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Characterization of fly-ash cenospheres from coal-fired power plant unit

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ABSTRACT

Cenospheres are one of the most desired byproducts of coal combustion process nowadays. They are small hollow spheres with roughly 10–1000 μm in diameter and constitute about 1–2% of the fly ash obtained from the coal combustion processes. Because of their specific properties, namely their low density and high mechanical strength, cenospheres are an important subject of coal fired power plants. In this study, several fly ash samples from a coal-fired power plant located in Poland were analyzed in terms of fly ash composition, cenosphere content and its relation with glass formation principles and combustion conditions. The cenosphere samples, with different size, color and shape, were characterized, chemically and structurally, in order to establish the conditions that favor their formation. For this purpose, cenospheres have been collected and characterized by techniques such as SEM, EDS, XRD, XRF and Raman spectroscopy. Results indicate that cenospheres from coal combustion are constituted by aluminosilicate glasses with some crystalline phases like quartz, mullite and calcite. The high alumina content – roughly 25–27 wt.% – is responsible for the high mechanical strength, while density of most cenospheres is lower than 1 g/cm^3. Regarding the formation process, there are correlations between the amount of cenospheres and the sodium and calcium content, in the different fly ash samples.

1. Introduction

Cenospheres are hollow ceramic microspheres that 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 and cenosphere recovery process can add value to the main coal fired power plant activity. 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]. Cenospheres present a mixed glass and crystalline structure with 76% of glass, 22% of mineral matter and 2% of char, being comprised mainly of aluminosilicate glass, quartz, mullite, calcite, iron oxides, calcium silicates and sulfates [2]. Vassilev et al. [2] indicate that cenosphere diameter can vary from 8 μm up to 1000 μm while Kolay and Bhusal [3] correlate the average diameter with density – for particles with density lower than 0.857 g/cm^3, 80% of them have diameter between 50 and 150 μm, 15% diameter between 150 and 200 μm and 5% between 200 and 250 μm. For particles with density lower than 1.282 g/cm^3, 10% of them have diameter between 40 and 50 μm, 50% between 50 and 100 μm, 20% between 100 and 110 μm and 20% have diameter between 110 and 150 μm.

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. On the other hand, if the temperature is high enough and the fall distance is enough, any droplet of melt will become spherical due to surface tension forces [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 [2,6] - all those reactions can occur at temperatures below 1000 °C, while the time needed to form a 50 μm cenosphere is about 0.3 ms [6]. Vassilev et al. [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 temperatures higher than 1500 °C, gas evolution will be so rapid that ash particles escape from melting. The major objective of this work is to determine which factors influence the yield of cenospheres recovered from different fly ash samples. This work was

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done in cooperation with EDF (Electricité de France) coal fired power plant located in Poland, which provided the samples.

2. Materials and methods

Cenospheres were obtained from fly ash samples collected from the hard coal-fired boiler OP-430. Separation was done by wet method – fly ash samples were poured with water, stirred and left for sedimentation during 1 h. Next, floating particles were skimmed, dried at 105 °C for 2 h and then burnt for 1.5 h at 800 °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 (around 7 days), 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 400 g. Because the agent used for separation, was demineralized water, all collected cenospheres have density lower than 1 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 PANanalytical diffractometer, with CuKα radiation, generated at 40 kV and 35 mA, at room temperature, with a step of 0.05 and a scan step time of 200 s. Scanning Electron Microscopy (SEM) and Electron Dispersive Spectroscopy (EDS) were used to investigate differences between particle morphology, shape and size, as well as to determine the chemical composition of those samples. A Bruker Nano GmBH microscope, equipped with an 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 1 mm^2 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 100× 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°) charge-coupled device (CCD) detector allowing a spectral resolution of ca. 4 cm^{-1}. All spectra were recorded in the 100–4000 cm^{-1} range with an integration time of 10 s and 3 accumulations per spectrum.

3. Results and discussion

3.1. Cenosphere separation

Table 1 presents the weight fraction results obtained 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. Table 1 also indicates the amount of unburned matter measured in each fly ash sample.

Table 1
Weight fraction results obtained from cenosphere separation.

Fly ash sample	Unburned fraction (wt.%)	Cenospheres 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

Fig. 1 presents a typical microphotography of the obtained cenospheres. It can be seen that particles present different size and color with diameters varying 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 the 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 [2]. 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.

3.2. XRF

Results from XRF analysis 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. There is a general correlation, for the obtained samples, 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 evident. 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 Fig. 2 along with regression line. A general correlation seems to occur, where the amount of cenospheres increases with the Na/Ca ratio. Samples with higher cenosphere yield present higher Na/Ca ratio, which means, more sodium and less calcium can be found in those samples.

3.3. XRD

The XRD pattern for sample no. 8 is presented in Fig. 3 and is illustrative of all samples. The broad ovoid shape of the main curve indicates the presence of an amorphous phase, while the sharp

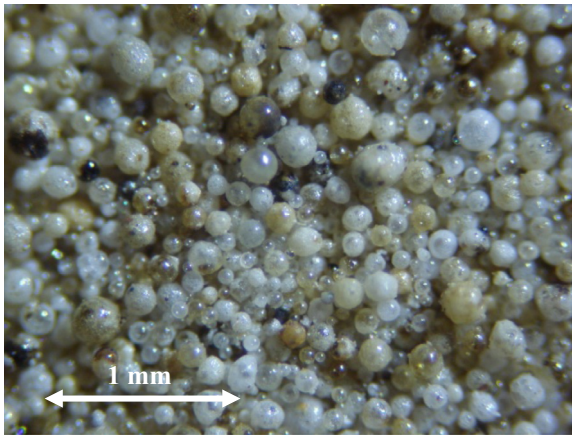

Fig. 1. Microphotography of obtained cenospheres.