XRD analysis of dust and ash deposits from the biomass combustion plants in Lienz and Kufstein

[wt%]	Lienz			Kufstein
	Industrial wood chips		Forest wood chips	Forest wood chips
	impactor < 1 µm	impactor > 1 µm	impactor < 1 µm	Ash deposits on the corrosion probe Ash deposits without SNCR
K ₂ SO ₄	46.9	58.0	47.5	42.6
KCl	53.1	42.0	17.6	7.6
KHCO ₃			33.6	48.6
CaSO ₄				16.4
CaCO ₃				14.4
K ₃ Na(SO ₄) ₂				9.3
Ca ₁₀ (PO ₄) ₆ O				8.1
MgO				9.6

4 SUMMARY AND CONCLUSIONS

The results of test runs with a new online low temperature corrosion probe performed to gather important knowledge concerning low temperature corrosion and its influencing parameters are presented in the paper.

Test runs at two grate-fired biomass combustion plants have been performed. In Lienz corrosion measurements have been executed using two different wood fuels (industrial softwood chips without bark, moisture content 55.6 wt% w.b. and forest softwood chips with bark, moisture content 29.7 wt% w.b.). In the CHP plant in Kufstein the influence of two different operation conditions (with and without urea injection of the SNCR

unit) have been investigated, using forest wood chips of low quality and a water content of 43.3 wt% w.b. as biomass fuel.

The results gathered in the heating plant in Lienz showed a relevant impact of the flue gas water content on the initial temperature at which the corrosion signal starts to rise. During the plant operation with wet industrial wood chips and water contents in the flue gas of about 20 – 24 vol%, the rise of the corrosion signal started at about 73 – 81°C. A change of the biomass fuel to dry forest wood chips and a reduced flue gas water content of 8 – 16 vol% caused a decrease of the initial temperature where a rise of the corrosion signal occurred to 50 – 61°C. Measurements at the CHP plant in Kufstein utilising forest wood chips identified an initial temperature of 64 – 70°C at a mean flue gas' water content of 22 vol% at operation conditions without urea injection and a slightly elevated temperature range of 70 – 76°C with operation of the SNCR unit at a mean water content of the flue gas of 24.3 vol%. Due to the relevant influence of the flue gas' water content on the initial temperature at which the corrosion signal starts to rise, the water content of the flue gas could have been identified as an important influencing parameter for low temperature corrosion. It could also be determined, that the initial temperature at comparable moisture contents of the flue gas varies in a certain range implying that also the chemical composition of the dust deposits seems to have an influence.

Comparing the acid dew points of SO₃, SO₂, HCl and NO_x present in the flue gas of biomass combustion plants fired with chemically untreated wood chips it has been determined, that only the SO₃ dew point is significantly above the water dew point of the flue gas and could therefore be detected by the low temperature corrosion probe. For this reason only the sulfuric acid dew point has been taken into account within this paper. The SO₃ content in biomass combustion plants is significantly lower than e.g. in coal-fired plants wherefore empirical models for the prediction of the sulfuric acid dew point or guiding values for the volumetric conversion rate of SO_x to SO₃ have to be handled with care. Within this work a new measurement method for the determination of SO₃ contents in flue gases from biomass combustion plants has therefore been developed and successfully tested. The results gained from the test runs in Kufstein delivered SO₃ contents of 0.06 – 0.07 mg/Nm³ (dry flue gas, 13% O₂) which correspond to a conversion rate of 0.2 – 2.1 vol% from SO₂ to SO₃. In Lienz the SO₂ contents were under the detection limit of 0.5691 – 1.017 mg/Nm³.

In all test runs performed the rise of the corrosion signal occurred at temperatures considerably higher than the water dew point of the flue gas at given conditions. Especially due to the negligible amounts of SO_x in Lienz it is likely, that the rise of the corrosion signal has not been induced by acid dew point corrosion. This can also be affirmed by the calculated acid dew point for the test runs in Kufstein which are in a range of 97 – 104°C and thus significantly higher than the initial temperatures detected with the low temperature corrosion probe. Due to the 50 to 100 times higher amount of dust related to the sulfuric acid concentrations in the flue gas it is likely, that deposits on the corrosion probe have a buffering effect binding acid droplets. For this reason it can be assumed, that corrosion due to the deliquescence of hygroscopic salts is of major importance.

Results of chemical analyses of dust and ash deposit samples from Lienz and Kufstein show that potassium

chloride is the dominating salt formed and seems to be of relevance for low temperature corrosion by deliquescence of hygroscopic salts. K₂CO₃ may also have a relevant influence. The presence of these salts is also confirmed by XRD analyses. In addition ZnCl₂ or CaCl₂ or mixed salts may also be of relevance. An influence of ammonium salts with and without operation of the SNCR unit, however, could not be detected.

Derived from the measurement results the recommendations regarding the minimum tube surface temperatures of heat exchangers in order to avoid deliquescence corrosion when utilising chemically untreated wood chips are 70°C at flue gas moisture contents up to 15 vol% and 90°C at flue gas moisture contents up to 20 - 25 vol%.

Future work will be focused on data collection for deliquescent salt mixtures and the investigation of the low temperature corrosion behaviour of non-wood fuels and waste wood as well as the evaluation of suitable materials that can withstand deliquescence corrosion in order to achieve an efficient heat recovery.

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