Fly ash from coal combustion - characterization

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Extended abstract

This work aims at characterizing a fly ash sample received from EDF Polska S.A. R&D Center, in terms of morphology using scanning electron microscopy (SEM), elemental composition using Energy dispersive X-ray analysis (EDX) and phase composition using X-ray diffraction (XRD). The fly ash samples were divided into five fractions with fly ash diameter sizes: under 63 μm, 63-100 μm, 100-200 μm, 200-320 μm and above 320 μm. This separation aims to finding a tendency between the size of fly ash particles and their morphological properties, elemental composition and phase composition. Furthermore, fly ash particles were also submitted to size range measurements using a Malvern Mastersizer 2000 instrument, which provided detailed information about the amount of particles in volume percentage.

The results indicate that the morphology of the different fractions shows significant differences. The elemental composition of the individual fractions depends on the particles size and it was observed that, some elements such as P, Mg, S, Fe, Cu were the ones, evidencing the more marked dependencies.

1. Introduction

Presently, electricity and heat are essential for the development and functioning of the modern civilization. Through the years, an increased demand for electrical energy has been recorded. The world's production of electricity is still greatly based on the thermal conversion of solid fossil fuels, which produces a significant number of wastes. Annually, the energy sector uses approximately $3.5 \cdot 10^9$ tonnes of coal, which allows to produce about 38% of the world's electricity [1,2].

Wastes are all the by-products produced during the combustion processes. The combustion of coal originates various types of by-products and, among these, fly ashes are the most abundant. Typically fly ashes distribution includes the fly ash (70 - 90%) and the bottom ash (10 – 20%). Other coal combustion by-products include boiler slag, flue gas desulphurisation, gypsum or other types of materials such as fluidised bed combustion ashes, cenospheres and scrubber residues.

In recent years, the power industry underwent a series of transformations, leading to significant technological and efficiency improvements. The actual targets of the sector aim at reducing the cost of

energy production, optimizing the use of fuel as well as reducing the impact of power plants on the environment. Therefore, new technologies are being introduced and existing ones have been improved. For example, in power plants, there is a trend to replace pulverized boilers by fluidizing bed boilers. Many plants also installed desulphurization and denitrification systems. In addition, the composition of the fuel changes, as well as the composition of bituminous coal and lignite. Moreover there is an increase of energy production from biomass. Therefore, the composition and properties of wastes changes and, in particular those referring to fly ash are essential to be known [3].

Fly ashes are mineral residues from coal combustion that leave the furnace together with the flue gases. Thereafter fly ash particles are captured using dust collection equipment, mainly electrostatic precipitators. It is estimated that each year, in the world, the production of fly ash is around $4.2 \cdot 10^8$ tonnes of fly ash – mostly in China and United States, while in Poland it is approximately $4.2 \cdot 10^6$ tonnes of fly ash (data from 2009). Fly ash physical, chemical and mineralogical properties combined with its large scale production make fly ash an attractive raw material for various applications. Therefore, in order to promote the usage of waste fly ashes, it is essential to study and to characterise in deep this material. This will allow its widespread use as raw materials in many areas of the economy [1,4].

Thus, the objective of this dissertation is to characterize various fractions of fly ash and in particular to detail its size distribution and its relation with chemical.

2. Experimental

2.1. Separation of the fractions

The first step was to divide the received sample of fly ash into various fractions using a series of sieves with different mesh sizes. With such equipment it was possible to obtain fractions with different granulometry and characteristic particle size. This step was crucial since it is necessary the characterization of the particles according to various characteristic diameters. To separate the different fractions of fly ash the following sieves (characteristic mesh size) were used: 320 µm with square mesh shape and 200 µm, 100 µm, 63 µm with round mesh shape. The sieving was done manually, except for the smallest fraction, under 63 µm, which was done mechanically.

During screening of the fly ash samples, each fraction was weighed and the weight percentage of each fraction was calculated with regard to the total ash mass. All calculations, including arithmetic averages and standard deviations are presented in table 1.

Table 1 Percentage of each fraction referring to the total mass of fly ash, arithmetic average and standard deviation.

Sample number / Fraction	1 [%]	2 [%]	3 [%]	4 [%]	Arithmetic Average	Standard deviation
Above 320 µm	0.18	0.22	0.2	0.2	0.200	0.016
320 - 200 µm	1.56	1.74	1.64	1.85	1.698	0.126
200 – 100 µm	16.8	17.11	16.45	15.5	16.465	0.698
100 – 63 µm	20.71	20.73	20.93	19.67	20.510	0.569
Under 63 µm	60.75	60.2	60.78	62.78	61.128	1.133

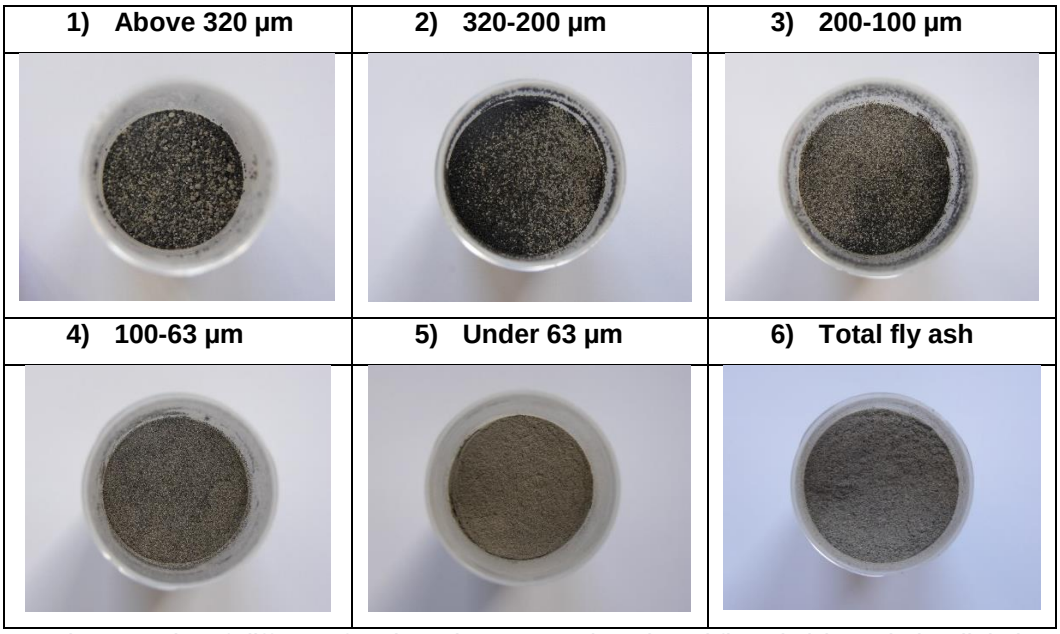

Figure 1 Photographs of different fractions (1, 2, 3, 4, 5) and total fly ash (6) made by digital camera.

Moreover, it is worth to notice that the obtained fractions, despite the differences in particle sizes, also differ visually in colour. The visual colour changes are presented in figure 1. The following trends can be outlined: the fraction of largest diameter contains more black particles; while the smallest fractions are almost entirely grey. It can be stated that according to the particle size, from the smallest to the largest, the colour gradually becomes more intense and darkens. In addition, by comparing the separated fractions with the initial (non-sieved) samples of ash, the dominant colour allows noticing which fractions are dominant.

2.2. Characterization techniques

2.2.1. Size range measurement

Measurements to detail the size of the fly ash particles were carried out using a Malvern Mastersizer 2000 equipment developed by the Malvern company.

Mastersizer 2000 is an instrument, which is based on laser light scattering. During the measurement, particles are passed through a focused laser beam. This equipment allows the measurement of particles sizes ranging between 0.02 – 2000 µm, with an accuracy better than 1% [5].

2.2.2. SEM and EDX

SEM and EDX analysis were carried out for the specified fractions at the microscopy laboratory of Instituto Superior Tecnico (IST) in Lisbon, using Hitachi SEM, model S2400, with a tungsten filament and image acquisition using the Quantax Esprit software, equipped with the detector SDD from Bruker. The measurements were performed using an electron beam with energy of 25 kV. Moreover, samples were covered with gold alloy to obtain conductivity, thus, gold signal can be observed in the EDX analysis. SEM and EDX analysis were performed for each fraction separately

The experiments of non-separated fly ash samples were performed in a microscopy laboratory at University of Science and Technology (AGH) in Kraków. The images of the powders were recorded using a FEI Nova NanoSEM 200 microscope equipped with low vacuum detector.

2.2.3. XRD

X-ray diffraction of fly ash samples were performed in the 10-110 degree range under the CuK_{α} radiation, using PANalytical Empyrean diffractometer. The tests were carried out in the X-Ray diffraction laboratory at University of Science and Technology in Kraków.

3. Results and discussion

3.1. Size range measurements

The size range measurement was carried out on 10 samples of fly ash (non-sieved). Each sample was analysed in terms of content of particle size in the specific range. The results show that there are no significant discrepancies, which means that all fly ash samples are nearly uniform. All 10 measurements were averaged and shown in Figure 2.

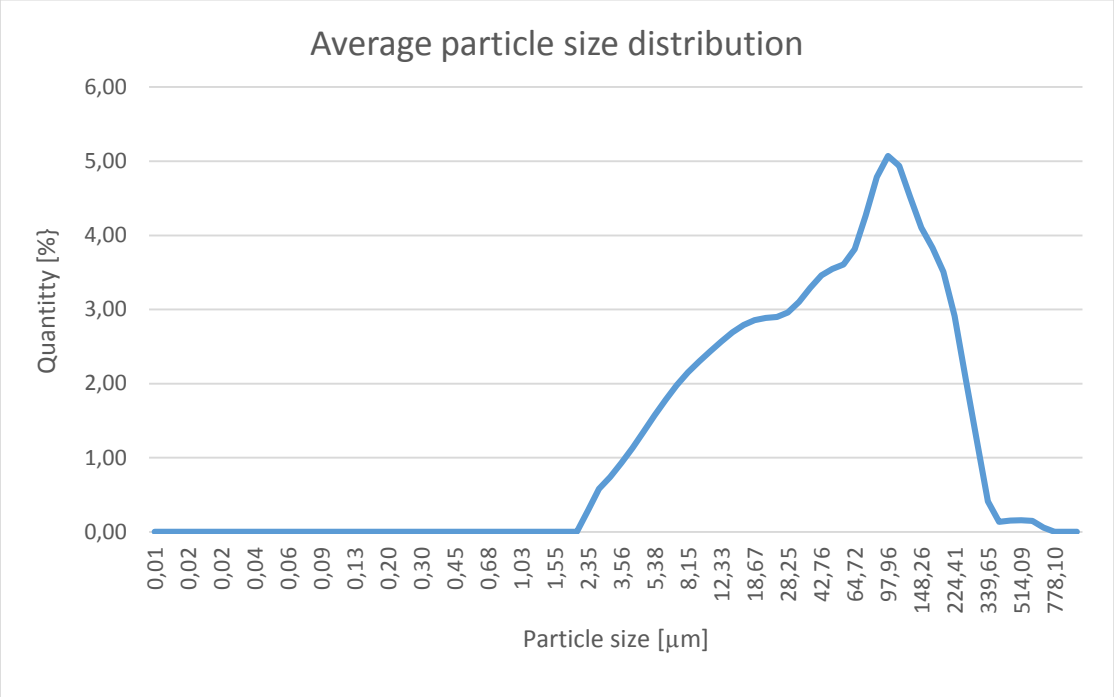

Figure 2 Average quantitative profile of fly ash particles as a function of the diameter size.

Generally, fly ash particles start to appear around 2 µm and the largest detected particles reach 700 µm. Graphical representation shows that there is a growing trend from 2 µm up to 100 µm and the highest peak of the function is observed in the area of 100 µm. Afterwards there is a highly decreasing trend until 320 µm. Then after 320 there is a slight growth which is a finish of the graph.

Consequently, the most numerous range of fly ash particles is when their size is around 100 µm. The second in terms of quantity is part between 100 µm up to 320 µm. Less numerous but appearing in larger area is part between 2 µm and 100 µm. Moreover, after a careful analysis it can be stated that this part, between 2 µm and 100 µm, embrace the largest percentage of the tested fly ash. On the other hand, almost quantitatively negligible is part above 320 µm.

3.2. SEM and EDX

3.2.1. "As received" fly ash characterization

The characterisation of the "as received" fly ash is essential to characterize the original by-product as a whole. Therefore, Figures 3 and 4 depict the SEM images of the "as received" fly ash samples. Particles presented on the figures are highly diversified concerning sizes and shapes. It is possible to find very large particles as well as much smaller ones. Moreover, the shape of the particles vary from very regular spherical shapes to completely irregular, weird shaped particles. In order to properly characterize fly ash, six different particles from each figure were selected and analyzed in terms of chemical composition.

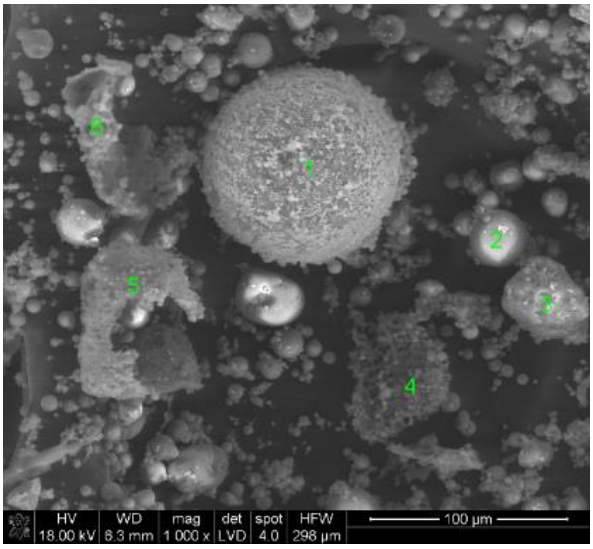

Figure 3 SEM image for fly ash sample, at 1000x magnification.

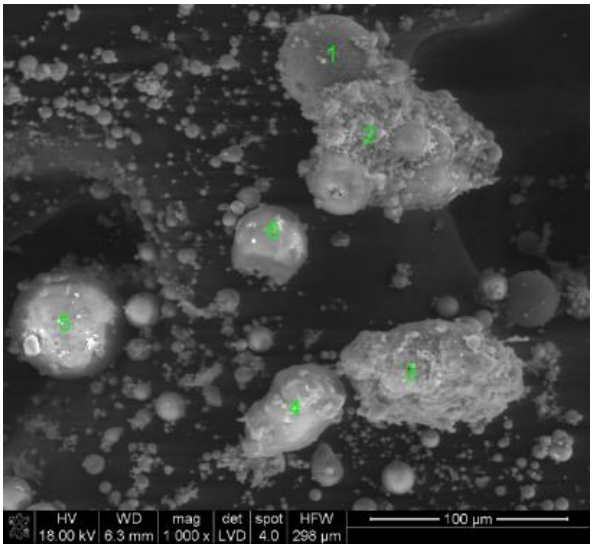

Figure 4 SEM image for fly ash sample, at 1000x magnification.

The results of EDX analysis shows that each particles vary in their elemental composition. In fly ash samples it is possible to find particles with higher content of iron which represents magnetic spheres or cenospheres with very regular shapes and unburnt carbon.

3.2.2. Fractions

SEM analysis was carried out for each fly ash fraction separately. SEM images of fractions are presented in ascending order, from the fraction with particle size under 63 µm up to fraction above 320 µm (Figures 5 – 10).

Figures 5 and 6 represent the morphological features of the smallest fraction of fly ash, that are characterized by the presence of very regular and spherical shapes. This morphology is typical of cenospheres. The particles diameter ranged from the limiting value 63 µm to spheres with a few µm diameter size. The fly ash fraction, with particle size in range of 63 - 100 µm depicted in figure 7 is quite distinct from those of the previous fraction. The particles are still spherical, but their shapes are more irregular. In addition, spheres are not uniform and they are covered with smaller particles and irregular deposits. Fly ash particles between 100 - 200 µm (Figure 8) are similar to those observed in the fraction 63 -100 µm. However the shapes of the particles are less uniform. The spheres are mixed with several particles, with irregular shapes, covered with smaller particles. The fraction in the range of 200 – 320

µm, shows particles with different shapes (Figure 9). Particles in this fraction are characterized by irregular dimensions and there are no spherical particles. Irregular shapes evidence porous structures with several smaller particles covering their shells. The largest fraction is shown in Figure 10 and represents fly ash particles larger than 320 µm. These are the biggest particles possible to find in received fly ash. The morphology of the particles included in this phase differ significantly from that of the other fractions. Generally, this fraction consists only of big, extremely irregular, edgy-sharped particles that seems hollow in most cases.

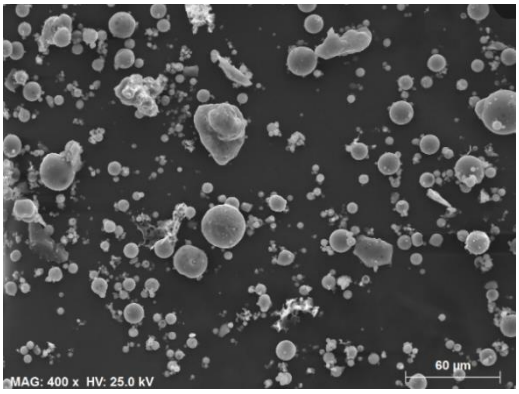

Figure 5 SEM image of FA, fraction under 63 µm, at 400x magnification.

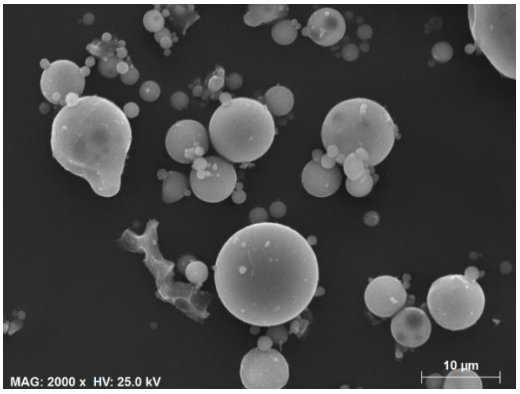

Figure 6 SEM image of FA, fraction under 63 µm, at 2000x magnification.

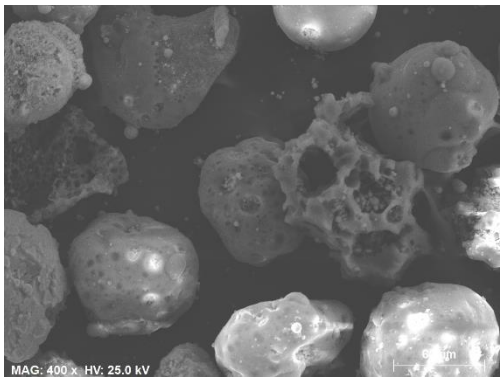

Figure 7 SEM image of FA, fraction between 63 - 100 µm, at 400x magnification.

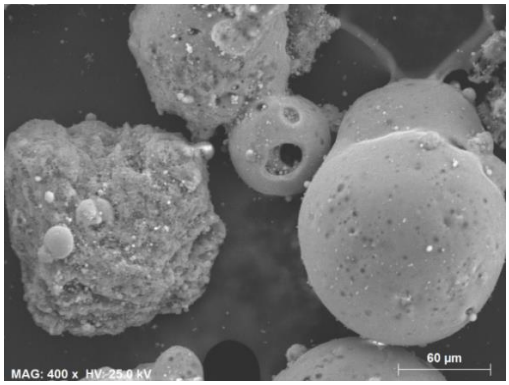

Figure 8 SEM image of FA, fraction between 100 - 200 µm, at 400x magnification.

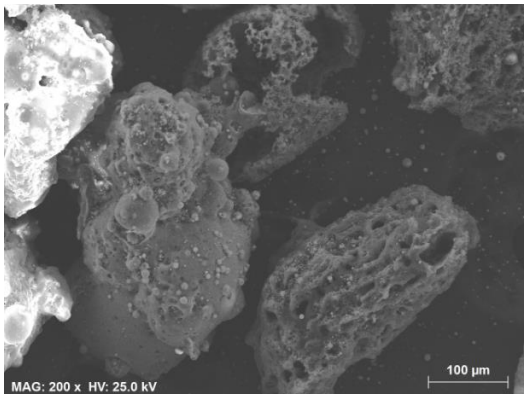

Figure 9 SEM image of FA, fraction between 200 – 320 µm, at 200x magnification.

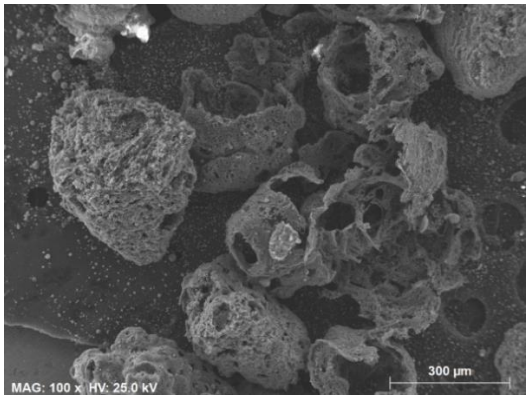

Figure 10 SEM image of FA, fraction above 320 µm, at 100x magnification.

3.2.3. Comparison of EDX results

The EDX measurements obtained for each fraction were compared, considering the content of the major and minor elements determined in the various fractions of fly ash. These plots represent only the elements that could be detected by the apparatus. Therefore, the analyzed elements Al, Ca, Fe, Mg, P, K, Si, Na, S, Ti and Cu were found. Generally, in every fraction, all elements are present, except phosphorus which is not detected in fractions 4 and 5. This means that it occurs in fly ash particles with diameter less than or equal to 200 μm.

Aluminum and silicon are the two abundant elements which are fairly constant in all fractions (Figure 11). The aluminum content oscillates in the range of 25 to 30 % wt., while silicon is within the range 42 to 46 %wt. and slightly decreases in fraction 5, being equal to 36 % wt.. This result suggests that the particles are mainly composed of aluminosilicates [6].

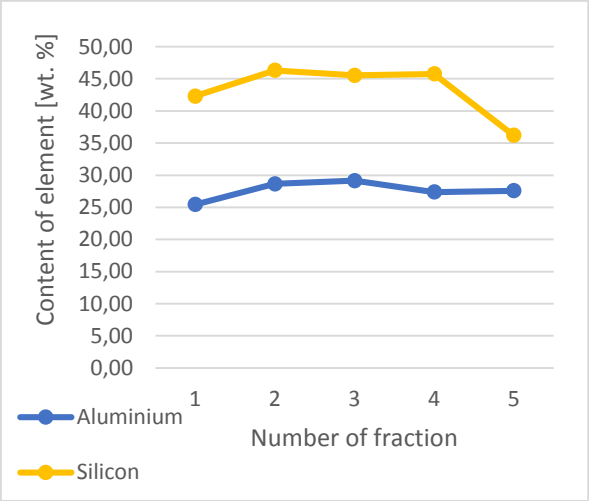

Figure 8 Aluminum and silicon distribution in all fractions of fly ash.

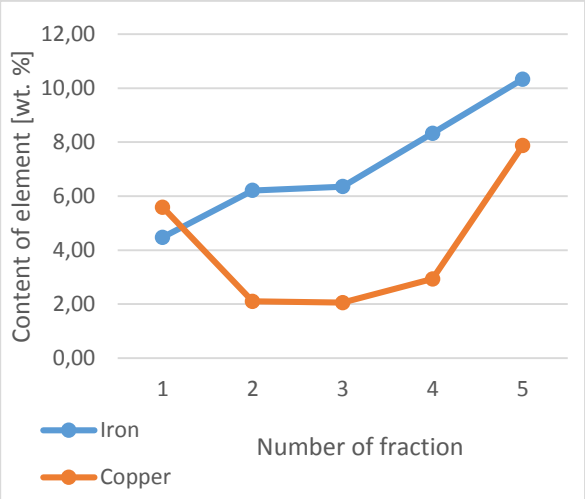

Figure 9 Iron and copper distribution in all fractions of fly ash.

Figure 12 shows that the content of Fe increases from fraction 1 (the smallest particles) to fraction 5 in which the particles are the largest. Iron content in fraction 1 is 4,47 % wt. in fraction 2 is 6,21 % wt. in fraction 3 is 6,35 % wt., in fraction 4 is 8,32 % and in fraction 5 is 10,33 % wt.. Fractions which are richer in iron show more marked higher magnetic properties. Another element presented in figure 12 is copper that is present in all fractions. As it is shown on the figure there is no clear trend. However its content is higher in the smallest fraction as well as in the largest fraction. The lowest content of copper, around 2%, can be found in fraction 2 and 3.

Another group of elements is characterized by a decreasing trend of their content as the particle size in the fraction increases (Figure 13). Thus, as the particle size increases, Mg and P contents decrease (indeed P vanishes for the two largest fractions). Sulphur also shows a decreasing trend, however, suddenly for the largest fraction it increases, probably because coal intended for combustion contained some amounts of sulphur which remains in unburnt carbon particles.

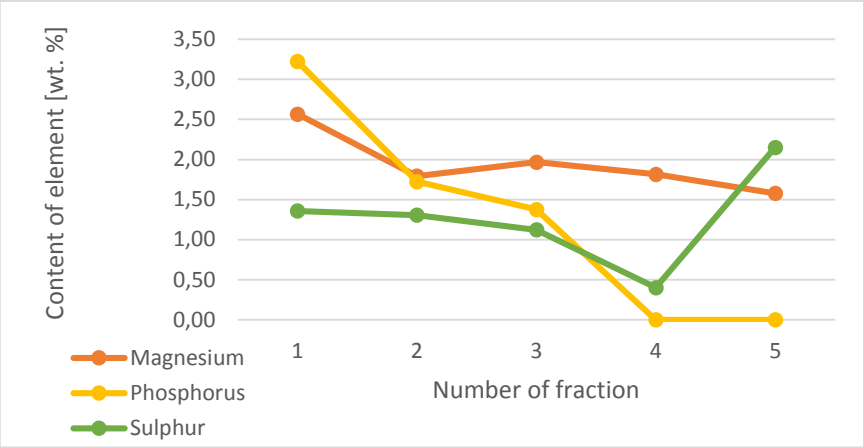

Figure 10 Magnesium, phosphorus and sulphur contents in all fractions of fly ash.

The phosphorus content gradually decreases from fraction 1 (above 3 % wt.) to fraction 2 (1,72 % wt.), fraction 3 (1,38 % wt.) and finally fractions 4 and 5 do not show phosphorous. Magnesium also shows a similar trend evolving from 2,56 % wt. in fraction 1 to 1,58 %wt. in fraction 5 (with some exception in fraction 2 where its content slightly increased). The next element which also shows this trend is sulphur. It decreases from 1,36% wt. in fraction 1 to 0,4 % wt. in fraction 4. In fraction 5 the content of sulphur increases again. Probably higher content (2,15% wt.) of sulphur is related to dominant carbon in this fraction which also contains suplhur in their composition.

3.3. XRD

XRD results show that all fractions, in terms of their phase compositions, were nearly similar. The most important difference between them is their weight proportions of compounds. The distribution of phases in all five fractions is shown in Figure 14.

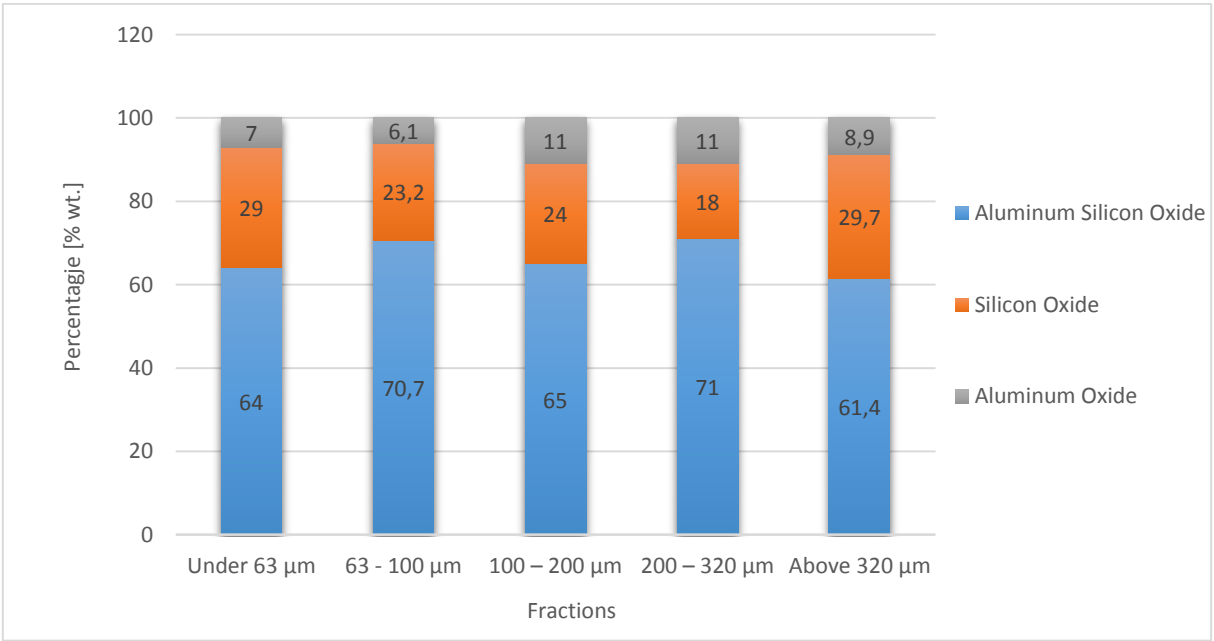

Figure 11 Distribution of different phases in the fractions of fly ash.

The most abundant compound in all fractions is the aluminum silicon oxide, which content ranges from 61,4 % wt. (in the fraction above 320 μm) to 71 % wt. (in the fraction with particles sizes from 200 – 320 μm). The second most frequent compound is silicon oxide. Its composition in fly ash fractions oscillates from 18 % wt. (in fraction 200 – 320 μm) up to 29,7 % wt. (in fraction above 320 μm). The content of silicon oxide is also high (29 % wt.) in the smallest fraction of fly ash with particles under 63 μm. The fraction with particles between 63 -100 μm and 100 – 200 μm indicates, 23,2 % wt. and 24 % wt. content of silicon oxide, respectively. The last compound is aluminum oxide, its content is in range between 6,1% wt. (in fraction 63 – 100 μm) up to 11 % wt. (in fractions 100 – 200 μm and 200 - 300 μm). Remaining values of aluminum oxide contents are as follows: 7% wt. in fraction under 63 μm and 8,9 % wt. in fraction above 320 μm.

4. Conclusions

Fly ash from coal combustion has been studied to obtain detailed information about its characterizatics. For this purpose, fly ash samples were separated into five different fractions with various particles sizes ranges (above 320 μm, 320-200 μm, 200-100 μm,100-63 μm and under 63 μm). Thus, it was possible to compare physical properties of the fractions and investigate them in terms of their morphology, elemental composition and phase composition.

Results clearly show that various fractions of fly ash differ from each other. In general they differ visually in terms of their color. The biggest fraction includes very dark, black particles and then the color of the particles becomes clearer, up to light grey, in the smallest fraction. This is due to higher content of unburnt carbon in the thickest fractions which is not so numerous in lower fractions.

Moreover the Malvern Mastersizer 2000 measurements provide details about the quantitative profile of fly ash. Fly ash particles start from 2 μm and vanish when they gain 340 μm. The dominant sizes of fly ash particles were in range between 60-200 μm with the maximum peak at 100 μm. However the most abundant particles were in range from 2 μm to 100 μm.

Results obtained from scanning electron microscope (SEM) show the morphological variation present in the different fractions of fly ash. It was proved that fly ash particles with diameter size under 63 μm (the smallest fraction) significantly vary from fly ash particles with diameter size above 320 μm (the biggest fraction). This is due to different formation in each fraction. In the smallest fraction the dominant are cenospheres which characterize with regular spherical shape while in the biggest fraction prevail formation is unburnt carbon with extremely irregular and jagged shapes of particles. Furthermore remaining fractions also vary from each other. The differences are analogous, in the fraction with particles in ranges between 63-100 μm there is a mixture of predominance spherical particles (cenospheres) with irregular particles, then with each fraction the amount of irregular particles successively increases up to mentioned fraction (above 320 μm) where they occur exclusively.

Moreover the elemental composition, received from electron dispersive X-ray spectroscopy (EDX), of the fly ash vary within the fractions. The dominant elements, which are silicon and aluminum show fairly constant amounts in all fractions. For other detected elements in general it is possible to find a trend. Phosphorous, magnesium and sulphur show a decreasing trend from the smallest fraction to the

largest. Iron and copper were elements, for which contents increased from the smallest fraction to the largest. The remaining elements did not revealed any particular trend.

X-ray diffraction (XRD), provided information of the phase composition. Results provided and overview of the fly ash phase composition which revealed three main phases (aluminum silicon oxide, silicon oxide and aluminum oxide). The most abundant phase is composed of aluminum silicon oxide, the second largest is silicon oxide and the least numerous aluminum oxide. The study showed that the individual fractions were not significantly different in their phase composition.

References

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