

# Characterisation of fly-ash cenospheres from coal-fired power plant unit

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*Key words: cenospheres, cenosphere yield, cenosphere formation, coal combustion, fly ashes.*

## Abstract

Cenospheres are one of the most desired byproducts of coal combustion process nowadays. They are small hollow spheres with roughly 10 – 1000  $\mu\text{m}$  in diameter and constitute about 1-2 % of the fly ash obtained from the coal combustion process. Because of their specific properties, namely their low density and very high mechanical strength, cenospheres are an important subject of coal fired power plants. The objective of this work is to characterize, chemically and structurally, different cenospheres in order to establish the conditions that favors their formation. For this purpose, several samples of cenospheres, obtained from fly ash from coal-fired power plant located in Poland, were analyzed in terms of composition of cenospheres and fly ash and its relation with glass formation principles and combustion conditions. They can present different size, color and shape. Moreover, detailed properties of cenospheres have been obtained and described by techniques such as SEM, EDS, XRD, XRF and Raman spectroscopy. Results indicate that cenospheres from coal combustion are aluminosilicate glasses with some crystalline phases. The high alumina content – roughly 25-27 wt. % - is responsible for the high mechanical strength, while density of most cenospheres is lower than 1  $\text{g}/\text{cm}^3$ . Regarding the formation process, there are interesting correlation between the amount of cenospheres and the sodium and calcium content, in different fly ash samples.

## 1. Introduction

Cenospheres constitute a small but important fraction of by-products from coal combustion process. Because of some distinctive properties, like their low density and high mechanical strength, they are suitable for a variety of applications in many branches of industry. This is why coal fired power plants are strongly interested in this issue and cenosphere recovery process is now under investigation. This work was done in cooperation with EDF (Electricité de France) coal fired power plant located in Krakow (Poland), which provided the samples. The major objective of this work is to find out, which factors influence the yield of cenospheres recovered from different fly ash samples. Cenospheres are hollow ceramic microspheres that are a by-product of coal burning power plants. When pulverized coal is burnt at power plants, fly ash is produced. Cenospheres are the lighter particles present in fly ash and constitute about 1-2% wt.% of the fly ash [1]. Vassilev [2] indicates that cenosphere diameter can vary from 8  $\mu\text{m}$  up to 1000  $\mu\text{m}$ . Kolay [3] correlates the average diameter with density – for particles with density lower than 0.857  $\text{g}/\text{cm}^3$ , 80% of them have diameter between 50 - 150

$\mu\text{m}$ , 15% diameter between 150 - 200  $\mu\text{m}$  and 5% between 200 - 250  $\mu\text{m}$ . For particles with density lower than  $1.282 \text{ g/cm}^3$ , 10% of them have diameter between 40 - 50  $\mu\text{m}$ , 50% between 50 - 100  $\mu\text{m}$ , 20% between 100 - 110  $\mu\text{m}$  and 20% have diameter between 110 - 150  $\mu\text{m}$ . Cenospheres present a mixed glass and crystalline structure and, according to Vassilev [2], the cenospheres are constituted by 76% of glass, 22% of mineral matter and 2% of char and are comprised mainly of aluminosilicate glass, quartz, mullite, calcite, iron oxides, calcium silicates and sulphates.

Cenosphere formation is similar to the glass blowing process [4]. In fact, silica-containing melts (as in the case of cenospheres), present high viscosity and form glass easily upon cooling [5]. The gases emitted from a char particle during combustion, or from ash particle during melting, inflate the melted inorganic mineral matter and if cooling is fast, amorphous cenosphere can be formed. Gases capable to inflate spherical particle can come from decomposition of calcium and magnesium sulfates, kaolinite, calcium carbonate, dolomite and pyrite oxidation [6] - all those reaction can occur at temperatures below  $1000 \text{ }^\circ\text{C}$ . Time needed to form a 50  $\mu\text{m}$  cenosphere is equal to about 0.3 msec [6]. Vassilev [2] points out, that chlorites and montmorillonites may show some catalytic properties for cenosphere formation, while illite works as a deterring agent. According to Karr [6], at temperature higher than  $1500 \text{ }^\circ\text{C}$ , gas evolution will be so rapid that it will escape from melting ash particle.

## 2. Experimental

Cenospheres were obtained from fly ash samples collected from boiler OP-430, installed in EDF Krakow power plant. Separation was done by wet method – fly ash samples were poured with water, stirred and left for sedimentation during 1 hour. Next, floating particles were skimmed, dried at  $105 \text{ }^\circ\text{C}$  for 2 hours and then burnt for 1.5 hour at  $800 \text{ }^\circ\text{C}$ . Fly ash was collected twice a day – at 5:00 AM and at 4:30 PM. In this study, only samples from ESP (electrostatic precipitator) zone I are considered because about 70 wt.% of all fly ash ends up there. What is more, all samples were collected within a considerably short period of time, which means that power plant's operation conditions, like load and the scale of energy production were very similar during that time. The average mass of each collected ash sample was about 400g. Because the agent used for separation, was demineralized water, all collected cenospheres have density lower than  $1 \text{ g/cm}^3$ .

Samples of cenosphere and fly ash were subjected to several tests. X-Ray Fluorescence (XRF) was done using a Philips PW1480 spectrometer, to determine any correlations between their composition and yield of cenospheres. X-Ray Diffraction (XRD) was done using a PANalytical diffractometer, with  $\text{CuK}\alpha$  radiation, generated at 40 kV and 35 mA, at room temperature, with step of 0.05 and a scan step time of 200s. Scanning Electron Microscopy (SEM) and Electron Dispersive Spectroscopy (EDS) were used to investigate differences between particle morphology, shape, size as well as to determine the chemical composition of those samples. A Bruker Nano GmBH microscope, equipped with a XFlash 5010 detector was

used and the measurements were performed at 20 kV. Based on EDS results, oxide composition of cenosphere and fly ash samples was determined. For each sample EDS analysis was performed three times for different areas of 1mm<sup>2</sup> and afterwards, the average values were calculated. Raman spectra were collected using a LabRAM HR Evolution Confocal Microscope (Horiba Scientific) with 532 nm excitation and a 100x objective lens (NA – 0.9). The laser power on the samples was ~10 mW. The collected Raman radiation was dispersed with a 600 lines/mm grating and focused on a Peltier-cooled (-70<sup>o</sup>) charge-coupled device (CCD) detector allowing a spectral resolution of ca. 4 cm<sup>-1</sup>. All spectra were recorded in the 100-4000 cm<sup>-1</sup> range with an integration time of 10 s and 3 accumulations per spectrum.

### 3. Results and Discussion

#### 3.1. Cenosphere separation

Table 1 presents data from cenosphere separation. The different fly ash samples are organized in terms of growing cenosphere content. Results indicate a strong difference between samples – from only 0.2 wt.% of cenospheres in sample no. 1 up to 1.9 wt.% in sample no. 10. Except for samples no. 8, 9 and 10, results are not impressive regarding a hypothetical industrial separation of cenospheres by the power plant. In Table 1, it is also given the amount of unburned matter measured in each fly ash sample. Figure 1 presents an example picture of the obtained cenospheres. It can be seen that particles present different size and color. Diameters vary from about 30 μm to about 350 μm, which is the most common size range for cenospheres. Although most particles are spherical, some of them have a somewhat irregular and distorted shape. Furthermore, some particles are fully transparent (especially smaller ones) while others are opaque. Color can change from white to yellow or brown. Different colors can originate from trace elements like Fe, Ti or Cu incorporated in the glass phase [1]. Transparent particles are clearly hollow inside, but in case of opaque particles it is not possible to state that, since some particles may have smaller cenospheres trapped inside, the so-called plerosphers.

Table 1 - Results from cenosphere separation

Fly ash sample	Unburned fraction [wt. %]	Cenosphere content [wt. %]
1.	6.26	0.2
2.	3.70	0.3
3.	7.02	0.4
4.	5.16	0.4
5.	3.22	0.4
6.	3.59	0.5
7.	0.59	0.6
8.	8.67	0.8
9.	4.08	1.0
10.	4.30	1.9

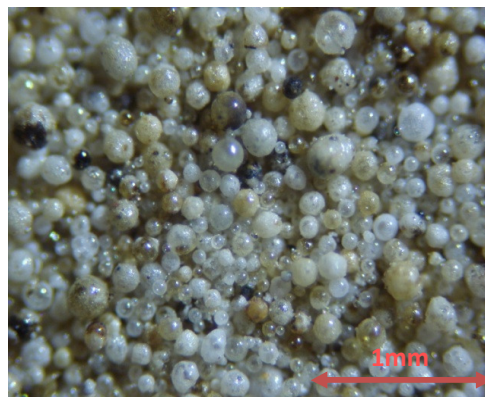


Figure 1 – SEM image of cenosphere sample.

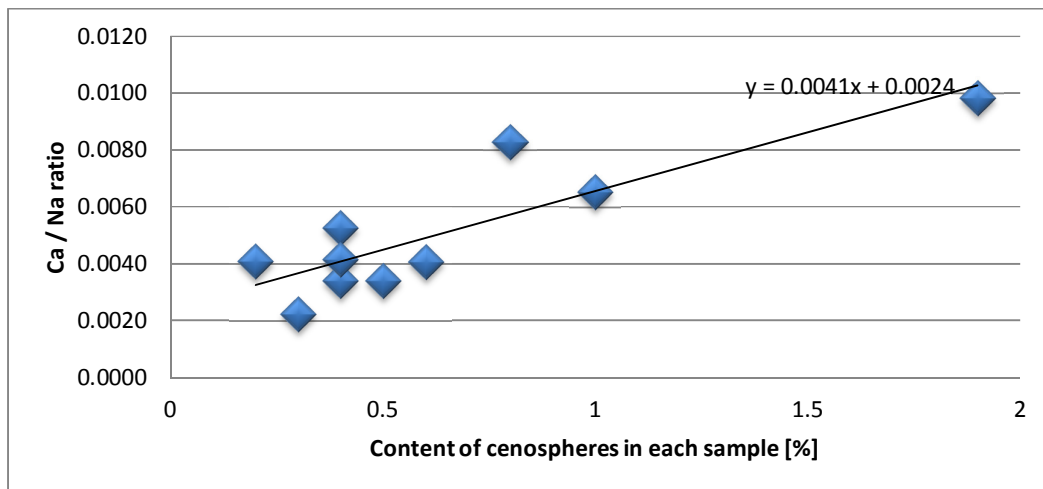
### 3.2. XRF

Results from XRF of the ten fly ash samples are summarized in Table 2, where all the elements are presented in the form of a ratio to silica. This makes the results and comparisons between them more reliable and accurate.

**Table 1 - Data obtained from XRF – elementary analysis of fly ash samples in ratio of silica (Si).**

Sample	Fraction <1g cm <sup>3</sup> [%]	Si / Al.	Si / Ca	Si / Na	Si / Mg	Si / K	Si / Fe	Na / Ca x1000
1.	0.2	1.463	0.761	186.150	17.586	1.614	0.105	4.088
2.	0.3	1.344	0.758	339.156	18.596	1.585	0.112	2.235
3.	0.4	1.394	0.850	249.818	19.430	1.593	0.116	3.402
4.	0.4	1.376	0.461	87.995	13.204	1.806	0.110	5.239
5.	0.4	1.392	0.605	146.416	15.690	1.689	0.113	4.132
6.	0.5	1.381	0.754	221.599	18.090	1.626	0.125	3.403
7.	0.6	1.423	0.949	233.575	20.400	1.437	0.140	4.063
8.	0.8	1.548	0.955	115.619	18.884	1.623	0.119	8.260
9.	1	1.646	0.679	104.121	16.939	1.504	0.109	6.521
10.	1.9	1.471	0.842	85.690	19.052	1.558	0.135	9.826

There is a clear correlation between the content of cenospheres and the amount of sodium in the XRF results. A correlation with calcium content can also be observed, but it is not so strong. However, the best correlation observed – in terms of level of deviations and curve slope – is the one combining the content of sodium and calcium altogether. In the end right column of Table 2, the ratio between sodium and calcium (Na / Ca) is also presented. Graphical description of this data is given in figure 2 along with regression line and respective equation. A general correlation seems to occur, where the amount of cenospheres increases with the Na/Ca ratio. Samples with most satisfactory results have higher Na/Ca ratio, which means more sodium and less calcium content can be found in that samples.



**Figure 2 - Correlation between Na/Ca ratio in fly ash samples and content of cenospheres obtained from given sample.**

### 3.3. XRD

XRD analysis disclosed that the crystalline phases present in the examined cenospheres, are quartz, mullite and calcite. Example XRD pattern for sample no. 8 is presented in Figure 3. The broad ovoid shape of the main curve indicates the presence of an amorphous phase, while the sharp peaks are related to the presence of crystalline phases. Because carbonates like calcite cannot be found at high temperature conditions – calcite is fully decomposed below 1400 °C [7], its occurrence could be an effect of later crystallization. The results obtained – presence of quartz, mullite and calcite - are consistent with the composition of cenospheres described by Vassilev [2].

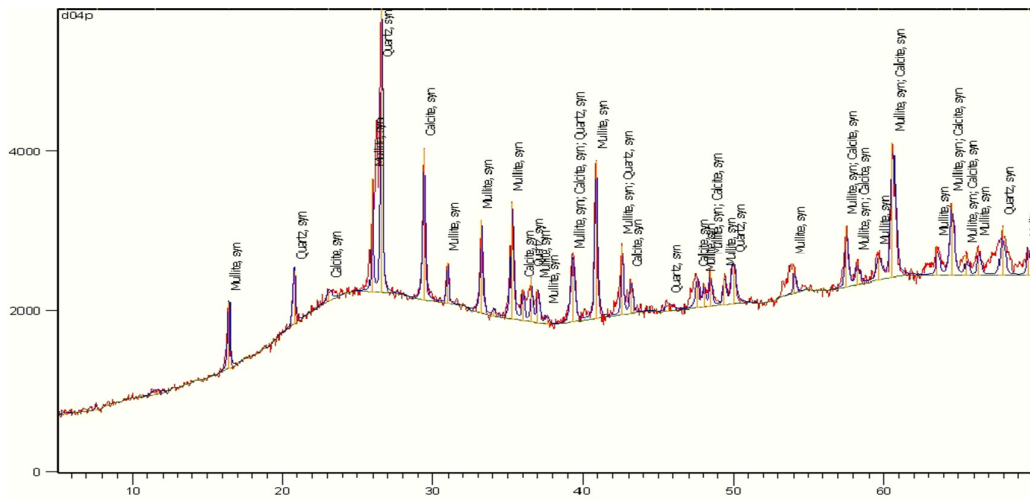


Figure 3 - XRD pattern for cenosphere sample no. 8.

### 3.4. SEM / EDS

Figure 4 presents images of cenospheres and fly ash obtained by Scanning Electron Microscope. Regarding cenospheres (left image), they are spherical and different particle sizes can be observed (~10 to 100 μm). Comparing to the average size of fly ash particles (right image), they have significantly smaller average diameter than cenospheres. The oxide composition of cenospheres and fly ash presented in Tables 3 and 4 was calculated based on results from EDS analysis.

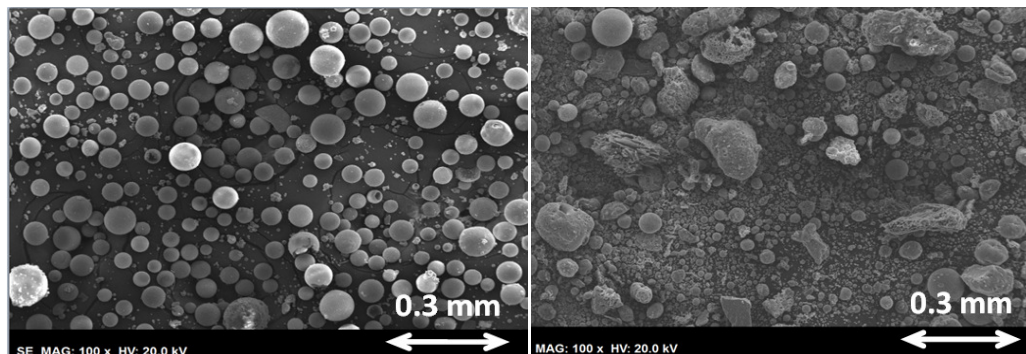


Figure 4 - SEM images of cenospheres (on the left) and fly ash (on the right)

Table 3 presents oxide composition of the cenospheres samples, whereas Table 4 presents results for four samples of fly ash. In particular, two of these samples contain the highest amount of cenospheres (no. 10 and no. 9) while the other two present small yield of cenospheres (no. 1 and no. 4). The composition of cenosphere samples lay between 49.49 – 60.45 % of SiO<sub>2</sub>, 23.20 – 28.30 % of Al<sub>2</sub>O<sub>3</sub>, 0.00 – 14.81 % of CaO, 1.61 – 7.83 % of MgO, 1.77 – 5.43 % of Fe<sub>2</sub>O<sub>3</sub>, 2.04 – 3.62 % K<sub>2</sub>O, 0.00 – 4.83 % of Na<sub>2</sub>O with trace content of TiO<sub>2</sub>. These results are quite interesting, because it is not common for aluminosilicate glasses to have such a high content of alumina. This, in turn, promotes high mechanical strength of cenospheres.

From Table 4, there is a correlation between Na<sub>2</sub>O and CaO content and the yield of cenospheres obtained from each fly ash sample. The content of sodium oxide is increasing with the amount of cenospheres, while the content of calcium oxide is decreasing. This confirms the previous assumption about sodium and calcium influence for cenospheres abundance in fly ash. Similar results were obtained by Itskos [7] – bigger fly ash particles (which are mainly cenospheres) contain more sodium oxide and less calcium oxide than smaller ones.

**Table 2 - Oxide composition of cenosphere samples in [%] arranged in order of growing cenospheres content.**

Sample	Fraction <1g/cm <sup>3</sup> [%]	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	MgO	K <sub>2</sub> O	SiO <sub>2</sub>	Na <sub>2</sub> O	TiO <sub>2</sub>
1.	0.2	23.20	14.81	4.46	2.55	3.01	51.53	0.43	0.00
2.	0.3	27.24	5.82	2.14	1.61	3.33	58.24	1.62	0.00
3.	0.4	28.30	8.53	1.77	7.83	2.04	51.53	0.00	0.00
4.	0.4	26.52	1.12	2.83	4.80	2.82	59.13	1.56	1.22
5.	0.4	26.32	6.56	3.16	1.63	3.41	54.10	4.83	0.00
6.	0.5	25.13	14.69	1.99	3.35	2.23	49.49	3.12	0.00
7.	0.6	25.81	0.00	5.20	2.28	3.62	60.45	1.09	1.56
8.	0.8	25.80	6.00	5.43	3.51	2.40	54.90	1.96	0.00
9.	1	25.13	14.69	1.99	3.35	2.23	49.49	3.12	0.00
10.	1.9	26.88	0.31	1.89	6.25	2.17	56.75	4.44	1.31

**Table 3 - Oxide composition of fly ash samples in [%] arranged in order of growing cenospheres content.**

Sample	Fraction <1g/cm <sup>3</sup> [%]	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	MgO	K <sub>2</sub> O	SiO <sub>2</sub>	Na <sub>2</sub> O	TiO <sub>2</sub>
1.	0.2	21.79	7.98	7.33	5.46	1.86	54.60	0.98	0.00
4.	0.4	22.76	8.10	5.47	7.06	1.52	52.83	1.51	0.75
9.	1	21.26	3.03	3.76	4.47	2.18	60.77	4.53	0.00
10.	1.9	22.91	4.83	5.24	5.75	2.14	55.52	3.20	0.39

According to Vassilev[2], the presence of chlorine can be beneficial for cenosphere formation. The presence of chlorine and fluorine in an aluminosilicate peraluminous melt can increase its viscosity - peraluminous melt occur when the fly ash molar content of Al<sub>2</sub>O<sub>3</sub> is higher than the sum of Na<sub>2</sub>O and CaO [8]. Chlorine alone can, in turn, increase the viscosity of Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> melts [9] and this can promote glass formation [5]. This chlorine effect can give a clue,

why melts containing sodium present higher viscosity than others. What is more, chlorine can possibly enter the combustion chamber and become part of a considered melt, as a component of sodium chloride (NaCl). We can also assume that sodium actually works as a chlorine carrier in fly ash. Another possibility of chlorine effect on cenosphere formation is derived from their formation principles. Fenelonov [10] indicates that sodium chloride (NaCl) is one of possible volatilizing components which are responsible for cenosphere swelling during formation process. In addition, Tomeczek [11] points out, that the vaporizing temperature for NaCl is equal to 1465 °C, which is consistent with preferable cenosphere formation temperature figured out by Vassilev [2] and Karr [6]. However, those hypotheses require further and more detailed investigations.

### 3.5. Raman spectroscopy

Figure 5 shows a Raman spectrum of a cenosphere particle from sample no. 1. The spectrum is typical of a silicate glass, with a broad band at 467  $\text{cm}^{-1}$ , thus confirming the amorphous nature of the cenospheres. However, other spectra (not shown), also presented a narrow peak at 457  $\text{cm}^{-1}$ , indicative of crystalline quartz, thus confirming the XRD results. The narrow peak observed at 1085  $\text{cm}^{-1}$ , also reveals the presence of a crystalline phases and is due to calcite, which again confirms its occurrence detected by XRD. Those two features are visible in most particles tested by Raman spectroscopy; however, a clear signature for mullite was not observed. Unburned carbon particles were also observed ( $\sim 1350$  and  $\sim 1590 \text{ cm}^{-1}$ ), but mainly in samples with lower cenosphere yield.

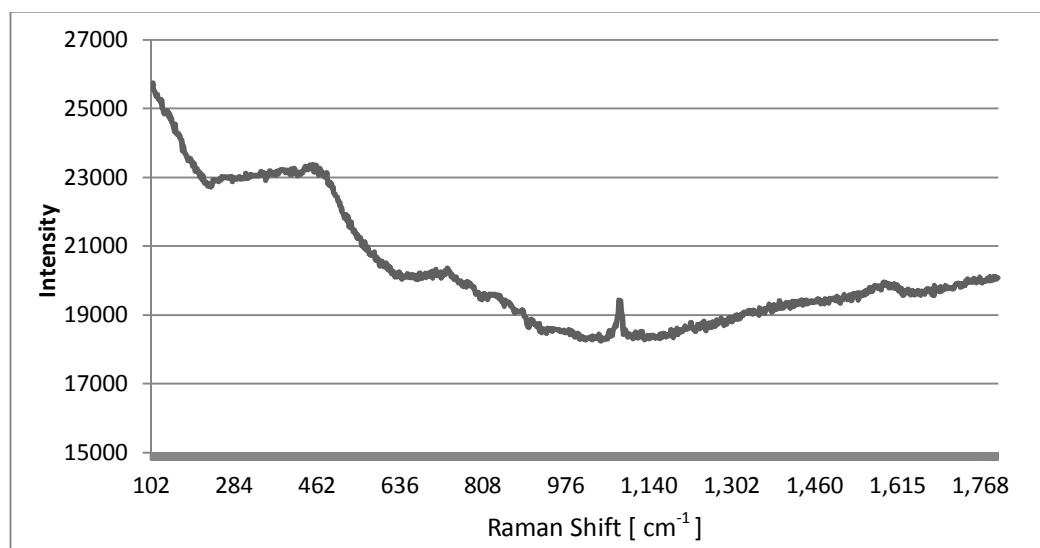


Figure 5 - Raman spectrum of a cenosphere particle from sample no. 1.

### 3.6. Viscosity

Viscosity is one of the most important parameter when glass formation is considered. Table 5 presents theoretical viscosity calculated for four samples of fly ash. Results are given for three distinctive temperatures which are relevant when the cenosphere formation is considered.

Viscosity was calculated using the model proposed by G. Urbain and modified by Kalmanovitch-Frank [12], based on data from Table 4.

**Table 4 - Comparison of viscosities for four fly ash samples for distinctive temperatures.**

Sample:	No. 1	No. 4	No. 9	No. 10
Fraction <1 g/cm <sup>3</sup> [%]	0.2	0.4	1	1.9
Temperature [°C]	Viscosity [Pa s]			
1000	43132	36075	258818	70644
1200	2048	1687	7979	2866
1500	73	64	193	93

From Table 5 it can be clearly seen that viscosity is indeed higher for the two samples with higher cenosphere content. However the correlation is not linear because sample no. 9 reveals more than twice as high viscosity as sample no. 10, whereas regarding content of cenospheres, it is almost the opposite. From Table 4 and 5, it looks like Na<sub>2</sub>O and SiO<sub>2</sub> content increases melt viscosity while CaO content, in opposite, decreases it. This is expected only in the case of CaO and SiO<sub>2</sub>, because sodium itself causes even higher decrease in melt viscosity than calcium [5]. Most probably the influence of calcium is much more visible than the influence of sodium, because the former has significantly more abundant in the examined material [13]. Despite that, the major component which influences viscosity is obviously silica, which is the major component used in glass industry [5]. Also Vassilev [2] points out, that a higher content of quartz and cristobalite (both comprised of Si) can be found in samples with higher cenosphere yield. The same is also visible in Table 5, however the correlation disclosed is not linear. It must be kept in mind, that viscosity calculations presented above are just a rough approximation. Moreover, they are based on oxide composition recalculated from EDS elementary analysis, which was performed on the limited area of the sample and thus may have some inaccuracy.

### 3.7 Analysis of combustion process

All investigated samples of fly ash, were obtained from pulverized coal combustion boiler OP-430 with tangential burners and air staging system, installed in EDF Krakow power plant. There are many parameters that are measured by power plant during its operation, like temperature and pressure distribution in the boiler, the amount of primary and secondary air delivering to the combustion process, parameters of exhaust gases and many others. By analyzing the correlation between these parameters and the amount of produced cenospheres, it turned out, that the yield of cenospheres is increasing with the decrease of temperatures measured upstream from bulkhead superheater. There is more cenospheres produced when temperature in this region is around 700 °C. This temperature drop results in a fast quenching of the melt and from glass formation principals [5], we know that in order to obtain amorphous structure and avoid crystallization, the melt must be quenched quickly enough. Glass transformation temperature for cenospheres should be lower than about 800



°C [2][5]. On the other hand, the range of temperatures in the OP-430 boiler is quite wide – from 130 °C to almost 2100 °C. Therefore, if we can find a path where fly ash particles slip from temperature of about 1500 °C - maximum temperature for cenosphere formation [6] - to temperatures below 800 °C, we could expect cenosphere formation in that region. In terms of boiler OP-430 it can presumably occur either in horizontal position – along the furnace height, or in the vertical position – close to the boiler walls.

#### **4. Conclusions**

Results disclose a strong disproportion in the content of cenospheres among the different fly ash samples. In terms of size and shape, cenospheres present spherical shape with diameters from about 10 to 1000 µm. The smaller particles are mostly transparent, while the larger particles are rather opaque and have different hues. Cenospheres presented high alumina content – about 25-27% and the structure of cenospheres turned out to be mainly amorphous, with the occurrence of crystalline phases such as mullite and quartz. This indicates the occurrence of glass formation process inside the pulverized coal combustion boiler. From glass formation principles, it is known, that to form an amorphous phase, fast quenching of a high viscous melt is necessary. High viscosity comes from cenosphere major component – silica, while fast quenching conditions occur inside the boiler. Therefore, cenospheres are, most probably formed in specific regions of the boiler, where temperature decreases rapidly from about 1500 °C to temperatures below 800 °C. In terms of boiler OP-430, this can presumably occur either in horizontal position – along the furnace height, or in the vertical position – close to the boiler walls. In the temperature zone higher than 1500 °C, gas pressure inside the cenosphere-forming melt, can be too high to maintain spherical shape of the forming particle. Also, temperatures lower than about 700 °C, in the region above bulkhead superheater, seem to be favorable when cenosphere yield is concerned. Based on EDS and XRF data, a correlation between cenosphere yield and the amount of sodium and calcium was observed. A higher amount of calcium in some samples may lead to a decrease in viscosity, which is not beneficial for the glass formation process. In these samples, the yield of cenospheres turned out to be lower. It is more difficult to explain the positive influence of sodium. One possible explanation is that sodium can act as a chlorine carrier (in sodium chloride NaCl) and chlorine itself can increase melt viscosity under certain conditions. Another possibility could be that chlorine especially increases viscosity in melts containing sodium, which in the aftermath give a correlation between sodium and the content of cenospheres in fly ash. Finally, sodium chloride is a compound which can be released during melting process in the favorable temperature range, and therefore it may play role in inflating cenospheres.

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