

## DISTRIBUTION OF SELECTED ELEMENTS DURING THE CO-COMBUSTION OF LIGNITE WITH WOOD AND WOOD WASTES

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### ABSTRACT

Combustion of lignite with limestone, co-combustion of lignite with limestone and wood, and combustion of wood were performed in a circulating fluidised bed in 7 different combustion regimes. The inorganic matter composition and properties of all input and output materials were characterized. For each combustion regime the material streams and the boiler outputs were calculated. The total inorganic mass and the mass of selected trace elements in fuels (Cl, Zn, As, Se, Hg, and Pb) were based on the output of a 1 GW circulating fluidised-bed boiler; additionally, the concentrations of volatile elements (As, Se, Hg) in fly ash (FA) were evaluated in relation to the mass of FA. Element (Cl, Zn, As, Se, Hg, and Pb) enrichment in FA compared with BA was related to the ratio R between the combusted mass of organic wood wastes and total combusted fuel. Additionally, the unburned carbon in bottom ash (BA) and fly ash (FA) was determined, and selected elements were studied in unburned materials separated from BA. The results show that combustion of wood and/or co-combustion of lignite with wood waste brings about significant environmental benefits.

**KEYWORDS:** lignite, wood wastes, ash, co-combustion, trace elements distributions

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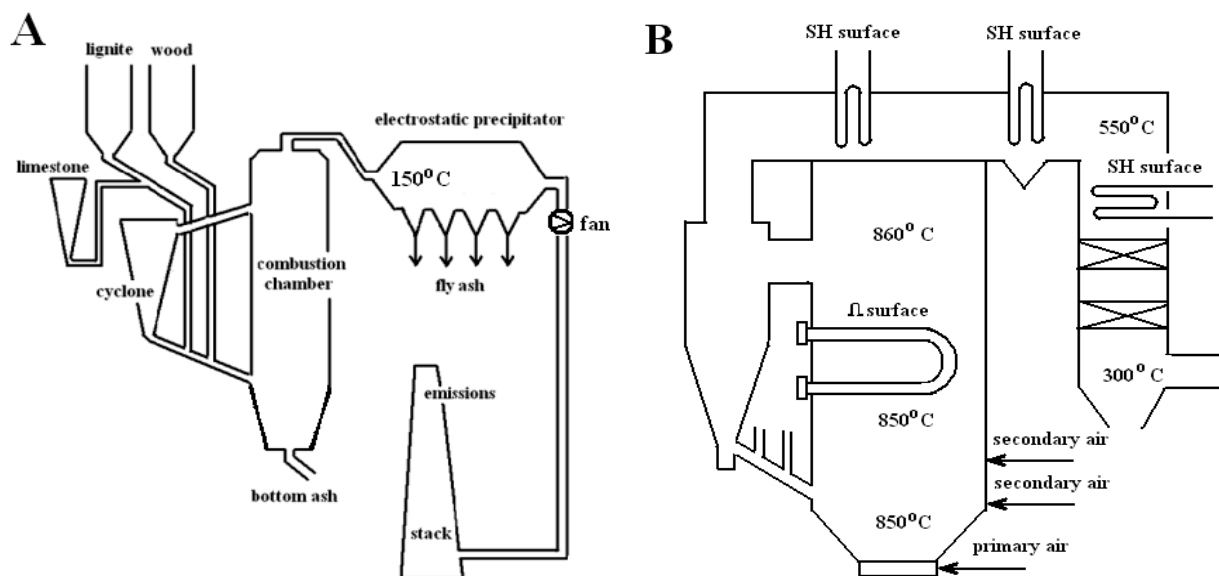
### 1. INTRODUCTION

Worldwide, there are many reasons in favour of the utilization of biofuels for energy purposes. Above all, this material brings significant environmental benefits (Kajikawa et al., 2008; Haykiri-Acma and Yaman, 2008; Van Loo and Kopperjan, 2008; Ogaji and Probert, 2009) and a reduction of dependency on imported oil. Biofuels are typically low in sulphur and ash content, and therefore their use brings about reductions in acid rain, CO<sub>2</sub> as a greenhouse gas, and hazardous elements that can enter the environment as a volatile species or can be dissolved from solid products of lignite combustion. Moreover, biomass is a renewable fuel, available for heat and power production in relatively substantial amounts (Escobar et al., 2009; Yilgin and Pehlivan, 2009; Petterson et al., 2009).

In general, there are two approaches when using waste biofuels for energy production: a) combustion in current power stations (originally designed for lignite combustion), or b) the use of new combustion facilities specifically designed for biofuels.

At present there is a strong tendency to prefer the first approach due to cost reasons. However, the different behaviour of waste fuel in the combustion chamber is connected with several unfavourable effects, such as fouling, slagging or corrosion. The predisposition of waste fuel to fouling or slagging is caused mainly by the composition of its ash, i.e. by the content of alkali metals – Ca, P, Cl, Si, Al, etc.

The compositions of different waste fuels vary greatly, and most biofuels are strongly prone to create fireside deposits during combustion. This is the reason why co-combustion of waste biofuels with lignite is usually preferred in order to diminish the unfavourable effects of simple biofuel combustion (Arvelakis and Frandsen, 2010). It was found that blending waste and fossil fuels resulted in changes of fuel characteristics that are consequently reflected in the different behaviour of these fuels in the combustion chamber. The blending of waste and fossil fuels leads to different volatilization of toxic pollutants during co-combustion and their different redistribution between bottom ash, fly ash and emissions (e.g. Díaz-Somoano et al., 2007; Steenari and Lindquist, 1999). This is why the composition of combustion ashes originating in coal combustion differs depending on whether or not waste materials were added. Of course, there are considerable differences in composition even among different coal ashes, as is presented e.g. by Asokan et al. (2005). The concentration range of As in Indian coal combustion ashes is 5–68 ppm; for Pb it is 10–144 ppm; in the case of Se, Cu and B their content reaches 1–10 ppm, 39–1000 ppm and 100–1000 ppm respectively. The content of Pb, Se, As, Cu, and Hg in coal combustion ashes collected at two Czech power stations (Klika et al., 2001; Bartoňová et al., 2007) was: Pb 17–223 ppm, Se 0.65–16.8 ppm, As 9.4–45.2 ppm, Cu 90.9 – 675 ppm, and Hg 0.004–



**Fig. 1** Diagram of the combustion facility.

A – Simplified diagram of the CFB, B – detail of the combustion chamber.

1.75 ppm. More information on coal combustion ashes, including their composition, can also be found in some other studies (e.g. Galbreath et al., 2000; Ratafia-Brown, 1994; Meij, 1995; Hower et al., 1996; Fulekar et al., 1983).

The comparison of elemental content in lignite ash and wood ash (in ppm) was reported e.g. by Skodras et al. (2002), who found the biggest differences in element content (in ppm) between coal and wood ashes for As (coal ash 13, wood ash 0.42), Cr (coal ash 29, wood ash 0.6), Ni (coal ash 20.4, wood ash 0.88), Pb (coal ash 3.62, wood ash 0.48) and Co (coal ash 5.2, wood ash 0.18). Significant variability in the composition of coal ash, coal/wood ash and wood ash was also found e.g. by Klika et al. (2010). In contrast to Skodras et al. (2002), the content of Cl, As, Pb, Zn, and Se in these ashes falls within a larger interval: Cl (303-836 ppm), As (140-438 ppm), Pb (41-65 ppm), Zn (25-268 ppm), and Se (< 1.3-12.5 ppm) but the quantity of ash from the combustion of coal/wood and wood is much less.

Many studies have focused on evaluating the content of Hg and other toxic elements in emissions from the combustion of lignite with different biofuels. Some of these studies are based on the evaluation of selected element mass flows (Åmand and Leckner, 2004; Klika et al., 2010; Elled et al., 2007); however, direct measurement of elemental content in emissions has been studied only sporadically (e.g. Skodras et al., 2002).

This contribution studies the mass flows of elements (Cl, Zn, As, Se, Hg and Pb) during the combustion of lignite, lignite with wood waste, and/or wood waste itself in a circulating fluidised-bed boiler (CFB). The aim of the study is to show the differences

in mass flows of selected elements related to the unit of CFB output for regimes with different ratios between lignite and wood wastes.

## 2. EXPERIMENT

At a power station situated at the Mondí Packaging paper mill in Štětí near Mělník (Czech Republic), lignite combustion and co-combustion of lignite/wastes were performed in a circulating fluidised-bed boiler (K11) at about 850-860 °C. Fluidisation air is brought into the furnace by a burner nozzle positioned at the bottom of the fire grate, while secondary air is introduced into the furnace from the side wall at different heights. This enables gradual combustion of fuel without the formation of a large quantity of redundant NO<sub>x</sub>. Flue gases go from the combustion chamber through a cyclone in which the coarse fractions of ash are separated and removed as bottom ash. Finer ash fractions are separated in an electrostatic precipitator. A diagram of the combustion facility is given in Figure 1.

In the everyday combustion regime, lignite is combusted with wood wastes from the production of cellulose in a circulating fluidised-bed boiler (K11) in the weight ratio 10:1. This paper describes 7 combustion regimes (I – VII) in which lignite is combusted and/or co-combusted with wood wastes from cellulose production in a wide variety of lignite/biofuel weight ratios. In the referential regimes I and IV, the lignite was combusted only with limestone; in regimes II, V, VI, and VII lignite was combusted with wood wastes; and in regime III only wood wastes (wood, sawdust and wood chips) were combusted.

**Table 1** Mass flows of lignite, limestone and biofuels ( $m_i$ ) for combustion regimes I -VII.

Fuel	$m_i$ (kg.h <sup>-1</sup> )						
	I	II	III	IV	V	VI	VII
Lignite (C)	25920	11840	-	29980	34960	26750	28550
Limestone (L)	2630	970	-	3490	4320	3240	2630
Sawdust (S)	-	5220	3114	-	-	-	-
Tree-bark (B)	-	5620	-	-	-	-	-
Wood (W)	-	-	14905	-	19728	15160	24260
Wood chips (WCh)	-	-	14870	-	-	-	-
Sewage sludge (SS)	-	-	-	-	-	15160	-
Alternative solid fuel (ASF)	-	-	-	-	-	940	-
Soap (So)	-	-	-	-	-	-	200

**Table 2** Moisture ( $W_i$ ) of lignite, limestone and other materials used for the combustion regimes I -VII.

Fuel	$W_i$ (%)						
	I	II	III	IV	V	VI	VII
Lignite (C)	14.7	16.4	-	19.7	25.6	25.6	20.8
Limestone (L)	0.45	0.45	-	0.79	0.91	0.63	0.79
Sawdust (S)	-	28.1	29.7	-	-	-	-
Tree-bark (B)	-	26.7	-	-	-	-	-
Wood (W)	-	-	12.8	-	58.0	58.0	29.9

Note: Moisture ( $W_i$ ) relates to the original moist basis; moistures of other fuels are: WCh (26.8 %), SS (67.0 %), ASF (4.5 %) and So (28.5 %).

Each combustion regime reached a steady state after 8-10 h. The samples of lignite, limestone, biofuels and ashes were collected at 2-hour intervals in quantities of approx. 2 kg. An average sample for each material was then prepared and used for analysis. The total sampling period was 12 hours.

Moisture ( $W_i$ ) of samples was determined gravimetrically by drying at 105-110 °C. The ash content ( $A_i^d$ ) of dried lignite and limestone was determined at 900 °C and the ash content of dried biofuels  $A_i^d$  (sawdust, tree-bark, wood, wood chips, sewage sludge, alternative solid fuel (ASF) and/or soap) at 450 °C. Recalculations of the ash content  $A_i^d$  (db, dry basis) on  $A_i$  (original moist basis) were performed using the formula  $A_i = 10^{-2} A_i^d \cdot (100 - W_i)$ ; where  $A_i$ ,  $A_i^d$  and  $W_i$  are given in wt. % and index  $i$  relates to the  $i$ -th input material (see Table 1). Chemical analyses of Pb, Cl, Zn, As, Se and Hg were performed from dried samples of lignite and limestone (105-110 °C) and from biofuel ashes prepared at 450 °C. Concentrations of the  $j$ -th element determined in dried lignite and limestone  $c_{i,j}^d$  (db) were recalculated on  $c_{i,j}$  (original moist basis) using the

formula  $c_{i,j} = 10^{-2} c_{i,j}^d \cdot (100 - W_i)$ , and concentrations determined from biofuel ashes  $c_{i,j}^A$  were recalculated on  $c_{i,j}$  (original moist basis) using the formula  $c_{i,j} = 10^{-2} c_{i,j}^A \cdot A_i$ , where  $c_{i,j}^A$  is the concentration determined in the ash (450 °C). The concentrations in BA ( $c_{B,A,j}$ ) and FA ( $c_{F,A,j}$ ) were determined from original samples of ashes. Elements Pb, Cl, Zn, As, and Se were determined by X-ray fluorescence spectrometry (SPECTRO XEPOS) and mercury content was determined using an AMA-254 spectrometer.

Unburned carbon (UC) from coal present in bottom ash (BA) and fly ash (FA) was determined by a method devised at our laboratory. This method is based on the removal of the carbonates by leaching with diluted HCl (1:4) at 90 °C. These samples are washed out with distilled water, dried at 105 °C, and the carbon content (unburned carbon) is determined using a CS-2000 analyzer (ELTRA).

### 3. RESULTS AND DISCUSSION

#### 3.1. MASS BALANCE OF INORGANIC MATTER

Chemical analyses of selected elements (Cl, Zn, As, Se, Hg, and Pb) were performed for lignite and

**Table 3** Ash content ( $A_i$ ) of lignite, limestone and other materials used in the combustion regimes I -VII.

Fuel	$A_i$ (%)						
	I	II	III	IV	V	VI	VII
Lignite (C)	18.3	16.8		22.9	24.3	24.3	22.9
Limestone (L) <sup>a)</sup>	65.9	65.9		66.3	66.7	66.5	66.3
Sawdust (S)		0.64	0.47				
Tree-bark (B)		4.8					
Wood (W)			0.25		2.7	2.7	6.8

Note: Ash content ( $A_i$ ) relates to the original moist basis; ash content of the other biofuels relates to the original moist basis: WCh (1.04 %), SS (0.9 %), ASF (8.1 %) and So (7.6 %).

<sup>a)</sup> Ignited limestone at 850 °C

**Table 4** Mass of inorganic matter ( $m_{IN,i}$ ) present in lignite, limestone and other materials used in the combustion regimes.

Combustion regime	Input streams $m_{IN,i}$ (kg/h)										Output streams $m_{IN,i}$ (kg/h)		
	C	L	S	B	W	WCh	SS	ASF	So	$m_{IN}$	BA	FA	
I	4743	1733	-	-	-	-				6476	3210	3266	
II	1989	640	33	750						3412	2020	1392	
III	-	-	14	-	37	155				206	5	203	
IV	6865	2314								9179	3670	5510	
V	8495	2881	-	-	532					11909	4770	7140	
VI	6500	2155			409		136	76		9277	3710	5570	
VII	6538	1743			1649				15	9946	3720	6226	

Note: Inorganic matter ( $m_{IN,i}$ ) relates to the original moist basis

limestone from dried samples (110 °C) and chemical analyses of all biofuels from ash prepared at 450 °C. Using the data of moisture and ash content (Tables 2 and 3) these analytical data have been recalculated on original moist samples basis (Table 6) necessary for mass balances. Analyses BA and FA are given in Table 7A and Table 7B, respectively. The mass flows of non-dried lignite, wood wastes and other alternative fuels in combustion regimes I –VII ( $m_i$ ) are given in Table 1. The data relate to as-received non-dried fuels. Lignite with limestone was combusted in regimes I and IV, wood wastes in regime IV, and co-combustion of lignite with wood wastes and alternative fuels took place in regimes II, V, VI, and VII. The moisture and ash content of fuels are shown in Tables 2 and 3 respectively.

The inorganic mass ( $m_{IN,i}$ ) present in lignite, limestone and other materials for various combustion regimes was calculated from Eq. (1); the results are given in Table 4. The mass flows of bottom ash (BA) and fly ash (FA) are also given in the same table.

$$m_{IN} = \sum_i m_{IN,i} = \sum_i m_i \cdot A_i \quad (1)$$

where: index  $i$  relates to lignite (C), limestone (L), sawdust (S), tree-bark (B), wood (W), wood chips (WCh), sewage sludge (SS), alternative solid fuel (ASF) and/or soap (So) in the input streams.

The mass of ash present in flue gas is negligible and therefore it is not included in the calculation. For example, the very fine solid particles determined in emissions reach about 0.42, 0.57 and 0.16 kg/h in combustion regimes I, II, and III, respectively.

### 3.2. BOILER OUTPUT

The relation between the boiler output and other parameters is given by Eq. 2:

$$Q_{out} = m_{CM} \cdot Q_{cal} \cdot \eta \quad (2)$$

where  $Q_{out}$  (MW) is boiler output,  $Q_{cal}$  (MJ.kg<sup>-1</sup>) is calorific value based on dry and ash-free fuel,  $m_{CM}$  is combustible mass of fuels (kg.h<sup>-1</sup>) for the combustion regimes I – VII, and  $\eta$  is boiler efficiency.

The combustible mass of lignite and other biofuels ( $m_{CM}$ ) was calculated for each of the combustion regimes I – VII from Eq. 3.

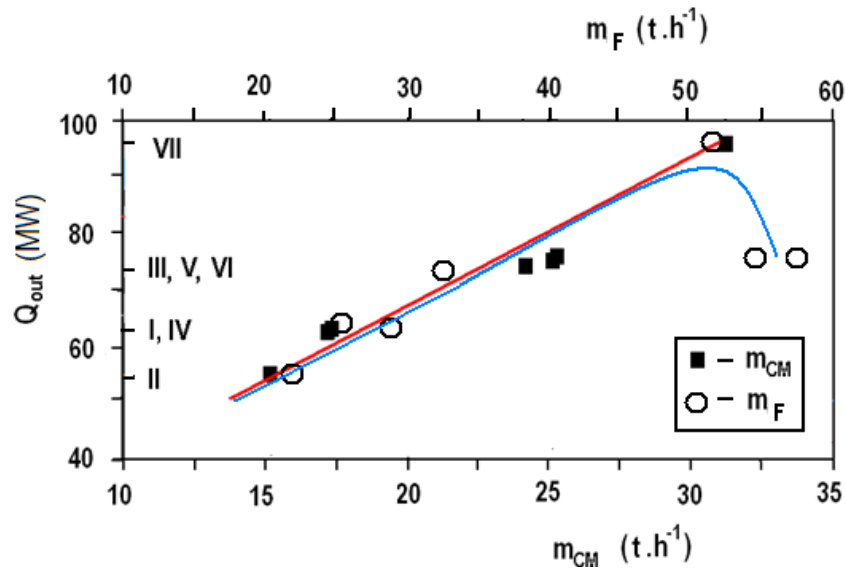
$$m_{CM} = \sum_i m_i \cdot [1 - 10^{-2} \cdot (W_i + A_i)] \quad (3)$$

where  $m_i$  is mass of the  $i$ -th fuel and/or biofuel (original moist basis) in a given regime (see Table 1).

The calculated boiler output  $Q_{out}$  and other parameters are given in Table 5 for each of the 7 combustion regimes. The parameter (R) is defined as the mass ratio between the combusted mass of organic

**Table 5** Parameters related to boiler output  $Q_{out}$ .

Combustion regime	$m_{CM}$ (kg/h)	$Q_{cal}$ (MJ.kg <sup>-1</sup> )	$\eta$	$Q_{out}$ (MW)	$m_F$ (kg.h <sup>-1</sup> )	$m_C$ (kg.h <sup>-1</sup> )	$R$ (%)	$m_{IN}/Q_{out}$ (kg.h <sup>-1</sup> .MW <sup>-1</sup> )
I	17366	15	0.89	64	25920	25920	0	101
II	15479	14	0.90	54	22680	11840	49	63
III	24410	12	0.90	73	32889	0	100	2.8
IV	17208	15	0.89	64	29980	29980	0	143
V	25268	12	0.90	76	54688	34960	36	157
VI	25047	12	0.90	75	58010	26750	54	123
VII	31558	12	0.90	95	53010	28550	46	105

**Fig. 2** Plot of boiler output and mass of fuel.  
 $m_F$  – total mass of fuels;  $m_{CM}$  – total combustible mass of fuels.

wood wastes and total mass of combusted fuel (Eq. 4).

$$R = 100 \cdot \frac{m_F - m_C}{m_F} \quad (4)$$

where  $m_F$  is the total mass of lignite (original moist basis) and biofuels and  $m_C$  is the mass of lignite (original moist basis) in a related combustion regime.

This ratio varies from 0 (for regimes I and IV) to 1 (for regime III). The other parameters related to boiler output are also given in Table 5. The ratio between the mass of inorganic matter ( $m_{IN,i}$ ) present in lignite/limestone and boiler output ( $Q_{out}$ ) was calculated from data given in Tables 4 and 5, respectively.

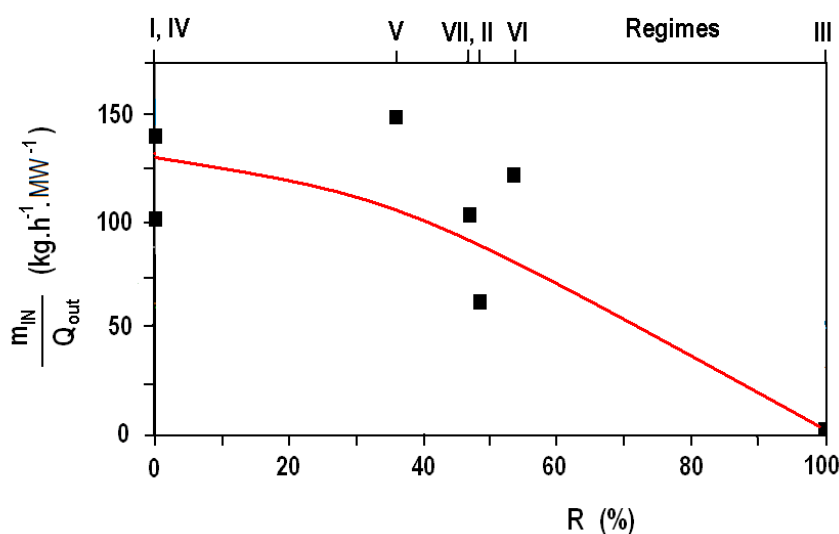
The boiler output ( $Q_{out}$ ) and the combustible mass of fuel are plotted in Figure 2. On the left side of the diagram the combustion regimes I – VII are denoted. The plot between  $Q_{out}$  and  $m_{CM}$  is practically linear with almost no dependence on the type of combustion regime. In contrast, the plot between boiler output  $Q_{out}$  and mass of fuel  $m_F$  shows two outsiders for regimes V and VI. The much lower boiler output  $Q_{out}$  for both regimes can be explained

by the combustion of a large amount of wood (regime V and VI) and sewage sludge (regime VI) containing very high moisture (Tables 1 and 2).

The higher moisture content in fuels of regimes V and VI is also reflected in Figure 3, which plots the ratio of total inorganic matter to boiler output ( $m_{IN}/Q_{out}$ ) and the ratio between combusted mass of organic wood wastes and total mass of combusted fuels ( $R$ ). The decrease of  $m_{IN}/Q_{out}$  with increasing ratio  $R$ , and extremely low  $m_{IN}/Q_{out}$  for combustion of wood with wood wastes ( $R = 100\%$ ), are observed.

### 3.3. SELECTED TRACE ELEMENTS

Chemical analyses of selected elements (Cl, Zn, As, Se, Hg, and Pb) were performed for all fuels (Table 6), for BA (Table 7A), and for FA (Table 7B). Samples of fuel, BA and/or FA were prepared as mean samples from approx. 7 sample portions collected during the measurement in each of the regimes I – VII. For regimes I – VII mean values and estimated standard deviations of element concentrations ( $c_{i,j} \pm 2s$ ) were calculated for lignite, limestone and wood (Table 6), while for S, B, WCh,



**Fig. 3** Plot between ratio of total inorganic matter to boiler output and ratio R between combusted mass of organic wood wastes and total combusted fuel.

**Table 6** Concentrations and estimated standard deviations ( $c_{i,j} \pm 2s$ ) of selected trace elements in lignite, limestone and other biofuels in regimes I - VII.

Fuel	$c_{i,j} \pm 2s$ (ppm)					
	Cl	Zn	As	Se	Hg	Pb
Lignite	407 ( $\pm 150$ )	26 ( $\pm 7$ )	87 ( $\pm 40$ )	1 ( $\pm 0.5$ )	0.16 ( $\pm 0.04$ )	11 ( $\pm 0.5$ )
Limestone	733 ( $\pm 300$ )	34 ( $\pm 3$ )	1.9 ( $\pm 1$ )	0.6 ( $\pm 0.25$ )	0.01 ( $\pm 0.001$ )	8 ( $\pm 4$ )
Sawdust	4	5.6	0.24	0.013	0.05	0.19
Tree-bark	16	41	0.18	0.038	0.06	1.7
Wood	258 ( $\pm 37$ )	59 ( $\pm 8$ )	0.32 ( $\pm 0.3$ )	0.05 ( $\pm 0.01$ )	0.05 ( $\pm 0.05$ )	4 ( $\pm 1$ )
Wood chips	11	3	1.2	0.05	0.05	0.43
Sewage sludge	22	3.4	0.08	0.02	0.003	0.6
Alternative solid fuel	128	208	0.48	0.2	0.7	37
Soap	364	49	0.18	0.11	0.001	0.8

SS, ASF, and So (for abbreviations see note to Table 1) mean concentrations were not calculated, because these fuels were used only for one or two regimes.

The concentrations of elements in BA and FA differ more than those of fuels, and therefore they are presented for each regime (I – VII) separately. They are given for BA ( $c_{BA,j}$ ) in Table 7A and for FA ( $c_{FA,j}$ ) in Table 7B.

The ratio of element concentrations in FA/BA against the ratio R is plotted in Figure 4.

In FA elements such as Cl, Pb and Zn are hardly enriched at all in contrast to Se, As and Hg. These results are in agreement with the conclusions of Elled et al. (2007), who studied the distribution of As, Cd, Hg, Pb, Se, Sb, and Hg during the combustion of sewage sludge and wood. They explain the higher ratio  $c_{FA,j}/c_{BA,j}$  of elements as a result of the higher specific surface area of fine-grained fly ash.

Higher enrichment of FA with volatile Se, As, and Hg is observed for the combustion of lignite

( $R = 0\%$ ), while for the co-combustion of lignite with wood wastes, and particularly for wood wastes only ( $R=100\%$ ), the enrichment is significantly decreased. This element diversity is also dependent on the mass of FA ( $m_{FA}$ ) in which these volatile elements (Hg, Se, As) can be captured (Fig. 5). It is particularly visible for the most volatile Hg, which does not condense and remains in flue gas if the mass of FA (about  $400 \text{ kg.h}^{-1}$  in regime III) is very low. In contrast, the mass of fly ashes, as well as their surface area, is much higher, enabling highly efficient capture of volatile elements at approximately similar volumes of flue gas in all combustion regimes. No data on the plot  $c_{FA,j}/c_{BA,j}$  in relation to R ratio or mass of FA have been reported up to now. Pedersen et al. (2010) studied the release of trace elements from waste materials when combusted. The study found that Pb, Zn, Cl, S, Na, K, and As were released to a significant extent and that this release was fuel specific. Lind et al. (2007) studied enrichment / depletion of trace elements in

**Table 7A** Concentrations of selected trace elements in BA for the combustion regimes I – VII.

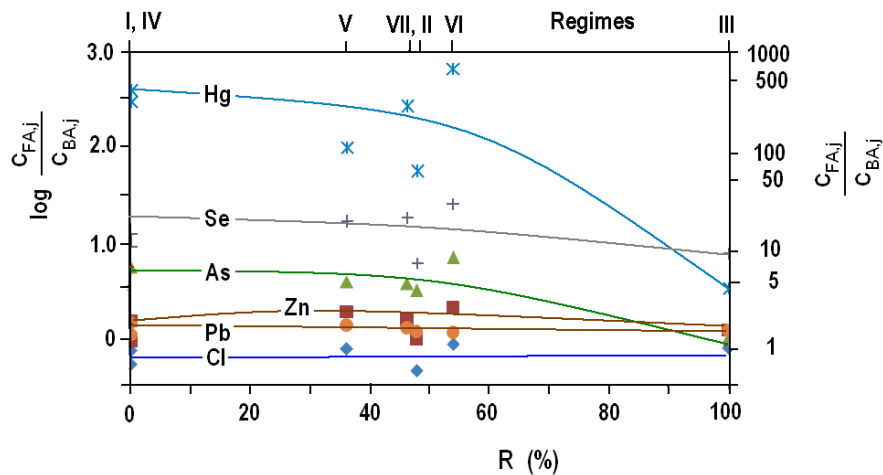
Combustion regime	$c_{BA,j}$ (ppm)					
	Cl	Zn	As	Se	Hg	Pb
I	569	188	248	1.4	0.002	41.2
II	836	251	140	1.3	0.005	56.0
III	566	223	298	1.0	0.003	48.5
IV	1568	151	97	0.6	0.002	33.4
V	1315	139	97	0.3	0.001	33.3
VI	1141	94	39	0.2	0.001	41.1
VII	490	170	158	0.4	0.002	32.9

Note: Concentrations  $c_{BA,j}$  of the j-th element present in BA

**Table 7B** Concentrations of selected trace elements in FA for the combustion regimes I – VII.

Combustion regime	$c_{FA,j}$ (ppm)					
	Cl	Zn	As	Se	Hg	Pb
I	303	172	375	12.5	0.605	58.9
II	375	243	438	7.9	0.280	65.0
III	440	268	291	7.8	0.010	57.4
IV	1163	225	535	7.4	0.779	36.1
V	1003	261	375	5.0	0.282	45.0
VI	975	196	268	5.1	0.672	46.6
VII	650	264	586	7.3	0.537	41.8

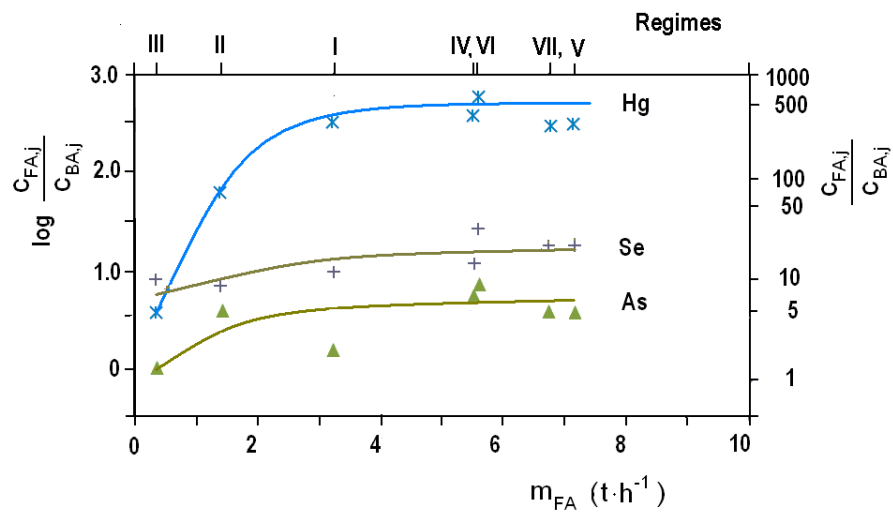
Note: Concentrations  $c_{FA,j}$  of the j-th element present in FA.



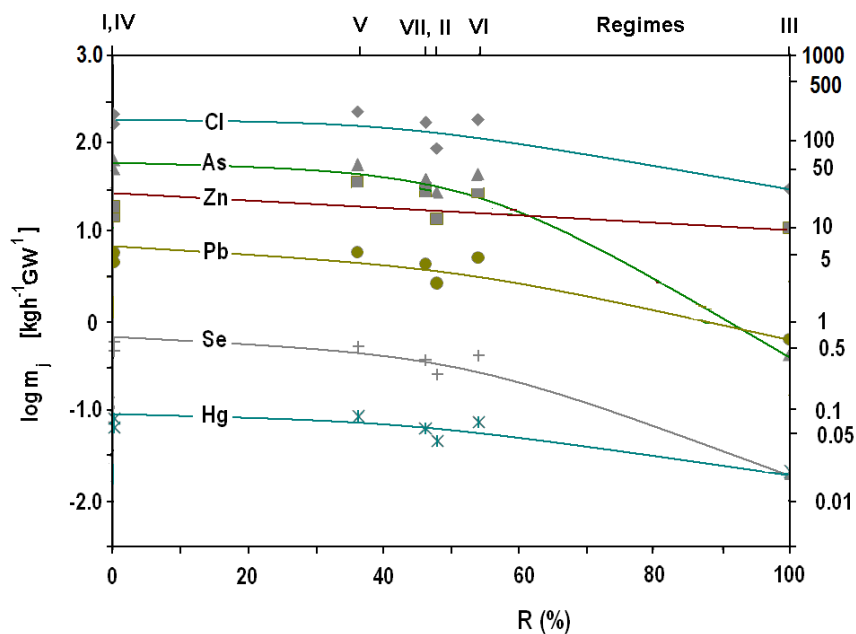
**Fig. 4** Plot of FA/BA ratio of element concentrations and ratio R between the combusted mass of organic wood wastes and total combusted fuel.

PM1.0 particles during waste combustion in grate firing and in fluidised bed combustion. It was found that the behaviour of As and Sb differed for these two combustion units. The above data shows that FA ashes are usually enriched with volatile elements, but the ratio  $c_{FA,j}/c_{BA,j}$  is very individual and depends on many parameters of fuel combustion (e.g. fuel rank, fuel composition and affinity of trace elements; combustion unit and condition of fuel combustion, temperature of combustion and FA separation, mass of FA, etc.).

Calculations of the mass of elements volatilized into flue gas from the mass balance are usually burdened by relatively high errors. These errors are brought about above all by the imprecise determination of lignite, limestone and other materials used for combustion and also by the imprecise determination of the mass of bottom ash and fly ash. The mass of fuel is usually determined in relation to the vapour output of the boiler, and/or determined with a certain imprecision from the volume of combusted fuels. The mass of fly and bottom ash is



**Fig. 5** Plot of FA/BA concentration ratio of Hg, Se and As concentrations versus mass flow of FA.



**Fig. 6** The plot between total input mass flows of elements (Cl, As, Zn, Pb, Se, Hg) and ratio R between the combusted mass of organic wood wastes and total combusted fuel.

usually calculated from the mass and ash content of the combusted fuel and from measured data related to BA and/or FA. Errors also arise from sampling and analyses of lignite, limestone and other biofuels used for combustion and also analyses of BA and FA. Because the calculation of the elements in flue gas based on the difference between input and output mass streams is burdened by high errors, only the comparison of mass flows of selected elements is

performed here, for various combustion regimes I – VII. Input mass streams were calculated (Eq. 5) for selected elements (Cl, As, Zn, Pb, Se, and Hg) using the data in Tables 1 and 6.

$$m_j = \sum_i m_i \cdot c_{i,j} \quad (5)$$

where:  $m_j$  is the total mass flow of the  $j$ -th element in lignite, limestone and other biofuels;  $c_{i,j}$  is the



**Table 8A** Percentages of unburned carbon ( $c_{UC}$ ) in BA and fractions from BA for combustion regimes I - III.

sample	$c_{UC}$ (%)		
	I	II	III
BA	1.60	0.72	0.28
fraction > 2.0 mm	4.66	2.42	1.11
fraction 0.4-2.0 mm	0.27	0.32	0.09
fraction < 0.4 mm	0.11	0.10	0.07

**Table 8B** Percentages of unburned carbon ( $c_{UC}$ ) in FA and fractions from FA for combustion regimes I - III.

sample	$c_{UC}$ (%)		
	I	II	III
FA	0.32	0.53	0.27
fraction > 0.09 mm	0.08	4.66	0.05
fraction 0.04-0.09mm	0.21	0.27	0.14
fraction < 0.04 mm	0.48	0.11	0.42

**Table 9** Chemical analyses of elements in separated UM from BA and BA in combustion regimes I – III.

samples	$c_i$ (ppm)					
	Cl	Zn	As	Se	Hg	Pb
I-UM	638	53	79	0.4	0.03	30
<i>I-UM-rec</i>	1960	163	243	1.23	0.09	92
I-BA	569	188	248	1.4	0.002	41.2
II-UM	716	62	165	2.4	0.03	36
<i>II-UM-rec</i>	1566	136	361	5.25	0.06	79
II-BA	836	251	140	1.3	0.005	56.0
III-UM	738	70	98	1.8	0.03	46
<i>III-UM-rec</i>	1180	112	157	2.9	0.05	74
III-BA	566	223	298	1.0	0.003	48.5

concentration of the  $j$ -th element in the  $i$ -th input stream (lignite, limestone and other biofuels);  $m_i$  is mass in the  $i$ -th input fuel stream.

The calculated total mass flows  $m_j$  of the elements in various combustion regimes were based on boiler outputs  $Q_{out} = 1$  GW. For this, the real boiler outputs for the regimes I – VII given in Table 5 were used. The calculated mass flows  $m_j$  of elements (Cl, Zn, As, Se, Hg, and Pb) are plotted versus the ratio R for each combustion regime (Fig. 6).

The results show that the total input mass flows of all the studied elements ( $m_j$ ) decrease with an increase of R ranging from 0 to 100 % (Fig. 6). In a circulating fluidised-bed boiler with an estimated output of 1 GW, the following decrease of total input mass of the elements ( $m_j$ ) was observed in regimes combusting lignite (regimes I and IV; R = 0 %) and regimes combusting wood wastes (regime III; R = 100 %):

For Cl: from 219 to 36 kg/h

For As: from 40 to 0.3 kg/h

For Zn: from 13 to 11 kg/h

For Pb: from 5 to 0.8 kg/h

For Se: from 0.5 to 0.03 kg/h

For Hg: from 0.10 to 0.02 kg/h

It can be supposed that the mass of these elements present in flue gas will follow the quantity of volatile elements in input fuel, i.e. the quantity of

volatile elements will decrease with increasing ratio R. This assumption was recently proved (Klika et al., 2010) for sulphur, balanced for the regimes I (R = 0 %) and III (R = 100 %).

### 3.4. UNBURNED MATERIAL

Unburned material (UM) is the unburned part of coal present in BA and FA after the combustion of coal. The content of unburned material in BA and FA reflects the efficiency of coal combustion; the higher the quantity of unburned material, the lower the efficiency of the combustion. Unburned material was studied in BA and FA from regimes I – III. The samples of BA and FA were sieved, and from each ash 3 fractions were separated and unburned carbon (UC) determined. The percentages of UC for the symplex of BA and their 3 fractions are given in Table 8A, for FA and their 3 fractions in Table 8B.

There is a higher content of UC in BA compared with FA. However, both in BA and FA the percentages of UC are low, so the combustion is very effective for all three combustion regimes I – III. The UM was mechanically separated from BA, while from FA it was not possible to perform a separation, either mechanically or in heavy liquids. This is due to the very small FA grain sizes. Ash content in the mechanically separated unburned material of BA ( $A_{UC}$ ) is 32.5 %, 45.7 % and 62.5 % for regimes I, II and III respectively. Chemical analyses of Cl, Zn, As, Se Hg and Pb in separated UM samples from BA were

performed. The results are given in Table 9 for UM, UM-rec and BA for combustion regimes I, II and III. UM-rec data were recalculated from related data of UM and the ash content of the unburned material. For example, the analysis of Cl in sample I-UM-rec (regime I) was calculated using the formula

$$c_{UC-rec} = 10^2 \cdot \frac{c_{UC}}{A_{UC}}, \text{ i.e. } 10^2(638/32.5) = 1960 \text{ ppm.}$$

This concentration relates to chlorine based on ash. Comparison of element concentrations in UM-rec with concentrations of elements in BA in a particular combustion regime shows that values for UM-rec are mostly somewhat higher than those for BA (Table 9). Such enrichment is usually expected in UM (e.g. Bartoňová et al., 2008). Taking into account the low mass of UM in BA (Table 8A), it can be concluded that the mass of elements in UM can not considerably influence other mass streams, e.g. volatilized elements in flue gas. The values for the content of unburned carbon in FA is even lower (Table 8B), and therefore we also do not expect this value to exercise a major influence over the distribution of the studied elements.

#### 4. CONCLUSION

This study focused on the comparison of some hazardous element mass flows in a circulating fluidised-bed power station in Štětí during the combustion of lignite and wood waste materials. Seven combustion regimes with different ratios of wood waste to total fuel mass (lignite and wood wastes) were used. It was shown that under similar combustion conditions, the concentration ratio between FA and BA ( $c_{FA,j}/c_{BA,j}$ ) for volatile elements (e.g. Hg, Se and As) increases with increasing mass of FA, i.e. for combustion of fuel with a higher proportion of wood wastes the efficiency of capture of volatile elements in FA is lower than that for the typical combustion of lignite. Because the input mass of volatile elements for the combustion of fuel with a higher proportion of wood wastes is much lower, the total mass of volatile elements in flue gas will be expected to be lower than that found in the typical combustion of lignite. The total input mass flows of the elements (Cl, Zn, As, Se, Hg, and Pb) in all combustion regimes were related to the 1 GW output of the circulating fluidised-bed boiler. It was found that using a higher ratio ( $R$ ) of wood waste to total fuel (lignite with wood waste) brings about a decrease in the mass flow of the elements (Cl, Zn, As, Se, Hg, and Pb) in the process of co-combustion of lignite with wood wastes, and this is expected to result in a lower volatilized mass of these elements. The study of unburned carbon in BA and FA showed that only a small part of the total mass of the element is captured in this material, and therefore it does not strongly influence the distribution of the studied elements.

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