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# Characterization of unburned carbon from ash after bituminous coal and lignite combustion in CFBs

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#### Abstract

This paper deals with the characterisation of carbon (UC) from bottom ash (BA) and fly ash (FA) samples from two fluidised-bed power stations burning bituminous coal and lignite. The laboratory results for the carbon determinations and its mass balances are evaluated. Chemical and mineral analyses and textural characteristics (specific surface area and pore-size distribution) are presented. Depletion/enrichment of selected elements (S, Cl, V, Cr, Ni, Cu, Zn, As, Se, Sb, Hg, and Pb) in carbon from the bottom ash are compared with both ash compositions. The strong positive relationships between the concentrations of some trace element contents (Hg, Se, As, Cu, Ni, V and Cl) in fly ash with the content of carbon and the specific surface area of FA are presented and expressed by regression equations with very high correlation coefficients. Laser ablation-ICP–MS has been used to obtain an insight into element distributions within carbon grains from the bottom ash.

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Keywords: Coal combustion; Unburned carbon; Trace elements

#### 1. Introduction

The presence of carbon (UC) in solid coal combustion products is a measure one of the efficiency of coal/lignite combustion [1–4]. Even if the carbon content in the ash is only several percent, the loss of energy is huge due to vast amount of coal combustion residues produced every year. In 1999, for example, 55 million tonnes of coal combustion products were produced in Europe (EU 15) [5]. With 2–5% carbon content in the ash this equates to 1.1-2.7 million tonnes of carbon lost each year. The amount of carbon and its properties are affected by the chemical composition of the coal, the coal petrography, coal preparation [6–8]

and by the combustion conditions (combustion temperature, air preheat, excess air, residence time, boiler output, etc. [6,9,10]). In addition to the loss of energy the presence of carbon in the ash increases the costs for ash transport and storage and makes ash utilization more difficult because of adverse effects on the material properties [11].

The amounts of toxic elements released from coal into flue gas depends on coal type, composition, modes of element occurrence and the combustion technology [12–14]. In recent years the possibility of utilizing the carbon for adsorption of volatile elements (e.g. Hg, Se) and their compounds from flue gas (at about 200 °C) has been intensively studied e.g. [15–18]. According to Maroto-Valer et al. [19] and Baltrus et al. [20] the specific surface area of carbon before activation usually ranges from 12 to 40 m<sup>2</sup>/g, which is insufficient for effective flue gas cleaning [19,20]. For the carbon to be more effective as a sorbent it is necessary to activate it by steam or by CO<sub>2</sub>. This process increases the specific surface area from about 40 m<sup>2</sup>/g up to about

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 $600-700 \text{ m}^2/\text{g}$  [9,21] depending on the bulk physicochemical properties [22]. Activated carbon could therefore be a very good low-cost sorbent.

This paper deals with properties of carbon present in bottom and fly ashes from two CFB power stations combusting bituminous coal and lignite respectively. This extends our earlier study based on these power stations looking at element partition between bottom ash, fly ash and emissions [23].

# 2. Experimental

#### 2.1. Samples

At power stations in Poříčí and Tisová bituminous coal and lignite are combusted in CFBs. In Poříčí Power Station electrostatic precipitators are installed for removing fly ash, whereas in Tisová Power Station this is achieved with fabric filters. Further technical data on the combustion facilities have already been presented [23].

Samples of coal and ash were collected at regular time intervals. Carbon particles were separated from the bottom ash by hand, but in the fly ash the particle size was too small for successful separation of the carbon even using laboratory flotation.

Ash samples were also fractionated using 2.0, 1.0, 0.4 and 0.2 mm sieves for the bottom ash and 0.15, 0.09 and 0.04 mm sieves for the fly ash. For the chemical and mineral analyses all samples were ground, milled and homogenized, while the determinations of pore size and specific surface area were performed using non-ground samples.

## 2.2. Methods

For the determination of UC in the ash samples (coal residue in ash expressed as carbon wt%) the infrared emission spectrometry [2,24], photo acoustic measurements [25] and the loss of ignition (LOI) at 815 °C are widely performed [7]. In this paper the content of UC (expressed as

carbon wt%) in ash samples was determined by oxidation of carbon with oxygen (forming  $CO_2$ ) followed by infrared absorption measurement (Leco CS-244). Before the UC determination the ash samples were treated with 15% HCl (1 h) at ambient temperature to remove carbonates.

Chemical analyses of major, minor and trace elements in solid samples were performed by means of XRF using an energy-dispersive spectrometer (EDS) SPECTRO X-LAB; Hg was determined using AMA 254. The mineral composition of the coal, UC samples and the bottom ash were identified using X-ray powder diffraction (INEL X with PCD, Ge monocrystal, and Cu-K<sub> $\alpha$ </sub> radiation) using low-temperature ash (380 °C) of these samples. Laser ablation-ICP–MS was used to determine the distribution of elements in the carbon grains separated from bottom ash. The analysis was performed on Cetac LSX–200 Nd YAG (266 nm) in combination with ICP–MS (Agilent Technologies–AT 4500).

BET surface area measurements were carried out on Sorptomatic 1990 (termo-Finnigan) using adsorption of nitrogen at 77 K and the pore-size distribution in carbon and coal samples was determined by means of mercury porosimetry (Micromeritics – Autopore IV). Photomicrographs of carbon particles were taken with a scanning electron microscope (SEM) Philips XL 30, equipped with energy-dispersive microanalyser EDAX.

## 3. Results and discussion

#### 3.1. Characterisation of coal and coal combustion products

#### 3.1.1. Chemical and mineral composition

The chemical analyses of selected elements and ash contents of coal (C), bottom ash (BA), fly ash (FA) and unburned carbon (UC) separated from BA are given in Table 1. Ash content (A) and sulphur are given in %, other elements in ppm.

In Table 2 mass flow of coal  $(m_{\rm C})$ , bottom  $(m_{\rm BA})$  and fly  $(m_{\rm FA})$  ashes are presented as well as weight percentages

Table 1

Chemical analyses of coal (C), unburned carbon from bottom ash (UC), bottom ash (BA) and (FA) at bituminous coal and lignite combustion

	Bituminous coal combustion				Lignite combustion			
	С	UC	BA	FA	С	UC	BA	FA
A (%)	31.66	37.42	97.86	95.07	26.80	52.65	92.41	97.03
S (%)	0.50	0.41	1.08	1.17	1.34	0.81	3.11	3.55
Cl (ppm)	348	276	193	184	155	164	189	186
V	90	137	115	211	239	496	277	631
Cr	42	62	88	115	56	107	98	154
Ni	34	44	48	108	27	54	35	80
Cu	43	76	91	159	186	548	182	577
As	7.1	5.6	9.4	29	14	12	24	28
Se	1.2	1.0	0.65	5.7	4.4	4.8	1.2	13.9
Sb	8.9	10	9.8	33.9	0.40	1.2	0.70	1.20
Hg	0.130	0.100	0.006	0.540	1.580	0.011	0.005	1.180
Pb	39	44	53	168	9.7	26	17	28

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