ASH CHARACTERISTIC IN CO-COMBUSTION OF COAL WITH WOOD RESIDUE, SEWAGE SLUDGE AND MUNICIPAL WASTE

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ABSTRACT

Samples of bottom ash and fly ash coming from the combustion of lignite with the addition of limestone, from the co-combustion of lignite and wood residue with limestone and from co-combustion of lignite, wood residue, biological sludges from the waste water treatment plant and municipal waste as well with the addition of limestone were examined. Scanning electron microscopy with X-ray microanalyser were used for study of morphology and chemical composition of ash particles. The results were compared with average composition of bottom ashes, fly ashes and input materials found by X-ray fluorescence spectrometry and with phase composition found by X-ray diffraction method. There were proved no significant differences in the character and the structure of individual samples coming from various regimes of combustion.

KEYWORDS: coal, bottom ash, fly ash, scanning electron microscopy, X-ray microanalysis

INTRODUCTION

Constantly increasing production of all kinds of wastes and decreasing stores of fossil fuels for the power industry leads to the reuse of waste material as a component of fuels in the power engineering. It is vital to consider the influence of processes like that, together with technological aspects, to the environment for the significant expansion of this co-combustion of fossil fuels and wastes. Possibility of harmful substances releases to the atmosphere belongs to that above all; these issues were solved in the paper (Klika et al., 2004).

A remarkable production of solid wastes, bottom ash and fly ash occurs during combustion as well. For the liquidation or utilization of these solid wastes it is necessary to know the character of these wastes, which means their structure, chemical composition and form of occurrence of single elements. The object of the work was to evaluate samples of bottom ash and fly ash coming from the co-combustion of lignite and different wastes with the additive of limestone and their comparison with ash and fly ash coming from the co-combustion of lignite only with the additive of limestone.

EXPERIMENTAL

Samples from bottom ash and fly ash from three tests of co-combustion of lignite from the basin in Northern Bohemia (Most) in the mixture with various waste materials were examined. The combustion was performed in the kettle operating on the principle of circulating fluid bed in FRATSCHACH ENERGO, a.s., Štětí. The combustion temperature in all three regimes was 870 °C.

In the regime I lignite was co-combusted only with the additive of limestone. In the regime II a wood residue (woodchips, bark) and in the regime III moreover biological sludge from the waste water treatment plant and municipal waste (textile, plastics, paper) were added in addition. The detailed description of the combustion process including mass flows of individual fuels and additives are described in the paper (Klika et al., 2004).

Samples of bottom ash and fly ash were examined by the scanning electron microscope PHILIPS XL-30 with energy dispersive X-ray microanalyser EDAX. The medium average fraction, which represented about 80% of the total amount of ash and represented therefore sufficiently the sampled unit, was taken from the samples of bottom ash for the analysis. The samples of fly ash were sufficiently homogeneous, the average representative parts of samples were taken for analyses. Samples were put on the self-sealing targets with electrically conductive graphite layer which was stuck to the sample holders. The surface of the samples was covered by the metal layer (AuPd) with the help of the sputter coater POLARON SC 7640, which allows parallel rotating and rocking of the samples holder. Relatively homogeneous coverage of the indented surface was allowed that way.

The surface of the samples was examined in the mode of secondary and backscattered electrons. Displaying in the secondary electrons mode gives information about the morphology of the samples surface. In the backscattered electrons mode so called material contrast shows and the display brings information about differences in the chemical composition of individual spots on the sample surface.

The chemical composition of selected particles on the sample surface was determined by the method of x-ray spectral analysis. This method allows analysing of very small particles on the surface of samples, the analytical signal comes from the area about 1 – 2 µm in diameter and from the depth about 1 – 2 µm similarly. It is therefore possible to reliably determine the chemical composition (concentration of single elements) for the specific particle with at least 5 µm in diameter and thickness and provided that this particle represents the chemical individual it is possible to determine the composition of the respective compound as well. As far as the particles on the surface are smaller or they consist of clusters of smaller particles the interpretation of the results is more difficult. In such cases the results of the analyses are given as the sum of the analyses of the examined particle and its surroundings. Even in the case of relatively great particles the results could be distorted by the signal from the material below the particle, as far as the thickness of the particle is not sufficient.

As well in this case it is vital to take into consideration that the samples were put on the graphite target which considerably affected the results of the carbon determination – the concentration of carbon for the most of analyses was higher that the content of non-combustible carbon in average samples determined by the combustion method (LECO CS 244) (Klika et al., 2004). Considering this fact and as well generally lower quality of light elements determination by energy dispersive X-ray spectrometry the results of the C and O determination cannot be taken as reliable.

For the comparison of the results of individual particles analyses on the bottom ash and fly ash samples surface the ratios of the representation of single elements (Si, Al, Ca, S, Mg, K, Na, Fe and Ti) were therefore evaluated. Concentrations of single elements were expressed in atomic percentage:

$$A_i = \frac{C_i / M_i}{\sum_i (C_i / M_i)} \cdot 100 \qquad (\%)$$

Where:
A_i - atomic percentage of the element i,
C_i - concentration of the element i in mass %,
M_i - molar weight of the element i.

Ratios of the number of atoms in the analysed sample volume with respect to aluminium were calculated from atomic percentage:

$$R_i = \frac{A_i}{A_{Al}}$$

Where:
A_{Al} - atomic percentage of Al in the analysed sample volume.

The calculated ratio thus represents the number of atoms of the single element corresponding to one atom of aluminium.

For the comparison atomic ratios of the elements with respect to Al were calculated from the total analyses by the XRF method of average samples of bottom ash and fly ash from all three regimes (Klika et al., 2004). Furthermore the same ratios were calculated in fuels and additives on the input to the combustion space. The results of analyses of individual input materials and their mass flows presented in the paper (Klika et al., 2004), were used for the calculation:

$$A_i = \frac{\sum_j [(C_i . m_{ij}) / M_i]}{\sum_j \sum_i [(C_i . m_{ij}) / M_i]} \cdot 100 \qquad (\%)$$

Where:
m_{ij} - the mass flow of the element *i* on the input of *j*, kg/hour,
C_{ij} - the concentration of the element *i* on the input of j in mass %.

The calculated atomic ratios of the basic elements in analysed particles were used for the estimation of the phase constitution of the single elements. The results were compared with the results of the phase analysis of average samples of bottom ash and fly ash by the method of X-ray diffraction analysis presented in the paper (Klika et al., 2004).

RESULTS AND DISCUSSION

The calculated results of the relative representation of basic elements (Si, Al, Ca, S, Fe, Ti, K and Mg) in input fuels and additives are graphically presented in the Figure 1. In the Figure 2 there are these ratios expressed from the average composition of bottom ash and in the Figure 3 from the average composition of fly ash. The ratios are expressed with respect to Al, thus they represent the number of atoms of the single element corresponding to one atom of Al.

The ratios of studied elements on the input for individual regimes do not differ significantly. A little higher proportion shows S in the regime I. It is obvious from the results of the analyses of input materials that the main source of sulphur is coal, other alternative fuels thus lower the proportion of S. Even the relatively higher addition of limestone (higher proportion of Ca in the mode I) corresponds to it. Higher proportion of S and Ca in the input materials shows also in the higher proportion of these elements in bottom ash and fly ash in the regime I. The Si/Al ratio in the input materials is about 2 : 1, in bottom

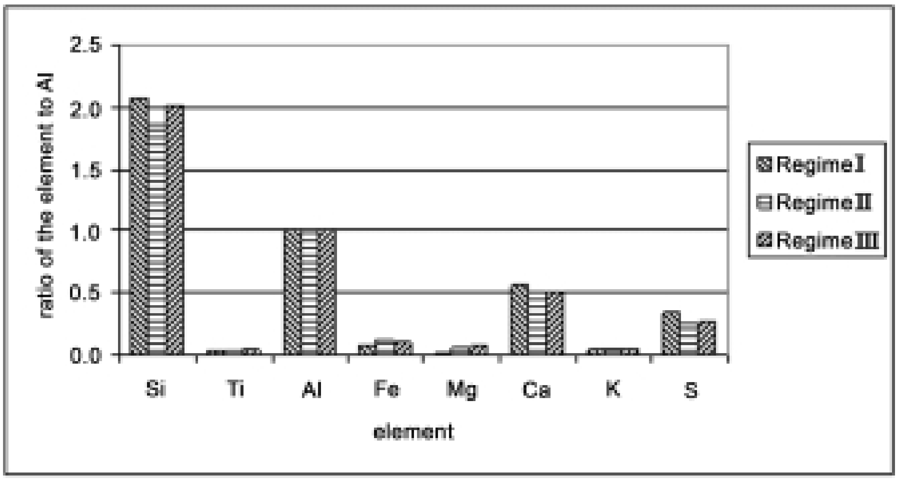


Fig. 1 Ratios of elements to Al in input materials for combustion

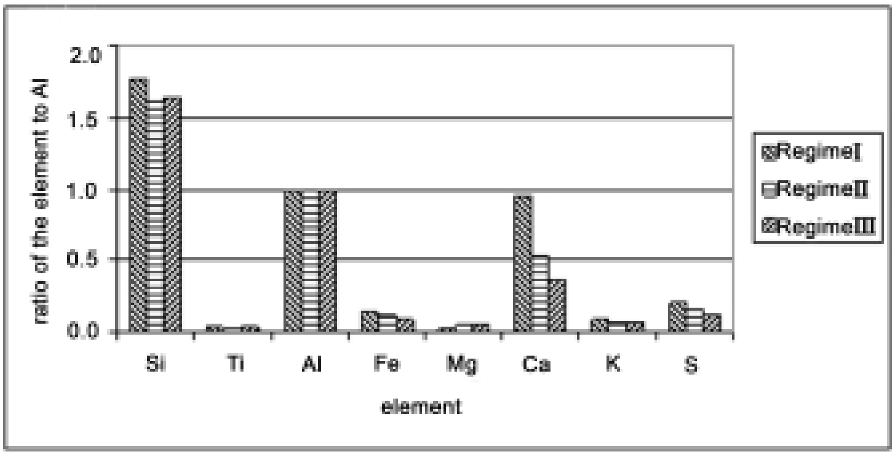


Fig. 2 Ratios of elements to Al in bottom ash

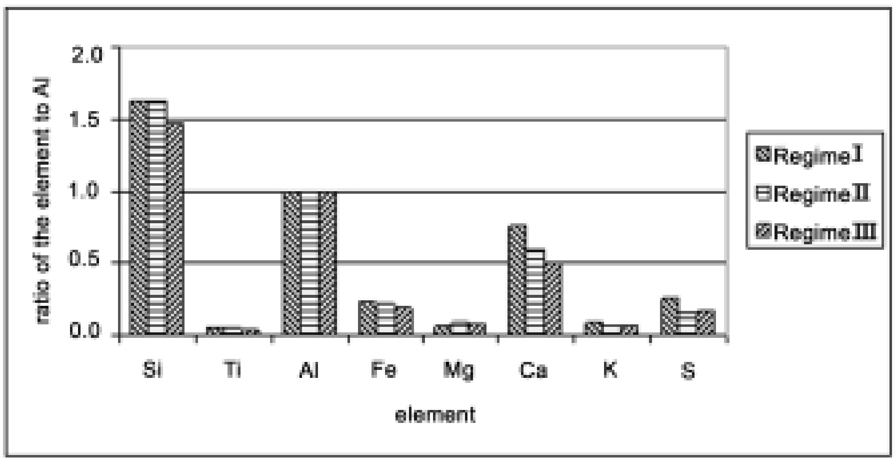


Fig. 3 Ratios of elements to Al in fly ash

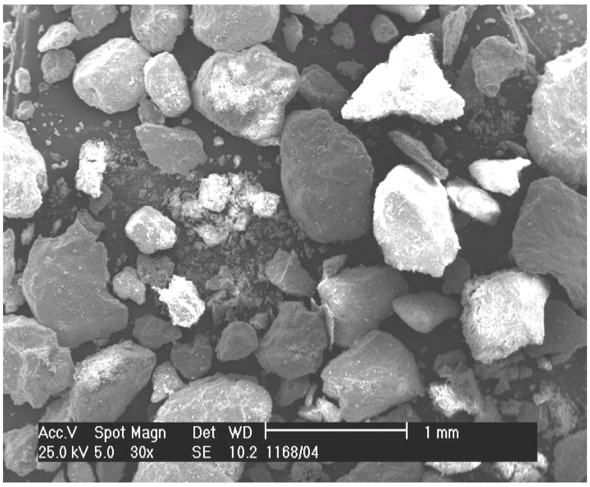


Fig. 4 Bottom ash, regime I, 30× magnification, secondary electrons

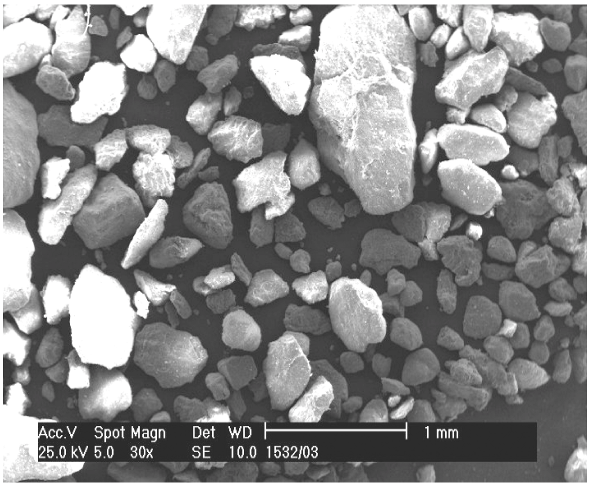


Fig. 5 Bottom ash, regime II, 30× magnification, secondary electrons

ash about 1.7 : 1 and in fly ash about 1.6 : 1. Among other elements Fe is of the highest proportion, in bottom ash about 0.1 and in fly ash about 0.2 atoms to one atom of Al.

It arises from the phase constitution of bottom ash and fly ash presented in the paper (Klika et al., 2004) that all the samples from three regimes of combustion contain quartz, potassium feldspar, anhydrite and hematite. All the samples except fly ash from the regime III contain mica and all the samples except bottom ash and fly ash from the regimes II and III contain calcium oxide. The sample of fly ash from the regime III contains calcium feldspar in addition to it and bottom ash from the regime II portlandite. It arises from the results that total sulphur in the samples of bottom ashes is bounded in the form of anhydrite ($CaSO_4$). Remaining calcium is generally bounded in the form of lime (CaO), in bottom ash from the regime II is then a part of calcium bounded in the form of portlandite ($Ca(OH)_2$), in fly ash from the regime III then in the form of calcium feldspar.

The estimation of the phase constitution of individual particles analysed by the method of X-ray microanalysis issued from the relative proportion of elements in individual particles. Sulphur was expressed as $CaSO_4$, remaining calcium as CaO. The occurrence of calcium in other forms (portlandite, aluminosilicates) was neglected. Considering the fact that the present feldspars and micas were aluminosilicates of various composition with different ratios of Si/Al and with different contents of other elements (Na, K, Ca, Mg) (Remy, 1972; Greenwood and Earnshaw, 1993), the found contents of Si and Al were expressed only by the number of atoms of Si to one atom of aluminium.

The pictures of the representative selection of particles of bottom ash samples from individual regimes of combustion are presented in the Figure 4 (regime I), Figure 5 (regime II) and Figure 6 (regime III). The pictures were obtained by the scanning electron microscope in the secondary electrons mode at 30× magnification. It is obvious from the pictures that the character and structure of all the individual particles are similar. The size of predominant majority of particles fluctuates between 0.1 – 1 mm, in the bottom ash from the regime II a higher proportion of smaller particles is noticeable. These particles are composed from a great number of very little grains of various composition as it will be documented later. The average chemical composition of basic particles (Figures 4 – 6) is very similar and it approximately corresponds to average composition of the bottom ash samples presented in the paper (Klika et al., 2004). Similar chemical composition of particles is confirmed as well by the pictures in the mode of backscattered electrons where no material contrast is noticeable at low magnification.

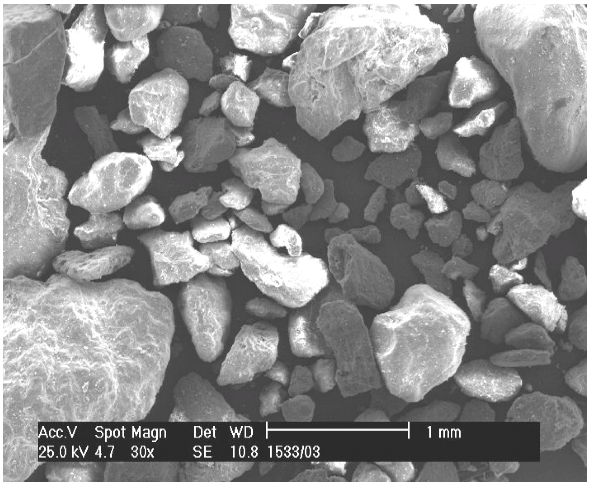
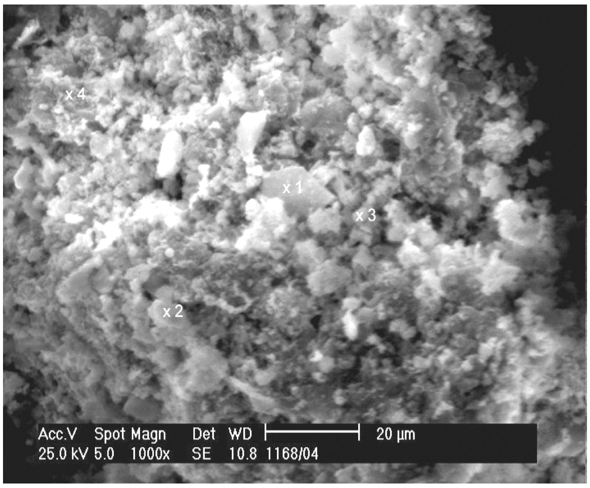
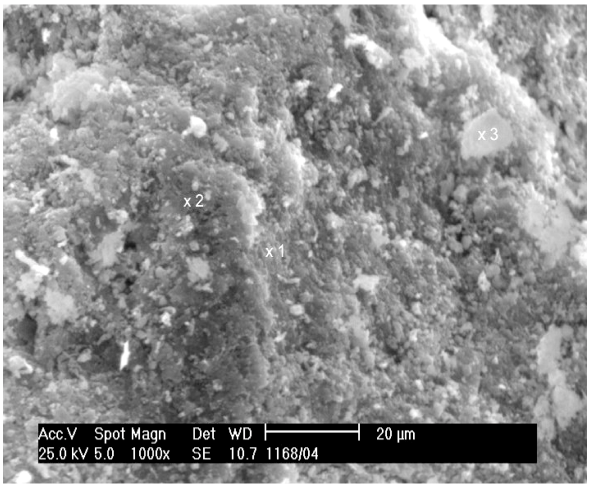


Fig. 6 Bottom ash, regime III, 30× magnification, secondary electrons



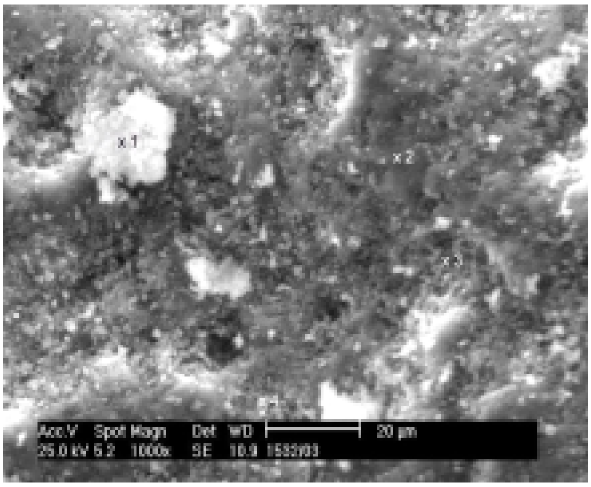
Analysed spot	1	2	3	4
Al	1	1	1	1
Si	1.20	2.12	1.38	6.95
$CaSO_4$	0.07	0.17	0.15	0.13
CaO	0.60	0.86	4.17	5.74

Fig. 7 Bottom ash – detail of the particle, regime I, 1000× magnification, secondary electrons



Analysed spot	1	2	3
Al	1	1	1
Si	1.87	1.98	1.72
$CaSO_4$	0.03	0.06	0.25
CaO	0.02	0.21	1.29

Fig. 8 Bottom ash – detail of the particle, regime I, 1000× magnification, secondary electrons

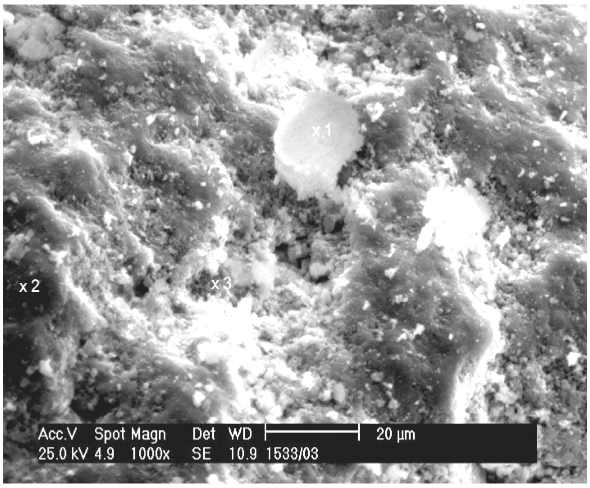


Analysed spot	1	2	3	4
Al	1	1	1	1
Si	1.09	1.39	1.31	1.40
$CaSO_4$	0.99	0.13	0.09	0.02
CaO	6.14	0.24	0.24	0.20

Fig. 9 Bottom ash – detail of the particle, regime II, 1000× magnification, secondary electrons

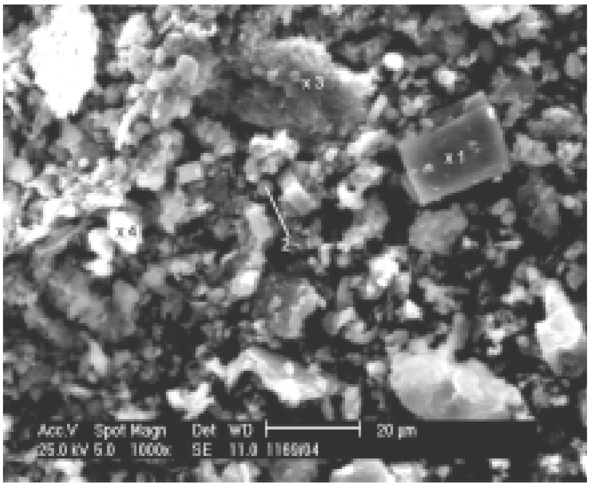
Analysed spot	1	2	3	4
Al	1	1	1	1
Si	0.89	1.19	1.21	1.03
$CaSO_4$	0.09	0.03	0.02	0.12
CaO	3.40	0	0.03	0.03

Fig. 10 Bottom ash – detail of the particle, regime III, 2000× magnification, secondary electrons



Analysed spot	1	2	3
Al	1	1	1
Si	1.29	1.44	1.37
$CaSO_4$	0.06	0.24	0.05
CaO	0.08	0.17	0.10

Fig. 11 Bottom ash – detail of the particle, regime III, 1000× magnification, secondary electrons



Analysed spot	1	2	3	4	5
Al	1	1	1	1	1
Si	1.19	1.59	1.85	1.32	1.72
$CaSO_4$	1.33	0.64	0.56	2.91	0.07
CaO	2.00	1.94	1.74	0.46	0

Fig. 12 Fly ash, regime I, 1000× magnification, secondary electrons

There are examples of the particle surface details of bottom ash from the regime I of combustion in Figures 7 and 8, from the regime II in the Figure 9 and from the regime III in the Figures 10 and 11. It is obvious from the pictures that these particles consist of a great number of small particles of the size 1 – 10 µm and smaller. Different chemical composition of these individual components is obvious from the display in the mode of backscattered electrons, especially the particles with a high content of Ca are different. Together with the pictures there are compositions of analysed spots presented together with the pictures. As well the ratios of the numbers of molecules or atoms corresponding to one atom of Al are mentioned.

All the analysed spots in Figure 7 contain relatively high proportion of Si, on the spot 2 and especially on the spot 4 predominantly in the form of SiO_2. Calcium in all three analysed spots occurs almost exclusively in the form of CaO, proportion of anhydrite is low here. On the spots 3 and 4 CaO is a majority component.

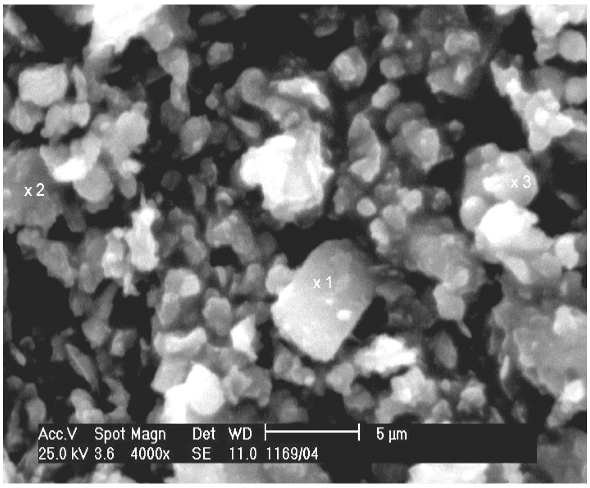
The particle, the detail of which is in Figure 8, consists predominantly of aluminosilicates with a high proportion of SiO_2. The content of Ca is low here, on the spot 1 practically negligible. The character of the particle 3 is quite different than its surroundings, there is a higher content of Ca, predominantly in the form of CaO, in this particle. It is probably the particle of CaO with a lower content of $CaSO_4$, contents of Si and Al probably come from the material below this particle.

Figure 9 demonstrates diversity of the composition of the bottom ash particles from regime II, spot 1 represents the particle with a high content of Ca, predominantly in the form of CaO. The ratio of atoms Si/Al is about 1 : 1 on this spot, at other analysed places with low content of Ca it is about 1.3 – 1.4 : 1. A very fine substructure of the basic ash particles is obvious from the picture as well the smallest particles are of the size 1 µm and smaller.

There is a detail of the ash particle surface from the mode III in Figure 10. No occurrence of $CaSO_4$ was noticed, only on the spot 1 a high content of Ca in the form of CaO was found. The ratio of Si/Al is near 1 : 1. Although the chemical constitution of the particles 2, 3 and 4 is very similar, their character is very different. While it is possible to consider the crystalline character of the particle 2, the particle 3 with the diameter of about 5 µm probably consists of many smaller particles. The particle 4 is of a globular character with the diameter of about 1 µm.

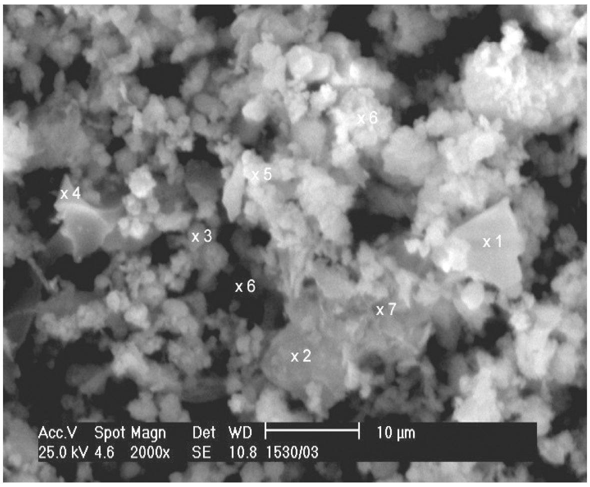
As well the bottom ash particle surface in the Figure 11 from the regime III of combustion is very various, although the chemical composition on various spots is very similar. Slightly higher concentration of Ca was found on the spot 2, which was the aluminosilicate particle with the Si/Al ratio about 1.3 – 1.4 : 1.

During the study of the surface of bottom ash particles from all three regimes no significant differences in the character and structure of individual particles were found. The bottom ash from the regime II contained rather higher proportion of smaller



Analysed spot	1	2	3
Al	1	1	1
Si	1.44	1.54	1.04
$CaSO_4$	3.70	0.16	0.18
CaO	0.70	0.03	0.39

Fig. 13 Fly ash, regime I, 4000× magnification, secondary electrons



Analysed spot	1	2	3	4	5	6	7
Al	1	1	1	1	1	1	1
Si	1.22	1.58	1.75	1.18	1.83	1.38	1.50
$CaSO_4$	1.93	0.14	1.53	0.37	0.23	0.19	0.29
CaO	0.18	0.12	0.32	0.45	0.54	0.35	0.56

Fig. 14 Fly ash, regime II, 2000× magnification, secondary electrons

particles (< 0.5 μm). Also the chemical composition of the individual particles was similar. It can only be stated that the occurrence of the particles with a high content of Ca was the highest in the bottom ash from the regime I, the lowest from the regime III, which corresponds to the average composition of bottom ash samples (see Figure 2). The average Si/Al ratio on the analysed spots was about 1.7 : 1 for the bottom ash from the regime I, about 1.4 : 1 from the regime II and about 1.3 : 1 from the regime III. In the bottom ash sample from the regime I particles with a very high content of Si (the ratio Si/Al up to 7 : 1) were found, which means they consisted mostly of SiO_2. Particles like that were not found in other two samples.

In Figures 12 and 13 there are examples of the character of fly ash from the regime I of combustion, in the Figures 14 and 15 from the regime II and in the Figures 16 and 17 from the regime III.

The shapes of individual particles of the fly ash samples are very various, there can be seen crystals with a high content of CaO and $CaSO_4$ (spot 1) in Figure 12. There are similar chemical compositions of the small globular particles 2 and 3, both of them with a higher proportion of CaO. The particle with the prevailing proportion of $CaSO_4$ was conversely found on the spot 4. There is the aluminosilicate particle with the ratio of Si/Al about 1.7 : 1 and with the negligible content of Ca on the spot 5.

As well in Figure 13 there can be seen the crystalline particle with a high content of $CaSO_4$ (spot 1) and also aluminosilicate particles with a low content of Ca (spots 2 and 3). At high magnification in Figure 13 it is obvious that the size of basic fly ash grains is about 1 μm, bigger particles are formed by clusters of these basic grains. Crystals of $CaSO_4$ are of bigger dimensions (5 – 20 μm), CaO tends to form small globular particles with the diameter of about 1 μm.

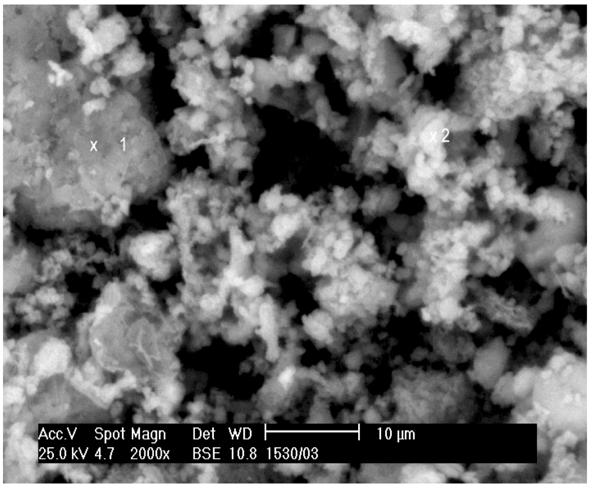
In Figure 14 there can be seen two particles with a high content of $CaSO_4$ of a completely different shape – on the spot 1 crystalline, on the spot 3 globular. On other analysed spots no higher contents of Ca were found, the ratios of Si/Al ranged from 1.4 – 1.8 : 1.

In Figure 15 there are sintered agglomerates of smaller grains. On the spot 1 it is an aluminosilicate particle with a higher content of SiO_2 and a negligible content of Ca. On the spot 2 a cluster of particles of aluminosilicates and $CaSO_4$ with the content of CaO was analysed.

In Figure 16 there can be seen aluminosilicate particles with a minimal content of Ca and with the Si/Al ratio about 1.5 : 1 (spots 1 a 2). Furthermore a globular particle with a high content of Ca predominantly in the form of CaO (spot 3) was found.

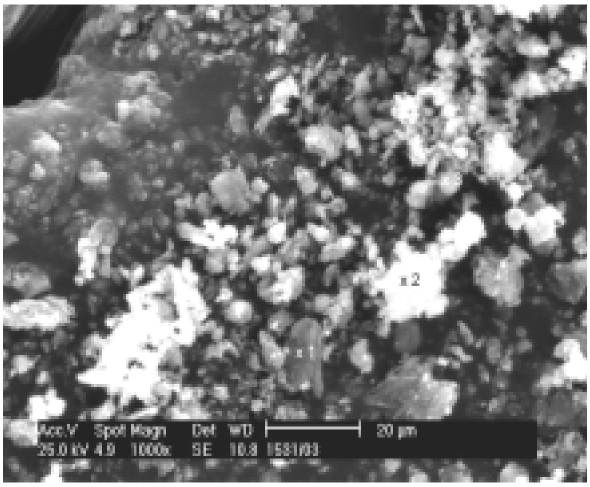
It is obvious from Figure 17 that particles of the size about 10 μm are formed by sintering of smaller grains. On the spot 4 a high concentration of Ca in the form of CaO and $CaSO_4$ was measured. On other spots aluminosilicate particles with the lower content of Ca were found.

Identically as for the samples of bottom ash it is possible to state for the samples of fly ash that no significant changes were observed in the character and



Analysed spot	1	2
Al	1	1
Si	1.95	1.57
$CaSO_4$	0.07	0.59
CaO	0.08	0.23

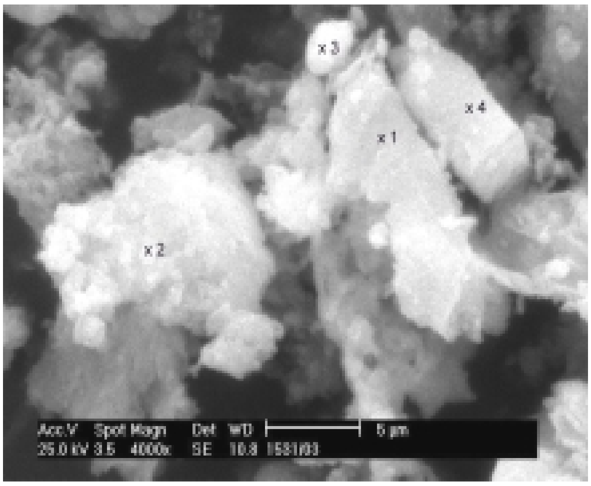
Fig. 15 Fly ash, regime II, 2000× magnification, secondary electrons



Analysed spot	1	2	3
Al	1	1	1
Si	1.57	1.54	0.41
$CaSO_4$	0.13	0.07	0.67
CaO	0.08	0.04	1.01

Fig. 16 Fly ash, regime III. 1000× magnification, secondary electrons

the structure of samples coming from the different regimes of combustion. Only for the sample from the regime III a slightly higher occurrence of agglomerates of the size 5 - 20 µm composed from smaller grains of the size 1 µm and smaller was observed. Identically as for the samples of bottom ash a higher occurrence of particles with a higher content of $CaSO_4$ and CaO was observed at the samples from the regime I, the lowest from the regime III, which corresponds to the average composition of the bottom ash samples. In contrast to the results of X-ray diffraction analysis where in the bottom ashes from the regime II and III no occurrence of lime was proved, the particles with a high content of CaO were found. These particles were mostly of a globular character with the diameter of about 1 µm and therefore there was no expression of them in the diffraction record. The average Si/Al ratio in the analysed particles of bottom ash from all the regimes ranges within 1.5 – 1.6 : 1.



Analysed spot	1	2	3	4
Al	1	1	1	1
Si	1.07	1.51	1.53	1.00
$CaSO_4$	0.09	0.09	0.12	2.30
CaO	0.34	0.02	0.26	4.34

Fig. 17 Fly ash, regime III. 4000× magnification, secondary electrons

CONCLUSION

Samples of bottom ash and fly ash coming from the combustion of lignite with the addition of limestone (regime I), from the co-combustion of lignite and wood residue with limestone (regime II) and from co-combustion of lignite, wood residue, biological sludges from the waste water treatment plant and municipal waste as well with the addition of limestone (regime III) were examined.

There were proved no significant differences in the character and the structure of individual samples coming from various regimes of combustion. Only at the bottom ash sample from the regime II a slightly higher proportion of smaller particles and at the fly ash sample from the regime III a higher proportion of agglomerates of the size 5 – 20 µm composed from smaller grains were found. At the samples of bottom ash and fly ash from the regime I a higher proportion of particles of $CaSO_4$ and CaO, with the lowest occurrence at the samples from the regime III, was recorded. The average ratio of Si/Al on analysed spots was about 1.7 : 1 for the bottom ash from the regime I, about 1.4 : 1 for the bottom ash from the regime II and about 1.3 : 1 for the bottom ash from the regime III. The average ratio of Si/AL in the analysed particles of fly ash from all the regimes does not differ very much and ranged within 1.5 – 1.6 : 1.

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