

On Unburned Carbon in Coal Ash from Various Combustion Units

L. Bartoňová, D. Juchelková, Z. Klika, and B. Čech

Abstract—Work is focused to the study of unburned carbon in ash from coal (and wastes) combustion in 8 combustion tests at 3 fluidised-bed power station, at co-combustion of coal and wastes (also at fluidized bed) and at bench-scale unit simulating coal combustion in small domestic furnaces. The attention is paid to unburned carbon contents in bottom ashes and fly ashes at these 8 combustion tests and to morphology of unburned carbons. Specific surface area of coals, unburned carbons and ashes and the relation of specific surface area of unburned carbon and the content of volatile combustibles in coal were studied as well.

Keywords—Coal combustion, emissions, toxic elements, unburned carbon.

I. INTRODUCTION

ACCORDING to International Energy Agency (2008) and World Coal Association, coal covers about 41% of electricity generation today in worldwide scale; in some countries the proportion is even significantly higher, e.g. in South Africa (93%), Poland (92%), PR China (79%), Australia (77%), India (69%), USA (49%), Germany (46%) etc. In the Czech Republic the share is about 60%. Moreover, the importance of coal in electricity generation in near future is thought to increase up to 44% worldwide [1]. Even if modern coal combustion technologies are being tested and used, coal combustion is still accompanied by negative impact on the surrounding environment, from which the release of emissions containing toxic elements is one of the most significant. Since the efficiency of particulate control devices is generally high, the most problematic elements are those that remain in flue gas in gaseous form coming through the precipitator or fabric filter. For the retention of these volatile elements (such as Hg, Cl, Br, As, Se etc.) many adsorbents are being tested [2-4], from which the most common is the adsorption of Hg on activated carbon [5-7]. Even if the adsorption efficiency of activated carbon is generally good, rather problematic is somewhat high cost of this material. This is the reason why some new precursors are being sought. Many waste materials are being tested because their possible utilization would bring another benefit. This work deals with unburned carbon – carbonaceous particles of unburned coal present to greater or lesser extent in all ashes. The particular attention was paid to the unburned carbon content in ashes collected at various coal combustion units as well as to unburned carbon adsorption characteristics in terms of the

retention of volatile elements from flue gas during the coal combustion.

II. EXPERIMENTAL

A. Combustion Units and Samples

This work was focused to the study of unburned carbon from ashes collected at the coal combustion at various combustion units. In Poříčí and Tisová power stations the bituminous coal and lignite were combusted along with limestone (due to desulphurization of emissions) in circulating fluidized bed. These two power stations were labeled in tables and figures as FC1 and FC2 (i.e. fluidized combustion 1 and 2) [8,9]. At the third atmospheric fluidized-bed power station (FC3) lignite was combusted also with limestone. In this power station three samples of fly ash from the three sections of electrostatic precipitator were collected. At Štětí two combustion tests were carried out, where lignite, limestone and various waste materials we co-combusted. During Test 1 waste wood and tree-bark were used (FWC1 – fluidized waste combustion 1), during Test 2 it was wood, tree-bark, waste paper, fabrics, rubber and sewage sludge (FWC2). And for the comparison also 3 combustion tests were carried out in the bench-scale combustion unit simulating coal combustion in small domestic combustion furnaces. In this combustion unit three different coals (lignites with different ash and S content) were combusted without the addition of limestone (labeled as “house combustion” HC 1-3). All coal and ash samples collected at the combustion units were ground, milled and homogenized in order to prepare representative analytical samples. Unburned carbon particles were separated from bottom ash by hand.

B. Methods

Unburned carbon content in ash samples was determined on Leco CS-244 equipment (the determination is based on infrared absorption measurement). Prior to the measurement itself the samples were leached in dilute HCl (1:1) in order to dissolve carbonates, which could misrepresent the results. Specific surface area determination was performed on Sorptomatic 1990 (Thermo Finnigan) using BET method and nitrogen adsorption. Analysis of Cl, Br and Ni was carried out by polarized-beam X-ray fluorescence spectrometry on SPECTRO XEPOS. The scanning electron micrographs were taken on SEM Philips XL-30. The determination of volatile combustible matter was performed in covered crucible in muffle furnace at 850°C for 7 minutes.

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III. UNBURNED CARBON CONTENT IN ASH

So far, unburned carbon in ash has represented above all the decrease in combustion efficiency, but currently its content in ash is important also in terms of the possible utilization of this material, e.g. as an adsorbent preparation. Unburned carbon contents in ashes collected in 8 various coal combustion tests in 4 combustion units are given in Table I.

TABLE I

UNBURNED CARBON CONTENT IN ASH AT VARIOUS COMBUSTION TESTS
(BA = BOTTOM ASH, FA = FLY ASH)

Combustion unit	Ash type	Unburned carbon content (%)
FC 1	BA	1,23
	FA	5,57
FC 2	BA	0,64
	FA	0,05
FC 3	BA	0,38
	FA Section 1	1,29
	FA Section 2	3,98
FWC 1	BA	1,26
	FA	1,30
FWC 2	BA	0,43
	FA	0,76
HC 1	BA	32,90
	FA	-*
HC 2	BA	26,18
	FA	-*
HC 3	BA	21,15
	FA	-*

* Not measured (small amount of soot sample)

Data given in Table I indicates quite low contents of unburned carbon in fluidized-bed combustion units, usually lower than several %. The comparison of unburned carbon contents in the three fluidized-bed power station where only coal and limestone (without wastes) were combusted showed that the slightly higher contents of unburned carbon were obtained in FC1 differing from the other two power stations by the fact that it was the only combustion test where bituminous coal was combusted. So generally lower reactivity of bituminous coal (related to low rank coals) likely brought about the slightly higher unburned carbon content in ashes. Unburned carbon contents determined for lignite and wastes co-combustion are nearly the same as those measured for lignite combustion at fluidized-bed power stations without the addition of wastes. The highest unburned carbon contents occurred in ashes from the combustion unit simulating the coal combustion in small domestic furnaces. Specific Surface Area of Coal, Unburned Carbon and Ash Specific surface areas of coals, unburned carbons separated from bottom ashes and bottom ashes are given in Table II.

TABLE II

SPECIFIC SURFACE AREA (SBET) OF COAL, UNBURNED CARBON AND BOTTOM ASH (m^2/g)

	Coal	Unburned carbon	Bottom ash
FC 1	39	44	9
FC 2	16	154	18
FC 3	30	168	21
FWC 1	31	80	13
FWC 2	21	59	20
HC 1	48	152	21
HC 2	33	201	28
HC 3	21	254	26

The data given in Table II suggest that the highest specific surface areas were determined in all combustion tests for unburned carbons; the values obtained for coals and ashes were significantly lower. The highest unburned carbon porosity could be explained through the liberation of volatile combustible matter out of the coal particle leaving pores and ruptures in the resulting unburned carbon grain. The effect of coal rank (expressed as V^{daf}) on the specific surface area of unburned carbon was studied as well and the results are given in Fig. 1.

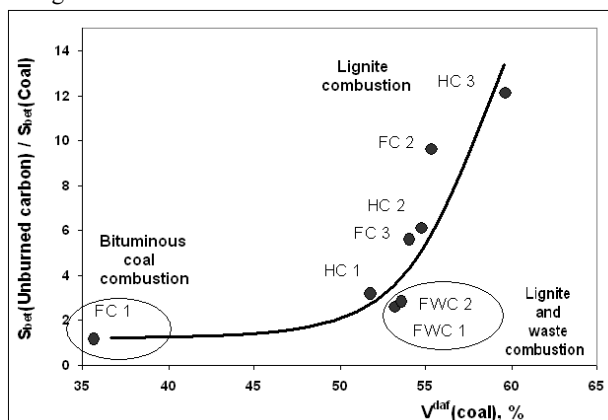


Fig. 1 Increase in specific surface area of unburned carbon in the dependence of the content of volatile combustibles in coal

Owing to the different values of specific surface area of the parent coals these values were taken into account - therefore against the V^{daf} values of parent coals not S_{bet} of unburned carbons but the ratio of $S_{\text{bet}}(\text{unburned carbon}) / S_{\text{bet}}(\text{Coal})$ was plotted. Fig. 1 suggests that the content of volatile combustible matter in coal has a strong effect on the porosity of unburned carbons originating from these coals. Generally low content of volatile combustibles in bituminous coal brought about also very low increase in specific surface area when this coal was combusted and unburned carbon created. On the other hand, significantly high content of volatile matter in lignites increases the porosity of unburned carbons considerably. The specific surface area of unburned carbon can be even 12-times higher than that of coal if the coal contains about 60% of volatile combustibles (V^{daf}). In Fig. 1

the results for co-combustion of lignite and waste materials were plotted as well and it can be observed that these two values (FWC1 and FWC2) nearly do not differ from the other values obtained for the combustion without wastes.

IV. CORRELATIONS BETWEEN UNBURNED CARBON AND ELEMENTAL CONTENT IN ASH

In FB 3 power station, three fly ashes from three sections of electrostatic precipitator were available in sufficient amount. Therefore these three fly ash samples were subjected to dry fractionation on sieves, which provide altogether 29 fly ash particle-size fractions. In all these fractions the unburned carbon contents were determined as well as the contents of Cl, Br and Ni. The contents of the three elements were plotted against the unburned carbon contents in order to examine the mutual relations. The graph obtained for Cl is given in Fig. 2, for Br in Fig. 3 and the same for Ni is shown in Fig. 4.

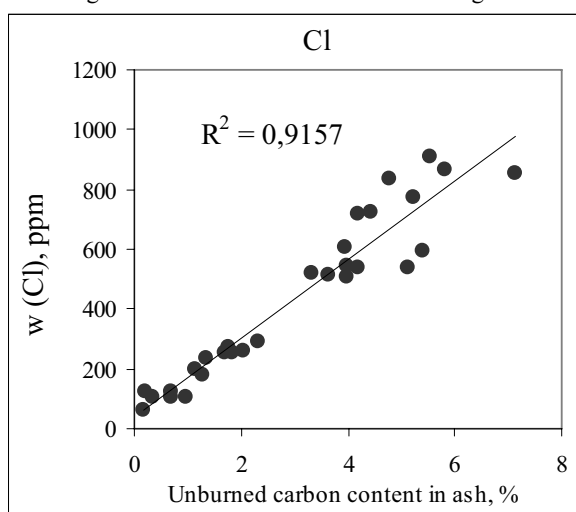


Fig. 2 Content of Cl vs. unburned carbon content in 29 particle-size fractions of fly ash (FC 3)

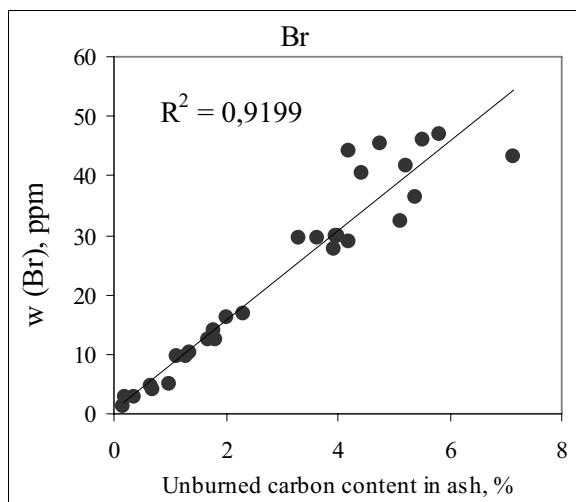


Fig. 3 Content of Br vs. unburned carbon content in 29 particle-size fractions of fly ash (FC 3)

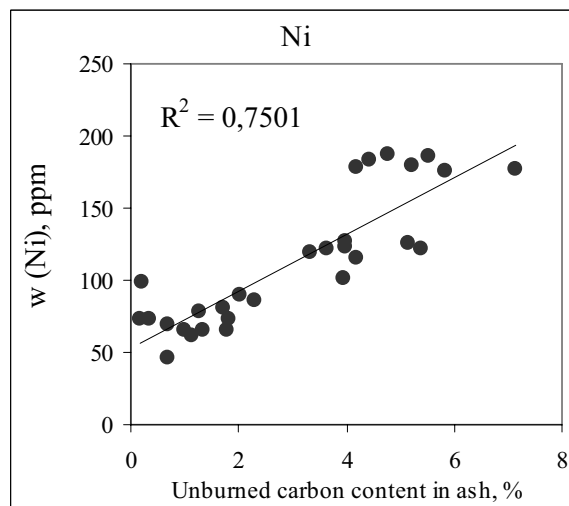


Fig. 4 Content of Ni vs. unburned carbon content in 29 particle-size fractions of fly ash (FC 3)

The values plotted in Figs. 2-4 indicate strong and significant relation between the content of Cl, Br or Ni and unburned carbon content, since the correlation coefficients are very high, especially in case of Cl and Br. Significant relation between Hg, Se, As, S, Ni and Cu and unburned carbon content was also observed in case of FC 1 and FC 2, which has already been reported earlier [10]. This observation could have a significant importance in terms of the preparation of adsorbents using unburned carbon, which is currently only a waste material that even complicates the utilization of fly ashes in cement production.

V. MORPHOLOGY OF UNBURNED CARBON PARTICLES

Since the unburned carbon is promising material for the preparation of adsorbents, its surface structure and morphology were studied using scanning-electron-microscope micrographs, which are given for two different unburned carbons in Figs. 5 and 6. The former micrograph was taken from unburned carbon originating from bituminous coal and the latter relates to unburned carbon from lignite (combusted in CF 3 power station).

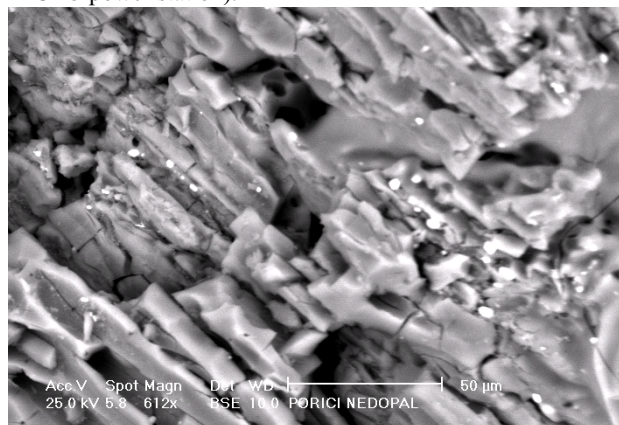


Fig. 5 Morphology of unburned carbon particle originating from bituminous coal (combusted in CF 1)

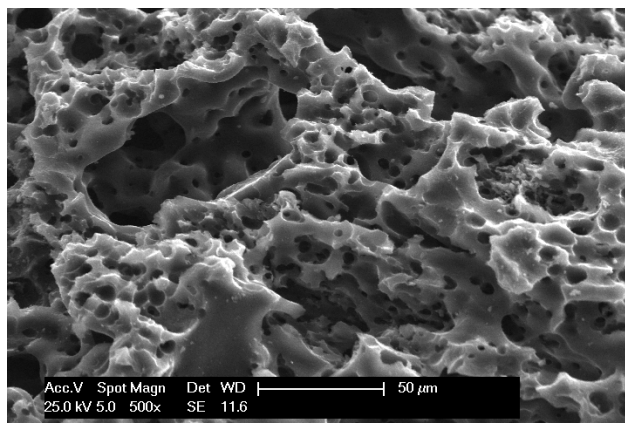


Fig. 6 Morphology of unburned carbon particle originating from lignite (combusted in CF 3)

Figs. 5 and 6 show that the surface structure of both carbons are rather different coming from different nature of parent coals (especially different content of volatile combustible matter). The magnification shown in Figs. 5 and 6 can be used also for the approximate assessment of pore sizes – the pores shown in these SEM micrographs are macropores. Therefore some caution is needed in evaluation of this structure in relation to specific surface areas given above, since specific surface area increases above all with the increasing abundance of micropores that cannot be seen in Figs. 5 and 6. Nevertheless, large pores are also of some significance in adsorption processes because they enable the access to small pores where adsorption itself takes place.

VI. CONCLUSION

As the results presented in this work suggest, it can be concluded that unburned carbon particles separated from coal-combustion ash show advantageous properties in terms of adsorbent preparation and that it could be a promising and cheap precursor of activated carbon production.

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