Influence of chemical composition of fly-ash cenospheres on their grains size

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Abstract
Cenospheres, which are the by-product of hard coal combustion, are characterized by properties allowing for a broad use of this material. The article presents the results of the chemical composition analysis of the cenospheres obtained from various power plants. It has been exhibited that depending on the place of origin, their chemical composition is similar and comparable to fly ash produced in hard coal combustion. A great majority of analysed cenospheres may be classified similarly as the sialic ashes—slightly acidic. The analysis of dependence of refractoriness of the cenospheres on their chemical composition confirmed the correlation between this parameter and the content of SiO2 and Al2O3. At the same time, the content of each of the chemical components indicates a correlation with the size of the cenospheres. A trend of SiO2/Al2O3 ratio decreasing along with the increasing size of the cenospheres has been noted. Also the content of K2O and—to a lesser extent—Na2O decreases along with increasing diameter of grains. An inverse correlation was noted in case of Fe2O3. The higher the diameter of the grains, the higher the content of this component. In view of the obtained results, it should be assumed that the division of cenospheres into grain-size classes before further industrial use could extend the current range of use of this material.

Keywords Cenospheres · Chemical composition · Fly ash · Size of cenospheres

Introduction
Cenospheres are a by-product, but also one of the more valuable coal combustion products (Ranjba and Kuenze 2017). Most often, cenospheres are spherical and filled with gas (mostly CO2 and N2) (Li 2012; Pichór 2005; Pétrich and Petri 2003; Acar and Atalay 2016; Novoselova et al. 2008). Cenospheres are particles of ash with a density lower than the density of water, which facilitates their separation by floatation in sedimentation tanks of power plants (Manocha et al. 2011). Their size usually fits within the range from 5 to 500 μm, usually from 20 to 200 μm (Pichór 2005; Joseph et al. 2013; Soh et al. 2016). Sporadically, also larger particles have been noted in some ashes (Vassilev et al. 2004; Žyrkowski et al. 2016; Strzałkowska and Stanienda Pilecki 2018). The thickness of the walls of cenospheres usually constitutes from 5 to 10% of their diameter (Pichór and Petri 2003; Strzałkowska and Stanienda Pilecki 2018). One of the key parameters determining the possible use of waste is the chemical composition (Ulíasz-Bocheńczyk and Mokrzycki 2018). The largest part is constituted by SiO2 silica (45–60%) and Al2O3 white clay (20–30%) (Żyrkowski et al. 2016; Haustein and Quant 2011; Kapuściński and Strzałkowska 2008; Senthamarai Kannan et al. 2016; Fomenko et al. 2012), which ensures their high mechanical strength (Żyrkowski et al. 2016; Dey and Pandey 2016). The remaining components: Fe2O3 and CaO, MgO, SO3, K2O, Na2O and TiO2, occur in low concentrations (Vassilev et al. 2004; Strzałkowska 2017; Ng et al. 2007). The chemical composition of cenospheres is determined by the type of the mineral substance present in coal, which is a subject to transformations related to high temperature: dehydration, decarbonatization or oxidation. Reduction in iron oxides is considered one of the most important reactions in the process of mineral substance expansion, as it reinforces the processes of coal oxidation and combustion. According to
Raask (1968), the content of iron oxides is an important factor determining the formation of microspheres. The authors of the work (Ngu et al. 2007; Yu et al. 2012) do not share this opinion, stating that iron oxide is the main component of the magnetic fraction of ashes but is not necessary in the formation of cenospheres. The presence of Fe₂O₃ and TiO₂, on the other hand, causes a change of colour of cenospheres from white to yellow or brown (Żyrkowski et al. 2016).

Authors of the works (Żyrkowski et al. 2016; Itskos 2010) provide that a correlation exists between the content of Na₂O and CaO and the amount of cenospheres obtained from fly ash. The increase in sodium content—at a simultaneously decreased content of calcium, facilitates the intensification of the cenosphere formation in ash. According to the authors, a larger amount of calcium causes a lower viscosity, which is adverse in terms of the glass formation process. The positive impact of sodium in the cenosphere formation process is, on the other hand, debatable. One possible explanation is the fact that sodium may be supported by NaCl and the chlorine itself may increase the viscosity of alloy in certain conditions (Vassilev et al. 2004; Żyrkowski et al. 2016). According to Łączny and Wałek (2011), the amount of cenospheres obtained from fly ash results mostly from the parameters of combustion process and not the composition of the feed material. The dependence of the chemical composition and the size of microspheres is rarely mentioned. It has been observed that the high value of the SiO₂/Al₂O₃ indicator facilitates the formation of particles with a smaller diameter (Haustein and Quant 2011; Ngu et al. 2007), while the content of iron oxide, magnesium and sodium decreases along with the increasing cenosphere diameters (Haustein and Quant 2011). The earlier findings by Itskos (2010) have not been thus confirmed, as he observed that larger particles contain more sodium and magnesium oxides and less calcium oxide. The literature also notes the fact that the concentrations of Cu, Zn, Pb, Ni and Cr are increased along with increasing particle diameters (Haustein and Quant 2011; Bradlo 2016). This dependence was not confirmed for cadmium (Haustein and Quant 2011). Although the content of the elements in cenospheres is highly variable, the highest concentrations were exhibited by alkaline metals, mostly Ba, Sr and Rb (Bradlo 2016).

The purpose of this study was to determine the extent to which the size of the cenospheres is related to their chemical composition. The study encompassed samples of cenospheres available at the domestic and foreign markets.

**Materials and methods**

For the purpose of the study, samples of microspheres from sedimentation tanks of three power plants were acquired (Dolna Odra, Opole and Kazakhstan).

The granulometric composition of the acquired samples was established using the sieve method. In the tests, the following mesh sizes were used: 0.8; 0.7; 0.6; 0.5; 0.25; 0.125; 0.071; 0.063; and 0.045 mm.

The chemical composition was established by means of X-ray fluorescence method using the ZSX PRIMUS spectrometer manufactured by RIGAKU.

The study was extended to microanalyses using a Hitachi SEM SU3500 vacuum microscope with variable concentration.

**Fig. 1** Cumulative grain-size composition curves of cenospheres
scanning microscope, cooperating with an X-ray spectrometer with EDD UltraDry energy dispenser from the Thermo Scientific NORAN 7 system. X-ray microanalysis was carried out using the following parameters: accelerating voltage—15 keV, working distance (WD)—10 mm, pressure—30 Pa, vacuum—variable. Four grain classes of cenospheres were selected for the tests, namely < 0.045 mm; 0.045–0.063 mm; 0.125–0.25 mm; and 0.25–0.50 mm.

Results and discussion

Granulometric composition of the cenospheres

Nine grain classes were distinguished in granulometric analysis. Based on the calculated percentage of each of the grain classes, cumulative curves of size composition were prepared (Fig. 1) The largest grain sizes were exhibited by the sample of cenospheres from Kazakhstan. The class

| Grain class (mm) | Value | SiO₂ | Al₂O₃ | SiO₂/Al₂O₃ | Fe₂O₃ | Na₂O | K₂O | MgO | CaO | No. of measurement points |
|-----------------|-------|------|-------|-------------|-------|------|-----|-----|-----|---------------------------|
| Below 0.045     | Min.  | 44.60| 18.55 | 1.11        | 0.00  | 0.00 | 0.00| 0.00| 0.00| 43                        |
|                 | Max.  | 81.45| 43.22 | 4.39        | 12.33 | 7.52 | 10.63| 3.23| 4.12|                           |
|                 | Mean  | 59.23| 33.06 | 1.92        | 1.47  | 1.21 | 3.26| 0.89| 0.39|                           |
| 0.045–0.063     | Min.  | 48.81| 10.83 | 1.15        | 0.00  | 0.00 | 0.00| 0.00| 0.00| 41                        |
|                 | Max.  | 89.17| 44.64 | 8.23        | 8.31  | 2.98 | 6.34 | 5.07| 4.87|                           |
|                 | Mean  | 57.84| 34.16 | 1.83        | 2.03  | 0.85 | 3.09| 1.47| 0.30|                           |
| 0.125–0.25      | Min.  | 40.0 | 14.2  | 1.2         | 0.0   | 0.00 | 0.00| 0.00| 0.00| 43                        |
|                 | Max.  | 80.7 | 45.6  | 5.7         | 28.4  | 3.3  | 7.4 | 9.06| 10.9|                           |
|                 | Mean  | 56.05| 33.64 | 1.79        | 3.38  | 0.56 | 2.86| 1.50| 1.04|                           |
| Over 0.25       | Min.  | 35.24| 19.37 | 1.09        | 0.00  | 0.00 | 0.00| 0.00| 0.00| 45                        |
|                 | Max.  | 78.88| 46.37 | 3.73        | 24.67 | 3.10 | 6.24| 4.97| 12.95|                          |
|                 | Mean  | 55.26| 32.78 | 1.78        | 5.03  | 0.61 | 2.25| 1.74| 1.84|                           |
exceeding 0.125 mm constituted as much as 95% of the sample, while it was only 23% of the sample acquired from the Dolna Odra plant. The location of the cumulative curve, which represents a sample of microspheres from the Dolna Odra power plant, near the left-bottom corner of the graph, confirms the high content of fine grains below 0.3 mm (almost 100%) in the material.

**Chemical composition of cenospheres (XRF)**

In the microspheres from Opole, Dolna Odra and Kazakhstan power plants, SiO$_2$ and Al$_2$O$_3$ were the dominant chemical components. Their total content exceeded 80% of the mass and reached as much as 90% of the mass in case of the power plant in Kazakhstan (Table 1). In case of the latter, characterized by the largest grains, the value of the SiO$_2$ to Al$_2$O$_3$ indicator was the lowest. The content of components, such
Fig. 4 Variability of the mean SiO₂/Al₂O₃ ratio in selected grain classes of cenospheres.

Fig. 5 Position of the Opole Power Plant cenospheres in the classification of fly ash produced in coal combustion (Vassilev and Vassileva 2007).
as TiO$_2$, Fe$_2$O$_3$, MgO, CaO and K$_2$O, reached only several per cent in all the samples, while the content of remaining components has not reached 1% of the mass. The chemical composition of cenospheres which were a subject to the study was similar to the composition of fly ash (Adamczyk and Białecka 2005; Kurdowski 2010; Haustein and Quant 2011; Giergiczny et al. 2016).

The sample of the cenospheres from the power plant in Kazakhstan, characterized by the highest total content of silica and white clay (over 90% of mass), and the low content of fluxes (approx. 6%), has exhibited the highest refractoriness, that is, 1685 °C. In case of the sample of cenospheres from the Opole Power Plant, that is, the one with the lowest refractoriness, the lowest content of Al$_2$O$_3$ was also noted, while the total of oxides classified as fluxes exceeded 14% of the sample’s mass.

Microanalysis of the chemical composition of cenospheres (SEM)

To make the results more precise, the study was complemented with a chemical microanalysis of the selected grain-size classes of the cenospheres. The results are listed in Table 2 and presented in Figs. 2, 3, 4, 5, 6, 7 and 8. The performed analyses have indicated local variability of the chemical composition of cenospheres, while the following has been noted: increase in the Fe$_2$O$_3$, MgO and CaO contents along with the increase in the size of the cenospheres (Fig. 2, 3) and decreasing trend of K$_2$O content along with the increasing size of cenospheres.

A similar dependence as K$_2$O was observed for Na$_2$O, but it was not that strong (Fig. 3).

Higher contents of alkalis (K$_2$O and Na$_2$O) in smaller-size microspheres are probably related to their melting point. As is well known, K$_2$O and Na$_2$O lower the melting point; components such as Fe$_2$O$_3$ and MgO lower it slightly, whereas SiO$_2$ and Al$_2$O$_3$ increase its value (Vassilev et al. 1995; Jing et al. 2012; Drzymała et al. 2014; Mishra et al. 2016). Therefore, mineral components containing alkalis will melt faster than the components without them. Drops of an alloy with a higher content of K$_2$O and Na$_2$O, in the stream of flue gas, will be characterized
by lower viscosity than a drop of an alloy with a smaller amount of these components. Due to the fact that all solid and liquid components (alloy drops) contained in the flue gas stream are in motion, they must collide with each other. An alloy drop after hitting a solid grain may: (1) splash (very low viscosity of the alloy—higher contents of K2O and Na2O), (2) spread on its surface (higher viscosity of the alloy—low contents of K2O and Na2O) or (3) adhere to it (the highest viscosity of the alloy—the lowest contents of K2O and Na2O), forming aggregates (Fig. 8d). In the first case, they will form cenospheres with the smallest dimensions, which will grow as the contents of K2O and Na2O decrease.

At the same time, a considerable decrease in the value of the SiO2/Al2O3 ratio has been noted along with the increase in the size of cenospheres (Fig. 4).

The projection of chemical composition of the cenospheres (constituting a prepared part of fly ash) in a classification triangle presented in Vassilev and Vassileva (2007) indicates that a vast majority of tested cenospheres is classified similarly to sialic ashes, irrespective of their place of origin (power plant) (Figs. 5, 6, 7). The remaining cenospheres are also of different types, mostly ferrisialic and rarely calsialic.

**Conclusion**

The presented results of the study have exhibited that cenospheres originating in different power plants may vary considerably in terms of grain sizes. Irrespective of the place of origin, however, their chemical composition is similar and comparable to fly ash produced in hard coal combustion. The analysis of dependence of refractoriness of cenospheres on their chemical composition has confirmed a positive correlation between the refractoriness of a sample and the content...
of SiO₂ and Al₂O₃. The projection of chemical composition in the classification triangle indicates that most of the analysed cenospheres may be classified as sialic ashes, or—least frequently—ferricalsialic and calsialic. At the same time, the content of individual chemical components is correlated to the size of the cenospheres. A trend of SiO₂/Al₂O₃ ratio decreasing along with the increasing size of the cenospheres has been noted, which had been indicated in the professional literature earlier. The increase in the diameter of the cenospheres was simultaneously related to the increase in the iron content. It may be thus assumed that the presence of iron oxides facilitates the formation of larger cenospheres, but is not necessary in their formation. The formation of larger diameters of the particles is dependent on gases causing an outward pressure in the particle. According to Raask (1968), this requires a certain amount of iron oxide. In wet separation of cenospheres, the larger particles will float more easily in the sedimentation tank, because the gravity force exerted on the cenosphere will have a smaller value than the buoyant force. A similar correlation between the increase in the content of a component and the increasing diameter of the particles has been noted for magnesium oxide and—to a lesser extent—for calcium oxide. The correlation previously provided in the professional literature has not been thus confirmed (Itskos 2010). A detailed interpretation of SEM (scanning electron microscope) results allows for a partial explanation of this phenomenon. The coarser class of grains often contains particles with much lower sphericity and inclusions of finer particles (Fig. 8). These grains might disturb the dependencies found earlier. It should be noted that the study by Itskos did not concern cenospheres, but ashes produced in the combustion of brown coal. It is common knowledge that ashes of that type exhibit a high content of calcium oxides.

K₂O and Na₂O are important chemical components of cenospheres, because as their content increases, the diameter

Fig. 8 An example of a SEM image of cenospheres according to grain class and power plants: a <0.045 mm (Dolna Odra); b 0.045–0.063 mm (Opole); c 0.125–0.25 mm (Kazakhstan); d 0.25–0.50 mm (Dolna Odra)
of cenospheres decreases. The mechanism of the formation of cenospheres with different contents of these components is quite complicated and remains correlated with the temperature and viscosity of molten mineral components.

The conducted study has confirmed that size of cenospheres is related to their chemical composition. In view of the obtained results, it should be assumed that the division of cenospheres into grain-size classes before their further industrial use could extent the current range of use of the material. Both chemical composition and sizes of cenospheres are main parameters that are decisive for their further use. A continuous control over these parameters may allow to obtain a product characterized by a higher quality. Due to the high demand, also the cost of production is of significance.

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