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CHARACTERIZATION AND ENVIRONMENTAL IMPACT OF FINE FLY ASH PARTICLES

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Abstract: *Fine dust and ash particles (less than 10 μm) pose a serious risk to the environment and human health. A few million tons are only the fly ashes generated annually by the thermal power plants in Bulgaria. Since they are most often kept in open landfills, they are potential pollutants with harmful elements not only of the air but also of soil and water. The method of electron microanalysis of individual ash particles proposed herein has the advantage of characterizing and classifying them by size, elemental composition, morphology, etc. The most harmful inhaled particles of fly ash enriched of heavy metals are studied in detail.*

ХАРАКТЕРИЗИРАНЕ НА ФИНИ ПЕПЕЛНИ ЧАСТИЦИ И ВЪЗДЕЙСТВИЕТО ИМ ВЪРХУ ОКОЛНАТА СРЕДА

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Ключови думи: *пепелни частици, ТЕЦ, SEM, EDX, замърсяване на околната среда*

Резюме: *Фините частици на прах и пепел (по-малки от 10 μm) представляват сериозен риск за околната среда и човешкото здраве. Няколко милиона тона са само летливите пепели, генерирани годишно от топлоелектрическите централи в България. Тъй като най-често те се съхраняват в открити депа, те са потенциални замърсители с вредни елементи не само на въздуха, но и на почвата и водите. Предложеният тук метод на електронен микроанализ на отделни пепелни частици има предимство при характеризирането и класифицирането им по размер, елементен състав, морфология и т.н. Най-вредните частици на летливата пепел с инхалаторен размер и богати на тежки метали са изследвани подробно.*

Introduction

In recent years a very large number of investigations worldwide have been devoted to the characterization of fly ashes (FA) in order to estimate the potential environmental impact of this waste [1-4]. The chemical composition of coal ashes indicates that they contain a number of toxic and harmful elements (As, Cd, Cl, Co, Cr, Hg, Mn, Ni, Pb, Sb, Tl, U, etc.) [5-10]. The impact on the environment in the long term is difficult to predict sufficient reliability [11, 12]. Coal combustion is estimated as the second serious source of trace element contamination of the environment [10]. Unused fly ash is one of the main problems of all coal-fired power plants. Several million tonnes of this waste product is generated annually by power plants in Bulgaria and most often are disposed in open landfills [13]. The many-tones nature of this waste, as well as some features in the distribution of toxic elements in them, is linked to a number of environmental problems. The physicochemical properties of the fly ash and the respectively released into the environment trace elements depend on the origin of coal, the type of coal burning process, the availability of emission control, the disposal methods, and so on. This can lead to different environmental problems such as air pollution or contamination of soil and groundwater due to leaching of heavy metals. Circulation and accumulation of the finest ash particles (less than 10 μm) further endanger all surrounding populations, including the health of people.

The purpose of this presentation is to determine not only the average chemical composition of the fly ash, generated in some of the biggest Bulgarian thermal power plants but also to clarify the specific characteristics of the individual ash particles. It is also useful to know the distribution of the harmful elements between the ash particles and to predict the possibility of their spontaneous extraction under environmental conditions.

Experimental

Results from some investigations of the chemical composition and morphology of individual particles of fly ashes from six of the biggest coal-burning thermo-power plants in Bulgaria TPPs: "Varna" (V), 2000 MW, "Maritza-3" (M-3), 120 MW, "Bobovdol" (Bd), 660 MW, "Maritza-1" (M-1), 150 MW, "Republika" (Rep), 460 MW, and "Russe Iztok" (RI), 400 MW (fly ash mixed with slag), are briefly presented. All fly ash materials are previously sieved and the finest fractions are analyzed, namely fractions < 0.125 mm for V, Bd, M-1, M-3, and Rep, and a fraction < 0.2 mm for RI.

Scanning electron microscopy (SEM) for determination of the shape and sizes of the ash particles is used. Images in both SEI (formed by secondary electrons) and BEI (formed by back-scattered electrons) modes are obtained and compared. SEI mode is used to observe details in the morphology and surface structure of the particles, while BEI regime is used to search for particles enriched of heavy metal, i.e. having average atomic number higher than that of the background particles. An illustration of one and the same ash objects in both modes is presented in Fig. 1.

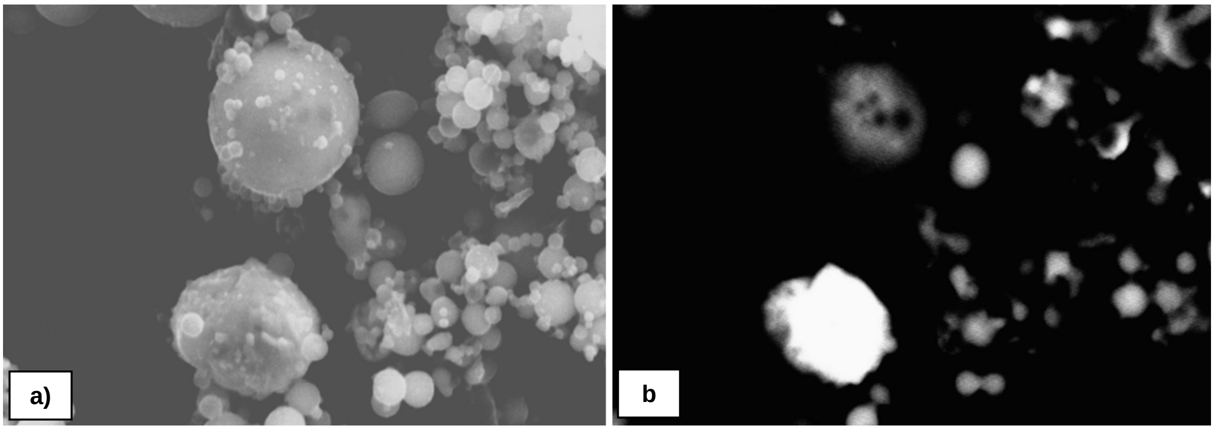

Fig. 1. Group of several fly ash particles taken in SEI (a) and BEI (b) mode at the same magnification. The heavy metal rich particles from (a) are visible as bright spots in (b).

An energy dispersive X-ray microanalysis (EDX) of fly ash elemental content is applied. Concentration of heavy metal in different particles determined by EDX analysis is studied as well as their affinity to other elements.

Detailed information about bulk composition and various physicochemical properties of the investigated ashes is available in our previous studies [8, 9, 13-15]. Most of these physical, chemical, morphological and magnetic peculiarities of these wastes are initially studied by one of the authors in her PhD dissertation [13]. They include various methods and apparatus for investigation, namely laser analysis of particle size distribution, inert gas absorption for determination of pore volume and specific surface, pycnometer for specific weight. The bulk chemical composition of ashes with respect to macro, micro and trace elements (silicate analysis, atomic absorption spectroscopy, X-ray luminescence and fluorescence analysis) are also studied in detail as well as the leaching behavior under acid conditions. A few of these results are presented here as well.

Results and discussion

The studied fly ashes represent inhomogeneous powders, consisting of particles of different shapes - from almost ideal spherical to highly irregular, having in the same time different surface structures - from glassy flat surfaces to highly rough ones, see Fig. 2. The shapes and surfaces of the particles reflect in great extend the high temperature processes of coal burning.

The fly ash from “Varna” consists of single spherical particles with perfect smooth surface (Fig. 2a). Similar smooth and flat surface is typical for the ash and slag particles (spherical and irregularly faceted ones) of “Russe Iztok” (Fig. 2f). Most of ash particles from “Bobovdol” (Fig. 2b) are almost spherical, but mixed with some amount of irregular ones. Their surface is sometimes even, but most often porous, ribbed, lamellar, etc. The ash particles from “Maritza-1 (Fig. 2c), “Maritsa-3” (Fig. 2d) and “Republika” (Fig. 2e), are with rather irregular shapes and rough-structured surfaces.

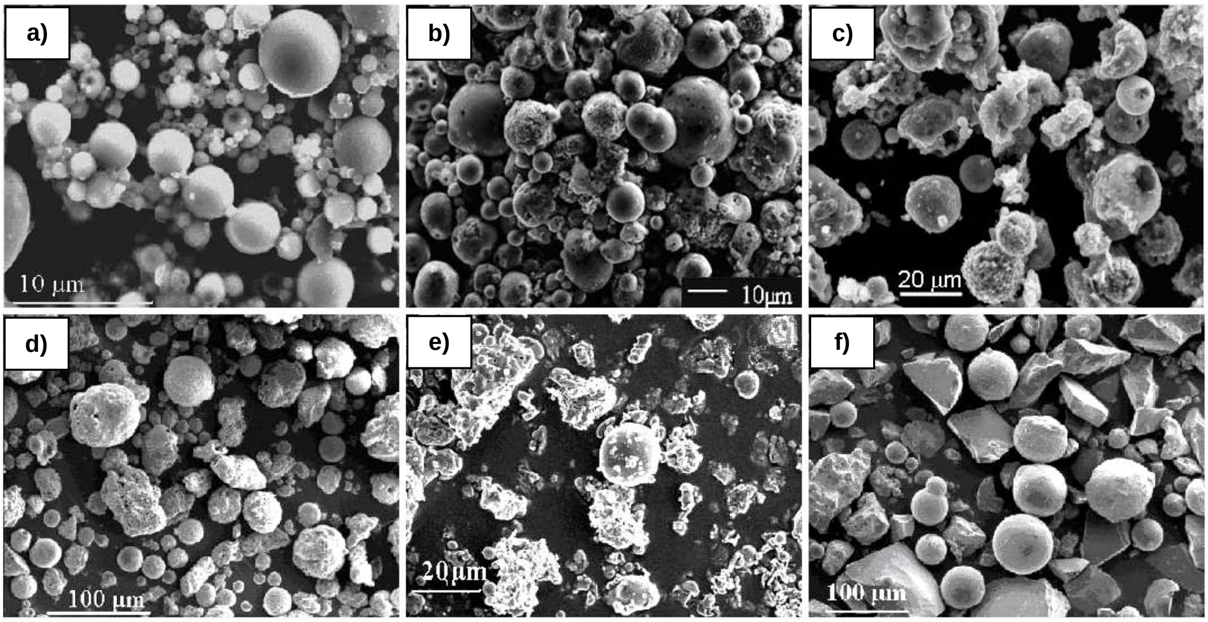

Fig. 2. SEM micrographs of fly ash particles: Varna (a), Bobovdol (b), Maritza-1 (c), Maritza-3 (d), Republika (e), and Russe Iztok (f). All photos are taken in SEI mode, and the magnification bar is given below each one.

Table 1. Chemical composition (in weight %), expressed as oxides, based on silicate analysis and atomic absorption spectroscopy, according to [9]

Fly ash	Chemical composition, wt%						
	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	Fe_2O_3
Varna	0.9	3.0	23.5	46.7	2.9	5.2	8.6
Bobovdol….	0.6	3.4	20.8	50.9	2.1	13.6	8.5
Maritza-1	0.4	1.4	13.5	23.4	1.1	7.1	26.9
Maritza-3	1.1	3.1	19.9	42.1	1.2	10.7	12.9
Republika	0.3	1.0	27.6	57.1	2.5	3.2	5.8
RusseIztok	0.7	2.3	29.5	54.6	1.8	3.5	4.6

Table 2. Elemental composition (in weight %), based on EDX-analyses of several thousand single particles

Fly ash	Elemental composition, wt%							
	Na	Mg	Al	Si	S	K	Ca	Ti	Fe
Varna	1.3	1.4	24.1	43.4	2.1	7.4	5.0	1.7	13.7
Bobovdol….	0	3.2	19.3	40.8	2.3	4.9	16.7	0	12.9
Maritza-1	0	0	8.4	12.4	20.8	0	6.9	0	51.5
Maritza-3	1.9	2.5	20.8	35.4	5.0	1.5	14.5	0.6	18.0
Republika	0	1.7	26.2	53.4	0	6.4	2.3	1.9	8.4
RusseIztok	0	2.0	24.6	45.7	0	4.9	4.5	0	18.4

Average composition of the six fly ashes is given in Tables 1 and 2. The most reliable chemical composition (in weight %), expressed as oxides (not normalized to 100%), is based on application of standard silicate analysis for macro elements Si, Al, Fe, Ca and Mg, and atomic absorption spectroscopy for microelements K and Na. The presented in Table 2 elemental composition (in weight %) is based on the so-called “integral spectra” taken by EDX-analysis at low magnification from an area comprising hundreds particles. Although there exist some differences, the main tendencies could be accepted as similar.

The content of some trace elements detected in fly ashes is presented in Tables 3 and 4. Table 3 gives it in ppm, determined with methods of bulk analysis (atomic absorption spectroscopy, X-ray luminescence and fluorescence). According to [10], some of the presented here metals, such like As, Cd, Hg, Pb are potentially the most toxic elements of the periodic chart. Many of them are established by EDX analysis of individual ash particles and this statistics is given in Table 4.

Table 3. Content of several trace elements, in ppm, according to [9]

Trace elements, ppm	Fly ashes					
	Varna	Bobovdol	Maritza-1	Maritza-3	Republika	Russelztok
Ag	4	4	5	5	1	5
As	458	1032	298	177	71	32
Ba	1773	1461	1227	523	663	929
Cd	4	2	20	5	0	2
Ce	236	107	13	59	56	111
Co	10	70	84	41	35	10
Cu	740	590	295	613	180	240
Hg	1,3	0,04	0,41	0,19	0,33	0,09
La	106	80	41	95	11	43
Nd	19	0	0	34	0	0
Ni	140	122	111	80	65	62
Pb	426	310	67	82	101	210
Sn	56	45	62	37	13	43
Sr	3926	1942	2081	2445	350	1089
Tl	36	17	51	26	28	0
W	193	96	72	151	25	215
Y	194	124	124	83	82	132
Zn	979	819	602	469	301	1869
Zr	1090	529	301	434	113	437

Table 4. Number of single particles rich of iron and non-ferrous heavy metals

Heavy metal rich particles, number	Fly ashes					
	Varna	Bobovdol	Maritza-1	Maritza-3	Republika	Russe Iztok
Fe	103	54	131	32	29	55
Ba, Sr, Ba+Sr	14	2	2	6	3	
Ba, Ba+Cu+Tl	10	10				
Pb	3	22		2		
Pb(+Cd,+Zn,+Cu,+Ni)		7		2		
Cd, As, Hg		4				
Cu, Zn, Ni	2	5	5		6	1
W (+Ni)		1			5	1
Ag (+Pd)	2			1	4	1
Co, Sn, Zr	1	11	1		2	
La,Ce,Nd,Sm,Gd	3					
Y (+Gd, +Er, +Yb)	1	1				
Non-ferrous HM particles	**36**	**63**	**8**	**11**	**20**	**3**
All studied particles	**207**	**240**	**196**	**75**	**74**	**98**

About 900 individual ash particles are analyzed (see Table 4). The majority of them are aluminosilicates. In four of the ashes (“Varna”, “Bobovdol”, “Maritza-1” and “Maritza-3”) particles rich of Fe, Ca or Si are often observed and these macro-elements are uneven spread. Most of the analyzed particles in “Republika” and “Russe Iztok” have chemical content very close to that of the bulk ash, given in Table 1. Some of the heavy metals are usually found in typical combinations, namely Ba - with Cu, Sr, Ca, Tl; and Sr- with S, Ti, Ca. Fe and Cu are enriched in single individual particles, and the Fe-rich ones are predominated. Spots of Pb are met sometimes on the surface of aluminosilicate particles. Rare elements and lanthanides are also detected. Many other elements, including some rare elements and Lanthanides are detected in high concentrations. Some of them are usually found in typical combinations.

The sample of ash and slag of “Russe Iztok” is characterized by a very homogeneous distribution of the elements. Detailed search in BEI mode revealed only a few heavy metal enriched particles (3 out of 98 analyzed), see Table 4. The predominant part of the Maritsa-1 bright particles is iron-rich (Fe> 50%) particles (131 of 196 studied), which often contain Mn. Rarely encountered there are non-iron particles of heavy metals (8 out of 196). 11 particles of non-ferrous heavy metals out of a total of 75 analyzed were found in Maritsa-3 and 32 other bright particles were enriched with Fe. In these three samples (RI, M-1 and M-3), Mn, V and Ti are rarely detected in individual particles, and therefore these elements are evenly distributed among all particles in the ash.

SEM-EDX of “Varna” and “Bobovdol” shows (see Table 4) that these two ash samples contain significant number and variety of particles enriched of heavy metals. In all fly ashes the detected non-ferrous heavy metals are concentrated in particles having low iron content (Fe < 30 wt%). Fe-rich particles (Fe > 50 wt%) from “Varna” (103 of 207 investigated) most often contain small quantities of Mn, Cr and V, while those from “Bobovdol” (54 of 117 analyzed bright particles) contain traces of Mn, Ti and V. “Republika” ash also contains relatively high quantity of single particles rich of heavy elements. Although the bulk analysis has shown that Ni content is correlated with iron, SEM-EDX has detected Ni-rich particles with low Fe content.

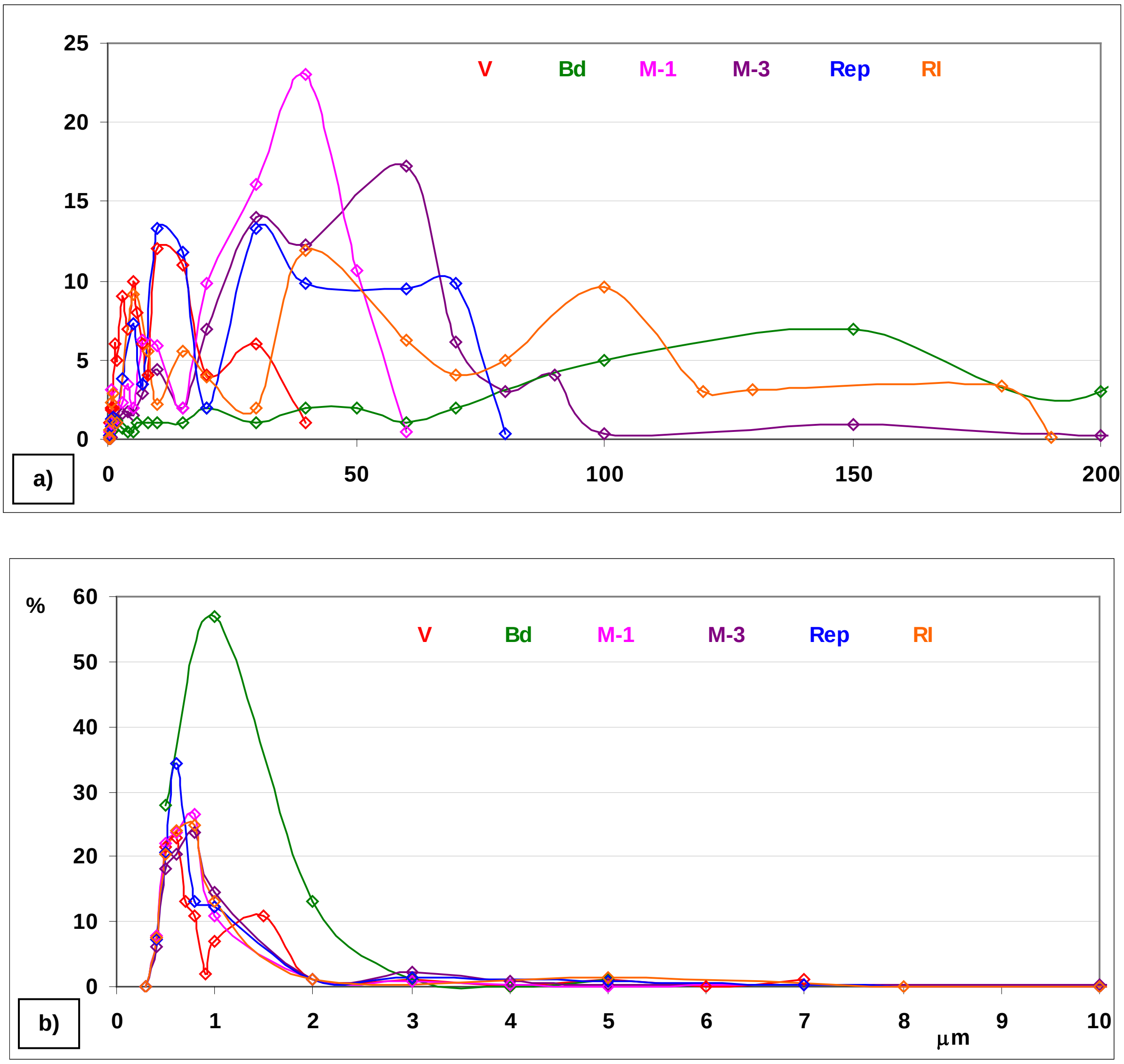

Fig. 3. Distribution (in percents) of the size (in micrometers) of fly ash particles presented by their volume (a) and number (b) statistics

Data on the distribution of ash particles by size, expressed by volume and number statistics are presented in Fig. 3a,b. As can be seen from Fig. 3, the disperse composition of the ashes is highly inhomogeneous. They contain particles that differ in size from 2 to 4 orders of magnitude (see Fig. 3a). According to [9], the average particle size, calculated on the basis of volume statistics, for the different ashes varies within a broader range d_{50}(volume) = 5 ÷ 45 μm. In the same time their size distribution calculated on the basis of statistics by number is almost the same for all materials - d_{50}(number) = 0.56 ÷ 0.64 μm. In other words, according to the number statistics (Fig. 3b), all the samples consist exclusively (> 99.9%) of particles with respirable size (< 10μm) and most of them (> 80%) are submicron ones. Microscopic observations confirm the presence of significant quantity of submicron particles in all fly ashes, as well.

As a result of the above analysis, we can conclude that if most of the fly ash particles rich in heavy metals and rare elements have a respiratory size (<10μm), this is a prerequisite for increased reactivity and easier solubility. The fact that more than half of the particles in all studied ashes are of submicron size also implies easier transport of ash material from air streams, facilitated inhalation and increased risk of extraction of toxic components in the environment and in the organisms.

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