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## ASSESSMENT OF ONLINE CORROSION MEASUREMENTS IN COMBINATION WITH FUEL ANALYSES, AEROSOL AND DEPOSIT MEASUREMENTS IN A BIOMASS CHP PLANT

Stefan Retschitzegger<sup>1\*</sup>, Thomas Brunner<sup>1,2,3</sup>, Ingwald Obernberger<sup>1,2,3</sup>, Barbara Waldmann<sup>4</sup>

<sup>1</sup>BIOENERGY 2020+ GmbH, Inffeldgasse 21b, 8010 Graz, Austria Tel.: +43/316/48130071; Fax: +43/316/4801004; E-mail: stefan.retschitzegger@bioenergy2020.eu \* corresponding author

<sup>2</sup>BIOS BIOENERGIESYSTEME GmbH, Inffeldgasse 21b, 8010 Graz, Austria

<sup>3</sup>Institute for Process and Particle Engineering, Graz University of Technology Inffeldgasse 21b, 8010 Graz, Austria

<sup>4</sup>Corrmoran GmbH, Buchenstraße 13, 86179 Augsburg, Germany

## ABSTRACT

In order to systematically investigate high temperature corrosion of superheaters in biomass CHP plants, a long-term test run (5 months) with online corrosion probes was performed in a CHP plant (28 MW<sub>NCV</sub>, steam parameters: 32 t/h, 480°C, 63 bar) firing chemically untreated wood chips. Two corrosion probes were applied in parallel in the radiative section of the boiler at average flue gas temperatures of 880°C and 780°C using the steel 13CrMo4-5 for the measurements. Corrosion rates were determined for surface temperatures between 400°C and 560°C. The results show generally moderate corrosion rates and a clear dependence on the flue gas temperatures and the surface temperatures of the corrosion probes. The data are to be used to create corrosion diagrams in order to determine maximum life steam temperatures for superheaters in future plants, which are justifiable regarding the corrosion rate.

Dedicated measurements were performed at the plant during the long-term corrosion probe test run to gain insight into the chemical environment of the corrosion probes. Fuel analyses and an assessment of the results based on indexes indicated only a low risk for high temperature corrosion due to a rather high molar 2S/Cl ratio (mean: 6.0). Chemical analyses of aerosols sampled at the positions of the corrosion probes showed that no chlorine is present in condensed form at the positions investigated. Deposit probe measurements performed at the same positions and analyses of the deposits also showed only small amounts of chlorine in the deposits mainly found at the leeward position of the probes. Subsequent to the test run, the corrosion probe have been investigated by means of SEM/EDX. The results confirmed the deposit probe measurements and showed only minor Cl-concentrations in the deposits and no Cl at the corrosion front. Since in the case of Cl-catalysed active oxidation a layer of Cl is known to be found at the corrosion front, this mechanism is assumed to be not of relevance in the case at hand. Instead, elevated S-concentrations were detected at the corrosion front but the corrosion mechanism has not been clarified yet.

**Keywords:** *biomass combustion, high temperature corrosion, online corrosion measurements* 

## **1 INTRODUCTION**

High temperature corrosion still poses an insufficiently investigated problem in biomass combustion plants. Failures of heat exchangers due to corrosion are a major problem and may cause a substantial reduction of the lifetime of these parts. The problem occurs especially in plants firing biomass fuels with elevated chlorine contents but also in plants firing wood chips and bark, when increased life steam temperatures are applied. To minimise these failures, life steam temperatures are often kept on a rather moderate level, which results in a reduced degree of efficiency regarding the electricity generated.

High temperature corrosion has already been extensively investigated in plants firing municipal solid waste (MSW) (an overview is given by [1, 2, 3, 4, 8 and 9]) and also in plants firing biomass rich in chlorine [2, 5, 6 and 7] such as straw. Yet no detailed investigations of corrosion rates 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 been performed. Therefore, the aim was a systematic investigation of high temperature corrosion in plants firing these fuels.

# **2 OBJECTIVES**

The aim of the work presented was a detailed investigation of superheater corrosion by the application of newly developed corrosion probes in a biomass combined heat and power (CHP) plant fired with forest wood chips. The material investigated was the heat-resisting steel 13CrMo4-5 which corresponds to the material of the final superheater in the plant. Corrosion probes have already been applied in MSW plants [8, 9, 10] and from these measurements it is known that the most relevant parameters influencing the corrosion rate are the surface temperature of the tube, the flue gas temperature, the chemical compositions of the flue gas as well as of the deposits and the flue gas velocity. Therefore, long-term corrosion probe test runs with variations of the parameters tube-surface temperature, flue gas temperature and flue gas velocity should be performed. Moreover, in order to identify the framework conditions of the long-term test run, dedicated measurements at the positions of the corrosion probes and the continuous recording of operating data of the CHP plant have been performed.

From the data gained from the long-term corrosion probe test run corrosion diagrams for the fuel investigated and the superheater material used should be developed. Moreover, a better understanding of the corrosion mechanism prevailing should be gained. These corrosion diagrams shall provide the basis to determine maximum life steam temperatures for superheaters in future plants, which are justifiable regarding the corrosion rate, in order to increase the electric efficiency of biomass CHP plants. In future similar test runs and measurements are foreseen in plants firing other biomass fuels. Moreover, different superheater materials are planned to be investigated.

# **3 MATERIALS AND METHODS**

The test run at the biomass CHP plant was started in the middle of May, 2011 and lasted 25 weeks until the beginning of November. Dedicated accompanying measurements were performed during three blocks, each consisting of one week. The timetable of the test run

is shown in Figure 1. After about one month, one corrosion probe had to be replaced due to a failure of the cooling unit. In August an unexpected plant shutdown took place which required about three weeks to gain a stable corrosion signal after the restart of the plant. The discontinuous measurements performed during the accompanying measurement weeks as well as the continuous measurements during the whole test run are explained in the chapters 3.1 to 3.5.



Figure 1: Timetable of the test run at the biomass CHP plant

#### 3.1 Plant description and measurement positions

The biomass CHP plant is fired with chemically untreated woody biomass (wood chips). The plant consists of a grate-fired combustion unit with a 4-path boiler consisting of two radiative sections followed by a convective section which contains three superheater bundles and five economiser bundles (steam parameters: 32 t/h at  $480^{\circ}\text{C}$  and 63 bar). The nominal fuel power input is  $28 \text{ MW}_{\text{NCV}}$ , corresponding to an electric capacity of 5 MW and a thermal capacity of 18 MW (district heat supply). The plant is operated in heat controlled mode and covers the base load of the district heating network. A multi-cyclone and an electrostatic precipitator are applied for flue gas cleaning. Figure 2 shows the scheme of the plant, fuel sampling and corrosion measurement positions as well as relevant temperature and flue gas measurement points.

During the test run relevant operating data of the plant as well as results from the continuous  $O_2$  and CO measurements have been recorded from the process control system in 1-min intervals in order to characterise the operating conditions of the plant and to investigate the influence of relevant parameters on the corrosion rate. The flue gas temperatures at the positions of the corrosion probes were measured and recorded with thermocouples, which were inserted close to the corrosion probes. The calibration of the thermocouples was performed with a suction pyrometer during the first block of the dedicated measurement campaigns.



Figure 2: Scheme of the biomass CHP plant investigated as well as relevant measurement and sampling points

Explanations: HTI ... high temperature impactor

## 3.2 Fuel sampling

Fuel sampling took place during each day of the three blocks of dedicated measurement campaigns on site. Samples were taken from the conveyor belt, which transports the fuel from the storage to the boiler three times a day. One mixed sample was prepared for each day that was forwarded to chemical analyses, which resulted in 14 probes analysed in total during the test run (see section 3.6.1).

### 3.3 Aerosol measurements

Aerosols (fine particulate matter with a particle size  $< 1 \ \mu$ m) consist mainly of volatile and semi-volatile elements such as K, Na, Zn, Pb, S and Cl if a complete burnout is achieved. During combustion, these elements are partly released from the fuel into the gas phase where they undergo gas phase reactions. If one of the compounds formed becomes supersaturated, gas to particle conversion takes place.

The concentrations and the particle size distributions of aerosols in the flue gas at the positions of the corrosion probes were determined with a high-temperature low-pressure impactor (HTI). The HTI (Figure 3) is an innovative development of the Graz University of Technology, Institute for Process and Particle Engineering [15] which enables in-site aerosol sampling at temperatures up to 1000°C. With the HTI particles are segregated in 8 size classes. The cut diameter of each stage is defined by the volumetric flow rate through the impactor, the number and diameter of identical orifices, the distance between the orifice plate and the stagnation plate and the flue gas temperature (see Figure 3). As sampling media Pt-foils are used to ensure thermal and chemical stability. Prior to the

sampling the HTI is positioned directly in the flue gas at the measurement position for 20 minutes for pre-heating. Pre-heating is needed to avoid cooling of the flue gas and particle formation by nucleation as well as ash vapour condensation in the HTI [11]. The sampling time (time during which flue gas is sucked through the HTI) itself is restricted to some minutes in order to avoid particle overloading. The Pt foils are weighed prior and after the sampling and based on the weight gain and the flue gas flow through the HTI during the sampling period the particle concentration for each stage is calculated (in mg/Nm<sup>3</sup>).



Figure 3: Scheme of the high-temperatur impactor (HTI) and cut diameters of the stages as a function of the flue gas temperature.

Aerosols sampled with the HTI were analysed regarding their chemical composition by means of SEM/EDX (see section 3.6.2). The high temperature aerosol measurements in combination with the fuel composition and the sampling temperature provide information about the concentration of aerosol forming elements in gaseous and solid phase at the corrosion measurement positions.

#### 3.4 Deposit probe measurements

Deposit probe measurements allow the investigation of particle deposition formation on heat exchanger surfaces. The deposit probe consists of a carrier-lance with a test ring on top (Figure 4), which is cooled by air and is inserted into the flue gas for a certain time at a certain temperature. The temperature of the test ring is measured with a thermocouple, which is located on the inside of the carrier lance nearby the test ring. A PID controller that regulates the amount of cooling air controls the temperature. This setup allows the simulation of heat exchanger tubes with different surface temperatures. Variation of the exposure time to the flue gas allows for the investigation of the time dependent deposit build-up.



Figure 4: Scheme of the deposit probe Explanations: TIC ... temperature indicator controller

The deposit probe measurements were used for calculating the deposit build-up rate by gravimetric measurement of the test ring before and after the exposure to the flue gas.

Furthermore, the chemical compositions of the deposits were determined by means of SEM/EDX subsequently to the measurements (see section 3.6.2).

#### 3.5 Corrosion probes

The corrosion probes provided by Corrmoran GmbH (Augsburg, Germany) are based on a system which has been developed at the Institute of Physics, Augsburg University during the PhD Thesis of Waldmann [8]. The system is designed to simulate a superheater tube in the flue gas of a combustion system. The following description was provided by Corrmoran GmbH.

A temperature-controlled sensor (Figure 5 - right) is placed on the top of a water-cooled carrier-lance, which is about 200 cm long (Figure 5 - left). The corrosion probe is inserted into the flue gas of a combustion plant via an opening in the boiler casing. The sensor on top of the corrosion probe is cooled by air to a defined temperature. When exposed to the flue gas, a layer consisting of deposits and corrosion products is formed on the sensor surface. This layer represents an electrolyte and allows the measurement of the corrosion rate. The system is based on the measurement of a linear polarisation resistance.

For the measurement a voltage is applied between the working electrode and the counter electrode resulting in a current between the two electrodes. The voltage applied cannot be accurately measured between the two electrodes due to the chemical corrosion reactions on the electrodes. Therefore, the reference electrode is connected to the working electrode via a high-resistance voltage metering and hence not influenced by the corrosion processes. Between the reference electrode and the working electrode the unbiased voltage can be measured.

The applied voltages are shifted around a value of zero which result in different currents and allow the recording of a current-voltage-characteristic. The linear content of the slope of the characteristic is called the linear polarisation resistance, which is proportional to the actual corrosion rate. The factor describing the relation between the linear polarisation resistance and the corrosion rate is determined subsequently to the test run by gravimetric measurement of the mass loss of a mass loss ring. A detailed description of the system can be found in the PhD Thesis of Maisch [9].

The material investigated during the test run was 13CrMo4-5 (1.7335), a heat resisting steel commonly used for heat exchanger tubes in steam boilers. Its chemical composition is shown in Table 1.



Figure 5: left: Corrosions probe; right: sensor with three electrodes (1 - 3) and the mass loss ring (M).

Table 1: Composition of 13CrMo4-5 (1.7335)

Element		С	Si	Mn	P	S	Al	Cu	Cr	Мо	Ni	Fe
min.	[wt%]	0.10		0.40					0.70	0.40		rest
max.	[wt%]	0.17	0.35	0.70	0.025	0.02	0.04	0.30	1.15	0.60	0.30	rest

Two corrosion probes were inserted into the flue gas at the positions M1 and M2, shown in Figure 2 to investigate high temperature corrosion parallel at different flue gas temperatures.

An existing CFD-simulation of a boiler with similar dimensions was used for an estimation of the flue gas temperatures and the flue gas velocities at the measurement positions. The flue gas temperatures were estimated to 930°C and 775°C, flue gas velocities were estimated to 5.0 m/s and 8.7 m/s at the positions M1 and M2 at a fuel power of 23.2  $MW_{NCV}$ , which is comparable to partial load operation at the CHP plant investigated. Flue gas temperatures measured during the test run are mentioned in section 4.1.

During the start phase of the corrosion measurements the corrosion probes were set to a surface temperature of 480°C which is the nominal temperature of the final superheater of the plant investigated in order to gain a stable and meaningful corrosion signal. This phase is necessary for the layer build-up and the achievement of a chemical balance on the surface of the corrosion probe. The layer build-up phase lasted about one month. After establishment of a stable corrosion signal stepwise variations of the surface temperature (400 - 560°C) were performed. Thus, superheater tubes with different life steam temperatures were simulated and the influence of the variations on the corrosion rate was investigated.

## 3.6 Chemical and SEM/EDX analyses

#### 3.6.1 FUEL ANALYSES

The moisture content of fuel samples was determined according to ÖNORM CEN/TS 14774. Fuel sample preparation was carried out according to CEN/TS 14780. The ash content was determined according to CEN/TS 14775. In addition, the corrected ash content was calculated by reduction of the ash content by the amounts of carbonates in the ash. This is necessary, since during the ash determination at 550°C carbonates are formed which normally do not occur during combustion in a real plant due to higher temperatures.

The determination of C, H and N-contents was carried out according to  $\ddot{O}NORM$  CEN/TS 15104. The determination of Cl was carried out according to  $\ddot{O}NORM$  CEN/TS 15289. Major and minor ash forming elements were determined by multi-step pressurised digestion of the fuel with HNO<sub>3</sub> (65%) / HF (40%) / H<sub>3</sub>BO<sub>3</sub> followed by measurement by inductively coupled plasma optical emission spectroscopy (ICP-OES) or inductively coupled plasma mass spectroscopy (ICP-MS) depending on detection limits.

#### 3.6.2 SEM/EDX ANALYSES

SEM/EDX analyses (Scanning Electron Microscopy / Energy Dispersive X-ray Spectroscopy) were used to determine the chemical composition of aerosols (HTI) and deposits (deposit probe). Subsequently to the test run the electrode rings of the corrosion

probes were also analysed regarding the chemical compositions and structures of the corrosion layers and the deposits by means of SEM/EDX.

Aerosol and deposit samples were coated with carbon prior to analyses to ensure the conductance of the surface and to prevent electrical charging of the surface during the analyses. The electrode rings of the corrosion probes were embedded in resin and grinded with sand papers with decreasing grain sizes until a smooth, plane surface was achieved. Afterwards, the rings were also coated with carbon. The equipment used for analyses of the aerosols and the deposit samples consisted of a Zeiss Gemini 982 (SEM-system) and a Noran Voyager (EDX-system). For the analyses of the electrode rings a Zeiss Ultra 55 (SEM-system) equipped with an EDAX Pegasus (EDX-system) was used.

The composition of aerosols was determined by area scans using magnifications between 100 and 2000 to compare overall average compositions with local compositions. The same principle was used for the analyses of deposit samples with magnifications of 100 and 500. In case of the deposit probe samples Fe, Cr and Ni were excluded in the analyses since the test rings consist of these elements and results of these elements originate most likely from the test rings. O was not measured in the aerosol and deposit probe samples but stoichiometrically calculated.

The electrode rings of the corrosion probes were analysed using area scans and point analyses using magnifications between 100 and 2000. Elemental mappings were performed to detect the distribution of certain elements. In these analyses O was measured to detect oxides and separate them from uncorroded steel and compounds that do not contain oxygen.

## 4 RESULTS

#### 4.1 Plant operation

Figure 6 shows weekly mean values as well as the standard deviations of relevant plant operating data. The plant was operated at rather stable conditions except for the weeks 15 and 16 where an unexpected plant shutdown took place. The shutdown happened in the middle of week 15 and lasted seven days which resulted in high standard deviations of the weekly mean values of measurement data, as shown in Figure 6. This shutdown affected the corrosion probe measurements to the effect that after the re-start of the plant the corrosion signals were rather unstable and it required about three weeks to regain a stable and meaningful corrosion signal. In the weeks 21 to 25 the boiler load was increased due to an increased demand from the district heating network, as it can be seen in the life steam flow. The life steam flows of 25.1 t/h (week 2) and 29.0 t/h (week 25) correspond to boiler outputs of 21.4 MW and 24.7 MW. The increased boiler load in weeks 21 to 25 resulted in increased flue gas flow rates but the mean values of the flue gas temperatures remained almost the same as at lower boiler load.

Consequently, for the whole corrosion measurement period stable and well comparable constraints regarding flue gas temperatures prevailed.

The continuous  $O_2$ -measurements show rather constant values, the variations of the COconcentrations can be caused by variations of the fuel moisture content, the fuel composition and the boiler output as well as by inhomogeneous distributions of the fuel on the grate. In general, a very good flue gas burnout is achieved.



Figure 6: Operating data of the CHP plant during the test run <u>Explanations</u>: operating data were recorded in 1 minute intervals, shown are mean values of one week and the corresponding standard deviations; TFG ... temperature of the flue gas; SH ... superheater; ECO ... economiser; CO emissions related to dry flue gas and 13 vol% O<sub>2</sub>

#### 4.2 Dedicated measurement campaigns

#### 4.2.1 FUEL ANALYSES

A comparison of the results of the fuel analyses with database values (Table 2) shows that the fuel used in the biomass CHP plant investigated can be compared with wood chips with bark, with elevated bark content. The analyses show rather constant fuel compositions without extreme deviations. The most relevant elements regarding corrosion (K, S, Cl) are within typical variation ranges. Heavy metal concentrations (e.g. Zn) are small as expected for a chemically untreated wood fuel. The fuel is representative for forest wood chips and was rather homogenous during the test run campaign. Therefore, relevant impacts from fuel quality variations on the results are not likely.

The molar ratio of 2S/Cl can be used as an indicator for the high temperature corrosion risk [12, 13, 14]. Both elements are relevant for aerosol and deposit formation since in the gas phase they form alkaline sulphates and alkaline chlorides which subsequently form particles or condense on heat exchanger surfaces. For fuels with high 2S/Cl ratios, a protective sulphate layer is formed at the tube surfaces. According to literature, only minor corrosion risks have therefore to be expected for 2S/Cl ratios > 4.

The mean value of the 2S/Cl ratio of the fuel analysed was calculated with 6.0 with a standard deviation of 2.4. These values indicate that only a minor risk for high temperature corrosion has to be expected.

		Wood	chips -	Database values					
		corrosio	n test run	wood	l chips	bark			
		n = 14 samples		with bark		Dark			
		mean	stddev.	mean	stddev.	mean	stddev.		
moisture content	wt.% w.b.	31.6	3.9						
ash content (550°C)	wt.% d.b.	2.7	1.2	0.8	0.5	4.4	1.3		
ash content corr.	wt.% d.b.	2.2	1.1						
С	wt.% d.b.	48.1	0.4	49.6	1.3	49.8	0.5		
н	wt.% d.b.	6.0	0.1	6.2	0.5	5.7	0.0		
N	wt.% d.b.	0.3	0.1	0.2	0.1	0.2	0.3		
S	mg/kg d.b.	262	70	120	48	537	135		
CI	mg/kg d.b.	117	71	49	31	172	52		
Са	mg/kg d.b.	4,723	1,207	2,105	1,158	12,472	3,558		
Si	mg/kg d.b.	3,654	3,009	570	495	3,538	1,081		
Mg	mg/kg d.b.	614	193	256	198	1,268	262		
AI	mg/kg d.b.	615	424	134	132	795	219		
Na	mg/kg d.b.	128	92	25	23	131	32		
К	mg/kg d.b.	1,875	449	812	381	2,480	445		
Fe	mg/kg d.b.	313	237	82	56	574	125		
Р	mg/kg d.b.	242	71	85	87	484	72		
Mn	mg/kg d.b.	88	26	95	43	653	266		
Zn	mg/kg d.b.	14.8	5.4	11.7	5.5	124.2	24.5		
Pb	mg/kg d.b.	4.1	4.6	0.7	0.9	1.6	0.5		
2S/CI	mol/mol	6.0	2.4	5.4		6.9			

Table 2: Results of the fuel analyses as well as database values for comparable fuels <u>Explanations:</u> d.b. ... dry basis; w.b. ... wet basis; std.-dev. ... standard deviation; ash content corr. ... ash content corrected by the amount of carbonates in the ashed samples

#### 4.2.2 AEROSOL MEASUREMENTS

High temperature aerosol measurements were performed at the positions of the corrosion probes. Figure 7 shows the particle size distributions of aerosols sampled with the high temperature impactor (HTI). The measurements were performed during the second accompanying measurement week (test run week 11), fuel compositions mentioned in this section are mean values of this week. At this time, the plant was operated at a mean life steam flow rate of 24.0 t/h (boiler output: 20.0 MW).

The particle size distributions show a typical maximum clearly below 1  $\mu$ m which tends to slightly increase from position M1 to M2 (aerodynamic diameters of the maxima are 0.17  $\mu$ m and 0.19  $\mu$ m). The particle growth takes place due to decreasing flue gas temperatures and therefore enforced surface condensation on aerosols as well as by agglomeration. The average aerosol concentration (sum of particles < 1  $\mu$ m sampled with the HTI) at position M1 amounts to 22.8 mg/Nm<sup>3</sup> respectively 24.4 mg/Nm<sup>3</sup> at position M2. These results are comparable to values found by Brunner [15] for wood fuels such as wood chips without bark (spruce) (aerosol concentration: 7.5 mg/Nm<sup>3</sup>) and bark (aerosol concentration: 32.0 mg/Nm<sup>3</sup>), sampled in a pilot-scale grate combustion plant in the secondary combustion zone.

Table 3: Average aerosol concentrations at the measurement positions <u>Explanations:</u> flue gas temperatures ... average temperature at the measurement position during the HTI measurements; measurement positions ... see Figure 2

Measurement position		M1	M2
Number of single measurements	[-]	3	2
Average flue gas temperature	[°C]	912	776
Standard deviation	[°C]	3.2	3.5
Average aerosol concentration (dry flue gas; 13 vol.% $O_2$ )	[mg/Nm <sup>3</sup> ]	22.8	24.4
Standard deviation	[mg/Nm <sup>3</sup> ]	4.2	2.6



Figure 7: Particle size distributions of aerosols sampled at the positions of the corrosion probes

Explanations: all concentrations are related to dry flue gas and 13 vol.% O2; ae.d. ... aerodynamic diameter

SEM/EDX analyses of the aerosols were performed for one HTI measurement from each position. The results of the analyses are shown in Figure 8. At both positions, all size classes  $< 1 \mu m$  show K and S as main elements. Their ratio indicates K<sub>2</sub>SO<sub>4</sub> to be the main component. In addition, Na is found in minor amounts, most probably in the form of Na<sub>2</sub>SO<sub>4</sub>. Particles  $> 1 \mu m$  contain besides K<sub>2</sub>SO<sub>4</sub> also Ca and Mg compounds, most likely sulphates and oxides. These are typical results for the combustion of chemically untreated wood fuels.

No Cl was found in the aerosols analysed. This is an expected result since it is known that Cl forms alkali chlorides and HCl which are expected to be in gaseous form at the flue gas temperatures at the measurement positions (Figure 8) [15].





Explanations: dp ... geometric mean diameter of the respective impactor stage (aerodynamic diameter); O has been stoichiometrically calculated

Chemical analysis of aerosols sampled by Brunner [15] in a pilot-scale grate combustion plant showed similar compositions regarding K and S but somewhat higher concentrations of Zn and Ca. These differences regarding Ca and Zn can be mainly explained by different fuel compositions as well as different fuel bed temperatures.

According to calculations regarding the modelling of aerosol formation of Jöller [16] for wood chips without bark and bark, using the fuel compositions from the measurements of Brunner [15], the gaseous phase mainly consists of KOH, KCl, HCl, SO<sub>x</sub>, K<sub>2</sub>SO<sub>4</sub> as well as NaOH and NaCl (in decreasing concentrations for a temperature range between 950°C and 750°C; only aerosol forming species mentioned). The calculations showed that K<sub>2</sub>SO<sub>4</sub> is the only component relevant for condensation at the temperatures prevailing at the positions M1 and M2 in Baden. These calculations are in good agreement with the aerosol compositions found during the corrosion test run.

#### 4.2.3 DEPOSIT PROBE MEASUREMENTS

The rates of deposit build-up (RBU) as well as the chemical compositions of deposits were investigated with a deposit probe at the positions of the corrosion probes. First measurements were performed in week 4, where the plant was operated at an average life steam flow of 24.4 t/h and an average flue gas flow of 29,900 Nm<sup>3</sup>/h. A second series of measurements was performed in week 23, where the plant was operated at an increased boiler load (life steam flow = 29.5 t/h, flue gas flow = 37,700 Nm<sup>3</sup>/h).

The probe surface temperatures were defined with 480°C and 560°C for all measurements. Exposure times were defined with 2h and 10h for both positions in week 4. For the measurements in week 23 the exposure times at position M1 were the same as in week 4, at position M2 the exposure times were changed to 2h and 38h to investigate deposit formation and if the deposits react at longer exposition times of the probe in the flue gas (e.g. sulphation).

Deposit build-up rates in week 4 were determined with 5-6 g/( $m^2 \cdot h$ ) for position M1 respectively 4-5 g/( $m^2 \cdot h$ ) for position M2 in case of 2h exposure time. The measurements at increased boiler load showed higher build-up rates of 6-10 g/( $m^2 \cdot h$ ) for position M1 respectively 19-23 g/( $m^2 \cdot h$ ) for position M2. An increase in the boiler load typically results in increased entrainment of fuel, charcoal and coarse fly ash particles from the grate into the flue gas, as known from investigation of Brunner [15]. This explains the increased build-up rates in week 23.

For all measurements, the higher probe temperatures resulted in higher deposit build-up rates. The longer the exposure time was, the lower the build-up rates determined were.

The trends regarding increasing deposit build up rates with increasing probe temperatures and decreasing sampling times were also found in deposit probe measurements performed in a real scale plant fired with waste wood [17] as well as in a pilot-scale plant fired with wood chips without and with bark [18] at similar flue gas temperatures as during the corrosion test run. The values of the build-up rates were in the range of measurements performed in the pilot-scale plant (between 6 and 10 g/(m<sup>2</sup>·h)) with slightly higher values for bark compared to wood chips without bark, with the exception at position M2 in week 23. In this case the build-up rates exceeded comparable measurements, which can be explained with the increased boiler load and the corresponding enhanced entrainment of fly ash particles with the flue gas.

Subsequently to the sampling, the deposits on the test rings were analysed by means of SEM/EDX at 3 positions of the ring - at the windward side, at windward+50° and at the leeward side - in relation to the flow direction of the flue gas to investigate possible relevant differences.



Figure 9: Results of SEM/EDX analyses of the deposits sampled at the positions of the corrosion probes

<u>Explanations</u>: the caption of each analysis characterises the sampling point, the surface temperature of the test ring and the sampling time - e.g.  $M1 - 480^{\circ}C - 2h$ 

The analyses of the deposits sampled (Figure 9) generally show, that the variation of the surface temperatures of the test rings did not significantly influence the chemical composition of the deposits. Analyses of deposits at position M1 show that at lower boiler load the deposits mainly consist of  $K_2SO_4$  independently of the point analysed. With increased boiler load, higher concentrations of Ca and Mg are found in the deposits, especially at the windward side. A similar trend is seen for the deposit composition at position M2, although not as distinctive as at position M1, since at position M2 Ca is also found in higher quantities at the windward side at lower boiler load due to different flow conditions. Measurement position M2 is located in the main flue gas flow whereas Position M1 is located outside of the main flow. This evaluation is based on the CFD-simulation, see section 3.5. The increase of Ca and Mg in the deposits in week 23 can be explained by the higher entrainment of particles from the grate since these elements are typical constituents of coarse fly ashes.

Analyses of the deposits sampled in the pilot-scale plant [18] showed K, S and Ca to be the main components when burning wood chips with and without bark. These are similar results to the results of the corrosion test run. The deposits of the test run in the pilotscale plant showed increased values of Ca at the windward side for both fuels investigated. This also is a similar result which has been found during the corrosion test run and can be explained by the deposition of coarse fly ash particles. The deposits sampled in the pilot-scale plant showed measureable Zn-concentrations in all deposits for both fuels investigated. This discrepancy compared to the results of the corrosion test run can be explained by the different fuel compositions, see section 4.2.2 (deposit probe measurements at the pilot-scale plant were performed at the same test runs at which the aerosol measurements were performed).

Cl is generally only found in small quantities in the deposits during the corrosion test run. Nevertheless, general trends were found during these measurements: Cl-concentrations were higher at position M2 compared to position M1. This can be explained by the lower flue gas temperatures and therefore higher saturation of chlorides in the flue gas which increases the condensation rate on cooled surfaces. Cl-concentrations were higher at lower probe temperatures which can also be explained by higher condensation rates. Clconcentrations were higher on the leeward-side compared to the windward-side. These trends are known and were also found i.e. in the pilot-scale plant already mentioned [18]. Maximum values for the Cl-concentrations were found during week 23 at position M2, 480°C at the leeward side with 4.6 mol% and 0.1 mol% at the windward side. At position M1, 480°C a value of 1.0 mol% was found at the leeward side and 0.2 mol% at the windward side during this week. The measurements in the pilot-scale plant showed Clconcentrations of 0.7 mol% (windward side) and 3.7 mol% (leeward side) for wood chips and 0.7 mol% (windward side) and 5.7 mol% (leeward side) for bark at probe temperatures of 450°C (sampling time: 2 h). This comparison shows, that chlorine concentrations found during the corrosion test run are in good agreement with other measurements when burning comparable fuels.

#### 4.2.4 CONCLUSIONS FROM DEDICATED MEASUREMENT CAMPAIGNS

The dedicated measurement campaigns showed rather constant fuel compositions during the long-term corrosion probe test run. K, S and Cl, which are the most relevant elements for high temperature corrosion were within the usual range of deviation. Compared to database values, the fuel could be described as wood chips with bark, with elevated bark contents.

Sampling and analyses of aerosol at the positions of the corrosion probes showed typical aerosol concentrations in the range of 20 - 25 mg/Nm<sup>3</sup> (13 vol% O<sub>2</sub>), with slightly increasing values along the flue gas path with decreasing flue gas temperatures. The maximum of the particle size distribution lies clearly below 1  $\mu$ m. The aerosol compositions show K<sub>2</sub>SO<sub>4</sub> to be the main component, which is in good agreement with the result of measurements with similar fuels [15] and the modelling of aerosol formation [16].

Deposit probe measurements at the positions of the corrosion probes showed deposit build-up rates in the range of 6 - 10 g/(m<sup>2</sup>·h) which is a typical result for chemically untreated wood fuels [18]. Increasing probe temperatures and decreasing measurement times were found to increase the deposit build-up rates which has also been found in [18]. The deposit built-up rates exceeded typical results in case of position M2 which was caused by the operation of the plant at increased boiler load resulting in increased entrainment of fuel, charcoal and coarse fly ash particles from the fuel into the flue gas. Analyses by means of SEM/EDX showed that deposits mainly consisted of K, S, Ca and Mg. With increased boiler load, higher amounts of Ca and Mg were found in the deposits caused by the already mentioned increased coarse fly ash particle concentrations in the flue gas. Cl-concentrations in the deposits were generally below 1 mol%, highest concentrations were found at position M2 at the leeward side for deposit probe temperatures of 480°C with 4.6 mol%. This value is comparable to results of measurements in a pilot-scale plant burning wood chips as well as bark. In these cases, the maximum concentrations were also found at the leeward side and resulted to 3.7 mol% (wood chips) and 5.7 mol% (bark), sampled at 450°C.

#### 4.3 Corrosion probe measurements

The corrosion probe measurements were performed over a period of about 5 months. Due to a failure of the cooling unit, corrosion probe 1 had to be replaced after about 1.5 months, which resulted in a decreased measurement time of this probe, compared to corrosion probe 2. Corrosion probe 1 had a total measurement time of 2,880 h at a mean flue gas temperature of 880°C (standard deviation:  $30^{\circ}$ C). Corrosion probe 2 had a total measurement time of 780°C (standard deviation:  $20^{\circ}$ C).

For the establishment of a stable corrosion signal in the beginning of the test run, a probe temperature of 480°C was chosen, since this represents also the life steam temperature of the CHP plant where the test run has been performed. The probe temperature of 480°C was later on used as a reference temperature to study the long term characteristics of the corrosion rates measured.

After establishment of a stable signal, the probe temperatures were stepwisely varied in the range of 400°C to 560°C for certain times. Figure 10 and

Figure 11 show selected results of the corrosion probe measurements at position M1 to illustrate the correlations found.

# 4.3.1 INFLUENCE OF THE FLUE GAS AND THE PROBE SURFACE TEMPERATURE ON THE CORROSION RATE



Figure 10: Corrosion rates of the corrosion probe at position M1 in dependence on the flue gas temperature at constant surface temperatures of the corrosion probe <u>Explanations:</u> TP ... temperature of the corrosion probe; right figure: mean values at certain flue gas temperatures (+/- 10°C) and certain corrosion probe temperatures (+/- 1°C); exponential fit of data for TP = 480°C; error bars show the standard deviations

Figure 10 - left shows the corrosion rates at a constant probe temperature of 480°C. Figure 10 - right shows mean values of corrosion rates for certain flue gas temperatures

and probe temperatures. The data in Figure 10 - right were gained over the whole corrosion test run. A clear trend of increasing corrosion rates with increasing flue gas temperatures can be seen. It has to be noted, that a mathematical description of the corrosion rates has not been developed yet and the exponential fit for the probe temperature of 480°C serves just for the purpose of investigating a possible influence of the flue gas velocity on the corrosion rate, see section 4.3.2.

Furthermore, it can be seen that increasing corrosion probe temperatures result in increasing corrosion rates too. To illustrate this correlation, corrosion rates are shown during variations of the corrosion probe temperature in Figure 11.

Figure 11 - right shows data gained during the whole corrosion test run in dependence of the corrosion probe temperature for certain flue gas temperatures.



Figure 11: Corrosion signal of the corrosion probe at position M1 in dependence on the probe temperature and the flue gas temperature

Explanations: TFG ... temperature of the flue gas

right figure: mean values of corrosion rates for certain flue gas temperatures (+/- 10°C) and corrosion probe temperatures (+/- 1°C); error bars show the standard deviations

In Figure 11 it can be seen that the slope of the corrosion rates increases with probe temperatures between 400°C and about 520°C. When exceeding 520°C the slope decreases with increasing probe temperatures. This behaviour is not consistent with results found in waste incineration plants, in which cases the relation between the corrosion rate and the corrosion probe temperature was described via an Arrhenius function [8, 9]. This function indicates exponentially increasing corrosion rates with rising probe temperatures. Moreover, a relation between corrosion rates and probe temperatures following an exponential function has been found by Gruber [19], during corrosion test runs in a pilot-scale combustion plant using similar fuels as in the case at hand. The Arrhenius-correlation is based on the assumption, that the dissolution of the metal into the corrosion layer is the rate-determining step, which is a thermally activated process.

The data at hand suggest that at higher corrosion probe temperatures this reaction is not the rate-determining step any more and the increase of the corrosion rate is slowed down by another process. A possible explanation could be a limitation by mass transport. This could be the transport of corrosive species to the corrosion front as well as the transport of corrosion products from the corrosion front. A comparison to the results of Gruber shows considerably thicker deposit layers on the corrosion probes, which are some mm up to about 1 cm in the case at hand compared to about 0.05 mm in the case of Gruber. Since the corrosion mechanism in the case at hand is yet not known (see section 4.4), it was no possible to identify a rate-determining step yet.

A comparison of the corrosion rates of the corrosion probes at the positions M1 and M2 show that the data can be combined quite well (Figure 12). It has to be noted that for this comparison only data gained after the plant shutdown has been used. Since before the shutdown no variations of the corrosion probe temperature have been performed in case of corrosion probe M1, only this reduced period could be used. For a probe temperature of 480°C, which was the reference temperature and is therefore the temperature for which most data is available, the corrosion rates merge almost without deviation. The data below a flue gas temperature of 810°C originates from corrosion probe M1.



Figure 12: Comparison of corrosion rates of corrosion probe M1 and M2 in dependence of the flue gas temperature for certain probe temperatures <u>Explanations:</u> TP ... temperature of corrosion probe, error bars show the standard deviations

Mean flue gas velocities at the positions of the corrosion probes during the period of the data shown in Figure 12 were 4.7 m/s (standard deviation: 0.5 m/s) in case of position M1 and 8.3 m/s (standard deviation: 0.3 m/s) for position M2.

#### 4.3.2 INFLUENCE OF THE FLUE GAS VELOCITY ON THE CORROSION RATE

Corrosion probe measurements in waste incineration plants have shown a dependency of the corrosion rate on the flue gas velocity, reported by Maisch [9]. Also the measurements in the pilot-scale plant using chemically untreated wood fuel have shown increasing corrosion rates with increasing flue gas velocities [19]. To investigate an influence of the flue gas velocity in the case at hand, the exponential correlation between the corrosion rate and the flue gas temperature at corrosion rate. This reduced corrosion rate (red line in Figure 13 - left) is gained by subtracting the difference between the calculated corrosion rate at a constant flue gas temperature, therefore variations caused by the flue gas velocity should be identifiable. For this purpose the period of the last days of the test run have been chosen, since during this time the boiler load and as a result also the flue gas

velocity fluctuated in relatively high ranges due to increased demands of the district heating network, especially during the morning and the evening hours. The calculation of the flue gas velocities was based on the air flow measurements from the process control system and the CFD-simulations mentioned in section 3.5.

Figure 13 - left shows the corrosion rates as well as flue gas temperatures and flue gas velocities (divided by 50 to fit on the primary axis) for corrosion probe M1. In Figure 13-right the reduced corrosion rates are plotted against the flue gas velocities.



Figure 13: Corrosion rates at a constant probe temperature of 480°C as well as flue gas temperatures and flue gas velocities

Explanations: left figure: the flue gas velocities were divided by a factor of 50 to fit on the primary axis of the figure; right figure: reduced corrosion rates

From Figure 13 it can be seen that no clear correlation between the corrosion rate and the flue gas velocity can be identified. The results are not in line with the results from Gruber [19] and Maisch [9]. A similar result was found for the data of corrosion probe M2. Besides the attempt to find an influence of the flue gas velocity on the corrosion rate by calculating a reduced corrosion rate, Figure 12 already indicated that there is no such influence in the case at hand since the flue gas velocities were on different levels at position M1 (mean: 4.7 m/s) and M2 (mean: 8.3 m/s) and yet the corrosion rates merge quite well.

A possible reason for the discrepancy to the results of Gruber, who used a similar fuel is the range of variation of the flue gas velocity. Gruber varied the velocity in the range of 2.8-10 m/s whereas in the case at hand variations occur mainly between 4-5.5 m/s (for position M1, a similar range occurs for position M2). Another possible reason are the fluctuations of the corrosion signal which can be seen in the standard deviations in the Figures 10 to 12. Gruber reported quite stable and well defined conditions regarding flue gas temperature, flue gas composition and flue gas velocity in the pilot-scale plant which do not occur in a real scale plant. At last, in the case at hand a much thicker deposit layer was found on the surface of the corrosion probes compared to the measurements of Gruber. These deposits could shield the corrosion probes and reduce a possible influence of the flue gas velocity.

#### 4.4 Analyses of the corrosion probes

Subsequently to the test run, the electrode rings of the corrosion probes were analysed by means of SEM/EDX. Analyses were performed for the same positions, for which the deposit probes have been analysed (windward, windward  $+50^{\circ}$ , leeward).

The deposit layers hat a thickness of some mm up to about 1 cm, with the thickest layer on the windward side. The overall thickness of the corrosion layers were in the range of 200 to 500  $\mu$ m with no correlation between the thickness differences and the position regarding the flue gas direction.

Generally, the deposits consist of Ca, K, S and O (Figure 14) indicating the deposits to be K- and Ca-sulphates and -oxides. This result is in good agreement with the results from the analyses of the deposit probe samples. S is also found in inner layers of the corrosion product and since K was also found in these areas, a layer-like formation consisting of corrosion product and deposits can be assumed. This could be caused by spallation of the corrosion product caused by the plant shutdown that happened during the test run and by the variations of the surface temperature of the probe.

Cl was only detected in small amounts in the inner deposit layers in some analyses (e.g. Figure 14 at windward+50°C) but no Cl was detected at the corrosion front in any analyses performed. Instead of Cl, an enrichment of S was found at the interface steel - corrosion layer. The general compositions of the deposits and the corrosion layer are the same for both corrosion probes including the S-enrichment on the corrosion front.

Since elevated Cl-concentrations are known to be found in inner corrosion layers and at the corrosion front if Cl-catalysed active oxidation takes place [20, 21], it is supposed that this mechanism, which is normally assumed to be the leading corrosion mechanism in MSW and biomass combustion plants, is not the dominant mechanism for corrosion in this case. The enrichment of S at the corrosion front indicates a participation of S in the corrosion mechanism. Nevertheless, a specific corrosion mechanism cannot be stated yet and therefore further work has to be done to identify the corrosion mechanism in case of chemically untreated wood fuels.



Figure 14: EDX-mappings of one ring from the corrosion probe at position M1

# **5 SUMMARY AND CONCLUSIONS**

Fuel analyses during the dedicated measurement campaigns showed rather constant fuel compositions during the long-term corrosion probe test run. The most relevant elements for high temperature corrosion, such as K, S and Cl were within the usual range of deviation. The assessment of the fuel analyses indicated a rather low risk for high temperature corrosion due to Cl-catalysed active oxidation.

Recording of relevant operating data showed, that during the test run, the CHP plant operated rather stably with the exception of one unplanned shutdown. For the first 20 weeks the plant was operated at a life steam flow of about 25 t/h corresponding to a boiler output of about 21 MW. In the last 5 five weeks the boiler load was increased to a life steam flow of about 29 t/h corresponding to a boiler output of about 25 MW.

High temperature impactor measurements at the positions of the corrosion probes showed aerosol concentrations of 22.8 mg/Nm<sup>3</sup> for position M1 and 24.4 mg/Nm<sup>3</sup> for position M2. Maxima of the particle size distributions were clearly below 1  $\mu$ m, with slightly increasing values with decreasing flue gas temperatures. The aerosols sampled consisted mainly of K<sub>2</sub>SO<sub>4</sub> with increasing concentrations of Ca in particles bigger than 1  $\mu$ m. Results from measurements in a pilot-scale plant [15] using similar fuels are in good agreement with the results at hand. Differences in the compositions can be explained by different fuel compositions. Calculations regarding the formation of aerosols show, that at the temperatures prevailing ZnO and K<sub>2</sub>SO<sub>4</sub> are the only relevant components for the formation of aerosols. The calculations also show that alkali metal chlorides exist only in gaseous form at these temperatures. The lack of Zn which was also found in the measurements in the pilot-scale plant can be explained by different fuel compositions, the gas phase relevant for particle formation mainly consists of KOH, KCl, HCl, SO<sub>x</sub> and K<sub>2</sub>SO<sub>4</sub> at the temperatures prevailing.

Deposit probe measurements at the positions resulted in deposit build-up rates in the range of 5-10 g/(m<sup>2</sup>·h). These are values also found during measurements when firing similar fuels in a pilot-scale plant. Measurements at the increased boiler load resulted in deposit build-up rates of 5-10 g/(m<sup>2</sup>·h) for position M1 and 19-23 g/(m<sup>2</sup>·h) for position M2 which exceeds comparable measurements. It is known that an increase in the boiler load typically results in increased deposit build-up rates due to increased entrainment of fuel, charcoal and coarse fly ash particles [15]. The high values at position M1 is located outside of the main flow.

The deposits consisted mainly of K<sub>2</sub>SO<sub>4</sub> and the elements Ca and Mg. At increased boiler load, increasing values of Ca and Mg are found, especially on the windward side. This is a result of the increased concentration of coarse fly ash particles in the flue gas which are mainly deposited by impaction on the windward side. Cl was found generally in minor concentrations in the deposits, mainly with values below 1 mol%. A maximum concentration of 4.6 mol% was found at position M2 for a deposit probe temperature of 480°C at the leeward side. Comparable measurements in a pilot-scale plant resulted in Cl-concentrations of 3.7 mol% for wood chips and 5.7 mol% for bark, analysed at the leeward side for probe temperatures of 450°C. General trends were increasing deposit build-up rates with increasing probe temperatures and decreasing sampling times. Increasing probe temperatures due to enhanced condensation rates. Cl-concentrations were generally higher on the leeward side compared to the windward side. These trends are known from previous measurements [18].

With the corrosion probe measurements corrosion rates for probe temperatures in the range of 400°C to 560°C were investigated parallel at two positions in the radiative section of the boiler. The measurements performed show a clear dependence between the corrosion rate and the parameters probe temperature and flue gas temperature. Increasing

values of both parameters result in increasing corrosion rates. For corrosion probe M2 data with flue gas temperatures in the range of 730°C to 810°C are available whereas flue gas temperatures for corrosion probe M1 were in the range of 810°C to 950°C. It has to be noted that only for a probe temperatur of 480°C an overlap of the data exists, whereas for the other probe temperatures a gap remains. For the probe temperature of 480°C the corrosion rates merge almost without deviation and also corrosion rates for the other probe temperatures are in good agreement.

Corrosion probe measurements in waste incineration plants [9] have shown an exponential increase of the corrosion rates with increasing corrosion probe temperatures. In addition, measurements performed in a pilot-scale combustion plant [19] have shown this relation. This behaviour has been described using an Arrhenius function which is based on the assumption that the dissolution of the metal into the oxide layer is the rate determining step. In the case at hand, this relation seems to be valid for probe temperatures from 400°C up to about 520°C. When probe temperatures exceed 520°C, the slope of the corrosion rates decreases which indicates another mechanism to become the rate determining step. A possible explanation could be a limitation by mass transport, but has not been proven yet. Therefore, further work has to be done to explain this result.

Furthermore the influence of the flue gas velocity was investigated since the measurements in waste incineration plants [9] as well as the measurements in the pilot-scale plant using chemically untreated wood chips [19] have shown an influence on the corrosion rate. The investigation of data gained from periods with fluctuating flue gas velocities in the test run at hand has shown no correlation between the flue gas velocity and the corrosion rate. The corrosion rates of the positions M1 and M2 are in good agreement despite somewhat different flue gas velocities (4.7 m/s in comparison to 8.3 m/s).

SEM/EDX analyses of the corrosion probes showed similar compositions as they were found during the deposit probe measurements. The deposit layers on both corrosion probes consisted mainly of K, S and Ca. Only small amounts of Cl were found in the deposits on the corrosion probes and no Cl was found at the corrosion front. Since a Cl-enriched layer at the corrosion front is typical for Cl-catalysed active oxidation, this mechanism is assumed not to be relevant in the present case. S was not only found in the deposits, but also at the corrosion front and therefore its participation in the corrosion mechanism is suspected. Nevertheless, yet no particular corrosion mechanism can be stated to have caused the corrosion and further work has to be done to identify a plausible corrosion mechanism for chemically untreated wood fuels.

The data gained from the corrosion probe measurements are to be used for the calculation of corrosion diagrams in order to support more efficient CHP plant design in the near future in terms of achievable electric efficiency at moderate or acceptable corrosion rates. Therefore, in future projects test runs with different biomass fuels and different superheater materials are intended.

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