

# COMPARATIVE CHARACTERISATION OF HIGH TEMPERATURE AEROSOLS IN WASTE WOOD FIRED FIXED-BED AND FLUIDISED-BED COMBUSTION SYSTEMS

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**ABSTRACT:** Fly ashes emitted from biomass combustion plants can generally be divided into coarse fly ashes and aerosols. To gain more detailed knowledge about aerosol formation processes and pathways in fixed-bed and bubbling fluidised-bed (BFB) combustion plants test runs have been performed, regarding aerosol characterisation by taking particle samples from the flue gas in the hot zones as well as downstream the economiser. The measurement results showed lower aerosol concentrations in all boiler sections of the BFB system as well as significant differences in the chemical compositions of the aerosols. The main reasons for these differences are the lower combustion temperatures and higher concentrations of coarse fly ash particles in the BFB combustion plant. Lower temperature levels reduce the release of aerosol forming elements (e.g. K, Na and Zn) from the fuel to the gas phase and subsequently aerosol formation as well as the sulphation of already formed KCl, consequently reducing the concentration of S in aerosols. Higher concentrations of coarse fly ash and bed material particles provide additional surfaces for chemical surface reactions (e.g. formation of Zn- and K-silicates as well as of Ca-sulphates) and also for the condensation of ash forming vapours. Both effects decrease aerosol concentrations emitted from BFB combustion systems. The higher amounts of KCl in aerosols from BFB combustion systems may enhance corrosion on superheater tube bundles by active oxidation.

**Keywords:** aerosol, waste wood, fixed bed, fluidised bed, chemical composition

## 1 INTRODUCTION

Fly ashes emitted from biomass combustion plants can generally be divided into coarse fly ashes (particles >1 µm) and aerosols (particles <1 µm). Thereby coarse fly ashes originate from ash and fuel particles which are entrained from the fuel bed with the flue gas. A part of these particles is precipitated in the furnace and the boiler (so-called furnace and boiler ashes) as well as on heat exchanger surfaces (deposit formation). The remaining fraction leaves the boiler as coarse fly ash emission [1]. Coarse fly ash particles mainly consist of refractory species such as Si, Ca, Mg, Fe, Al and P as well as semi-volatile elements such as K and Na.

Aerosols on the other side originate from K and Na as well as easily volatile species such as S, Cl, Zn and Pb which are partly released from the fuel to the gas phase during combustion. There they undergo gas phase reactions and form alkaline and heavy metal chlorides and sulphates as well as heavy metal oxides. As soon as the vapour pressure of such a compound exceeds the saturation vapour pressure aerosol particle formation by nucleation and particle growth by condensation of ash forming vapours on already existing aerosol particles takes place. Supersaturation can thereby be reached either by high formation ratios of a certain compound or due to the cooling of the flue gas. In the following, aerosol particles also grow by coagulation effects. Additionally, condensable ash forming vapours can also condense on heat exchanger surfaces and thereby contribute to deposit formation.

Coarse fly ash particles can be precipitated in cyclones while for aerosol precipitation more advanced filter systems such as baghouse filters and electrostatic precipitators are needed due to the small particles sizes (<1 µm) of aerosols.

Therefore, knowledge about aerosol formation processes in biomass combustion systems is of high relevance regarding particulate emissions and concerning deposit formation and corrosion processes. Detailed information about the different processes involved in

aerosol formation has already been gained from several research projects [1, 2, 3, 4, 5]. However, these investigations were mainly based on the determination of the concentration and chemical composition of aerosol particles sampled downstream the boiler. No detailed information about these characteristics of aerosol in the hot zones of the furnace and the boiler was available so far. Therefore, a high-temperature low-pressure impactor has been developed at the Institute for Process and Particle Engineering, Graz University of Technology, with which in-situ sampling of aerosols at temperatures up to 1,100°C is possible [6].

In this paper, data concerning the concentrations, particle size distributions and chemical compositions of aerosols sampled with this new device in different sections of a fixed-bed and a bubbling fluidised-bed (BFB) combustion systems fired with waste wood are presented. From these data relevant information about the differences concerning the aerosol formation processes taking place in fixed-bed and BFB combustion are derived which can be used to identify the parameters influencing aerosol formation in both systems as well as a basis for aerosol formation and deposit formation modelling.

### 1.1 Objectives

This paper aims at the investigation and comparison of aerosol formation processes in waste wood fired fixed-bed and BFB boilers. Therefore, measurement campaigns at a grate-fired combustion plant as well as at a BFB combustion plant have been performed. The objectives of these test runs were:

- The determination of the concentration, particle size distribution (PSD) and chemical composition of aerosols sampled at different measurement points along the flue gas pathway from the furnace over the superheater downstream the economiser by sampling and measurements with a high-temperature as well as conventional low-pressure impactor and subsequent analyses of the samples.

- Identification of the aerosol formation processes in fixed-bed and BFB combustion systems based on the evaluation of the impactor measurements, analyses as well as of process data recorded during the test runs.

## 1.2 Methods and materials

During the test runs performed the following samples were taken as well as measurements and analyses were performed:

- Characterisation of the waste wood used (fuel samples were taken every 2 hours during the test runs and from these samples daily mixed samples were produced) by wet chemical analyses regarding the ash content as well as the concentrations of the most relevant ash forming elements (Si, Ca, Mg, K, Na, Zn, Pb, S, Cl, Al, Fe, Mn and P). The ash content of the samples was analysed according to CEN/TS 14775 (loss of ignition at 550°C). For the determination of the Cl content bomb combustion in oxygen, absorption in NaOH and element detection with ion chromatography has been applied. All other elements were determined by pressurised multi-step digestion of the dried fuel samples with HNO<sub>3</sub>/HF/H<sub>3</sub>BO<sub>3</sub> and subsequent element detection with ICP-MS or AAS [8, 9].
- Characterisation of samples taken during the test runs from the bottom ash and the boiler ash (fly ash precipitated in the radiative boiler, superheater and economiser section) by wet chemical analyses regarding the concentrations of Si, Ca, Mg, K, Na, Zn, Pb, S, Cl, P, Fe, Al and Mn. Cl was determined by elution in deionised water and subsequent detection by ion chromatography while for all other elements pressurised multi-step digestion of the samples (HNO<sub>3</sub>/HF/H<sub>3</sub>BO<sub>3</sub>) followed by element detection with ICP-MS or AAS was applied [8, 9].
- Determination of the particle size distribution (PSD) and concentration of aerosols in the flue gas in the hot furnace and the superheater section with an 8-stage high-temperature low-pressure impactor (HT-LPI, see section 1.2.1).
- Determination of the particle size distribution (PSD) and concentration of aerosols in the flue gas at boiler outlet (downstream economiser) with 9-stage Berner-type low-pressure impactors (BLPI).
- Determination of the fly ash concentration in the flue gas at boiler outlet (downstream the economiser) using a sampling equipment according to VDI 2066.
- Determination of the chemical composition of aerosol and fly ash samples by SEM/EDX as well as by wet chemical measures applying the same methods as for bulk ash samples [8, 9].
- To define the operation mode of the respective combustion plant during the test runs, plant operation data such as furnace temperatures, flue gas temperatures, the plant load as well as the O<sub>2</sub> and the CO-concentrations in the flue gas were continuously measured, recorded and evaluated.

- Verification of the flue gas temperatures measured and recorded by the plant process control system using a suction pyrometer according to IFRF and VDI.

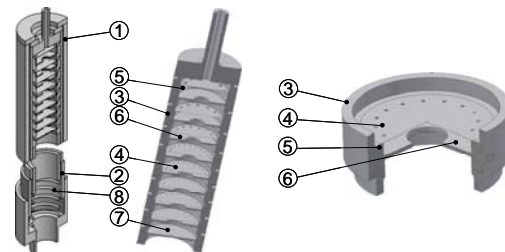
Based on these analyses data and on the plant operation data during the respective test runs mass and element balances were calculated over the combustion plants in order to determine the behaviour and fluxes of ash and aerosol forming elements.

### 1.2.1 High-temperature low-pressure impactor (HT-LPI)

For aerosol particle sampling at high temperatures a special high-temperature low-pressure impactor (HT-LPI) was developed at the Institute for Process and Particle Engineering (IPPT), Graz University of Technology, Austria. The HT-LPI is based on the common design of a Berner-type low-pressure impactor. It consists of 8 stages (Fig. 1) with cut diameters between 0.09 µm and 2.60 µm. Each stage consists of an orifice plate, a spacer ring and a stagnation plate. The flow rate is controlled by a critical orifice.

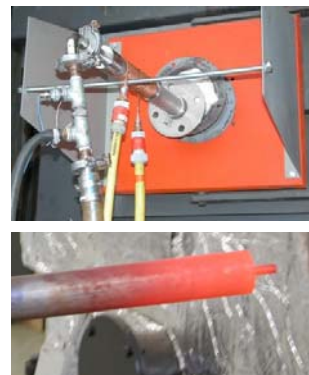
To facilitate an operation at temperatures of up to 1,100°C special materials have been applied for the HT-LPI itself (heat resisting steel 15 X CrNiSi 25 20 and Inconel 600) as well as for the sampling foils (platinum) and the sealing (quartz). Since the HT-LPI is directly placed in the furnace, it facilitates an in-situ measurement of the concentration and PSD of aerosols in the high temperature zones (Fig. 2). Thereby it has to be taken care that the HT-LPI is pre-heated in the furnace for a certain period of time (about 15 min), to avoid condensation of ash forming vapours in the HT-LPI.

Samples taken with the HT-LPI can subsequently be analysed by SEM/EDX or wet chemical methods.



**Figure 1:** Basic design of the HT-LPI

**Explanations:** 1...outer casing, 2...inner casing, 3...shell, 4...orifice plate, 5...spacer ring, 6...stagnation plate, 7...critical orifice, 8... spring



**Figure 2:** HT-LPI during and after a measurement

### 1.2.2 Ash balancing and determination of the concentration of coarse fly ashes at boiler inlet

The total ash mass flow was calculated based on the ash content and the mass flow of the waste wood fired which has been calculated from overall mass and energy balances. The amount of the bottom and boiler ashes was calculated subtracting the fly ash emissions measured downstream the economiser from the total input of ash forming elements. For the BFB plant additionally the bed material input was considered. The fractionation into bottom ash as well as boiler, superheater and economiser ash was determined based on data supplied from the plant operators.

Based on wet chemical analyses of the different ash fractions and the mass flows of all ash fractions, element balances over the plants were calculated.

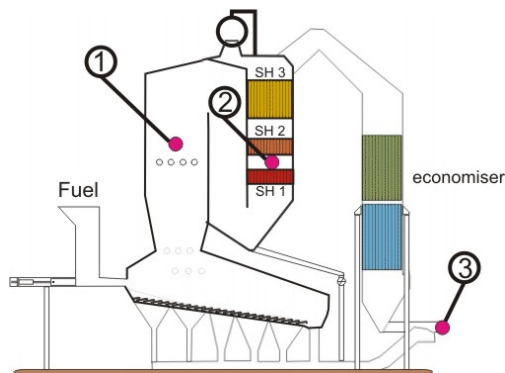
The concentrations of the coarse fly ashes at boiler inlet (above the fuel bed) was calculated by summing up the coarse fly ash precipitated in the boiler, superheater and economiser as well as the coarse fly ash emissions measured at boiler outlet.

### 1.3 Plant description

Measurement campaigns at a grate-fired waste wood combustion plant as well as at a BFB waste wood combustion plant have been performed. A strong focus was put on stable process conditions during the test runs in order to achieve representative results.

In the grate-fired waste wood combustion plant (Fig. 3) an inclined moving grate is fed with waste wood by a hydraulic stoker. The plant is equipped with a water-tube steam boiler (membrane walls), 3 superheaters as well as an economiser. For furnace temperature control flue gas is recirculated below and above the grate. Flue gas cleaning is done by a double cyclone and a baghouse filter. SNCR is applied for  $\text{NO}_x$  reduction and a dry sorption system is applied for HCl,  $\text{SO}_x$  and PCDD/F-emission control. The nominal boiler capacity of the plant is 44  $\text{MW}_{\text{th}}$  (steam parameters: 66 bar, 452°C).

During the test runs the combustion plant was operated at approximately 90% of its nominal load. Waste wood of quality A1 to A4 according to German quality standards [10] was utilised. The chemical characterisation of the fuel is given in section 1.4.



**Figure 3:** Scheme of the grate-fired waste wood combustion plant investigated

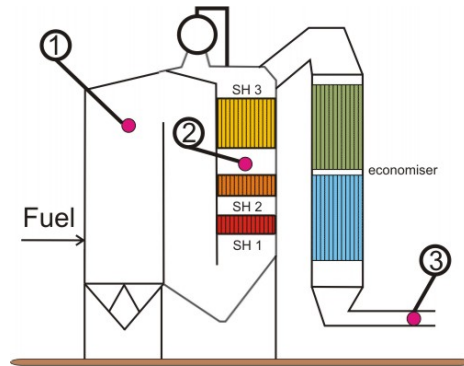
**Explanations:** HT-LPI measurements: 1<sup>st</sup> boiler duct (1), convective section downstream superheater 1 (2); BLPI and coarse fly ash measurements downstream economiser (3); SH...superheater

In Fig. 3 a scheme of the furnace, boiler and economiser is shown. Moreover, the positions of the HT-LPI, BLPI and dust sampling ducts are marked.

In the BFB combustion plant (Fig. 4) the fuel is fed into the plant with recirculated flue gas. The bed material used is quartz sand ( $\text{SiO}_2$ ). The plant is equipped with a water-tube steam boiler (membrane walls), 3 superheaters as well as an economiser. The flue gas is cleaned by a baghouse filter and a dry sorption system is applied for HCl and  $\text{SO}_x$  emission control. The nominal boiler capacity of the plant is 37.2  $\text{MW}_{\text{th}}$  (steam parameters: 61 bar, 453°C).

During the test runs the combustion unit was operated at approximately 95% of its nominal load. Waste wood of quality A1 to A3 according to German quality standards [10] was utilised. The chemical characterisation of the fuel is given in section 1.4.

In Fig. 4 a scheme of the furnace, boiler and economiser is shown. Moreover, the positions of the HT-LPI, BLPI and dust sampling ducts are marked.



**Figure 4:** Scheme of the BFB waste wood combustion plant investigated

**Explanations:** HT-LPI measurements: 1<sup>st</sup> boiler duct (1), convective section downstream superheater 2 (2); BLPI and coarse fly ash measurements downstream economiser (3); SH...superheater

### 1.4 Waste wood applied during the test runs

In Table 1 and Table 2 results of fuel analyses concerning the waste wood utilised during the test runs are presented.

The concentrations of major ash forming elements (Si, Ca, Mg, Al, Fe, P) were significantly higher in the fuel used in the fixed-bed combustion plant (68,022 mg/kg (d.b.)) than the one used in the BFB combustion plant (7,496 mg/kg (d.b.)) resulting in significantly higher ash contents (16.4 wt% (d.b.) compared to 2.2 wt% (d.b.)). The concentrations of the most relevant aerosol forming elements (K, Na, Zn, Pb) were also higher in the fuel used in the fixed-bed combustion plant (6,095 mg/kg (d.b.) compared to 1,918 mg/kg (d.b.)). In addition, the 2S/Cl ratio was higher for the fuel used in the fixed-bed system (2.8 mol/mol compared to 1.82 mol/mol).

**Table 1:** Characterisation of the waste wood used during the test runs at the fixed-bed combustion plant

Explanations: d.b. ... dry basis; Si+Ca+Mg+Al+Fe+P ... main ash forming elements; K+Na+Zn+Pb ... aerosol forming elements

		average	standard deviation
Al	[mg/kg (d.b.)]	5,263	321
Ca	[mg/kg (d.b.)]	8,289	1,028
Cl	[mg/kg (d.b.)]	1,127	330
Fe	[mg/kg (d.b.)]	6,123	663
K	[mg/kg (d.b.)]	2,453	162
Mg	[mg/kg (d.b.)]	1,337	145
Mn	[mg/kg (d.b.)]	262	44
Na	[mg/kg (d.b.)]	2,707	495
P	[mg/kg (d.b.)]	354	32
Pb	[mg/kg (d.b.)]	141	22
S	[mg/kg (d.b.)]	1,427	252
Si	[mg/kg (d.b.)]	46,657	8,646
Zn	[mg/kg (d.b.)]	794	352
ash content	[wt% (d.b.)]	16.4	2.3
Si+Ca+Mg+Al+Fe+P	[mg/kg (d.b.)]	68,022	
K+Na+Zn+Pb	[mg/kg (d.b.)]	6,095	
2S/Cl	[mol/mol]	2.80	

**Table 2:** Characterisation of the waste wood used during the test runs at the BFB combustion plant

Explanations: d.b. ... dry basis; Si+Ca+Mg+Al+Fe+P ... main ash forming elements; K+Na+Zn+Pb ... aerosol forming elements

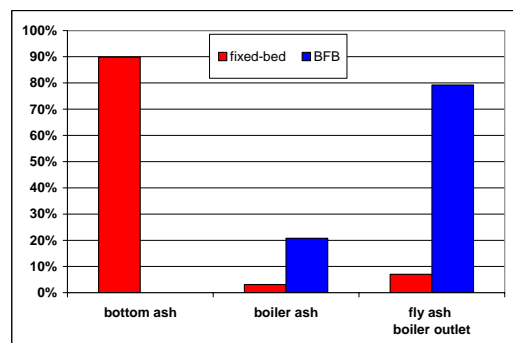
		average	standard deviation
Al	[mg/kg (d.b.)]	466	134
Ca	[mg/kg (d.b.)]	3,547	829
Cl	[mg/kg (d.b.)]	596	153
Fe	[mg/kg (d.b.)]	426	233
K	[mg/kg (d.b.)]	1,198	299
Mg	[mg/kg (d.b.)]	506	74
Mn	[mg/kg (d.b.)]	116	10
Na	[mg/kg (d.b.)]	542	93
P	[mg/kg (d.b.)]	168	46
Pb	[mg/kg (d.b.)]	56	32
S	[mg/kg (d.b.)]	490	63
Si	[mg/kg (d.b.)]	2,383	713
Zn	[mg/kg (d.b.)]	122	38
ash content	[wt% (d.b.)]	2.2	0.6
Si+Ca+Mg+Al+Fe+P	[mg/kg (d.b.)]	7,496	
K+Na+Zn+Pb	[mg/kg (d.b.)]	1,918	
2S/Cl	[mol/mol]	1.82	

## 2 ASH MASS FLOW DISTRIBUTION

In fixed-bed combustion systems the bottom ash is the dominating ash fraction representing 60 - 90% of the total ash mass flow [11]. About 10 - 40% of the ashes is entrained from the fuel bed and can be found as boiler ash, cyclone ash and filter fly ash. On the contrary in BFB units most of the ash is entrained from the BFB and can be found as boiler ash, cyclone ash and filter fly ash. Additionally, in a BFB boiler bed material particles are entrained from the furnace and also contribute to the coarse fly ash.

The results of the ash mass balances over the plants investigated follow these typical tendencies (Fig. 5). In the fixed-bed combustion system about 90% of the ash was found as bottom ash, 3% as boiler ash and 7% as fly ash emitted at the boiler outlet. In the BFB combustion system almost no bottom ash was found while 21% of the

total ash was separated in the boiler section. 79% of the ashes left the economiser as fly ash emission. About 16% of the total ash originates from bed material. Almost 70% of the entrained bed material was precipitated with the boiler ash, while 30% ended up in the coarse fly ash emissions at boiler outlet.

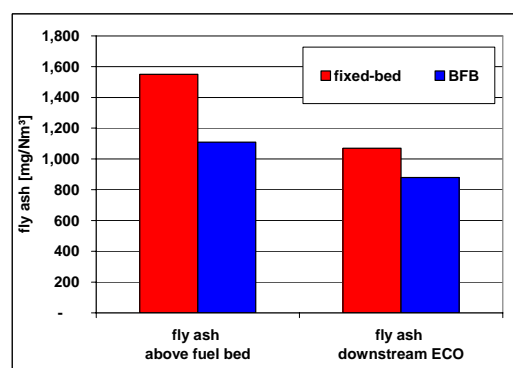


**Figure 5:** Distribution of the ashes among the different ash fractions in the plants investigated

Explanations: fixed-bed...fixed-bed combustion system; BFB...bubbling fluidised-bed combustion system

## 3 CONCENTRATIONS OF FLY ASH PARTICLES IN THE FLUE GAS

As shown in Fig. 6, the total fly ash concentrations above the fuel bed amounted to 1,550 mg/Nm<sup>3</sup> for the fixed-bed combustion system and to 1,110 mg/Nm<sup>3</sup> for the BFB unit (related to dry flue gas and 13 vol% O<sub>2</sub>). The concentrations of the fly ashes in the flue gas emitted downstream the economiser decreased to 1,070 mg/Nm<sup>3</sup> for the fixed-bed and to 879 mg/Nm<sup>3</sup> for the BFB plant.

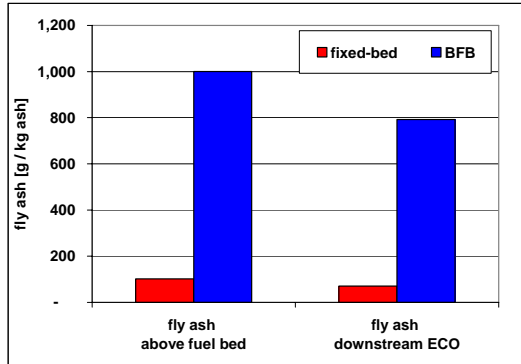


**Figure 6:** Fly ash concentrations in the flue gas above the fuel bed and downstream economiser in the plants investigated

Explanations: fixed-bed...fixed-bed combustion system; BFB...bubbling fluidised-bed combustion system; ECO...economiser; data related to dry flue gas and 13 vol% O<sub>2</sub>

However, when evaluating these results, the different ash contents of the fuels have to be considered, since with increasing ash contents also in fixed-bed combustion systems the fly ash emissions increase [1]. Therefore, the concentrations of fly ash particles in the flue gas were related to the ash mass flow into the combustion systems in order to evaluate the results (Fig. 7).

In the BFB system the share of fly ashes on the total ash in the flue gas above the fuel bed as well as downstream the economiser was, as expected, significantly higher (1,000 g/kg ash compared to 102 g/kg ash respectively 792 g/kg ash compared to 70 g/kg ash).

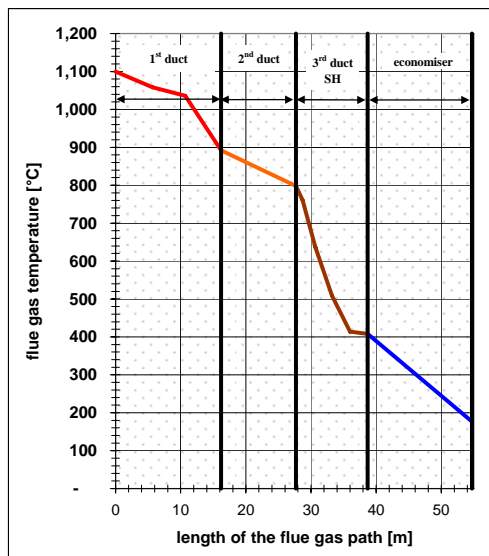


**Figure 7:** Share of the fly ash concentrations above the fuel bed and downstream the economiser related to the total mass of ashes formed

**Explanations:** fixed-bed...fixed-bed combustion system; BFB...bubbling fluidised-bed combustion system data related to the total ash mass flow; entrained bed material from the BFB included in the calculations of the total ash mass flow

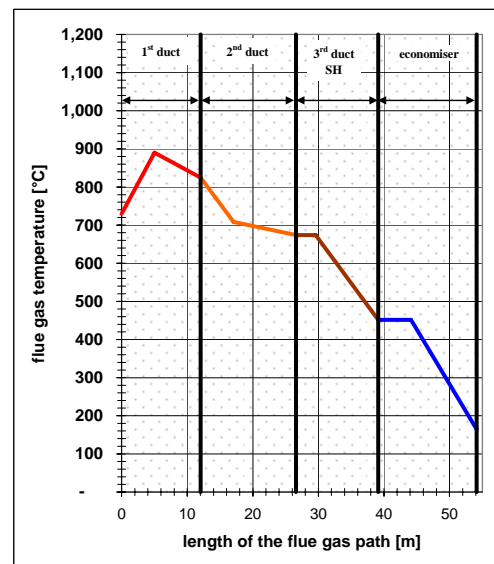
#### 4 TEMPERATURE PROFILES OF THE COMBUSTION PLANTS

In aerosol formation processes the temperature profile of a combustion plant plays an important role. In Fig. 8 and Fig. 9 the temperature profiles of the two combustion plants investigated are presented. The temperatures were taken from data recorded by the process control systems and were averaged over the period of the test runs. Moreover, suction pyrometer measurements were performed at the HT-LPI sampling positions to check the temperature data.



**Figure 8:** Temperature profile of the fixed-bed combustion plant

As Fig. 8 and Fig. 9 clearly show, the temperature level in BFB systems is generally lower. In the BFB unit the average flue gas temperatures decrease from about 890°C at the end of the 1<sup>st</sup> duct over 673°C upstream the superheater section to 450°C upstream the economiser and finally 164°C at economiser outlet. In the fixed-bed combustion system the average temperatures decrease from about 1,100°C at the end of the 1<sup>st</sup> duct over 800°C at the inlet of the superheater section to 410°C upstream the economiser and finally 177°C at economiser outlet. The starting temperatures displayed in the profiles are the first temperature measurements by the plant process control system directly above the fuel bed. Those are the most relevant temperatures for the release of ash forming vapours to the gas phase. In the BFB unit this temperature is significantly lower than in the fixed-bed system.



**Figure 9:** Temperature profile of the BFB combustion plant

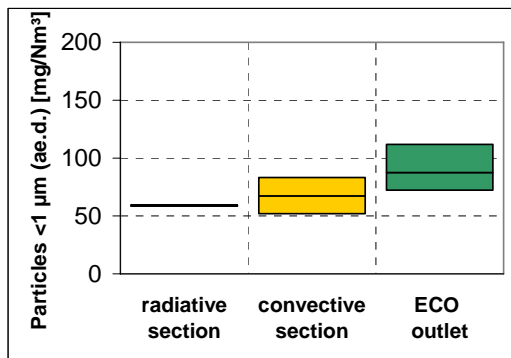
#### 5 AEROSOL FORMATION AND CHEMICAL COMPOSITION OF THE AEROSOLS

##### 5.1 Aerosol concentration

In order to determine the concentration and particle size distribution (PSD) of aerosols, HT-LPI measurements have been performed at the sampling points presented in Fig. 3 and Fig. 4. Moreover, BLPI measurements were done downstream the economiser.

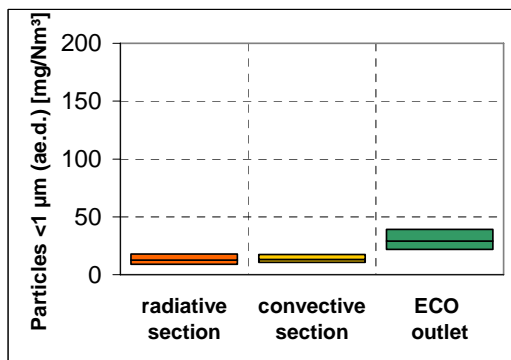
In Fig. 10 and Fig. 11 the aerosol concentrations measured in the radiative section (mean flue gas temperatures: fixed-bed: 889°C, BFB: 826°C) and the convective section (mean flue gas temperatures: fixed-bed: 400°C, BFB: 601°C) of the boilers as well as downstream the economiser (mean flue gas temperatures: fixed-bed: 182°C, BFB: 163°C) are presented. Generally, in both systems the aerosol concentrations increase, as expected, with decreasing flue gas temperatures. In the fixed-bed system the aerosol concentrations increase from the radiative section (59.0 mg/Nm<sup>3</sup>) over the convective section (67.2 mg/Nm<sup>3</sup>) to the measurement point downstream the economiser (87.4 mg/Nm<sup>3</sup>). The aerosol concentrations in the BFB unit increase from

12.6 mg/Nm<sup>3</sup> in the radiative section over 13.2 mg/Nm<sup>3</sup> in the convective section to 29.0 mg/Nm<sup>3</sup> at the measurements point downstream the economiser.



**Figure 10:** Aerosol concentrations determined at the different sampling points in the fixed-bed combustion plant

**Explanations:** measurement points according to Fig. 3; radiative and convective sections: HT-LPI measurements; ECO outlet... BLPI measurements; ae.d...aerodynamic diameter; data related to dry flue gas and 13 vol% O<sub>2</sub>



**Figure 11:** Aerosol concentrations determined at the different sampling points in the BFB combustion plant

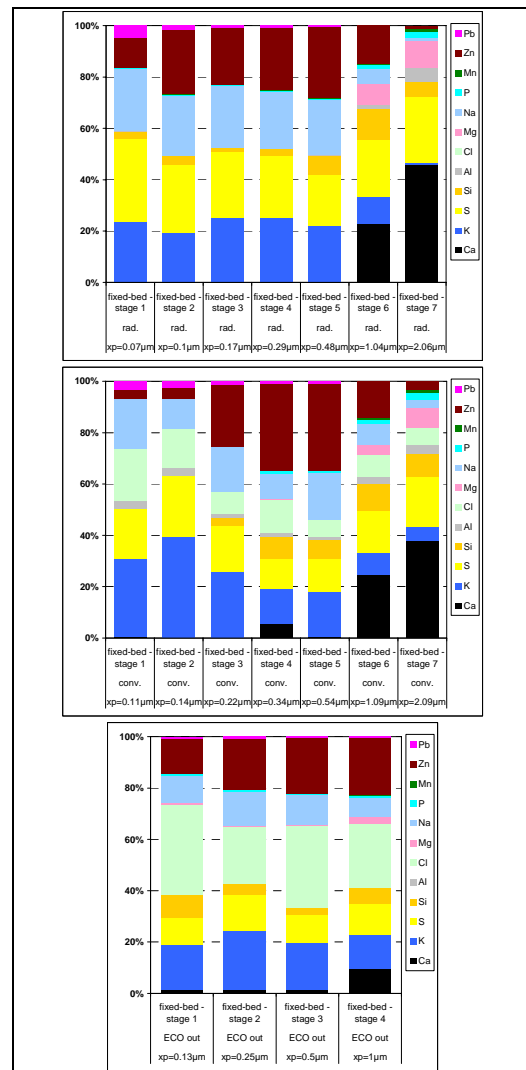
**Explanations:** measurement points according to Fig. 4; radiative and convective sections: HT-LPI measurements; ECO outlet... BLPI measurements; ae.d...aerodynamic diameter; data related to dry flue gas and 13 vol% O<sub>2</sub>

In the BFB combustion plant the aerosol concentrations in all sections are lower than in the fixed-bed combustion plant. Firstly, this is a result of the different compositions of the biomass fired since the concentration of aerosol forming elements in the waste wood fired in the fixed-bed combustion system is higher (6,095 mg/kg (d.b.)) compared to the one used in the BFB combustion system (1,918 mg/kg (d.b.)). Secondly, the high concentrations of coarse fly ashes as well as the bed material particles (quartz sand) in the BFB combustion system provide additional surfaces for condensation of ash forming vapours and consequently particle formation by nucleation is partly suppressed. Higher concentrations of coarse fly ash particles also lead to increased reactions of aerosol forming elements with those particles. In this respect it is known that Zn and K react with Si-rich bed material particles [13, 14]. Furthermore, the release of aerosol forming elements (e.g. K, Na and Zn) from the fuel to the gas phase and consequently aerosol formation is reduced by the lower

temperatures in the fuel bed of the BFB combustion plant [12, 13].

## 5.2 Chemical composition of the aerosols

The aerosols collected with the HT-LPI as well as the BLPI were investigated by wet chemical and SEM/EDX analyses concerning their chemical composition (Fig. 12 and Fig. 13) in order to identify differences in the aerosol compositions in fixed-bed and BFB systems.

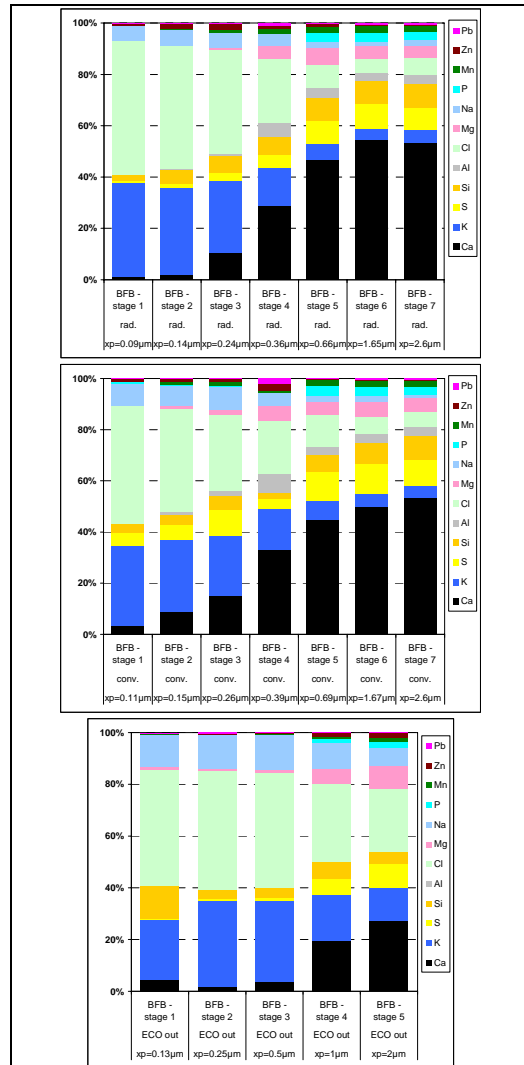


**Figure 12:** Chemical composition of the aerosols sampled with the HT-LPI as well as the BLPI at the fixed-bed combustion plant

**Explanations:** xp...cut diameter of the impactor stage; concentrations in [mol %]; HT-LPI: SEM/EDX analyses; BLPI: wet chemical analyses

In the 1<sup>st</sup> duct (mean flue gas temperature 889°C) of the fixed-bed combustion system the aerosols mainly consist of K and Na-sulphates as well as Zn-oxide and lower amounts of Si and Pb-oxides [1, 13 and 14]. With decreasing temperatures over the superheater (mean flue gas temperature 400°C) and the economiser (mean flue gas temperature 182°C) condensation of chlorides starts, as it is confirmed by the higher Cl-concentrations in the particles sampled in these sections. With increasing

particle size the concentrations of Si, Ca and Mg increase in all boiler sections.



**Figure 13:** Chemical composition of the aerosols sampled with the HT-LPI as well as the BLPI at the BFB combustion plant

**Explanations:** xp...cut diameter of the impactor stage; concentrations in [mol %]; HT-LPI: SEM/EDX analyses; BLPI: wet chemical analyses

The chemical composition of the aerosols sampled at the BFB boiler significantly differs from the one in the fixed-bed system. In the 1<sup>st</sup> duct (mean flue gas temperature 826°C) the aerosols mainly consist of K and Na-chlorides as well as smaller amounts of sulphates. Moreover, small amounts of Si, Ca and Mg-oxides are found (stage 3 to 7). Again the Ca, Mg and Si-concentrations increase with increasing particle sizes which indicates that these particles originate partly from defragmentation processes. With decreasing temperatures downstream superheater 2 (mean flue gas temperature 601°C) and the economiser (flue gas temperature 163°C) the chemical composition of the aerosols does not change significantly.

The most obvious difference concerning the aerosol compositions determined for the fixed-bed and the BFB

combustion system is the significantly lower amount of S in the aerosols sampled in the BFB system. This may be a result of the different biomass compositions since the higher molar 2S/Cl ratio of the waste wood fired in the fixed-bed boiler (2.80) compared to the one used in the BFB boiler (1.82) contributes to a higher sulphation ratio.

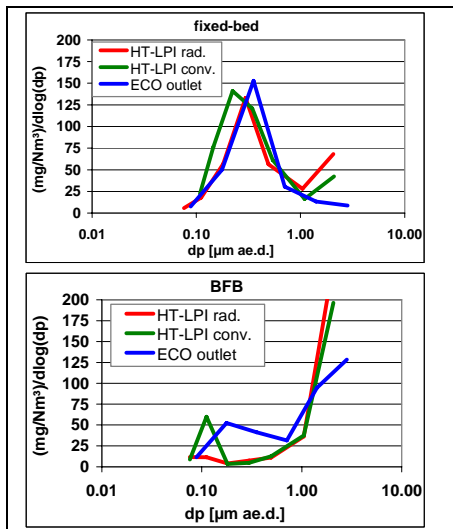
However, this argument alone does not explain the extremely low S-concentration found in the aerosols in the BFB system. Also the typical characteristics of BFB combustion plants, which are the high concentrations of fly ashes and the presence of bed material as well as the comparably low combustion temperatures, have an influence. The lower temperature levels in BFB systems retard the SO<sub>2</sub>-SO<sub>3</sub>-kinetics and consequently reduce the sulphation of already formed KCl. Moreover, the considerably higher amount of Ca-containing particles in the PM<sub>10</sub> fraction in comparison to fixed-bed systems enhances the formation of Ca<sub>2</sub>SO<sub>4</sub>.

Another interesting difference concerning the aerosol composition is that in the aerosols sampled in the BFB boiler almost no Zn was found while Zn is a relevant aerosol forming element in the fixed-bed combustion system. Firstly, this is assumed to be a result of the comparably low combustion temperatures in the BFB, which lead to a lower release of Zn to the gas phase. Secondly, it is known that Zn reacts with coarse Si-containing fly ash particles entrained from the bed material in the BFB combustion plant [13, 14]. The concentration of Pb in the aerosols sampled in the BFB boiler is as well lower than in the fixed-bed combustion system. Once more besides the lower Pb-concentration in the fuel, reactions of Pb with coarse Si-containing fly ash particles can be named as a reason [13, 14].

## 6 BEHAVIOUR OF RELEVANT ELEMENTS IN AEROSOL FORMATION PROCESSES

Based on the SEM/EDX analyses of HT-LPI samples as well as wet chemical analyses of BLPI samples presented in Fig. 12 and Fig. 13 and the particle size distributions derived from the single aerosol measurements, the behaviour of relevant elements in the aerosol formation processes was studied. The aim was to identify the contribution of these elements and their compounds to the aerosol formation processes in fixed-bed and BFB combustion systems.

The mean particle size distributions (PSD) of the aerosols sampled in the radiative and the convective section as well as at the boiler outlet of the fixed-bed and the BFB combustion plant are presented in Fig. 14. Generally, the aerosols formed in the fixed-bed combustion system are larger in particle size. While the peak diameter of the aerosol PSDs at boiler outlet for the BFB combustion system is placed on the 3<sup>rd</sup> impactor stage (0.18 μm ae.d.), the peak diameter of the PSDs at boiler outlet for the fixed-bed systems is located on the 4<sup>th</sup> impactor stage (0.35 μm). This is mainly due to the fact that in the BFB system less mass of aerosol forming vapours condenses and therefore, also the growth of aerosols by condensation on already existing particles is smaller.



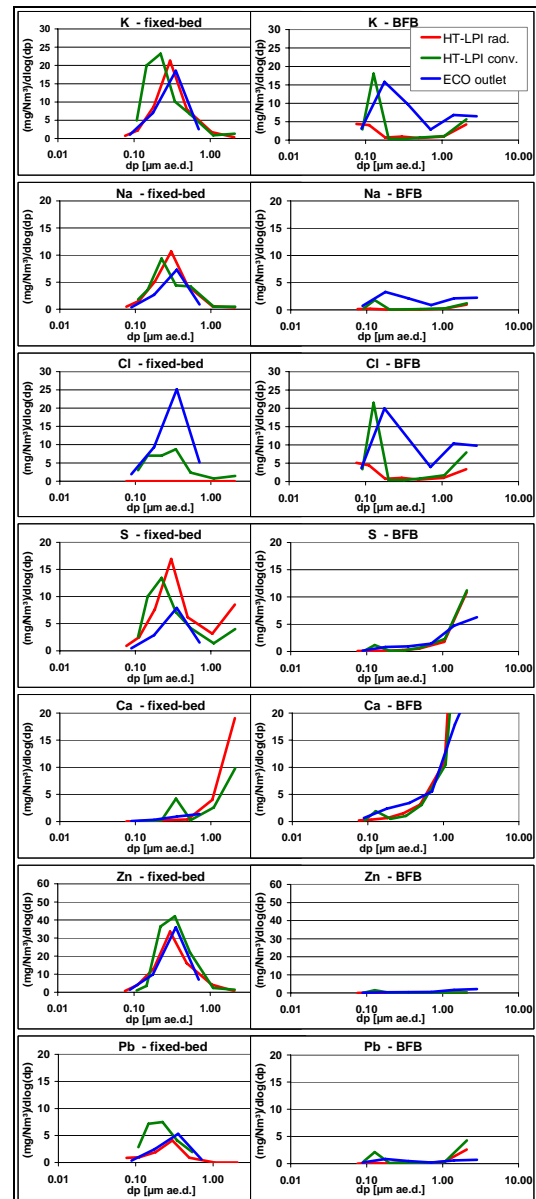
**Figure 14:** PSD of the aerosols in the flue gas in the radiative and the convective section as well as at boiler outlet in the fixed-bed combustion and the BFB combustion system

Explanations: all data related to dry flue gas and 13 vol% O<sub>2</sub>

In Fig. 15 the elemental distributions of K, Na, Cl, S, Ca, Zn and Pb among the different aerosol fractions of the fixed-bed and the BFB combustion plant are presented.

K and Na show about the same behaviour. The significant differences concerning the Na concentrations in the aerosol formed in the fixed-bed and the BFB combustion system are mainly due to their different concentrations in the fuels applied (2,707 mg/kg (d.b.) in the fixed-bed system respectively 542 mg/kg (d.b.) in the BFB system) as well as a lower Na release expected due to the lower bed temperature in the BFB system.

In the fixed-bed combustion plant K and Na compounds are formed at high temperatures in the radiative path of the boiler. As the comparison with the S-concentrations clearly indicates, the particles formed in the radiative section are mainly K<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub>. This is also confirmed by thermodynamic considerations, since, taking the saturation vapour pressure as well as the total concentrations of K, Na and S in the flue gas into account, supersaturation can be reached at about 1,000°C. With decreasing temperatures also the K and Na concentrations increase (sampling point downstream superheater 1). Besides the further condensation of sulphates, condensation of alkali metal chlorides is responsible for this effect which is clearly confirmed by comparing the K, Na, S and Cl distributions at sampling point 2 (convective section). A further increase of the Cl-concentrations can be seen at economiser outlet, which is assumed to be mainly due to the condensation of easily volatile heavy metal chlorides, which reach saturation at comparably low temperatures (show high saturation vapour pressures).



**Figure 15:** Concentrations of particle bound ash forming elements in the flue gas in the different boiler sections

Explanations: all data related to dry flue gas and 13 vol% O<sub>2</sub>

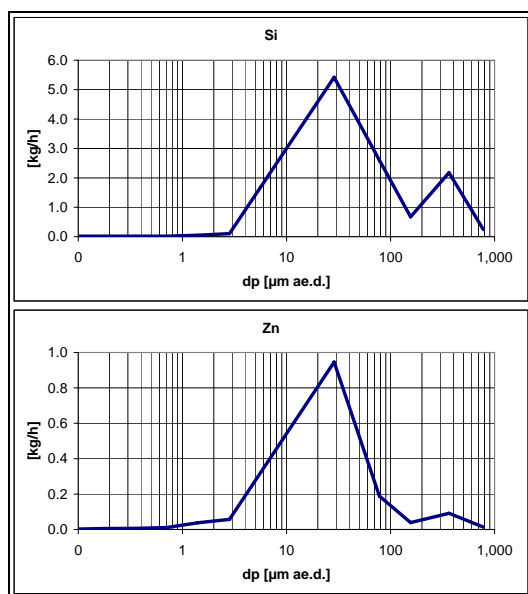
Concerning Zn, obviously almost the whole amount of Zn, which can be found in the aerosols downstream the economiser, already forms particles in the radiative section of the fixed-bed combustion plant upstream measurement point 1. The formation of ZnO particles in waste wood combustion systems has already been described in [1] and mainly results from the release of elemental Zn under reducing conditions and the subsequent formation of ZnO, which leads to instant nucleation due to the comparably low saturation vapour pressure of ZnO. A smaller part of the Zn may also form chlorides.

A considerable amount of Pb found in the aerosols at boiler outlet already forms particles in the radiative section of the fixed-bed combustion plant, most likely bound in oxides [1]. As the comparison with the Cl

concentrations clearly indicates, the further increase of the Pb-concentrations downstream the economiser is assumed to be mainly due to the condensation of Pb-chlorides.

Comparing the Ca distribution over the particle sizes at all measurement points with the distributions of all other elements analysed, no similarities and consequently no associations can be identified.

On the contrary, in the BFB combustion plant only a minor amount of K and Na has already formed particles in the radiative path (sampling point 1). Again, these particles consist of alkali metals, but in contrary to the fixed-bed combustion plant, K and Na are mainly bound as chlorides. This effect is assumed to be due to the lower combustion temperatures as the sulphation of alkali metal chlorides at temperatures below 800°C is kinetically limited. With decreasing temperature the K, Na and Cl concentrations increase indicating the further formation of KCl and NaCl in the convective section as well as to boiler outlet (as the sampling point in the superheater section was placed at high temperatures). Only minor condensation of sulphates in the submicron particle range occurs, while most of the S can be found in larger particle sizes. Comparing the concentrations of S and Ca over particle size, it can be concluded, that most of the S is bound to Ca-containing coarse fly ash particles forming Ca<sub>2</sub>SO<sub>4</sub>.



**Figure 16:** Particle size distribution of Si and Zn in the filter fly ash of the BFB combustion plant

Explanations: dp [µm ae.d.]...aerodynamic diameter

Concerning Zn obviously almost no nucleation or condensation processes take place. This indicates that the Zn release from the fuel particles is lower (due to the lower combustion temperatures in the BFB system) and most of the Zn released is embedded in Si-rich bed material particles by surface reactions. This effect is confirmed when comparing the PSD of Si and Zn for filter fly ash (Fig. 16).

The same effect is obvious for Pb. The Pb released from the fuel mainly reacts with silicates [13, 14] resulting in a high embedding ratio in coarse fly ash particles.

## 7 AEROSOL FORMATION PROCESSES IN FIXED-BED COMPARED TO BFB COMBUSTION SYSTEMS

Based on the results presented aerosol formation processes in waste wood fired fixed-bed and BFB combustion systems can be evaluated and compared.

### 7.1 Waste wood fired fixed-bed combustion system

In the fixed-bed combustion system the first step of aerosol formation results from the formation of ZnO particles. Zn is released under reducing conditions from the fuel bed to the gas phase. There it is oxidised and forms submicron particles by nucleation processes. This process takes place directly above the fuel bed. Pb is released under reducing conditions from the fuel bed to the gas phase, while under oxidising conditions PbO and PbCl<sub>2</sub> are formed [1]. As a next step the condensation of alkali metal sulphates takes place at temperatures around 1,000°C. During the further cooling of the flue gas in the radiative and the convective section, also alkali and heavy metal chlorides reach saturation and start to condense. Minor amounts of Ca which can be found in the particle size classes >0.5 µm are assumed to be results of defragmentation processes of Ca particles.

### 7.2 Waste wood fired BFB combustion system

Comparing the BFB system with the fixed-bed system, two main differences concerning aerosol formation obviously occur. Firstly, almost no Zn particles are found in the aerosols formed in the BFB system. This is a result of the lower temperatures in the fuel bed which lead to a significant decrease of the release of Zn to the gas phase. Furthermore, the Zn reacts with Si contained in the bed material and as a result Zn is embedded in the coarse fly ash fraction. Consequently, no ZnO nucleation can take place. The same effects are also valid for Pb resulting in low Pb-concentrations in the aerosols in the BFB boiler.

Secondly, only small amounts of S are found in the aerosol particles in the BFB system. Therefore, again the comparably low combustion temperatures but also the high amounts of entrained fly ash particles may be responsible. At temperatures below 800°C the reaction rate of SO<sub>2</sub> to SO<sub>3</sub> is limited and consequently, sulphation of alkali chlorides is hindered. Moreover, as the analyses have shown, most of the S reacts with Ca contained in the finer mode of the coarse fly ash particles.

Generally, the lower temperature levels in the BFB combustion plant compared to the fixed-bed system reduce the release of aerosol forming elements (e.g. K, Na and Zn) from the fuel bed to the gas phase subsequently less amounts of aerosols are formed.

Due to these reasons, aerosol formation in the BFB combustion plant is mainly dominated by nucleation and condensation of alkali metal chlorides.

### 7.3 Distribution of ash forming elements in the different ash fractions

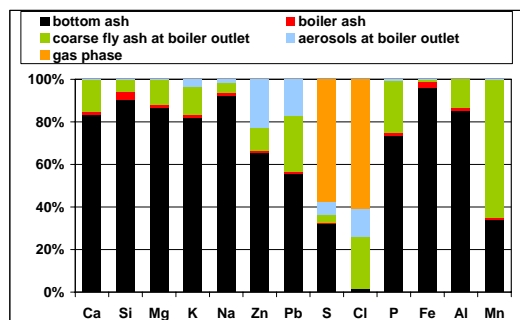
In order to confirm the aerosol formation mechanisms stated above, the distribution of certain ash forming elements between the different ash fractions and consequently the release of these elements to the aerosol fraction as well as the gas phase was evaluated (see Fig. 17 and Fig. 18).

In fixed-bed combustion systems non volatile elements (Ca, Si, Mg, Fe, Al, P, Mn) are mainly found in the bottom ash (about 90%), while minor parts of them

are found in the boiler ash (1 to 4%) respectively the coarse fly ash emissions (6 to 9%).

Semi-volatile elements such as K and Na are also mainly found in these ash fractions, however, a certain share of them contributes to aerosol formation (1 to 4%). This very low release is most likely due to the unusually high molar Si/K ratio of the waste wood used in the fixed-bed combustion system (about 10 times higher than for the waste wood fired in the BFB system) because Si embeds K due to silicate formation. For lower molar Si/K ratios in wood and waste wood fuels the K-release in fixed-bed systems is usually in the range of 20 - 35% [1]. In the actual case, about 20% of the easily volatile heavy metals Zn and Pb are transferred to the aerosol particle fraction.

While about 30% of the S is embedded in the bottom ash, 6% of S contribute to aerosol formation and about 55% are emitted as gaseous SO<sub>2</sub> emission. For Cl almost no embedding in the bottom ash occurs. About 35% are embedded in the coarse fly ashes and aerosols and about 65% leave the boiler as gaseous HCl emissions.



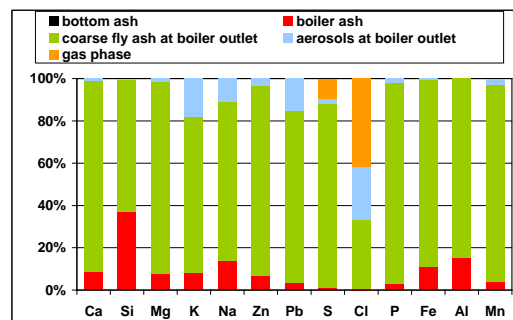
**Figure 17:** Distribution of elements among the ash fractions and the gas phase during the test runs at the fixed-bed combustion system

Explanations: gas phase at boiler outlet; data related to [wt%] of the total element output

Due to the fact that almost all ashes are entrained from the fuel bed with the flue gas in the BFB combustion plant, the non volatile elements Ca, Mg, Fe, Al, P and Mn are mainly found in the coarse fly ash emissions (85 to 94%). Simply Si differs from this behaviour as 37% of Si are found in the ash precipitated in the boiler due to the entrained bed material (quartz sand) from the furnace.

Again, a certain share (11 to 18%) of semi-volatile elements such as K and Na contributes to aerosol formation. In contrast with the fixed-bed combustion process, only 3% of Zn and 15% of Pb contribute to aerosol formation, while the major share (82 to 90%) of these elements is embedded in the coarse fly ashes.

S shows a totally different distribution compared to the fixed-bed system. Almost 87% of the S is embedded in the coarse fly ashes while only 3% contribute to aerosol formation and 9% to gaseous emissions. This is assumed to be, as already mentioned, an effect of the low furnace temperatures (decreased sulphation of chlorides) and the higher concentrations of relatively fine Ca-containing fly ash particles. Due to the reduced sulphation of chlorides, also the gaseous HCl-emissions are lower for the BFB system while a higher share of the Cl (25%) is bound in the aerosol fraction than in the fixed-bed system.



**Figure 18:** Distribution of elements among the ash fractions and the gas phase during the test runs at the BFB combustion system

Explanations: gas phase at boiler outlet; data related to [wt%] of the total element output

## 8 SUMMARY AND CONCLUSIONS

In order to study aerosol formation, test runs at a fixed-bed and a BFB waste wood combustion plant have been performed. Thereby, a high-temperature low-pressure impactor, which can be applied at temperatures up to 1,100°C, has been used as one important basis for these investigations. The concentrations, chemical compositions and particle size distributions of aerosols were investigated by taking particle samples from the flue gas in the radiative boiler section, the convective boiler section and downstream the economiser. Additionally, fuel and ash (bottom ash, boiler ash, coarse fly ash) sampling with subsequent analyses was performed.

The measurement results showed, as expected, an increase of the aerosol concentrations with decreasing temperatures along the flue gas pathway through the combustion plants. However, the mass of particles formed during BFB combustion was significantly smaller than the one formed during fixed-bed combustion. This effect may mainly be due to the high amount of coarse fly ashes and bed material particles in the flue gas of the BFB combustion system, which provide additional surfaces for the condensation of ash forming vapours. Moreover, the aerosol forming elements Zn and Pb react with Si-containing particles. Both effects reduce aerosol formation. Furthermore, the lower temperature levels in the BFB combustion compared to the fixed-bed combustion lead to a reduced release of aerosol forming elements (e.g. K, Na and Zn) from the fuel bed to the gas phase resulting in a lower aerosol formation.

Also concerning the chemical compositions of the aerosols sampled as well as their formation pathways significant differences became obvious. The main differences between a fixed-bed and a BFB combustion system are the lower temperature levels in the BFB boiler as well as the higher concentrations of coarse fly ash particles and entrained bed material particles. Aerosol formation processes are strongly influenced by these parameters.

Firstly, the lower temperature levels in the BFB system limit the sulphation of already formed KCl. Consequently, the concentration of S in the aerosols is low.

Secondly, the lower temperature level in the BFB

boiler reduces the release of Zn from the fuel to the gas phase and thereby the formation of ZnO aerosols.

Moreover, the higher concentrations of coarse fly ash particles also lead to increased reactions of aerosol forming elements, especially of S with coarse Ca-containing particles and Zn and Pb with Si contained in the bed material. Thus, S and Zn are stronger embedded in the coarse fly ash and consequently have only a minor reduced impact on aerosol formation.

Due to these different formation pathways, the aerosols at the BFB combustion plants are dominated by alkali metal chlorides, which may increase the risk of corrosion on superheater tubes due to sulphation reactions of condensed KCl layers with the bypassing SO<sub>x</sub> in the flue gas. Moreover, KCl shows in comparison to K<sub>2</sub>SO<sub>4</sub> a considerably lower melting point (640°C instead of 1,070°C) which could enhance the formation of sticky deposit layers. Those issues should be investigated in more detail as they are of great relevance regarding the appropriate choice of the steam parameters as well as the flue gas temperatures before the superheater inlet.

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