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## Effect of unburned carbon content in fly ash on the retention of 12 elements out of coal-combustion flue gas

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### Abstract

The aim of this study was to evaluate whether unburned carbon particles present in fly ash can help in the retention of S, Cl, Br, As, Se, Cu, Ni, Zn, Ga, Ge, Rb, and Pb out of flue gas during the coal combustion at fluidised-bed power station where the coal was combusted along with limestone. The competitive influence of 10%–25% CaO in fly ashes on the distribution of studied elements was studied as well to be clear which factor governs behaviour of studied elements. Except of S (with significant association with CaO) and Rb and Pb (with major affinity to  $Al_2O_3$ ) the statistically significant and positive correlation coefficients were calculated for the relations between unburned carbon content and Br (0.959), Cl (0.957), Cu (0.916), Se (0.898), Ni (0.866), As (0.861), Zn (0.742), Ge (0.717), and Ga (0.588) content. The results suggest that the unburned carbon is promising material in terms of flue gas cleaning even if contained in highly calcareous fly ashes.

**Key words:** unburned carbon; coal combustion; fluidised bed; trace elements; emissions; retention

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### Introduction

Total worldwide quantity of coal combustion wastes produced in large power stations (estimated in the early 1990s) exceeds undoubtedly 550 Mt per year (Adams et al., 2005; Manz, 1997). Fraction of unburned carbon (UC) in coal ashes varies considerably according to ash character (bottom ash, fly ash etc.) and mainly depending on coal rank and the type of combustion unit. Estimating average unburned carbon content in ash as 3% – there is 16.5 Mt of unburned carbon that is being produced annually. Unburned carbon properties depend mainly upon coal rank and operational conditions. Nevertheless, it is generally accepted that unburned carbon is a material with promising porous structure which leads to an effort to use this waste material as a low-cost adsorbent (Baltrus et al., 2001; Bartoňová et al., 2009, 2010; Batra et al., 2008; Bunt et al., 2009; Hurt et al., 1995; Izquierdo and Rubio, 2008; Maroto-Valer et al., 2001, 2002; Xu et al., 2009).

Another important problem when fossil fuels are used for electricity generation is the emissions of toxic pollutants. During the combustion, heavy metals and other toxic trace elements originally present in coal are redistributed among bottom ash, fly ash and emissions. The most problematic is the distribution of vaporized elements between the flue gas particles and gaseous phase because

the elements bound in solid particles are efficiently captured in electrostatic precipitator (ESP) or fabric filter whereas the gaseous fraction of toxic elements easily penetrates through the particulate control device directly into atmosphere.

This concerns above all the most volatile elements, such as Hg, As, Cl, Br, or Se. Depending on the coal characteristics and the operational conditions during the combustion, the fractions of these elements released into atmosphere in gaseous form can reach in some cases as much as 80%–90% or even more (Germani and Zoller, 1998; Huang et al., 2004; Klein et al., 1975; Klika et al., 2001; Meij et al., 1986, 1994; Xu et al., 2004; Yi et al., 2008).

This is the reason why many researchers directed their effort toward the retention of these vaporized elements on some fly ash constituents or using another adsorbent added during the combustion. Polluting gas can be cleaned by fly ash (Harja et al., 2008), promising results were obtained by unburned carbon particles in fly ash (Bartoňová et al., 2007; Hassett and Eylands, 1999; Hower et al., 1999, 2000, 2010; López-Antón et al., 2007; Sakulpitakphon et al., 2000) or by means of Ca-bearing additives, aluminosilicate adsorbents etc. (Furimsky, 2000; Chen et al., 1999; Senior et al., 2000; Sterling and Helble, 2003; Zhao et al., 2008).

Serre and Silcox (2000), Hower et al. (1999, 2000, 2010), Hassett and Eylands (1999), and Sakulpitakphon

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(2000) tested fly ashes from large-scale power stations for the retention of Hg from flue gas concluding that higher unburned carbon content in fly ash is advantageous for the retention of Hg. Unfortunately, works dealing with the possible retention of other elements on unburned carbon particles are rather rare (Bartoňová et al., 2007; López-Antón et al., 2007; Vassilev et al., 2000).

While the effect of unburned carbon is usually studied using real power-station fly ashes, the effect of other adsorbents is usually tested using bench-scale or pilot-scale furnaces due to the possibility of changing more parameters and conditions than it is possible in large power stations. Based on the bench-scale results the positive influence of some adsorbents (Ca-based adsorbents, kaolinite, alumina etc.) on the retention of trace elements were reported (Sterling and Helble, 2003; Furimsky, 2000; Chen et al., 1999; Zhao et al., 2008).

This work was focused on the evaluation of the effect of unburned carbon content on distribution of 12 selected elements (S, Cl, Br, As, Se, Cu, Ni, Zn, Ga, Ge, Rb, and Pb) in particle-size fractions of fly ashes collected at three ESP hoppers at fluidised-bed coal combustion power station.

There are at least three reasons why we decided to carry out this study: (1) this work is based on the real power-station samples (where all real operational conditions in power station are involved in the fly ash characteristics); (2) all these samples contain naturally also rather high CaO content (10%–25%), which enables us to take also this (maybe competitive) factor into account; (3) to the best of our knowledge – the effect of unburned carbon (in real and at the same time rather calcareous fly ashes) on the redistribution of as much as 12 elements have not been studied yet.

Thus, the main aim of this work was to evaluate whether unburned carbon in fly ashes can (or can not) help with the retention of many toxic elements out of the coal – combustion flue gas even in highly calcareous ashes.

## 1 Materials and methods

The samples were collected at Energetika Třinec – fluidised-bed power station where lignite and limestone was combusted at 850°C (the desulphurization of emissions was achieved by means of dry desulphurization method). The four-sectioned electrostatic precipitator (working at 142–145°C) is installed in this power station for the retention of solid particles out of the flue gas.

During the whole combustion test, at regular time intervals the partial samples of the fly ashes from the first three hoppers of electrostatic precipitator (ESP) were collected. Since majority of solid particles is captured in the first three rows of the precipitator, the fly ash from the fourth row was not studied due to insufficient amount. Fly ash was collected under the three hoppers separately, which enables us to study three separate fly ash samples within 1 combustion test. Each ash sample was then mixed properly and using quartering method about 5-kg samples of all the ashes were set apart for the analysis in the laboratory.

The three fly ash samples (collected under the three

ESP hoppers) were further separated into particle-size fractions using dry separation method on the following sieves: 0.032, 0.036, 0.040, 0.050, 0.053, 0.056, 0.063, 0.071, 0.080, 0.090, 0.100, and 0.125 mm and the yields of all the fractions were recorded.

In all fly ash samples (three bulks and all the particle-size fractions) the unburned carbon content was determined on Leco CS-244 (the determination is based on infrared absorption measurement). Prior to the measurement of carbon content, the samples were leached with dilute HCl (1:1, V:V) to dissolve carbonates, which could otherwise have misrepresented the results. In all ash samples the contents of major, minor and trace elements were determined by polarized-beam X-ray fluorescence spectrometry on SPECTRO XEPOS. Ash content in all the studied samples was determined gravimetrically in muffle furnace at 815°C. Calculations of pair correlation coefficients (including the evaluation whether they are statistically significant or not) was performed using Trilobyte statistical software QC Expert (v. 2.7).

## 2 Results and discussion

### 2.1 Analysis of fly ash samples

Fly ash samples collected under the three hoppers of electrostatic precipitator were dry-sieved providing altogether 26 particle-size fractions. All these fractions are listed in Table 1. All the results for the three bulk fly ashes (3 hoppers of ESP) and 26 particle-size fractions (prepared from them) are also summarized in Table 1.

Above all, this study was focused to the evaluation of the possible effect of UC content on the retention of 12 elements out of the flue gas: S, Cl, Br, As, Se, Cu, Ni, Ga, Ge, Pb, Zn, and Rb. Considering the results of other researchers (Furimsky, 2000; Chen et al., 1999; Senior et al., 2000; Sterling and Helble, 2003; Zhao et al., 2008), we can conclude an effect of Ca-bearing additives or aluminosilicate adsorbents on the retention of studied elements during bench-scale combustion tests, the effect of CaO and Al<sub>2</sub>O<sub>3</sub> content in the studied samples was evaluated as well to be clear that the distribution of elements is given by the very unburned carbon and not by CaO or Al<sub>2</sub>O<sub>3</sub> content.

Distribution of unburned carbon within the particle-size fraction of all the three fly ash samples is demonstrated in Fig. 1a, while the same for CaO and Al<sub>2</sub>O<sub>3</sub> is given in Fig. 1b.

Columns plotted in Fig. 1a suggest significantly higher UC content in fly ash samples collected under the 2nd and 3rd hopper of ESP, average UC content in fly ash from the 1st section is about 1%, the remaining two sections produced fly ash with 4%–5% UC. Distribution of CaO and Al<sub>2</sub>O<sub>3</sub> within the three sections (and particle-size fractions) varies not so significantly as in case of UC.

### 2.2 Correlations between the contents of 12 studied elements and unburned carbon, CaO, and Al<sub>2</sub>O<sub>3</sub> content

Pair correlation coefficients  $R$  between the contents of

**Table 1** Chemical analysis of bulk and particle-size fractions (mm) of fly ash collected at the 1st, the 2nd and the 3rd hoppers (including the yield of the fraction, ash content and unburned carbon (UC) content)

	Particle-size fraction (mm)														
	BULK 1	< 0.032	0.032– 0.036	0.036– 0.040	0.040– 0.050	0.050– 0.053	0.053– 0.056	0.056– 0.063	0.063– 0.071	0.071– 0.080	0.080– 0.090	0.090– 0.100	0.100– 0.125	> 0.125	
Fraction (%)	100.00	6.55	8.84	4.73	9.3	13.57	5.49	12.5	8.53	3.81	9.91	5.03	6.4	5.34	
Ash (%)	97.78	95.86	95.94	96.63	96.32	96.44	96.9	97.08	97.26	97.42	98.15	98.12	98.61	98.38	
UC (%)	1.29	2.31	2.03	1.78	1.70	1.83	1.35	1.14	0.99	0.70	0.68	0.36	0.17	0.20	
MgO (%)	0.42	0.50	0.51	0.36	0.42	0.44	0.48	0.34	0.35	0.32	0.45	0.32	0.37	0.33	
Al <sub>2</sub> O <sub>3</sub> (%)	19.85	18.11	18.61	17.83	17.78	18.20	19.05	19.17	21.76	19.92	22.60	23.52	25.57	28.00	
SiO <sub>2</sub> (%)	41.89	37.52	38.65	36.28	37.97	37.49	39.12	39.36	46.40	42.93	47.22	50.05	53.11	47.28	
P <sub>2</sub> O <sub>5</sub> (%)	0.39	0.47	0.49	0.43	0.46	0.46	0.43	0.34	0.35	0.29	0.40	0.36	0.35	0.38	
K <sub>2</sub> O (%)	1.53	1.28	1.32	1.32	1.31	1.34	1.42	1.51	1.85	1.69	1.99	1.97	2.19	1.81	
CaO (%)	20.25	24.02	22.52	24.74	23.99	23.27	21.59	22.75	15.83	21.12	15.22	12.90	9.63	12.04	
MnO (%)	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.06	0.05	0.04	0.04	
Fe <sub>2</sub> O <sub>3</sub> (%)	7.00	6.96	7.22	7.93	7.62	8.51	8.84	8.11	6.26	3.71	5.36	4.32	3.70	4.22	
S (%)	2.45	2.69	2.45	2.88	2.65	2.50	2.58	2.42	2.04	2.90	2.17	2.18	1.48	1.73	
Cl (ppm)	182	291	261	270	251	254	236	199	107	123	103	108	61	121	
Ni (ppm)	78	86	89	65	81	73	66	61	65	46	69	73	73	99	
Cu (ppm)	84	107	111	95	99	92	87	68	76	63	68	70	63	71	
Zn (ppm)	99	106	98	90	102	107	89	100	88	69	96	107	116	151	
Ga (ppm)	32	28	30	28	28	31	24	23	28	28	32	37	38	39	
Ge (ppm)	10.4	11.4	10.4	7.1	10.3	10.6	4.9	7.9	6.4	8.3	8.0	10.4	10.5	20.2	
As (ppm)	314	440	489	331	406	377	309	245	212	215	228	214	162	213	
Se (ppm)	5.5	13.5	9.9	7.8	9.7	8.3	7.0	3.7	3.2	1.1	3.1	1.1	1.7	0.6	
Br (ppm)	9.7	16.9	16.1	13.9	12.3	12.5	10.4	9.5	4.9	4.1	4.7	2.8	1.1	2.8	
Rb (ppm)	98	72	77	74	78	76	84	85	105	104	117	136	146	142	
Pb (ppm)	62.8	48.4	55.9	50.8	52.4	51.8	54.7	51.4	67.4	67.9	67.5	78.5	67.1	66.3	
	BULK 2	< 0.032	0.032– 0.036	0.036– 0.040	0.040– 0.050	0.050– 0.063	0.063– 0.080	> 0.080	BULK 3	< 0.040	0.040– 0.050	0.050– 0.053	0.056– 0.063	0.063– 0.080	> 0.080
Fraction (%)	100.00	7.82	8.77	24.41	14.45	27.49	7.58	9.48	100.00	12.10	13.17	32.74	16.37	9.25	16.37
Ash (%)	94.53	93.04	94.42	94.93	94.85	93.94	93.68	94.28	93.63	90.66	93.89	93.89	92.67	92.87	92.89
UC (%)	3.98	5.39	3.99	3.65	3.32	4.20	5.14	3.94	4.78	7.15	4.19	4.43	5.53	5.82	5.22
MgO (%)	0.64	0.66	0.69	0.64	0.64	0.61	0.55	0.67	0.72	0.68	0.70	0.70	0.65	0.71	0.77
Al <sub>2</sub> O <sub>3</sub> (%)	20.14	18.99	19.33	19.65	19.60	19.56	19.73	19.15	19.55	19.70	20.32	20.45	20.47	20.11	20.25
SiO <sub>2</sub> (%)	39.60	38.98	39.02	39.84	40.15	39.77	40.94	41.89	40.97	39.13	40.55	40.57	40.72	42.03	41.35
P <sub>2</sub> O <sub>5</sub> (%)	0.73	0.67	0.73	0.71	0.73	0.70	0.66	0.65	0.74	0.75	0.78	0.78	0.78	0.76	0.77
K <sub>2</sub> O (%)	1.65	1.57	1.62	1.61	1.63	1.61	1.65	1.65	1.57	1.60	1.67	1.67	1.64	1.61	1.60
CaO (%)	18.71	19.69	19.65	19.43	19.01	18.82	17.42	17.99	16.31	16.10	16.36	15.87	15.70	15.80	16.23
MnO (%)	0.06	0.06	0.06	0.06	0.06	0.06	0.05	0.05	0.06	0.05	0.06	0.06	0.06	0.05	0.05
Fe <sub>2</sub> O <sub>3</sub> (%)	6.60	6.16	6.78	6.48	6.72	6.65	5.97	5.88	6.80	6.20	6.50	6.67	6.42	6.32	6.79
S (%)	2.32	2.18	2.33	2.29	2.29	2.18	2.06	2.19	2.47	2.39	2.51	2.48	2.40	2.37	2.40
Cl (ppm)	546	592	507	516	517	541	540	607	834	851	715	722	911	863	772
Ni (ppm)	123	122	127	122	120	116	125	101	187	176	178	183	186	176	180
Cu (ppm)	132	136	132	127	137	121	117	137	158	153	160	165	161	156	170
Zn (ppm)	132	137	127	141	143	137	125	132	162	149	161	165	151	155	165
Ga (ppm)	36	35	34	36	39	31	31	34	41	43	45	42	40	44	44
Ge (ppm)	15.1	12.2	18.4	13.8	16.0	14.0	15.0	12.2	34.0	30.8	33.5	34.9	30.9	30.3	34.7
As (ppm)	470	402	503	481	481	440	461	383	641	602	665	685	651	690	672
Se (ppm)	10.2	12.8	11.7	11	11.8	9.5	11.8	8.6	15.1	18.8	15.3	16	15.7	14.2	13.4
Br (ppm)	30.0	36.4	29.9	29.4	29.6	28.9	32.3	27.7	45.5	43.1	44.1	40.5	46.0	47.0	41.8
Rb (ppm)	86	83	82	84	84	87	89	92	80	78	82	81	80	81	79
Pb (ppm)	61.8	59.0	59.7	63.3	63.5	58.9	61.4	61.6	67.1	69.3	68.1	71.6	68.7	68.4	72.1

12 studied elements and UC, CaO, and Al<sub>2</sub>O<sub>3</sub> contents are given in Table 2. All these calculated correlation coefficients were also subjected to evaluation whether they are statistically significant or not (significance level used was  $\alpha = 0.05$ ). For total number of evaluated data of 29 (3 bulk samples and 26 particle-size fractions) the critical value of correlation coefficient is 0.368 (with increasing number of measured data this value somewhat decreases).

For easier visualization of studied interrelations, the strength of mutual correlations of the 12 elements and UC and CaO content is demonstrated in Fig. 2, where the elements were divided into groups according to the strength of their relation to UC and CaO.

Statistically significant and positive values of correlation coefficient concerning relations with UC were calculated for Cl, Ni, Cu, Zn, Ga, Ge, As, Se, and Br, i.e., for 9 elements of 12 elements studied (they are all situated in the right third of the diagram). The strongest positive relation with unburned carbon was obtained for the most volatile elements: Br, Cl, Cu, Se, Ni, and As (all  $R$  values

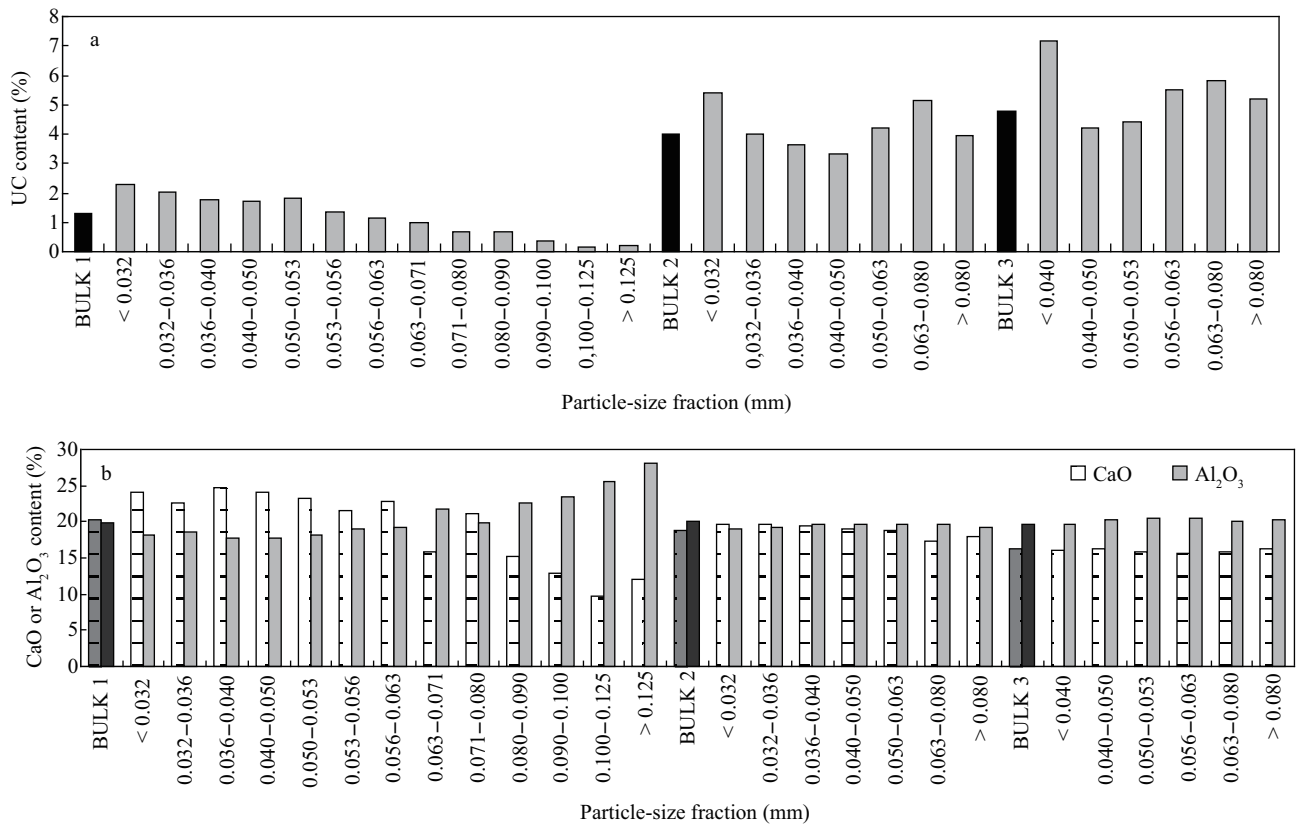
**Table 2** Mutual (pair) correlation coefficients  $R$  for the relations between the studied elements and unburned carbon (UC), CaO, and Al<sub>2</sub>O<sub>3</sub> contents

	UC	CaO	Al <sub>2</sub> O <sub>3</sub>
S	0.107	<b>0.755</b>	<b>–0.761</b>
Cl	<b>0.957*</b>	–0.153	–0.313
Ni	<b>0.866</b>	–0.358	–0.070
Cu	<b>0.916</b>	–0.085	–0.358
Zn	<b>0.742</b>	<b>–0.475</b>	0.144
Ga	<b>0.588</b>	<b>–0.655</b>	0.321
Ge	<b>0.717</b>	<b>–0.424</b>	0.065
As	<b>0.861</b>	–0.012	<b>–0.397</b>
Se	<b>0.898</b>	0.116	<b>–0.523</b>
Br	<b>0.959</b>	–0.113	–0.348
Rb	<b>–0.600</b>	<b>–0.693</b>	<b>0.908</b>
Pb	0.195	<b>–0.834</b>	<b>0.578</b>

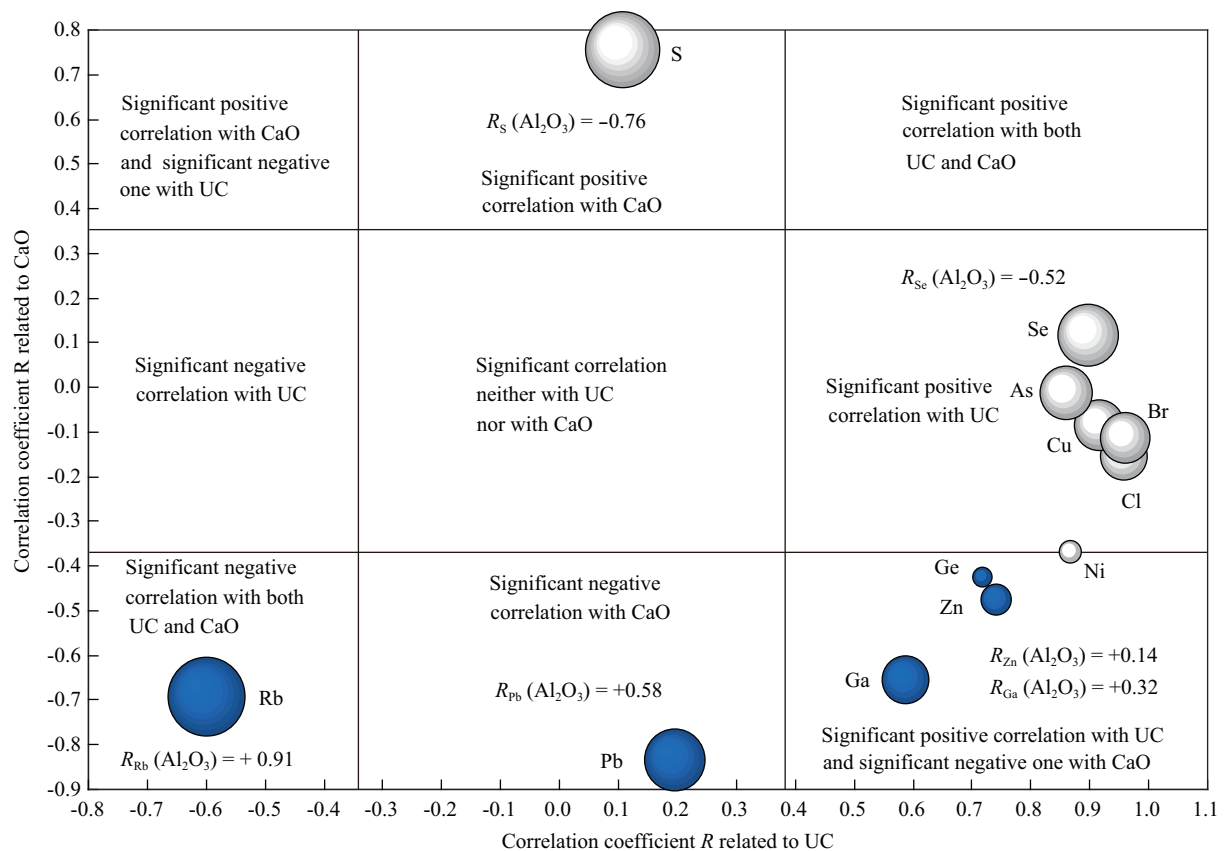
\* Bold-typed values were statistically evaluated as “significant”

are higher than 0.85). Correlation coefficients obtained for Ge, Zn, and Ga are somewhat lower (but still statistically significant).

Sulphur showed the only positive significant relation



**Fig. 1** Distribution of unburned carbon UC (a), CaO and Al<sub>2</sub>O<sub>3</sub> contents (b) within the particle-size fractions of fly ash collected at the 1st, 2nd and the 3rd hoppers of electrostatic precipitator.



**Fig. 2** Correlation coefficients for the relations of 12 elements and unburned carbon (UC), CaO, and Al<sub>2</sub>O<sub>3</sub> contents.

with CaO ( $R = 0.755$ ), it is the only element situated in the upper third of this diagram. This illustrates the interaction

of vaporized SO<sub>2</sub>/SO<sub>3</sub> with Ca-bearing minerals (calcium oxide, portlandite, calcite etc.). The relation between S

and UC was not of greater significance.

In the case of Rb and Pb it was the only  $\text{Al}_2\text{O}_3$  content, for which positive and significant correlation coefficient was calculated. Some caution is needed in the interpretation of this result, it should be reminded that it is the retention of vaporized element out of flue gas that is studied in this work. On the assumption that the elements are vaporized and then condensation/adsorption follows, their increasing contents with increasing content of UC indicates some retention. However, not all of the elements studied in this work are typically volatile. The typical example of non-volatile element in this work is Rb, a lithophile element bound in coal usually in aluminosilicates (which is the very reason of its rather low volatility). Therefore its strong relation with  $\text{Al}_2\text{O}_3$  content in fly ash may be a consequence of its occurrence in aluminosilicates in the coal combusted. Moreover, if very high correlation coefficient between Rb and  $\text{Al}_2\text{O}_3$  had been brought about by its condensation/adsorption out of the flue gas, absolutely no interaction with UC under such conditions would have been rather unlikely.

On the other hand, rather complicated is the situation of Pb, because the volatility of this element varies a lot depending on its association in coal, including sulphides, carbonates, but also aluminosilicates (Finkelman, 1994; Raask, 1985; Spears and Booth, 2002; Swaine and Goodarzi, 1995). Therefore, in case of Pb both explanations are possible, either adsorption of vaporized form onto aluminosilicates or its occurrence in aluminosilicate matrix of coal taking Pb into aluminosilicate matrix of ash.

Except for S, Rb, and Pb the remaining 9 elements (Cl, Ni, Cu, Zn, Ga, Ge, As, Se, and Br) showed dominant association with UC in ash (despite rather high CaO content in these samples); this observation was obtained even in case of acid-forming elements, such as Cl, Br, As or Se.

In this context it should be mentioned that the results supporting the efficient retention of As (or other volatile elements) presented in the literature (Furimsky, 2000; Chen et al., 1999; Sterling and Helble, 2003; Zhao et al., 2008) were usually obtained on bench-scale of pilot-scale combustion units where Ca-bearing adsorbents were tested without the occurrence of unburned carbon grains. Moreover, the combustion/adsorption conditions during these tests may have been somewhat different as in our fluidised-bed power station. The most common and the most significant differences can be the combustion temperature, flue gas composition and the temperature profile during flue gas cooling because the time interval available for the interaction of vaporized elements and the adsorbent may be the critical factor determining whether (even thermodynamically favored) reaction will actually be realized or not.

In other words, even if the reactions of some acid-forming elements (Cl, Br, As, or Se) with Ca-bearing adsorbent are thermodynamically favoured (which was also verified by bench-scale of pilot-scale combustion tests (Furimsky, 2000; Chen et al., 1999; Sterling and Helble, 2003; Zhao et al., 2008), under the conditions

of this fluidised-bed power station where also 1%–5% of unburned carbon was present in fly ash the dominant factor governing the distribution of Cl, Ni, Cu, Zn, Ga, Ge, As, Se, and Br was the unburned carbon content (while the effect of CaO content was not of greater significance). The results obtained in this work undoubtedly suggest that in this power station the condensation/adsorption of Cl, Ni, Cu, Zn, Ga, Ge, As, Se, and Br on unburned carbon particles was preferred to the interaction of these elements with Ca-bearing minerals.

### 3 Conclusions

The main aim of this study was to evaluate whether the unburned carbon particles present in fly ash can help with the retention of Cl, Br, As, Se, Cu, Ni, Zn, Pb, Rb, S, Ga, and Ge out of flue gas during the coal combustion at fluidised-bed power station where the coal was combusted with limestone. The main advantage of this work is that the effect of unburned carbon was evaluated in real fly ash samples containing also quite high CaO content.

It was found out that except of S (with significant association with CaO), Rb and Pb (with major affinity to  $\text{Al}_2\text{O}_3$ ), the statistically significant and positive correlation coefficients were calculated for the relations between unburned carbon content and Cl, Ni, Cu, Zn, Ga, Ge, As, Se, and Br content. The effect of unburned carbon in fly ash was significant and dominated even over the influence of CaO content. This observation could be brought about by unfavourable time and temperature profile in the power station for the interaction of these elements with CaO; under such conditions it was the very adsorption/condensation of elements onto UC, which was preferred behaviour.

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### References

- Baltrus J P, Wells A W, Fauth D J, Diehl J R, White C M, 2001. Characterization of carbon concentrates from coal-combustion fly ash. *Energy and Fuels*, 15(2): 455–462.
- Bartoňová L, Klika Z, Spears A D, 2007. Characterization of unburned carbon from ash after bituminous coal and lignite combustion in CFBs. *Fuel*, 86(3): 455–463.
- Bartoňová L, Kořistková M, Klika Z, Kolat P, Simha-Martynková G, 2009. Evaluation of elemental volatility in a fluidised bed power station in terms of unburned carbon study. *Chemical and Process Engineering*, 30(3): 495–508.
- Bartoňová L, Kořistková M, Kolat P, Klika Z, Čech B, 2010. Study of unburned carbon and volatility of elements during co-combustion of coal and waste alternative fuel. *Chemical*



- and *Process Engineering*, 31(4): 725–739.
- Batra V S, Urbonaite S, Svensson G, 2008. Characterization of unburned carbon in bagasse fly ash. *Fuel*, 87(13–14): 2972–2976.
- Bunt J R, Wagner N J, Waanders F B, 2009. Carbon particle type characterization of the carbon behaviour impacting on a commercial-scale Sasol-Lurgi FBDB gasifier. *Fuel*, 88(5): 771–779.
- Finkelman R B, 1994. Modes of occurrence of potentially hazardous elements in coal: levels of confidence. *Fuel Processing Technology*, 39(1–3): 21–34.
- Furimsky E, 2000. Characterization of trace element emissions from coal combustion by equilibrium calculations. *Fuel Processing Technology*, 63(1): 29–44.
- Germani M S, Zoller W H, 1998. Vapor-phase concentrations of arsenic, selenium, bromine, iodine, and mercury in the stack of a coal-fired power plant. *Environmental Science and Technology*, 22(9): 145–159.
- Harja M, Bărbuță M, Rusu L, Apostolescu N, 2008. Utilization of coal fly ash from power plants. I. Ash characterization. *Environmental Engineering and Management Journal*, 7(3): 289–293.
- Hassett D J, Eylands K E, 1999. Mercury capture on coal combustion fly ash. *Fuel*, 78(2): 243–248.
- Hower J C, Trimble A S, Eble C F, Palmer C A, Kolker A, 1999. Characterization of fly ash from low-sulphur and high-sulphur coal sources: partitioning of carbon and trace elements with particle size. *Energy Sources*, 21(6): 511–525.
- Hower J C, Maroto-Valer M, Taulbee D N, Sakulpitakphon T, 2000. Mercury capture by distinct fly ash carbon forms. *Energy and Fuels*, 14(1): 224–226.
- Hower J C, Senior C L, Suuberg E M, Hurt R H, Wilcox J L, Olson E S, 2010. Mercury capture by native fly ash carbons in coal-fired power plants. *Progress in Energy and Combustion Science*, 36(4): 510–529.
- Huang Y, Jin B, Zhong Z, Xiao R, Tang Z, Ren H, 2004. Trace elements (Mn, Cr, Pb, Se, Zn, Cd and Hg) in emissions from a pulverized coal boiler. *Fuel Processing Technology*, 86(1): 23–32.
- Hurt R H, Davis K A, Yang N Y C, Headley T J, Mitchell G D, 1995. Residual carbon from pulverized-coal-fired boilers: 2. Morphology and physicochemical properties. *Fuel*, 74(9): 1297–1306.
- Chen J C, Wea M Y, Ou W Y, 1999. Capture of heavy metals by sorbents in incineration flue gas. *Science of the Total Environment*, 228(1): 67–77.
- Izquierdo M T, Rubio B, 2008. Carbon-enriched coal fly ash as a precursor of activated carbons for SO<sub>2</sub> removal. *Journal of Hazardous Materials*, 155(1–2): 199–205.
- Klein D H, Andren A W, Carter J A, Emery J F, Feldman C, Fulkerson W et al., 1975. Pathways of thirty-seven trace elements through coal-fired power plant. *Environmental Science and Technology*, 9(10): 973–979.
- Klika Z, Bartoňová L, Spears A D, 2001. Effect of boiler output on trace element partitioning during coal combustion in two fluidised-bed power stations. *Fuel*, 80(7): 907–917.
- López-Antón M A, Díaz-Somoano M, Abad-Valle P, Matrínez-Tarazona M R, 2007. Mercury and selenium retention in fly ashes: Influence of unburned particle content. *Fuel*, 86(14 spec. iss.): 2064–2070.
- Manz O E, 1997. Worldwide production of coal ash and utilization in concrete and other products. *Fuel*, 76(8 spec. iss.): 691–696.
- Maroto-Valer M M, Taulbee D N, Hower J C, 2001. Characterization of differing forms of unburned carbon present in fly ash separated by density gradient centrifugation. *Fuel*, 80(6): 795–800.
- Maroto-Valer M M, Andrésen J M, Lu Z, Zhang Y, Jones A et al., 2002. Assessment of the commercial utilization of activated carbons produced from high carbon fly ashes. In: *Proceedings of the Technical Sessions Presented by the Conference on Unburned Carbon on Utility Fly Ash*. Pittsburgh, May 14, 2002.
- Meij R, Janssen L H J M, van der Kooij J, 1986. Air pollutant emissions from coal-fired power stations. *Kema Scientific and Technical Reports*, 4(6): 51–69.
- Meij R, 1994. Trace element behaviour in coal-fired power plants. *Fuel Processing Technology*, 39(1–3): 199–217.
- Raask E, 1985. The mode of occurrence and concentration of trace elements in coal. *Progress in Energy and Combustion Science*, 11(2): 97–118.
- Sakulpitakphon T, Hower J C, Trimble A S, Schram W H, Thomas G A, 2000. Mercury capture by fly ash: study of the combustion of a high-mercury coal at a utility boiler. *Energy and Fuels*, 14(3): 727–733.
- Senior C L, Helble J J, Sarofim A F, 2000. Emissions of mercury, trace elements, and fine particles from stationary combustion sources. *Fuel Processing Technology*, 65–66: 263–288.
- Serre S, Silcox G, 2000. Adsorption of elemental mercury on the residual carbon in coal fly ash. *Industrial and Engineering Chemistry Research*, 39(6): 1723–1730.
- Sterling R O, Helble J J, 2003. Reaction of arsenic vapour species with fly ash compounds: kinetics and speciation of the reaction with calcium silicates. *Chemosphere*, 51(10): 1111–1119.
- Spears D A, Booth C A, 2002. The composition of size-fractionated pulverised coal and the trace element associations. *Fuel*, 81(5): 683–690.
- Swaine D J, Goodarzi F, 1995. In: *Environmental Aspects of Trace Elements in Coal*. Kluwer Academic Publishers, The Netherlands. 168.
- Vassilev S V, Eskenazy G M, Vassileva C G, 2000. Contents, modes of occurrence and behaviour of chlorine and bromine in combustion wastes from coal-fired power station. *Fuel*, 79(8): 923–937.
- Xu M, Yan R, Zheng C, Qiao J, Han J, Sheng C, 2004. Status of trace element emission in a coal combustion process: a review. *Fuel Processing Technology*, 85(2–3): 215–237.
- Xu S, Zhou Z, Gao X, Yu G, Gong X, 2009. The gasification reactivity of unburned carbon present in gasification slag from entrained-flow gasifier. *Fuel Processing Technology*, 90(9): 1062–1070.
- Yi H, Hao J, Duan L, Tang X, Ning P, Li X, 2008. Fine particle and trace element emissions from an anthracite coal-fired power plant equipped with a bag-house in China. *Fuel*, 87(10–11): 2050–2057.
- Zhao Y, Zhang J, Huang W, Wang Z, Li Y, Song D et al., 2008. Arsenic emission during combustion of high arsenic coals from Southwestern Guizhou, China. *Energy Conversion and Management*, 49(4): 615–624.

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