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COMPARISON OF ELEMENTAL CONTENTS IN UNBURNED CARBON, COAL AND ASH DURING BROWN COAL COMBUSTION IN FLUIDIZED-BED BOILER

POROVNÁNÍ OBSAHŮ PRVKŮ V NEDOPALU, UHLÍ A POPELU BĚHEM SPALOVÁNÍ HNĚDÉHO UHLÍ VE FLUIDNÍM KOTLI

Abstract

This work was focused to behaviour of toxic minor and trace elements during coal combustion in circulating fluidised-bed power station. The evaluation was performed through the study of unburned carbon particles in terms of elemental and mineral composition as well as its textural characteristics.

Abstrakt

Tato práce byla zaměřena na chování toxických minoritních a stopových prvků při spalování uhlí v elektrárně s cirkulující fluidní vrstvou. Hodnocení bylo provedeno pomocí studia nedopalových zrn z hlediska elementárního a minerálního složení, stejně jako jeho texturní vlastnosti.

INTRODUCTION

Czech Republic belongs to the world´s largest brown coal/lignite producers; in 2007 about 48.9 million tones of brown coal and 0.5 million tones of lignite were produced in this region. In Czech Republic brown coal/lignite represents an important and indispensable supply of national fuel and energy policy [1,2]. But Czech brown coals/lignite are (at average) quite different from low rank coals coming from other European mining areas, especially in rather high ash content and some unfavorable characteristics of mineral matter [3]. This is the reason why this work was focused to elemental behavior during brown coal combustion in fluidized – bed boiler power station. Therefore the fluidized-bed combustion is widely used in the Czech Republic as a modern and ecological combustion technology. Low combustion temperature provides many advantages – lower volatility of many toxic trace elements, the decrease of thermal NOx emissions, high efficiency of sulphur capture due to limestone addition and so on. Even though the fluidized-bed is used as a modern and ecological technology, many problems still have not been satisfactorily solved, e.g. emissions of toxic minor and trace elements from the power stations into atmosphere.

EXPERIMENTAL COMBUSTION UNIT, SAMPLES, METHODS

The aim of this work was to evaluate the behaviour of 15 elements during combustion coal in circulating fluidised-bed power station in Tisová. The combustion temperature was about 850 ˚C. In regular time intervals the samples of coal, bottom ash and fly ash were collected. Unburned carbon particles were separated from bottom ash by hand. Analysis of major, minor and trace elements was

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carried out using X-ray fluorescence spectrometry on SPECTRO XEPOS. Analysis of mineral phases was performed by means of X-ray diffraction analysis using BRUKER D8 ADVANCE.Scanning electron microscope micrographs were taken by SEM PHILIPS XL – 30.

RESULTS AND DISSCUSSION

ANALYSIS OF MINERAL PHASES

The samples of coal (C), unburned carbon (UC), bottom ash (BA) and fly ash (FA) were analysed for mineral-phases occurrence using X-ray diffraction analysis and the diffraction patterns obtained for these samples are given in Figs. 1A,B,C and D.

Fig. 1. X-ray diffraction patterns of coal, unburned carbon, bottom ash and fly ash.
Q-quartz, L-lime, Cal – calcite, K – kaolinite, H – hematite, A – anhydrite,
Sid – siderite, AlSi - aluminium silicate, Ch - calcium hydroxide, G - goethite, T – anatase

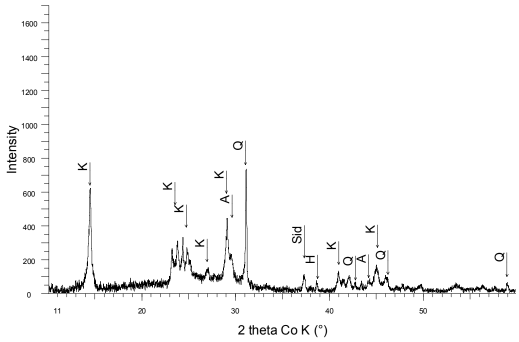

Fig. 1A. X-ray diffraction pattern of coal

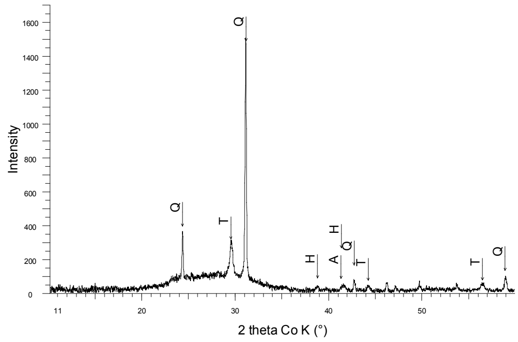

Fig. 1B. X-ray diffraction pattern of unburned carbon

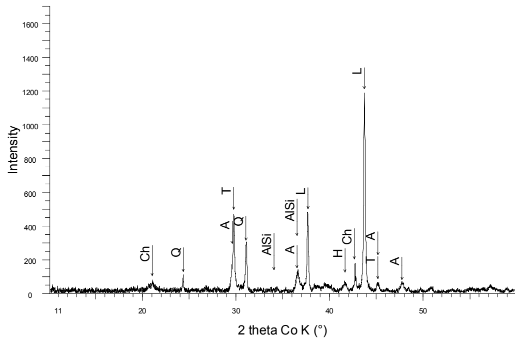

Fig. 1C. X-ray diffraction pattern of bottom ash

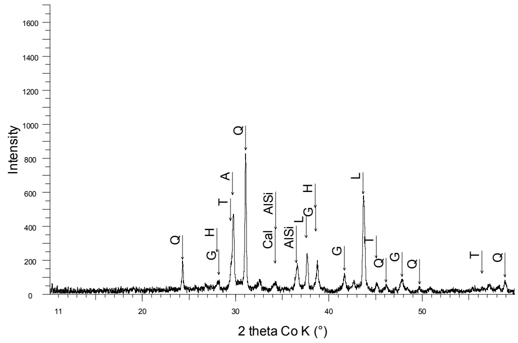

Fig. 1D. X-ray diffraction pattern of fly ash

ANALYSIS OF MAJOR, MINOR AND TRACE ELEMENTS

Contents of major, minor and trace elements in coal (V^{daf} = 52.61%), unburned carbon, bottom ash and fly ash as well as ash contents in these materials are given in Tab. 1

COMPARISON OF ELEMENTAL CONTENTS IN COAL, UNBURNED CARBON AND BOTTOM ASH

Since the ash contents of coal, unburned carbon and ashes are rather different, the elemental contents were recalculated to 100% ash content prior to comparison itself.

The recalculation was performed using Eqs. 1-4, where the addition of limestone during the combustion was taken into account as well.

$$W_{i,C} = 100\frac{w_{i,C}}{A_C} \qquad W_{i,UC} = 100\frac{w_{i,UC}}{A_{UC}} \qquad \text{Eqs. (1,2)}$$

$$W_{i,BA} = 100\frac{w_{i,BA}}{A_{BA} - w_{CaO,BA}} \qquad W_{i,FA} = 100\frac{w_{i,FA}}{A_{FA} - w_{CaO,FA}} \qquad \text{Eqs. (3,4)}$$

where w_i represents measured contents and W_i recalculated contents of studied elements in coal (C), unburned carbon (UC), bottom ash (BA) or fly ash (FA) and w_{CaO} are contents of CaO in bottom ash (BA) or fly ash (FA). A_C, A_{UC}, A_{BA} and A_{FA} are ash contents in studied materials.The recalculated elemental contents are given in Tab. 2.

Measured contents w_i				
Element	**Sample**			
	C	**UC**	**BA**	**FA**
Ash (%)	23.4	56.1	98.9	98.8
Na_2O (%)	< 0.2	< 0.2	< 0.3	< 0.3
MgO (%)	< 0.1	< 0.1	0.2	0.4
Al_2O_3 (%)	6.0	15.8	11.7	19.4
SiO_2 (%)	11.8	30.4	20.1	34.7
P_2O_5 (%)	0.1	0.2	0.2	0.4
K_2O (%)	0.1	0.2	0.5	0.4
CaO (%)	0.7	1.5	46.2	26.5
TiO_2 (%)	1.5	4.2	3.2	4.8
MnO (%)	0.02	0.02	0.07	0.05
Fe_2O_3 (%)	1.5	2.5	4.9	7.0
S (%)	1.1	1.1	3.8	2.9
V (ppm)	62.4	256.0	75.0	165.0
Cl (ppm)	41.5	58.6	49.8	122.2
Ni (ppm)	12.5	32.9	23.8	50.1
Cu (ppm)	67.0	222.5	91.5	166.2
Zn (ppm)	26.6	37.8	85.9	129.0
Ga (ppm)	14.4	26.0	20.3	47.1
Ge(ppm)	5.4	11.9	11.1	16.7
As (ppm)	39.0	40.0	81.0	145.2
Se (ppm)	1.2	1.5	1.3	6.6
Br (ppm)	1.8	2.4	2.4	6.5
Rb (ppm)	11.4	36.0	33.6	30.5
W (ppm)	19.1	64.9	22.7	48.0
Pb (ppm)	6.9	19.7	19.5	28.2
Th (ppm)	5.7	14.4	12.2	17.8

Table 1. Ash contents and concentrations of elements in measured samples

Contents recalculated W_i				
Element	**Sample**			
	C	**UC**	**BA**	**FA**
S (%)	4.7	2.0	7.3	4.0
V (ppm)	266.5	456.5	142.4	227.9
Cl (ppm)	177.2	104.5	94.5	169.0
Ni (ppm)	53.4	58.7	45.2	69.2
Cu (ppm)	286.1	396.7	173.7	229.6
Zn (ppm)	113.6	67.4	163.0	178.2
Ga (ppm)	61.5	46.4	38.5	65.1
Ge (ppm)	23.1	21.2	21.1	23.1
As (ppm)	166.5	71.3	153.7	200.6
Se (ppm)	5.1	2.7	2.5	9.1
Br (ppm)	7.7	4.3	4.6	9.0
Rb (ppm)	48.7	64.2	63.8	42.1
W (ppm)	81.6	115.7	43.1	66.3
Pb (ppm)	29.5	35.1	37.0	39.0
Th (ppm)	24.3	25.7	23.2	24.6

Table 2. Recalculated concentrations of elements in measured samples

The comparison of recalculated contents of elements in coal, unburned carbon and bottom ash was performed graphically using diagrams showed in Figs. 2-4, which demonstrates the relations between recalculated contents of elements in coal, UC and BA and the ash contents in these samples.

The gradual burn-up trend of coal particle is demonstrated only in Fig. 2A by dashed line (connecting the value for coal and BA). In other figures it has not been shown. The UC value was compared with the total burn-up trend – with the very dashed line. When the value for UC is situated below the general burn-up trend (Figs. 2A, B and C) the given element is depleted in UC, which indicated its volatile behaviour. If the value for UC is situated above the line (Fig. 3A,B), the element is enriched in unburned carbon relating the total burn-up trend and therefore this element shows non-volatile behaviour.

Fig. 4 demonstrates the behaviour of Ge, where the value for UC is situated approximately on the dashed line, i.e. the volatility of this element corresponds with the total burn-up trend.

Figs. 2A,B,C demonstrate typical volatile behaviour of As, S, Se, Br, Zn a Cl. Significant non-volatile behaviour was obtained in case of Ni, Rb, V, Cu and W, whereas the behaviour of Ga, Pb, Th a Ge did not show a clear trend. Ga was slightly volatile, Pb and Th showed non-volatile behaviour and the behaviour of Ge corresponds to average mineral matter volatility.

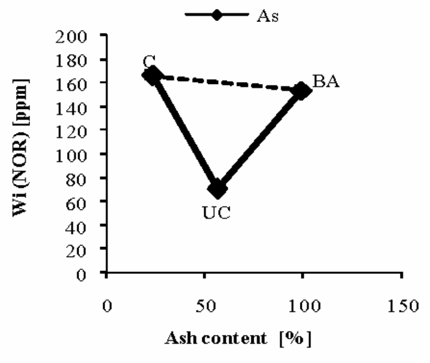

Fig. 2A. Comparison of recalculated elemental contents of As in coal, unburned carbon and bottom ash (volatile behaviour)

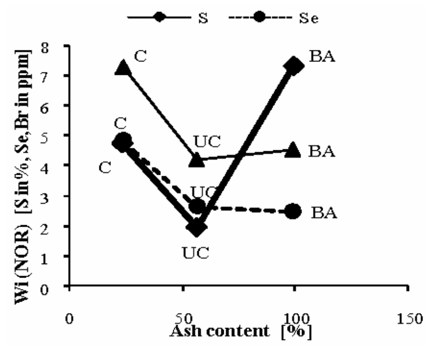

Fig. 2B. Comparison of recalculated elemental contents of S, Se and Br in coal, unburned carbon and bottom ash (volatile behaviour)

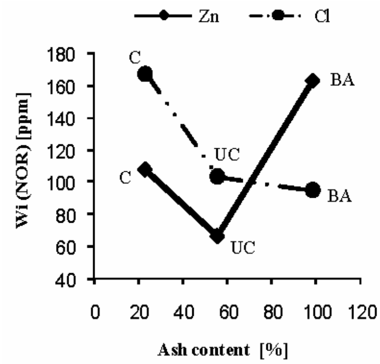

Fig. 2C. Comparison of recalculated elemental contents of Zn and Cl in coal, unburned carbon and bottom ash (volatile behaviour)

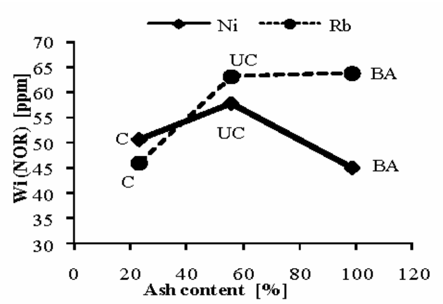

Fig. 3A. Comparison of recalculated elemental contents of Ni and Rb in coal, unburned carbon and bottom ash (non-volatile behaviour)

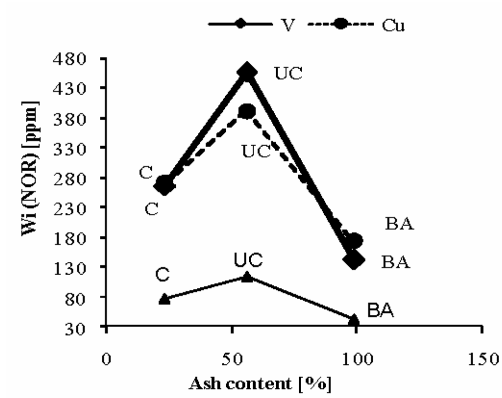

Fig. 3B. Comparison of recalculated elemental contents of V, Cu and W in coal, unburned carbon and bottom ash (non-volatile behaviour)

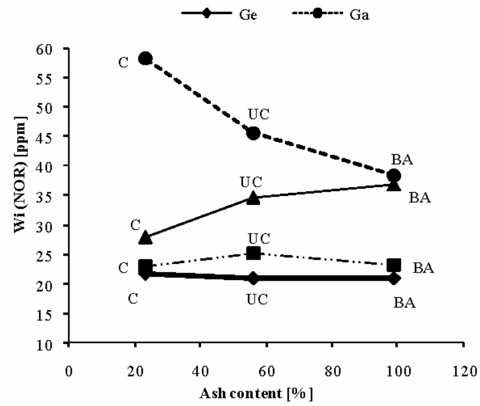

Fig. 4. Comparison of recalculated elemental contents of Ge, Ga, Pb and Th in coal, unburned carbon and bottom ash (no clear trend)

MORPHOLOGY AND PORE-SIZE DISTRIBUTION

SURFACE MORFPHOLOGY

The surface structure of coal, unburned carbon and bottom ash grains was studied by means of scanning electron microscopy using the secondary-electron beam method.

In Fig. 6-8 the SEM micrographs of a typical grain of coal (Fig.6), unburned carbon (Fig.7) and bottom ash (Fig.8) are given; for each particle two photographs were taken – a general view (with magnification of 50x) and a surface detail (with magnification of 1500x).

The comparison of the surface morphology of coal, unburned carbon and bottom ash particles suggests that the unburned carbon shows well-developed system of ruptures, pores and cavities whereas the porosity of coal and bottom ash is rather poor. The origin of the pores, ruptures and cavities in unburned carbon particles is created by the release of volatile combustibles out of the coal particle during the combustion process.

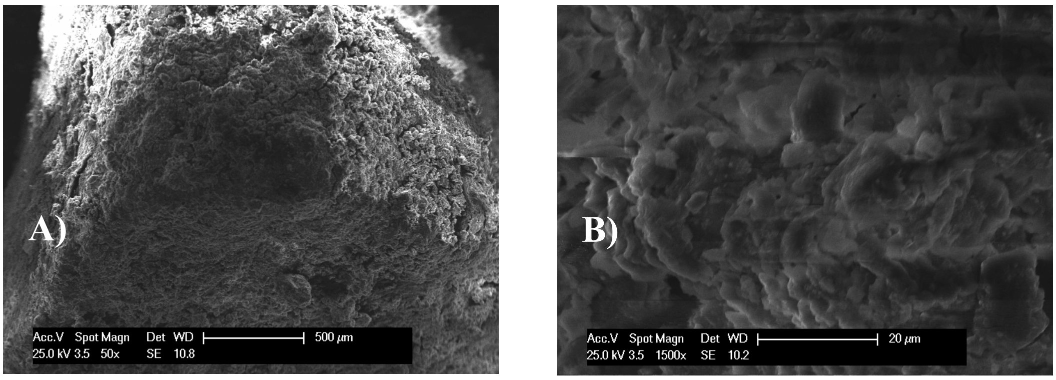

Fig. 6. SEM micrographs of coal particle

A) general view (magn. 50 X) B) surface detail (magn. 1500 X)

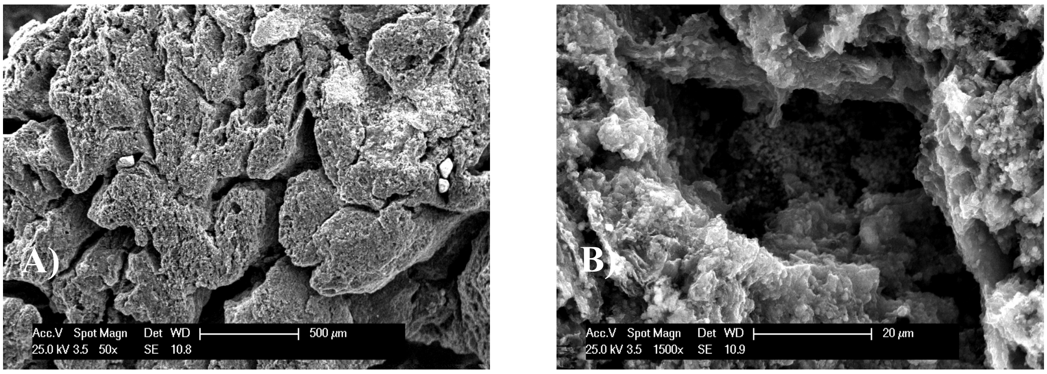

Fig. 7. SEM micrographs of unburned carbon particle

A) general view (magn. 50 X) B) surface detail (magn. 1500 X)

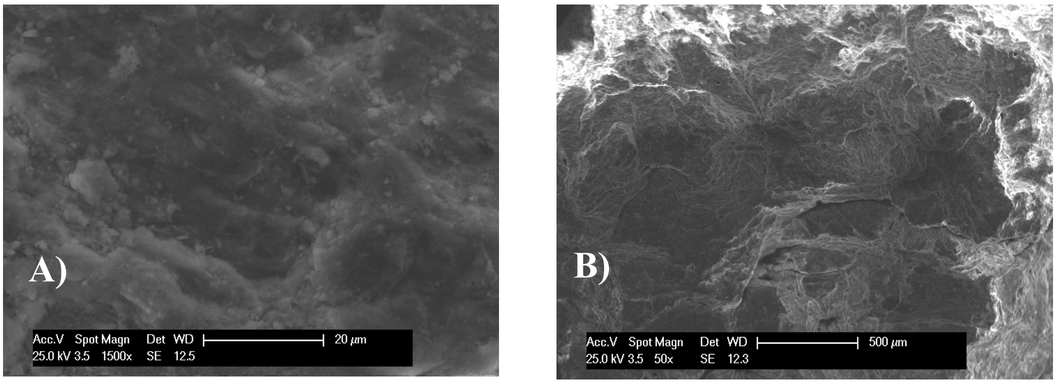

Fig. 8. SEM micrographs of bottom ash

A) general view (magn. 50 X) B) surface detail (magn. 1500 X)

CONCLUSIONS

Analysis of mineral phases indicated that the most abundant minerals in the coal were quartz and kaolinite and in unburned carbon it was quartz and anatase. In bottom ash and fly ash except quartz and anatase also Ca-bearing minerals were observed as the dominant phases – lime and anhydrite, which was brought about by the addition of limestone to coal during the combustion process.

Behaviour of elements within the combustion chamber was evaluated through the comparison of the elemental contents in the coal, unburned carbon and bottom ash. The volatile behaviour was obtained for As, Cl, Br, S, Zn, Se (and to a less extent also for Ga), typical non-volatile character was observed in case of Rb, W, V, Cu, Ni and rather slightly also for Pb and Th. Behaviour of Ge corresponded with average burn-up trend of coal particle.

The study of surface morphology of the coal, unburned carbon and bottom ash revealed the highly-developed system of pores and ruptures in unburned carbon grain, while the coal and bottom ash particle did not show such porous structure. High specific surface area of unburned carbon (194 m^2/g) corresponds with porous character of this material.

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