Acta Geodyn. Geomater.Vol.3, No.1 (141), 43-56, 2006

THE ELEMENTS DISTRIBUTION DURING THE CO - COMBUSTION OF COAL, WOOD, SLUDGE, PLASTICS AND SOAP

Martin STACH, Zdeněk KLIKA*, Martina NOVÁČKOVÁ and Václav ROUBÍČEK

[1] *Vysoká škola báňská – Technical University of Ostrava, Department of Chemistry,*
17. listopadu 15, 708 33 Ostrava-Poruba, Czech Republic
**Corresponding author's e-mail*: zdenek.klika@vsb.cz

(*Received* October 2005*, accepted* January 2006)

ABSTRACT

Combustion of coal with limestone (*a*) and co-combustion of coal with limestone with wood, sewage sludge, soap and PTP *(b)* were performed in CFB. Inorganic matter composition and properties of all input materials were characterized. For this, chemical and coal petrography analyses of solid samples as well as their leaching tests, unburned carbon, and other properties were determined. There are not striking differences in composition of bottom and fly ashes from combustion/co-combustion data. In fly ash samples higher concentrations of Hg (about 2 ppm), As (about 800 ppm) and chlorine (about 400 ppm) are present than they are in bottom ash (0.002 ppm Hg, 250 ppm As, and 220 ppm Cl). Also relating concentrations of above elements determined in emissions are very similar for combustion/co-combustion regimes (about 0.010 $mg.m^{-3}$ Hg, 0.027 $mg.m^{-3}$ As and 24 $mg.m^{-3}$ Cl). Content of unburned carbon in BA is below 2 wt.% and in FA below 0.6 wt.% in all combustion/co-combustion data. In FA samples the concentration of Hg, As, Se, etc. increases with increasing unburned carbon content, i.e. with decreasing grain size of FA. No significant differences in composition of emissions, bottom and fly ashes as well as in composition of water leachates were found from the combustion regimes I, II, III and IV.

KEYWORDS: co-combustion, lignite, wood, sludge, plastic, soap, elements distribution

1. INTRODUCTION

Fossil fuel combustion represents currently an important part of energy production in many countries. Due to the increasing energy consumption and decreasing fossil fuels reserves it is necessary in the future to take into account also alternative (secondary) fuels utilization. Of course, the problems related to the deposition of these materials in landfills are another good reason for the alternative fuel combustion because they contain much less percentage of ash.

The most promising alternative fuels there are native wood (wood chips, bark, and sawdust), biomass (agricultural wastes, straw, cereals, and grass), municipal solid waste (plastics, paper, and textiles) and sewage sludge. Native wood and wood waste are often preferred as a fuel for co-combustion due to their low ash content and large resources. Co-combustion of these material and lignite brings about the decrease of CO_2, NO_x and SO_2 emissions in dependence on mutual mass ratio of the fuels combusted and on the combustion temperature (Nussbaumer, 2003; Pederson et al, 1996; Gayan et al., 2004). Ashes originated from the wood combustion contain significantly higher amount of heavy metals (Cd, Co, Cr, Cu, Hg, Ni, Pb, Zn etc.) compared to the ashes originated from the straw and cereals combustion. This is brought about by longer growth period of wood, which enhances heavy metals accumulation, and by lower pH value of forest soils that increases the mobility of some heavy metals (Cd or Zn, e.g. Obernberger et al, 1997; Lind et al., 1999). On the other hand, straw and cereals contain higher amount of S, Cl and K, which are the elements playing an important role in corrosion processes.

Major combustible components of municipal solid waste (MSW) there are paper, plastics, and wet organic waste (wood, grass, food wastes, etc.). Heavy metals concentrations in MSW are relatively high in relation with biomass and lignite and are also rather variable for particular MSW fractions (Sørum et al., 2003; Kouvo and Backman, 2003). When MSW is co-combusted with lignite, emissions of N_2O and SO_2 are reduced, but the growth of CO can be observed owing to higher Cl content that decreases CO oxidation (Desroches-Ducarne et al., 1999). Municipal solid waste incineration has been identified as the most serious emission source of polychlorinated dibenzo–p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Among the possibilities how to minimize PCDD/PCDF emissions there is a utilization of S and Cl compounds as PCDD/PCDF-formation inhibitors (Zheng and Kozinski, 2003).

Sewage sludges contain often the significant concentrations of heavy metals (e.g. Cd, Cu, Hg, Pb, Sr, Zn etc.) in dependence on their original wastewater-cleaning technology used. Nevertheless, the retention of trace elements in ash after sewage sludge combustion is significantly higher that in case of other above-mentioned fuels (Lopes et al., 2003; Werther and Ogada, 1999).

Fundamental co-combustion idea is the utilization of existing units without further significant modifications. Thus, secondary-fuels combustion is convenient from either ecological or economical point of view. The major advantages are e.g. the reduction of dependence on fossil fuels import, utilization of local fuels, which decreases transportation and import costs, utilization of agricultural and forestry residues, industrial production and human activity wastes as well as the reduction of flue gas emissions compared to the coal combustion (Zheng and Kozinski, 2000; Spliethoff et al., 2000; and Steenari and Lindqvist, 1999). However, there are also some disadvantages of the co-combustion of secondary fuels and coal, such as high water content in alternative fuels, a seasonal variability in supply, high contents of some heavy metals as well as high content of Cl, alkali and alkaline earth metal, which can bring about some fouling and corrosion problems (Hansen et al., 1998; Hansen et al., 1999; Kaufmann et al., 2000).

In recent years the co-combustion of coal and secondary fuels is intensively studied above all in relation with the fate of heavy metals released during the combustion. Miller et al. (2002) paid attention to the emissions of heavy metals during the co-combustion of coal and biomass in fluidized bed and studied the trace elements in particular fuels that could be problematic during the combustion for their high concentrations, potential toxicity and volatility. They concluded that the most volatile heavy metals were (in case of majority of the co-combustion blends) Hg and Se followed by Cd, Pb, and As. On the other hand, the most significant retention of the elements in ash was obtained for Be, Co and Ni. Wang et al. (1999) studied NO_x, SO_2 and N_2O emissions released at the combustion and co-combustion of coal and biomass (wood chips and rice husk) in fluidized bed. They concluded that the addition of biomass during the coal combustion could reduce the NO_x emissions (about 8-11% when the ratios of coal to wood chip ranged between 20:1 and 10:1, and about 17-31% when the ratios ranged between 20:3 and 4:1). But with the increasing temperature the reduction effect somewhat decreased and at 920 °C there was no significant effect on the reduction of NO_x emissions. The co-combustion of coal and biomass led also to SO_2-emissions reduction by reason of both lower S and higher content of alkaline metals and/or metals of alkaline earths contained in biomass. The conclusion is in an agreement with the results of other researchers (e.g. Spliethoff and Hein, 1998; Pedersen et al., 1996).

In this paper the co-combustion of lignite with wastes is studied and compared with simple combustion of lignite. The combustion/co-combustion were performed in the fluidized-bed boiler situated in the paper-mill (Štětí, Czech Republic) where the sufficient amount of wood, paper and other waste materials are available.

2. EXPERIMENTAL

SAMPLES, METHODS AND MASS FLOWS

Four combustion tests were run in order to compare coal combustion results (regime I) with those of co-combustion of the same coal with various waste materials (regimes II, III and IV). During all the four combustion regimes the brown lignite from the North-West Bohemian Coal Basin was combusted together with limestone as a desulphurization additive. Regime I served as reference combustion test when only lignite and limestone were combusted. In the regime II also wood chips were added, while regime III was run for the evaluation of co-combustion of the same lignite and limestone together with wood, alternative solid fuel ASF (plastics, textile and paper wastes) and sewage sludge. In regime IV, lignite and wood bark were co-combusted with a little amount of soap.

All the tests were performed in a 175 MW circulating fluidized-bed boiler equipped with hot cyclones providing ash particles retention into the combustion chamber. As a particulate control device an electrostatic precipitator is utilized. The combustion temperature was about 870 °C. The composition of emissions (SO_2, NO_x, CO_2, and CO) was monitored using gas analysers (URAS 10E). The elements As, Se, Cd, Pb and Hg from flue gas (in regimes I, II and III) were adsorbed in two solutions with $H_2O_2 + HNO_3$ and K_2CrO_4 and HNO_3. They were analyzed by ICP-AES method on JOBIN YVON 24 except Hg, which was determined by AMA 254 equipment. Organic pollutants PCDD/F and PCB were determined using HRGC with MD detector and PAH using LC.

At regular time intervals the samples of all the solid input and output materials were collected in order to create representative average samples. After homogenization the quartering method was used for the laboratory solid samples preparation. Moreover, from bottom and fly samples the ash fractions were also prepared by sieve analysis (ANALYSETTE 3 SPARTAN). For separation of BA fractions the sieves 2.0 and 0.04 mm and for fly ash the sieves 0.09 and 0.04 mm were used. For all analyses samples were ground, milled and homogenized. The chemical composition of the solid samples was determined by X-ray fluorescence analysis (XEPOS, SPECTRO). From wood, PTP (plastics, textile and paper wastes), sewage sludge and soap the low temperature ashes were prepared (at 400 ^{o}C) and analyzed. The content of Hg was determined on AMA 254 spectrometer.

Moisture at 105 ^{o}C (W), ash content at 820 ^{o}C (A), loss of ignition at 1000 ^{o}C (L.O.I.), volatile matter (V), pH, elemental analyses were determined using standardized analytical methods.

The leaching behaviour of BA and FA was studied from the extract prepared from these materials

Table 1 Lignite, limestone and waste mass flows for regime I – IV

Type of regime	Input	Output
I	Lignite. 29980 kg.hr^{-1} (W = 19.7 wt.%, A = 22.9 wt.%) Limestone. 3490 kg.hr^{-1} (W = 0.79 wt.%, L.O.I. = 33.7 wt.%)	BA: 3670 kg.hr^{-1} FA: 5510 kg.hr^{-1} E_s : 2.53 kg.hr^{-1} E_g. 166570 Nm^3.hr^{-1}
II	Lignite. 34960 kg.hr^{-1} (W = 25.6 wt.%, A = 24.3 wt.%) Limestone. 4320 kg.hr^{-1} (W = 0.91 wt.%, L.O.I. = 33.3 wt.%) Wood. 19728 kg.hr^{-1} (W = 58.0 wt.%. A = 2.7 wt.%)	BA: 4770 kg.hr^{-1} FA: 7160 kg.hr^{-1} E_s : 2.48 kg.hr^{-1} E_g : 241880 Nm^3.hr^{-1}
III	Lignite. 26750 kg.hr^{-1} (W = 25.6 wt.%, A = 24.3 wt.%) Limestone. 3240 kg.hr^{-1} (W = 0.63 wt.%, L.O.I. = 33.5 wt.%) Wood. 15160 kg.hr^{-1} (W = 58.0 wt.%. A = 2.7 wt.%) Sewage sludge. 15160 kg.hr^{-1} (W = 67.0 wt.%. A = 0.9 wt.%) Alternative solid fuel. 940 kg.hr^{-1} (W = 4.5 wt.%. A = 8.1 wt.%)	BA: 3710 kg.hr^{-1} FA: 5560 kg.hr^{-1} E_s : 2.52 kg.hr^{-1} E_g : 246820 Nm^3.hr^{-1}
IV	Lignite. 28550 kg.hr^{-1} (W = 20.8 wt.%, A = 22.9 wt.%) Wood. 24260 kg.hr^{-1} (W = 29.9 wt.%, A = 6.84 wt.%) Soap. 200 kg.hr^{-1} (W = 28.5 wt.%, A = 7.61 wt.%) Limestone. 2630 kg.hr^{-1} (W = 0.79 wt.%, L.O.I. = 33.7 wt.%)	BA: 3720 kg.hr^{-1} FA: 6760 kg.hr^{-1} E_s : 1,93 kg.hr^{-1} E_g : 276300 Nm^3.hr^{-1}

Note: W – moisture, A – ash content, L.O.I. – loss of ignition
BA – bottom ash; FA – fly ash; E_s – solid emission; E_g – flue gas emission

using appointed procedure given by Regulation 383/2001 Col. Water extract of the material was prepared using the ratio of dried (105 °C) solid/deionised water S/L=1 : 10. For the dynamic leaching procedure the Heidolph - REAX 20 equipment was used. The suspension was placed into rotating tubs and the material was extracted at about 10 rpm for 24 hrs. The solid phase was then separated by a diaphragm filter with pore size of 0.45 μm and the extract after the stabilization with conc. HNO_3 (5 $cm^3.dm^{-3}$) was used for the chemical analysis. The concentration of As, Sb and Se was determined using AAS with flameless atomization, the concentration of Hg using AMA 254 equipment and the concentration of the other elements was performed using ICP-AES method.

In Table 1 the materials basic characteristics from combustion and/or co-combustion of lignite are specified for regimes I, II, III and IV as well as their mass flows of the input and output streams. While I regime I lignite is combusted, in regime II wood to lignite in mass ratio 0.57 : 1, in regime III wood : sewage sludge : alternative fuel : lignite in mass ratio 0.57 : 0.57 : 0.035 : 1 and in regime IV wood : soap : lignite in mass ratio 0.85 : 0.007 : 1 were co-combusted, respectively.

3. RESULTS AND DISCUSSION

The results of ultimate, proximate and lignite petrography analyses are given in Table 2. The data relates to the lignite combusted during the regime II. The lignite used for the combustion/co-combustion in regimes I, III and IV, respectively comes from the same coal mine and was, in fact, of the very similar quality.

Table 2 Ultimate, proximate and maceral analyses of lignite from regime II.

LIGNITE	Wt. %
Moisture (W)	25.6
Ash content (A)	24.3
Volatile matter (V)	34.8
C (wt. % db)	53.34
H (wt. % db)	4.57
N (wt. % db)	0.87
S_{total} (wt. % db)	1.23
O (wt. % db)	15.74
Huminite (v/v %)	90.4
Liptinite (v/v %)	5.1
Inertinite (v/v %)	4.4

Note: ***db*** – related to dry base

The chemical composition of lignite, limestone, waste materials, BA and FA is given for regime I in Table 3A, for regime II in Table 3B, for regime III in Table 3C and for regime IV in Table 3D. All the results are related to the samples dried at 105 °C.

The data given in Tables 3A-3D indicate that the composition of lignite, limestone, and wood) for the regimes I-IV is similar one another. The tests under the regime II and III, were performed during six-day period and those ones of regime I and IV during five-day period. The tests I and IV were measured out 1 month after the tests II and III. It is probably a reason while the composition of coal and limestone from regimes I and IV somewhat little differ from that one of regimes II and III.

Lignite is principal carrier of the most hazardous elements. Into combustion and/or co-combustion process limestone brings (except CaO and CO_2) essential amount of Sr, Zn, Cd and Cl, wood essential amount of Ca and Zn,ASF namely Zn (Ba and Pb) and soap mainly Cl, Cd and Zn. Sewage sludge does not contain any significantly increased concentrations of hazardous element.

Generally, ash content in lignite (A ~ 23%) is much higher than those in wood (A ~ 2.7%) and/or wood bark (A ~ 6.7%), which is the main reason why also lower content of major and trace elements in those materials was determined (compared to the lignite). The exceptions are the contents of CaO and Zn that are higher in wood. The content of Cl in wood is almost the same as it is lignite from the North-West Bohemia Coal Basin.

In regime III sewage sludge and ASF (composed of plastic, textile and paper) was co-combusted with lignite and wood chips. The ash contents of sewage sludge and ASF are 0.9% and 8.1%, respectively. In the first case the very low ash content and in the second one low ratio of ASF : lignite (0.035) are reason while higher content of some trace elements (e.g. Cu, Zn, Cd, Hg, Pb) in ASF did not essentially influence the composition of output BA and FA samples.

The soap was co-combusted along with lignite and wood bark in regime IV. The little mass of added soap as well as its low ash content (A = 7.61%) resulted only in negligible contribution of trace elements from this material into input stream.

Using the chemical analyses data (Tables 3A – 3D) and mass flows (Table 1), mass balances of selected elements were performed. For this purpose the following equations were used:

Inorganic mass balance:
Input stream:

$$C \cdot 10^{-2} A_C + L \cdot 10^{-2}(10^2 - L.O.I) + 10^{-2} \cdot \sum_i W_i \cdot A_i \quad (1)$$

Output stream:

$$BA + FA + E \quad (2)$$

Elemental balance:
Input stream:

$$C \cdot w_{C,j} + L \cdot w_{L,j} + \sum_i W_i \cdot w_{i,j} \quad (3)$$

Output stream:

$$BA \cdot w_{BA,j} + FA \cdot w_{FA,j} + V \cdot c_j \quad (4)$$

where: *C* – mass of coal,
L – mass of limestone,
W – mass of waste,
BA – mass of bottom - ash,
FA – mass of fly ash,
E – total mass of emission (gas + solid),
V – volume of flue - gas,
A – ash content,
L.O.I– loss of ignition,
w_j – weight fraction *j*-th element in - C, L, W, BA and FA,
c_j – concentration of the *j*-th element in flue gas

Indexes: *C* for coal, *L* for limestone, *BA* – bottom ash, *FA* – fly ash, *i*-th type of waste, *j*-th element.

Table 3A Chemical composition of input and output materials for regime I.

Oxide/elements		Lignite	Limestone	BA	FA
A	Wt. %	22.9	66.3	97.7	97.3
SiO_2		11.6	18.4	40.1	37.9
TiO_2		0.37	0.29	1.18	1.68
Al_2O_3		5.77	5.26	19.2	19.8
Fe_2O_3		0.81	1.68	4.37	7.28
MgO		0.07	0.37	0.36	0.96
CaO		0.47	41.3	20.1	16.4
K_2O		0.35	1.09	1.67	1.64
P_2O_5		0.04	0.11	0.17	0.52
SO_3		2.51	0.22	6.06	7.75
Cl	ppm	518	398	1568	1163
Cr		30.0	< 25.3	32.4	131
V		105	< 22.4	179	419
Ni		21.5	13.2	35.8	107
Cu		23.2	3.9	35.8	127
Zn		29.2	36.8	151	225
As		110	2.9	97.2	535
Se		0.9	0.8	0.6	7.4
Sr		87.1	738	515	669
Cd		0.5	0.2	0.8	2.3
Ba		120	125	311	643
Hg		0.172	0.011	0.002	0.779
Pb		10.1	5.9	33.4	36.1

The percentages of the oxides and/or element mass in input materials are plotted in Figs. 1A, 1B, 1C and 1D for regimes I, II, III and IV, respectively. Limestome is carrier of about 90% Ca, 50% Sr, 15% Zn and Ba, 5 – 10% Cl, Ni and Pb mass from total mass of a given element in input stream (Fig. 1A). Wood is carrier of about 50% Zn and Cd, 40% P_2O_5, 30% Cl, 20% Ba mass from total mass of a given element in input stream (Fig. 1B). At mass flow used in regime III sewage sludge and/or ASF put into co-

Table 3B Chemical composition of input and output materials for regime II.

Oxide/elements		Lignite	Limestone	Wood	BA	FA
A	wt. %	24.3	66.7	2.7	99.5	96.9
SiO_2		12.2	17.6	0.98	44.0	42.9
TiO_2		0.44	0.25	0.01	1.07	1.58
Al_2O_3		6.80	5.83	0.13	23.2	22.4
Fe_2O_3		1.57	1.95	0.11	4.16	7.63
MgO		0.29	0.49	0.15	0.92	1.48
CaO		0.29	38.6	1.45	13.5	14.5
K_2O		0.32	1.05	0.20	1.49	1.34
P_2O_5		0.04	0.12	0.09	0.18	0.42
SO_3		2.25	0.38	0.09	5.65	5.76
Cl	ppm	302	811	264	1315	1003
Cr		41.2	25	2.0	78.6	221
V		69.4	49.2	1.4	155	336
Ni		21.6	20.4	1.5	41.6	99
Cu		22.8	7.2	4.2	49.5	120
Zn		31.8	33	57.5	139	261
As		90.0	1.9	< 0.15	96.8	375
Se		1.1	< 0.5	< 0.08	0.3	5.0
Sr		61.5	805	46.0	393	525
Cd		0.3	< 0.2	0.7	1.6	2.7
Ba		107	165	64.4	307	562
Hg		0.185	0.009	< 0.25	0.002	0.202
Pb		10.5	9.1	5.1	33.3	45.0

Table 3C Chemical composition of input and output materials for regime III.

Oxide/elements		Lignite	Limestone	Wood	Sewage sludge	Alternative solid fuel	BA	FA
A	wt. %	24.3	66.5	2.7	0.9	8.1	99.6	98.8
SiO_2		12.8	19.3	0.92	0.27	4.19	49.9	41.4
TiO_2		0.46	0.28	0.01	0.01	0.23	1.31	1.64
Al_2O_3		6.68	5.85	0.25	0.15	0.46	25.8	23.9
Fe_2O_3		1.39	1.89	0.10	0.04	0.26	3.60	7.10
MgO		0.28	0.73	0.13	0.03	0.11	0.93	1.37
CaO		0.29	37.5	1.10	0.33	0.94	10.1	13.2
K_2O		0.31	1.11	0.19	0.01	0.20	1.55	1.29
P_2O_5		0.04	0.11	0.07	0.02	0.07	0.14	0.42
SO_3		2.26	0.41	0.07	0.04	0.20	4.73	6.50
Cl	ppm	309	959	221	22.4	128	1141	975
Cr		42.1	< 25	3.0	0.58	20.3	89.0	172
V		79.3	21.5	1.4	0.9	4.4	161	331
Ni		20.9	17.1	2.3	0.29	4.5	30.4	93.4
Cu		29.6	6.2	4.0	2.5	50.8	55.8	132
Zn		18.8	32.0	68.3	3.4	208	93.7	196
As		61.2	1.7	< 0.15	0.08	< 0.48	38.6	268
Se		1.1	0.7	< 0.08	< 0.02	0.2	0.2	5.1
Sr		58.1	728	29.0	4.4	17.8	328	428
Cd		0.4	< 0.2	0.7	< 0.10	1.0	1.7	2.8
Ba		114	212	74.4	7.6	239	232	564
Hg		0.197	0.009	< 0.25	0.0032	0.66	0.001	0.672
Pb		11.0	8.9	3.1	0.6	36.5	41.1	46.6

Table 3D Chemical composition of input and output materials for regime IV.

Oxide/elements		Lignite	Limestone	Wood	Soap	BA	FA
A	wt. %	22.9	66.3	6.84	7.61	96.8	97.1
SiO_2		11.7	18.9	4.62	0.07	43.4	38.7
TiO_2		0.51	0.28	0.05	0.001	1.31	1.68
Al_2O_3		6.68	5.32	1.8	0.03	21.7	20.2
Fe_2O_3		1.23	1.64	0.32	0.005	3.62	6.56
MgO		<0.04	0.37	0.13	<0.0005	0.52	1.20
CaO		0.31	40.0	1.81	0.25	18.3	16.2
K_2O		0.32	1.05	0.29	0.28	1.68	1.75
P_2O_5		0.054	0.10	0.11	0.02	0.23	0.73
SO_3		2.05	0.22	0.18	0.20	4.65	5.20
Cl	ppm	618	320	290	364	490	650
Cr		30.3	26	13.3	<2.1	58.7	193
V		102	30.3	<3.6	<0.6	184	425
Ni		23.0	12.9	3.7	<0.43	45.8	106
Cu		22.3	3.20	20.7	1.76	53.6	157
Zn		26.6	33.8	51.8	48.9	170	264
As		131	<2.0	0.809	<0.18	158	586
Se		1.7	<0.2	0.06	<0.11	0.4	7.3
Sr		105	720	33.2	10.7	517	661
Cd		0.3	<0.2	0.4	3.40	0.7	3.5
Ba		161	99	78	29.2	361	726
Hg		0.122	0.01	0.05	<0.001	0.002	0.537
Pb		11.1	10.1	3.96	<0.8	32.9	41.8

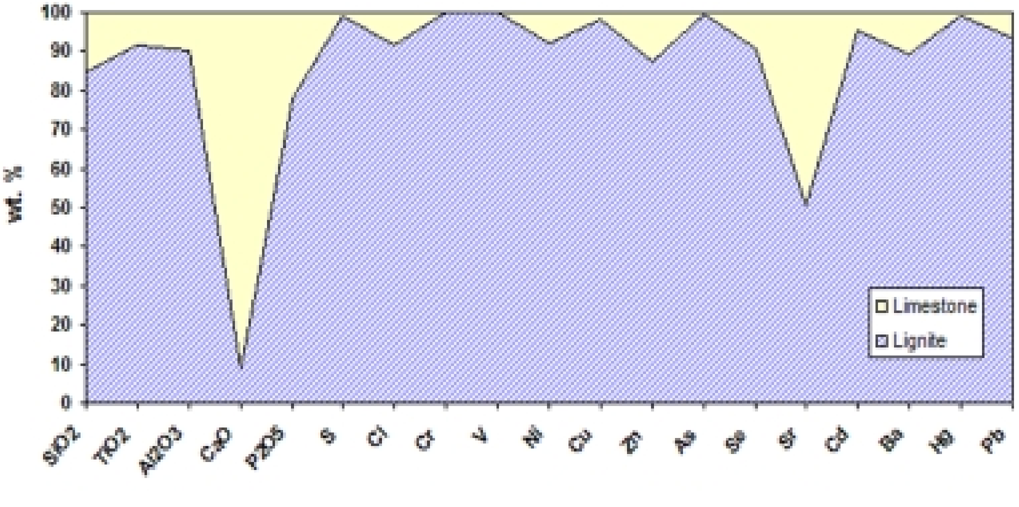

Fig. 1A The distribution of oxides and elements in input stream for regime I.

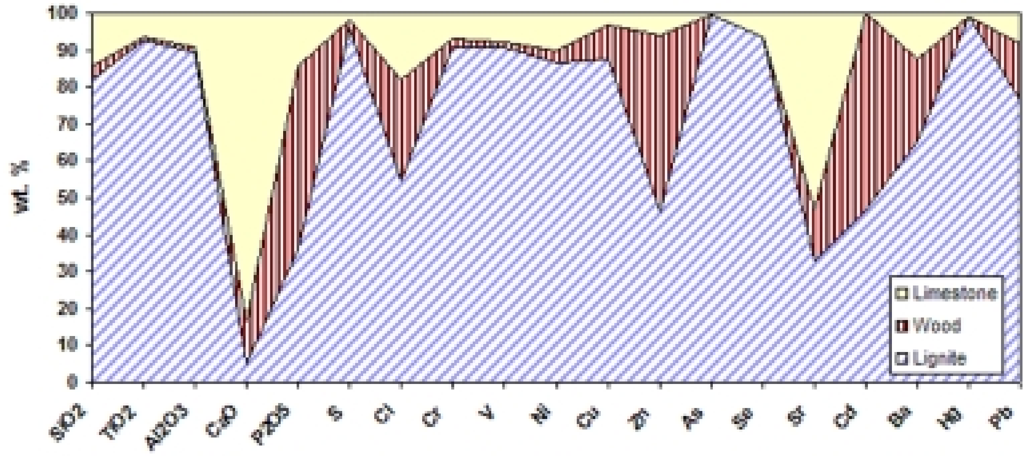

Fig. 1B The distribution of oxides and elements in input stream for regime II.

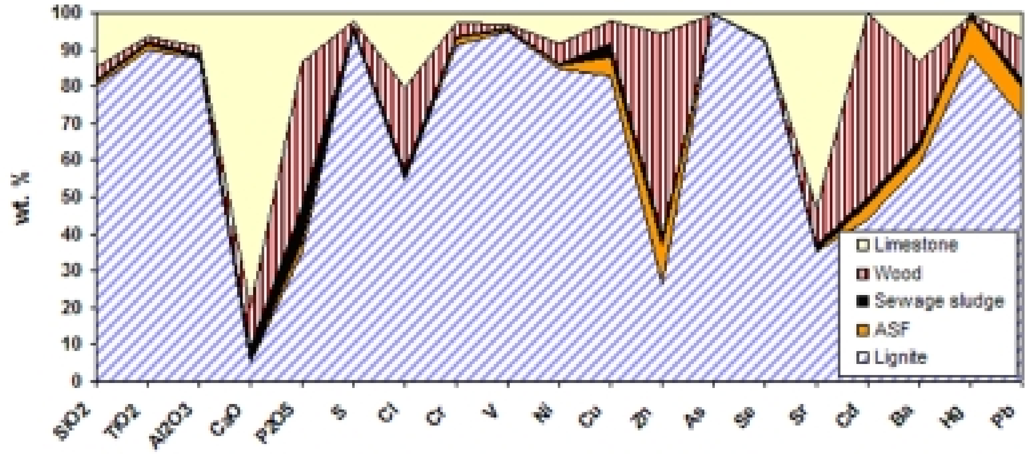

Fig. 1C The distribution of oxides and elements in input stream for regime III.

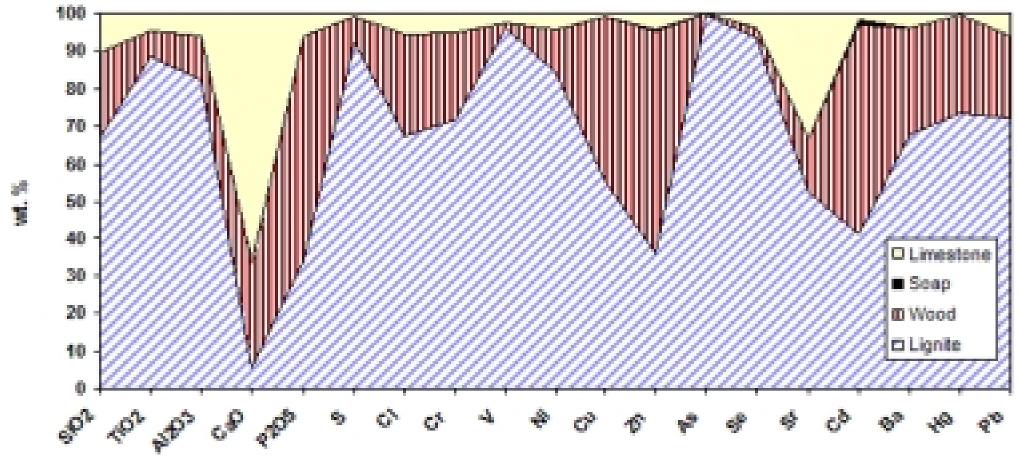

Fig. 1D The distribution of oxides and elements in input stream for regime IV.

combustion much less hazardous elements than lignite, limestone and/or wood (Fig. 1C). In regime IV, wood bark is carrier of about 60% P_2O_5 and Zn, 55% Cd, 40% Cu, 30% Ba and 25% Hg mass in input mass stream. Contribution of soap to percentages of the oxides and/or element mass in input materials is very poor (e.g. 1.5% Cd and 0.5% Zn, see Fig. 1D).

Using the equations (1 – 4) the mass balances were performed for all oxides and trace elements. In Fig. 2 the distributions of S, Cl, As, Se, Cd, Hg and Pb among BA, FA and E are plotted. For regimes I, II and III these elements were determined in flue gas (Table 4), while all other oxides and/or elements were determined only in solid samples and the calculated percentages in emissions were usually burdened with error up to ± 15%. The distribution of S, Cl, As, Se, Cd, Hg and Pb in output streams is plotted in Fig. 2A for regime I, in Fig. 2B for regime II and in Fig. 2C for regime III. The results show that except Hg there are not bigger differences in emissions of above elements among regimes I, II and III. The highest Hg emission is in the regime II (77.8%), the lowest in the regime I (17.2%). For regimes I – III the content of Hg in lignite varies from 0.172 to 0.197 ppm and in BA from 0.0001 to 0.002 ppm. Evaporated mercury from lignite was partly condensed on FA particles and partly passed to flue gas in gaseous form. From Hg analyses of FA result that Hg condenses on FA particles in regimes I and III (0.779 and 0.672 ppm Hg, respectively) while in regime II the Hg-condensation is limited (0.202 ppm Hg in FA). Because the ratio between FA and BA (1.50) and limestone to lignite (0.120) are about the same for all three regimes the behavior of different Hg distribution can be expected by very sensitive relation of Hg to temperature in an electrostatic precipitator. This temperature was in regime II probably highest because the boiler worked at the highest output while in regime I lowest because the boiler worked at the lowest output (Table 1).

Except $S(SO_2)$, Cl, As, Se, Cd, Hg and Pb the oxides CO and NO_x and PCCD/PCCF, PAH and PCB were determined in flue gas (regimes I, II and III). The data are presented in Table 4. In the same table the emission limits valid for the Czech Republic are presented. The data show that each of components is almost constant, i.e. contents of CO and NO_x and PCCD/PCCF, PAH and PCB are practically independent on regime of combustion.

In Table 5 the bulk chemical analyses of UC samples from BA are presented. If the content of oxides and/or elements is normalized on coal ash content (eq. 5) the differences in major or trace elements among UC samples from regimes I – IV are relatively low.

The separation of UC from FA was unsuccessful even using gravimetric separation in heavy liquids or flotation procedure. For the comparison of trace element contents in lignite (C), UC (separated from

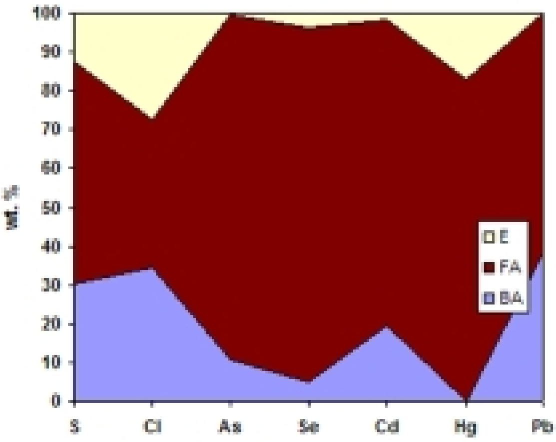

Fig. 2A The distribution of selected elements in output stream for regime I.

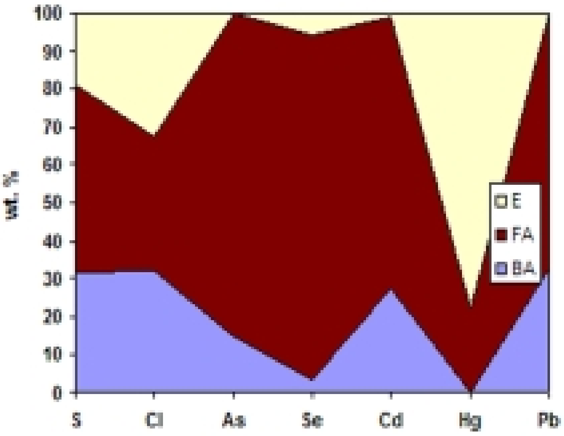

Fig. 2B The distribution of selected elements in output stream for regime II.

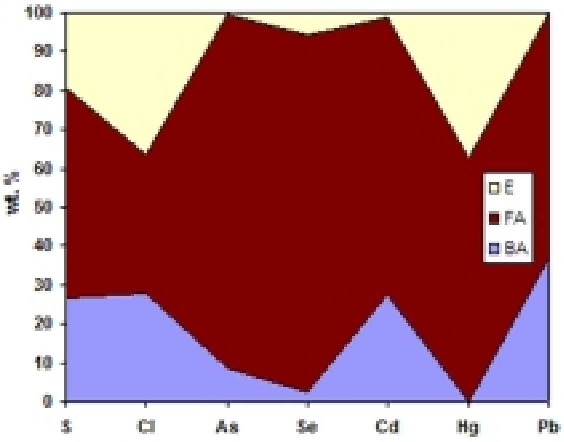

Fig. 2C The distribution of selected elements in output stream for regime III.

Table 4 Components determined in flue gas.

Components	Regime I	Regime II	Regime III	Regime IV	Limits
CO [mg/Nm^3]	28	24	34	31	250
NO$_x$ [mg/Nm^3]	220	212	196	200	400
SO$_2$ [mg/Nm^3]	450	514	400	380	500
Cl$^-$ [mg/Nm^3]	28.0	25.9	22.4	-	n.d.
F$^-$ [mg/Nm^3]	1.2	1.3	1.3	-	n.d.
As [mg/Nm^3]	0.0909	0.0304	0.0315	-	n.d.
Se [mg/Nm^3]	0.0101	0.0090	0.0070	-	n.d.
Cd [mg/Nm^3]	0.0014	0.0011	0.0011	-	n.d.
Hg [mg/Nm^3]	0.0054	0.0158	0.0090	-	n.d.
Pb [mg/Nm^3]	< 0.001	0.0038	0.0023	-	n.d.
PCDD/F [ng/Nm^3]	0.010	0.012	0.015	-	n.d.
PCB [ng/Nm^3]	< 0.001	< 0.001	< 0.001	-	n.d.
PAH [ng/Nm^3]	130	142	125	-	n.d.

n.d. - limits have not been determined

Table 5 The bulk chemical analyses of unburned carbon from BA.

Oxide/elements		Regime I	Regime II	Regime III	Regime IV
A	wt. %	54.7	74.7	79.6	44.5
SiO$_2$		28.7	34.7	45.9	22.5
TiO$_2$		1.04	1.27	1.77	1.00
Al$_2$O$_3$		15.8	19.5	27.0	12.4
Fe$_2$O$_3$		5.90	5.58	5.50	2.76
MgO		0.355	0.496	0.494	0.312
CaO		1.31	1.24	1.41	1.34
K$_2$O		0.922	0.997	1.06	0.594
P$_2$O$_5$		0.101	0.103	0.0797	0.105
SO$_3$		2.42	5.05	2.33	2.51
Cl	ppm	462	500	469	374
Cr		53.2	91.7	41	47.7
V		196	161	223	145
Ni		39.6	39.4	42.5	40.1
Cu		41.6	49.3	69.6	46.8
Zn		50.1	68.6	53.4	42.7
As		93.6	121	36.8	78.1
Se		2.4	1.6	1.7	2.3
Sr		194	141	167	211
Cd		< 4.8	< 5.2	< 5.1	< 4.5
Ba		176	228	255	206
Hg		0.009	0.02	0.009	0.02
Pb		21.8	27.7	35.1	18.9

BA), BA and FA the weight fractions of elements were normalized on 100% of ash in their matrix. The formula for the calculation of normalized weight fractions of the i-th element in the X-th material $(w_{X,i})_{NOR}$ is given in eq. (5):

$$\left(w_{X,i}\right)_{NOR} = 100 \cdot \frac{w_{X,i}}{A_X} \qquad (5)$$

Where: A_X - ash content of the C, BA and FA (Tables 3A, 3B, 3C and 3D) and that one for UC$_{BA}$ in Table 5;

$w_{X,I}$ - weight fraction of the i-th element in the C, BA and FA (Table 3A, 3B, 3C and 3D) and that one for UC in Table 5.

Comparison of the normalized weight fractions $(w_{X,i})_{NOR}/(w_{C,i})_{NOR}$ between UC/C, BA/C and FA/C is

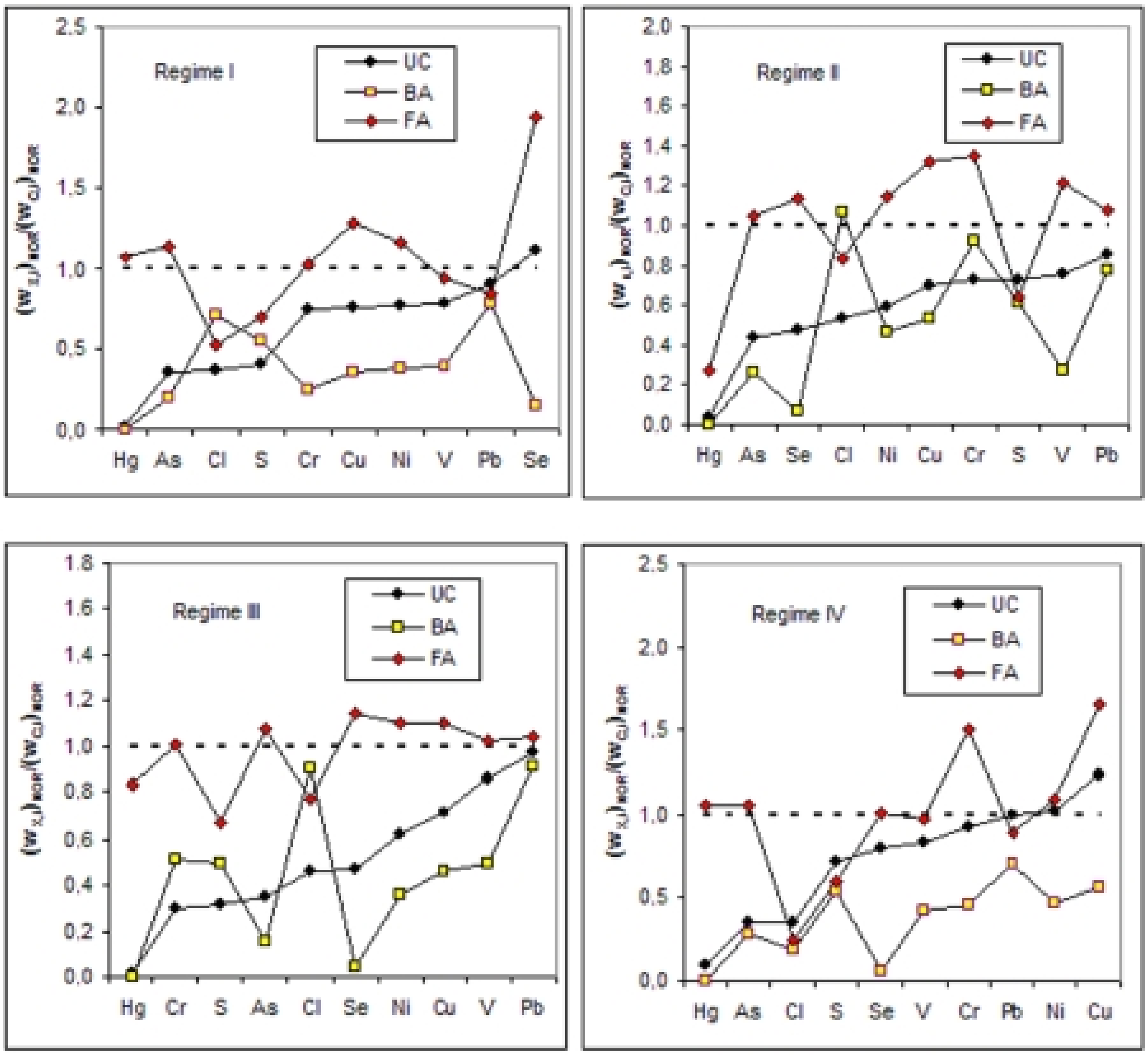

Fig. 3 The normalized weight fractions UC_{BA}/C, BA/C and FA/C of selected elements.

plotted in Fig. 3 for regines I, II, III and IV. The elements are ordered according to the increasing ratio ($w_{X,i}$ /$w_{C,i}$), where X is UC. Compared to coal the elements with $w_{X,i}$ /$w_{C,i}$ < 1.00 are in material *X* depleted and vice versa the elements with $(w_{X,i})_{NOR}/(w_{C,i})_{NOR}$ > 1.00 are enriched.

From the comparison of the results (Fig. 3), the normalized weight fractions for given elements can be ranged according to their increasing values into the following order: BA/C < UC_{BA}/C < FA/C. Only Cl, Cr and S show somewhat different results. Elements S and Cl are exception from above sequence. They are present in BA in higher content in forms $CaSO_4$ and $CaCl_2$ as a result of chemical reaction between them and $CaCO_3$. The highest enrichment of elements like Se (1.01 – 1.94), As (1.04 – 1.15), Cu (1.10 – 1.66), Ni (1.09 – 1.17) is in FA. It is due to their higher mobility and/or evaporation from lignite particles and the following fixation on fly ash particles. On the contrary these elements are depleted in BA, e.g. Se (0.04 – 0.16), As (0.15 – 0.29), Ni (0.35 – 0.47), Cu (0.36 – 0.57). Mercury is the most depleted element in BA (0.001 – 0.004) and UC_{BA} (0.01 – 0.10) from which it is mostly evaporated. However, evaporated mercury is then partly condensed on FA particles (0.84 – 1.07) and partly passes to flue gas (regimes I, III and IV). In regime II the highest Hg volatilization was observed, so that the condensation of mercury on FA particles was much lower than in previous regimes (Fig. 2B). As was given above we have not succeeded in separation of unburned carbon from FA and therefore in Fig. 3 only the data for UC_{BA} are plotted.

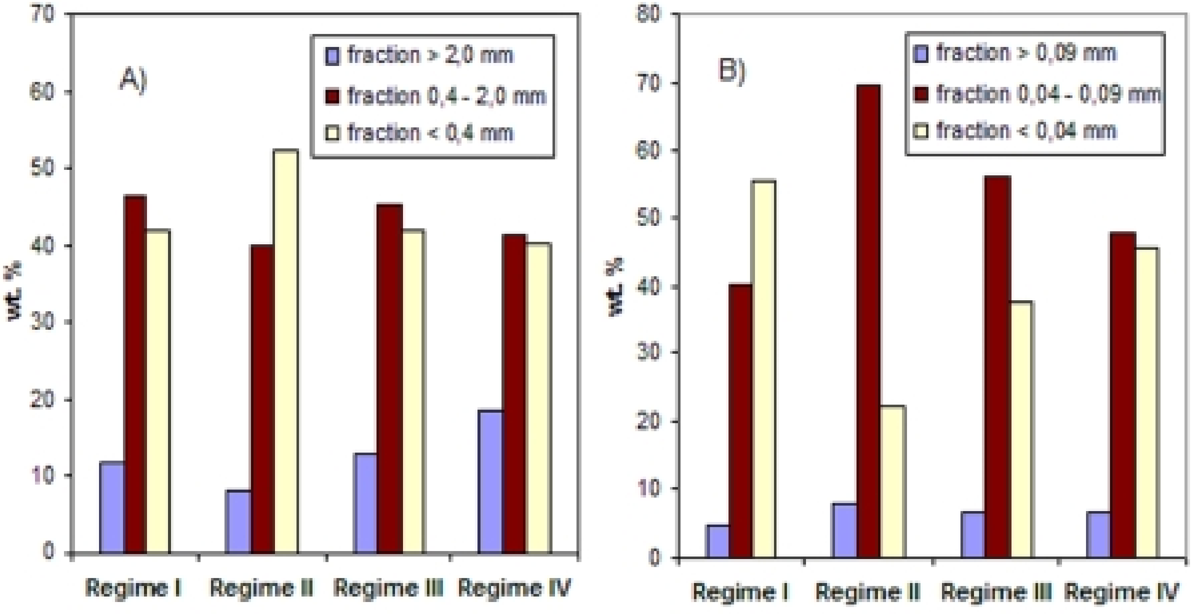

Fig. 4 The weight distribution of fractions in BA (A) and FA (B).

For the detail study of ashes the samples of BA and FA were separated into the three size fractions. The weight percentages of separated fraction from BA and FA are plotted in Fig. 4. From all regimes I – IV the fraction with most coarse size is included at least, both in BA and FA samples.

Unburned carbon contents in bottom and fly ash samples obtained from the co-combustion of lignite were in BA below 4.3 %, except BA from regime IV where the content reached up to 10.5%. The UC contents in FA were below 0.77% (Table 6). The contents of UC are greater in BA comparing them with those ones of FA. The UC content increases with increasing grain size of BA, while it is by contraries in FA. The maximal content of UC in BA fraction 3 (grain size > 2 mm) in regime IV (10.5%) can be explained by inferior lignite co-combustion with soap. This idea is also supported by lowest ash content (A = 42.6%) of this sample from all unburned carbon samples (Table 6).

The ash fractions from BA and FA were analyzed on major and trace element contents, as well as percentages of UC in FA and BA were determined (Table 6). From the analyses the relation between logarithm of selected element contents in FA fractions and UC contents are plotted in Fig. 5.

For the evaluation of element content in FA fractions in relation to their UC(FA) content the regression function given by equation (6) was selected:

$$w_{FA} = A \cdot e^{B \cdot (UC)} \tag{6}$$

where: w_{FA} - is content of the element in the size fraction of FA sample (in ppm for trace elements, in wt.% for sulphur and chlorine),

A, B - the regression coefficients.

The coefficient *A* relates to the content of element equals to zero for UC in FA;

Table 6 Unburned carbon contents in BA and FA fraction samples.

	I		II		III		IV	
	UC(BA)	UC(FA)	UC(BA)	UC(FA)	UC(BA)	UC(FA)	UC(BA)	UC(FA)
fraction 1	0.13	0.58	0.05	0.77	0.07	0.50	0.15	0.54
fraction 2	0.37	0.52	0.23	0.69	0.21	0.40	0.66	0.43
fraction 3	4.33	0.26	1.80	0.18	2.17	0.15	10.5	0.22
total	1.61	0.57	0.25	0.59	0.24	0.44	1.98	0.46

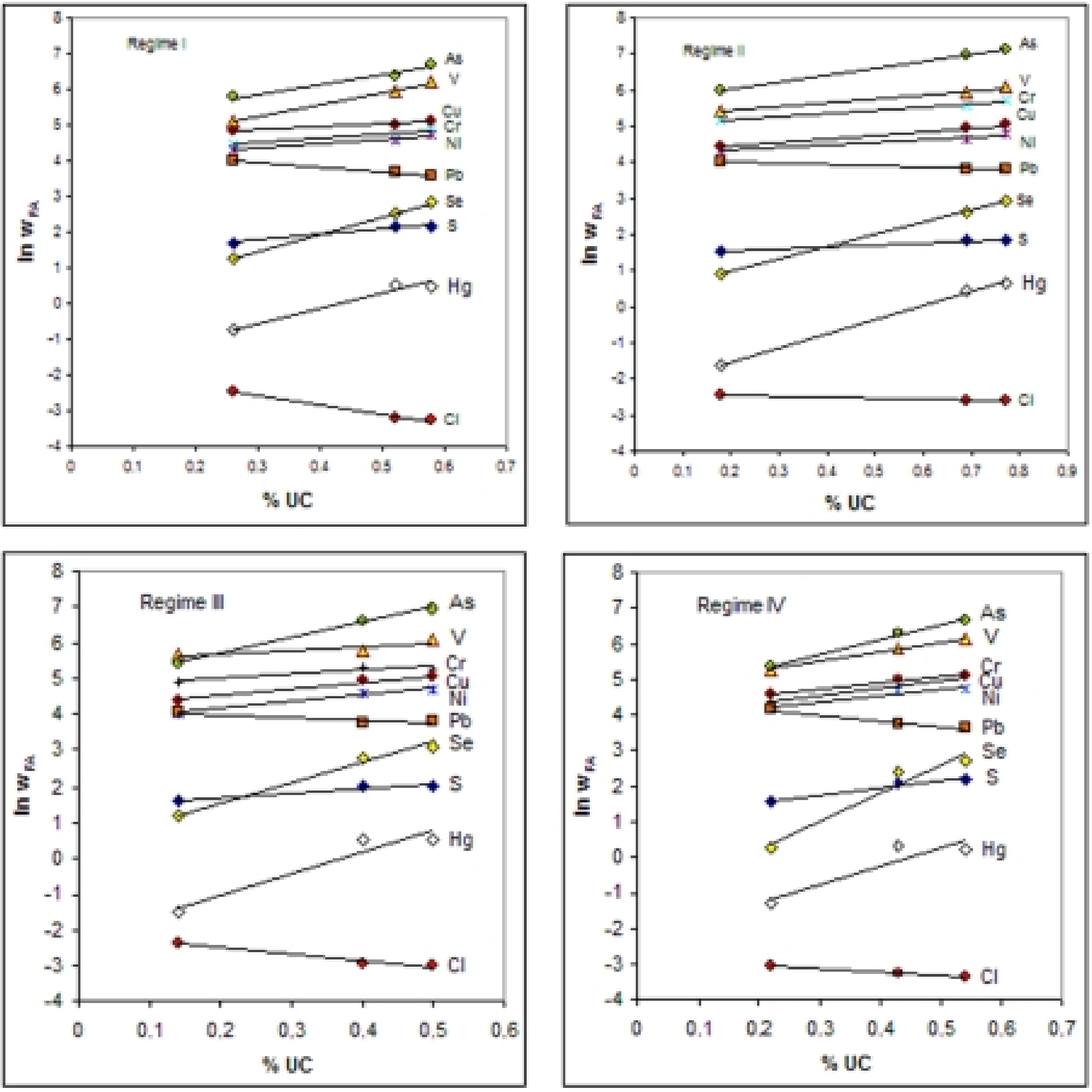

Fig. 5 The relation between logarithm of element contents in FA and percentages of UC in FA, (A – regime I, B – regime II, C – regime III and D – regime IV).

The coefficient *B* characterizes the slope of the regression function,

UC - content of the unburned carbon in fly ash fraction (in wt.%).

For all regimes, the regression coefficients A and B were calculated using logarithmic shape of equation (6). They are given in Table 7. Mainly Se, Hg, V and As exhibit an expressive growth of content with percentage of UC in FA. Elements Cl a Pb show inverse relation with unburned carbon content.

For the ash disposal or industrial utilization, its leaching behavior is very important. The determined data relating to the leaching of BA and FA from regimes I, II, III and IV are given in Table 8. In the same table also the concentration limits (the 1st degree) are given according to the Regulations 383/1 valid in the Czech Republic. (The 1st degree: the waste is allowed to be deposited on a waste dump; the 2nd and higher degrees: the waste is not allowed to be deposited on waste dump and must protected against the contamination of the environment). The higher degree of waste hazardousness the disposal site has to be more guaranteed against potential release of hazardous compounds).

Table 7 The regression coefficients of equation (6).

Elements	Regime I		Regime II		Regime III		Regime IV	
	A	B	A	B	A	B	A	B
Se	1.04	4.78	1.35	342	1.50	5.65	0.252	8.01
Hg	0.163	4.18	0.099	3.90	0.112	5.88	0.102	5.13
V	66.6	3.41	181.2	1.10	250.4	0.98	108.3	2.75
As	154.5	2.73	273.9	1.97	128.6	4.32	85.9	4.23
S	3.74	1.50	4.67	0.54	4.24	1.27	3.15	2.06
Ni	55.0	1.21	64.7	0.76	44.5	1.87	42.9	1.93
Cr	65.9	1.10	149.6	0.86	118.5	1.18	65.0	1.80
Cu	102.2	0.79	69.3	1.02	63.3	1.88	49.9	2.11
Pb	75.6	-1.28	59.8	-0.40	62.0	-0.71	89.2	-1.65
Cl	0.169	-2.64	0.0898	-0.28	0.120	-1.87	0.0570	-0.93

Table 8 Results of leaching tests of BA and FA. Concentrations are given in mg.dm^{-3}.

Parameter	I		II		III		IV		Limit I concentration according Czech Regulations 383/1
	BA	FA	BA	FA	BA	FA	BA	FA	
pH	12.4	12.2	11.7	11.1	11.5	11.3	11.9	11.2	5.5 - 11
NH_4^+	0.69	2.23	0.37	1.76	0.74	1.51	0.36	1.35	3.0
Cl^-	35	47	11.4	39	10.8	49			500
NO_3^-	< 5	< 5	51	47	< 2	52			100
NO_2^-	< 5	< 5	30	< 2	< 2	< 2			1.0
F^-	< 2	< 2	< 0.5	< 0.5	< 0.05	< 0.5			3.0
SO_4^{2-}	1650	1820	1790	1860	1720	1660			500
As	< 0.01	< 0.01	< 0.01	0.22	< 0.01	0.04	< 0.01	0.055	0.05
Ba	< 0.05	< 0.05	0.06	0.08	< 0.05	0.06	0.29	0.39	1.0
Cd	0.011	< 0.005	< 0.002	< 0.002	0.003	0.004	< 0.002	< 0.002	0.005
Cu	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	0.05	< 0.03	< 0.03	0.5
Pb	< 0.05	< 0.05	< 0.05	0.09	0.05	< 0.05	< 0.05	< 0.05	0.1
Se	< 0.01	< 0.01	< 0.01	0.011	0.013	0.01	< 0.01	< 0.01	0.05
Sb	< 0.01	< 0.01	< 0.01	0.021	< 0.01	0.021	< 0.01	< 0.01	0.05
V	< 0.03	0.06	< 0.03	0.06	< 0.03	< 0.03	< 0.03	0.19	0.2

The comparison of the measured data with the concentration limits suggests that almost all the parameters are below the limits valid for the 1st degree of the waste treatment. It is not true for pH of the extracts and sulphate concentration. Both these parameters fall outside the allowed interval valid for the 1st degree of waste deposition. This is the reason why samples of BA and FA have to be treated as wastes for which the regulations of the 2nd (according to sulphate concentration) and the 3rd degree (according to the pH) are valid. The data given in Table 8 also suggest that the addition of sewage sludge, plastic and wood doesn´t increase the pH value, sulphate, chloride and toxic element content in water leachates.

4. CONCLUSION

Combustion of lignite (I) and its co-combustion with wood (II), with wood, sewage sludge and ASF (plastics, textile and paper), and with wood and soap (IV) were performed in CFB with limestone. In regime II wood to lignite in mass ratio 0.57 : 1, in regime III wood : sewage sludge : alternative fuel : lignite in mass ratio 0.57 : 0.57 : 0.035 : 1 and regime IV wood : soap : lignite in mass ratio 0.85 : 0.007 : 1 were co-combusted, respectively.

Chemical composition of lignite, limestone, bottom and fly ashes as well as other co-combusted materials were determined and critically studied. For mass balances the concentrations S, Cl, As, Se, Cd, Hg and Pb in flue gas were determined for regimes I, II and III and the distribution of these elements among emission, bottom and fly ash evaluated. Moreover, in flue gas PCCD/F, PCB and PAH, in bottom and fly ash the unburned carbon content and leaching tests were determined. No significant differences in composition of emissions, bottom and fly ashes as well as in composition of water leachates were found from the combustion regimes I, II, III and IV.

ACKNOWLEDGMENT

The authors would like to gratefully acknowledge the financial support from Grant Agency of the Czech Republic by project No. 101/03/1402.

REFERENCES

Desroches-Ducarne, E., Marty, E., Martin, G. and Delfosse, L.: 1998, Co-combustion of coal and municipal solid waste in a circulating fluidized bed, Fuel, 77(12), 1311–1315.

Gayan, P., Adanez, J., de Diego, L. F., Garcia-Labiano, F., Cabanilas, A., Bahillo, A., Aho, M. and Veijonen, K.: 2004, Circulating fluidized bed co-combustion of coal and biomass, Fuel, 83(3), 277–286.

Hansen, P.F.B., Andersen, K.H., Wieck-Hansen, K., Overgaard, P., Rasmussen, I., Fradsen, F.J., Hansen, L. A. and Dam-Johansen, K.: 1998, Co-firing straw and coal in a 150 MW_e utility boiler: in situ measurements, Fuel Processing Technology, 54(1–3), 207–225.

Hansen, L.A., Fradsen, F.J., Dam-Johansen, K., Sørensen, H.S. and Skrifvars, B-J.: 1999, Characterization of ashes and deposits from high-temperature coal-straw co-firing, Energy & Fuels, 13(4), 803–816.

Kaufmann, H., Nussbaumer, T., Baxter, L. and Yang, N.: 2000, Deposit formation on a single cylinder during combustion of herbaceous biomass, Fuel, 79(2), 141–151.

Kouvo, P. and Backman, R.: 2003, Estimation of trace element release and accumulation in the sand bed during bubbling fluidised bed co-combustion of biomass, peat and refuse-derived fuels, Fuel, 82(7), 741–753.

Lind, T., Valmari, T., Kaupinnen, E.I., Sfiris, G., Nilsson, K. and Maenhaut, W.: 1999, Volatization of the heavy metals during circulating bed combustion of forest residue, Environmental Science and Technology, 1999, 33(3), 496–502.

Lopes, M.H., Abelha, P., Lapa, N., Oliveira, J.S., Cabrita, I. and Gulyurtlu, I.: 2003, The behaviour of ashes and heavy metals during the co-combustion of sewage sludges in a fluidised bed, Waste Management, 23(9), 859–870.

Miller, B.B., Kandiyoti, R. and Dugwell, D.R.: 2002, Trace element emissions from co-combustion of secondary fuels with coal: A comparison of bench-scale experimental data with predictions of a thermodynamic equilibrium model, Energy & Fuels, 16(4), 956–963.

Nussbaumer, T.: 2003, Combustion and co-combustion of biomass: Fundamentals, technologies, and primary measures for emission reduction, Energy & Fuels, 17(6), 1510–1521.

Obernberger, I., Biedermann, F., Widmann, W. and Riedl, R.: 1997, Concentrations of inorganic elements in biomass fuels and recovery in the different ash fractions, Biomass and Bioenergy, 12(3), 211–224.

Pedersen, L.S., Nielsen, H.P., Kiil, S., Hansen, L.A., Dam-Johansen, K., Kildsig, F., Christensen, J. and Jespersen, P.: 1996, Full-scale co-firing of straw and coal, Fuel, 75(13), 1584–1590.

Sørum, L., Fradsen, F.J. and Hustad, J.E.: 2003, On the fate of heavy metals in municipal solid waste combustion Part I : devolatilisation of heavy metals on the grate, Fuel, 82(18), 2273–2283.

Spliethoff, H. and Hein, K.R.G.: 1998, Effect of co-combustion of biomass on emissions in pulverized fuel furnaces, Fuel Processing Technology, 54(1-3), 189–205.

Spliethoff, H., Scheurer, W. and Hein, K.R.G.: 2000, Effect of co-combustion of sewage sludge and biomass on emissions and heavy metals behaviour, Process Safety and Environmental Protection: Transactions of the Institution of Chemical Engineers, Part B, 78(1), 33–39.

Steenari, B-M. and Lindquist, O.: 1999, Fly ash characteristics in co-combustion of wood with coal, oil or peat, Fuel, 78(4), 479–488.

Wang, J., Liu, H., Lu, J., Liu, D., Xia, X. and Ma, L.: 1999, Emission control during co-combustion of coal and biomass in a fluidized bed combustor, Developments in Chemical Engineering and Mineral Processing, 7(5), 501–511.

Werther, J. and Ogada, T.: 1999, Sewage sludge combustion, Progress in Energy and Combustion Science, 25(1), 55–116.

Zheng, G. and Kozinski, J. A.: 2000, Thermal events occurring during the combustion of biomass residue, Fuel, 79(2), 181–192.

Regulation 383/2001 Col. Ministry of the Environment of the Czech Republic. Praha: MŽP, 2001.