# DRYING OF CENOSPHERES RECOVERED BY THE WET-BASED METHOD FROM COAL FLY ASH FOR THEIR RATIONAL USE

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**Abstract.** Since slag and coal fly ash (CFA) are major global pollutants produced by thermal power plants (TPPs), special attention should be paid to their rational disposal. Scanning electron microscopy (SEM) was used to study the morphology of CFA and it was suggested that the use potential of CFA is high due to the presence of a large number of cenospheres (CSs), that can be recovered mostly by wet methods for the production of the wide range of products with improved properties. However, such decisions regarding the application of the cenospheres are largely related to the problem of their drying after removal.

The article is devoted to the investigation of the filtration method as less energy-consuming for the drying of cenospheres. The effect of the drying agent velocity on the mass transfer intensity has been established. The values of mass transfer coefficients have been calculated based on the thin-layer experimental data and equation  $\Delta W / \Delta \tau = \beta \cdot F \cdot x_{sat.} - (x_{sat.} + x_0) / 2 \cdot \rho$ . Calculated mass transfer coefficients for cenospheres have been correlated by the dimensionless expression  $Sh = 0.059 \cdot \text{Re}_e^{0.65} \cdot Sc^{0.33}$ , based on which equation  $\beta = 0.059 \cdot \text{w} \cdot d_e / \nu^{-0.65} \cdot \nu / D^{-0.33} \cdot D / d_e$  has been proposed to calculate the mass transfer coefficients, which is important at the filtration drying equipment design stage.

**Keywords**: thermal power plant (TPP), slag, coal fly ash, ash/slag dump, ash/slag settling pond, cenospheres, utilization, filtration drying method, mass transfer coefficient.

## 1. Introduction

Nowadays, approximately 40 % of global electricity is generated by coal-fired thermal power plants (TPPs). However, in addition to electricity, slag and coal fly ash (CFA) as by-products account for up to 16 % as a result of the coal burned, therefore millions of tons are produced annually. Ash/slag dumps and ash/slag settling ponds occupy large areas in the near vicinity of the TPPs. Since slag and CFA are air, soil, and water contaminants, particular attention should be given to their safe and rational disposal.

In general, slag is a valuable raw material for the production of building materials (Mammadov, Gadirov, 2018; Mitin et al., 2021; Kosivtsov et al., 2021), and the recovery of silicon and aluminum oxides (Hower et al., 2013). Due to the fact, that CFA is a complex system consisting of particles of different morphology and phase composition, and is characterized by fluctuations in composition and properties, only about 20–30 % of the CFA is used as secondary resources (Goga et al., 2013), especially for the production of cements (Badanoiu & Voicu, 2011), concretes (Zhuang et al., 2016), glass-ceramics (Cheng et al., 2002), while the remaining quantity is mainly deposited and thus constituting a

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chemical pollution source. But the potential of CFA is much higher due to the presence of large number of value-added structural elements formed as the result of the powdered coal combustion in TPPs furnaces at temperatures regime of 1000-1800 °C, during which the volatile matter and carbon are incinerated while impurities (clay, quartz, feldspar) melt and then condense, as the temperature is reduced, to form spherical particles with a diameter of several tens or hundreds of microns (Dzikuć et al., 2020). In general, these particles are represented by Al-Si-containing, hollow thin-walled spheres also called microspheres or cenospheres (CS) (Yadav et al., 2021). The variety of CSs is presented by plerospheres - encapsulated spheres with numerous smaller particles within them (Goodarzi, Sanei, 2009) and ferrospheres - ferrous-rich particles that are magnetic (Strzałkowska, 2021). There is a variation in the quantitative content of CSs and their chemical composition across the TPPs depending on the geological and chemical features of the coal type burned and on the combustion conditions. Given that CS total wt. fraction is only about 1-2 % in CFA (Zyrkowski et al., 2016), and, accordingly, there content is low in ash/slag mixtures, the methods applied for their recovery have to be reviewed.

#### 2. Statement of the problem and its solution

A hydraulic method is the most relevant to remove slag and ash from TPPs. After the pulp enters ash/slag settling ponds, the lightweight CSs float to the water surface, forming a "foam layer" and are collected by pumps. For the CSs recovery from CFA caught with the help of electrostatic precipitators and removed as a finely dispersed material, both dry and wet-based methods are used (Yadav et al., 2021). The dry-based method mainly uses air classifiers to separate CS particles from CFA and magnetic classifiers to separate ferrospheres from the total volume of material (Hirajima et al., 2010). In most cases, wet separation is applied to separate lowdensity cenospheres. The gravity separation or flotation methods implemented in liquid media such as water or an organic solvent, cenospheres are separated from ash in a laboratory plant or industrial conditions. Consequently, in the flotation tank fitted with an agitator or stirrer, heavier particles settle down, while lighter particles (CS) float at the top (Yadav et al., 2021; Walker, Wheelock, 2006). The efficiency of the CS recovery depends on several factors, including particle characteristics such as size, density, porosity, and texture of the surface (smooth-surfaced or rough-surfaced particles).

Due to micron sizes and exceptional properties, such as low weight and low bulk density, high thermal resistance and low thermal conductivity, high machinability, and high mechanical strength, cenospheres can be used for the production of the wide range of products with improved properties: cementitious (Adesina, 2020), concrete (Haustein, Kuryłowicz-Cudowska, 2020; Patel et al., 2019), ceramic/nano ceramic (Shao et al., 2008), plastics (Nakonieczny et al., 2020), high-temperature thermal barrier coatings (Arizmendi-Morquecho et al., 2012), cenosphere-based composites with insulating properties (Nithyanandam & Deivarajan, 2021). However, such decisions regarding the application of the cenospheres are largely related to the problem of their drying after removal from ash-slag dumps, ash-slag settling ponds, or CFA by using wetbased methods. A typical technological scheme for drying CSs consists of a vacuum filter; an intermediate storage hopper with a feeder; a dryer with a heat generator for preparing a drying agent; and a dust cleaning system (Progress, 2023). The drum dryer can be replaced with the filtration dryer as less energy-consuming equipment in which the drying agent is blown downward in a wide range of velocities through the material located on a perforated belt (Mitin et al., 2021; Kindzera et al., 2020). The filtration drying method allows intensifying mass and heat transfer processes. Therefore, it will be useful to know the values of mass transfer coefficients during the filtration drying of CSs as well as to create the equation to predict them in a wide range of velocities.

The aim of this work is to determine the mass transfer coefficients from the drying agent to the fixed bed of wet cenospheres (which were previously recovered by the wet-based method from coal fly ash) during the filtration drying and to estimate the equation that allows to calculation them at different actual velocities of gas flow.

## 3. Experimental part

#### 3.1. Materials

Coal fly ash (CFA) was collected from TPP electrostatic precipitators, in which ash is extracted from flue gases. CFA was the subject to wet separation of cenospheres. The sink-float method was employed to separate the lightweight cenospheres. Water was used as the medium and the cenospheres layer, as the floating part, was harvested from the surface of the liquid. Also, CSs were collected from ash/slag settling ponds.

#### 3.2. Experimental procedure

The scanning electron microscopy (SEM) was used to study the morphology of CFA and CS samples.

SEM images at 100 and 500 micron magnification were obtained by registering secondary electrons and scanning under the accelerating voltage of 14.27 kV on the samples with no coating.

Samples of CSs obtained by the sink-float method and collected from ash/slag settling ponds were dried by using the filtration-drying method. For the kinetics investigation, a set of experiments was performed by supplying a heat agent to the chamber with the fixed bed of material (Kindzera et al., 2020) ( $H_{CSs} = 12 \cdot 10^{-3} m$ ) with velocities ranging from 0.68 up to 2.03 m/s. Analytical scales were used to determine the loss of weight during the drying process. "Thinlayer" formed with CS particles provides exerlent distribution of the drying agent throughout the volume of the material, therefore experiments were also used for mass transfer coefficient determination.

## 3. Results and Discussions

SEM studies of CFA sample make it possible to visualize morphologically, shape and size different particles formation of which is depending on the combustion temperature and the cooling rate of the boiler and its operating conditions. Fig. 1 shows that most particles of the CFA, so called main CFA particles (carbon particles, i. e., unburned carbon soot and chars), have an



irregular shape ore are angular with the sizes ranging from 5 to 650 microns. Some of the particles appeared spherical – so called CSs, forming as the result of noncombustible minerals liquefying and rapidly cooling.

The sink-float method was employed to separate cenospheres from CFA, and after, they dried using the filtration dryer.

The SEM images of the CSs are shown in Fig. 2, a, b. As is seen in the low magnification image (Fig. 2, a), most CS particles have perfect shape-form or are close to it. Most cenospheres are intact, while damaged spheres or partially broken were observed in a slight amount.



Fig. 1. SEM images of CFA sample at 100 micron magnification



**Fig. 2.** SEM images of CS sample collected by wet-based method: a – at 100 micron magnification; b – at 500 micron magnification

Fig. 2, *b* shows, that the surfaces of most particles are smooth, some amount of particles have slight porosity surfaces. It should be noted, that small particles depositing on the CS surfaces (agglomerates and irregularly shaped particles) were observed, which were formed, probably, due to the melting of the mineral (e.g., quartz) around the inter-particle contact

and its rapid cooling. CSs are characterized by a high degree of dispersion (Fig. 2). Analysis of the granulometric composition of CS showed that the particle size falls in the range of 20–400 microns (mostly about 100 microns).

Samples of wet CSs (obtained by the sink-float method and collected from ash/slag settling ponds)

or

were dried using the filtration-drying method, and the results in the form of graphs are shown in Fig. 3. Kinetik curves (Fig. 2) show the decrease in drying time while the velocity increases.

Taking into account that the whole fixed layer of the CSs participated in the mass transfer process, the values of the mass transfer coefficient from the wet CS particles to the heat agent at different velocities of blowing were calculated based on the "thin layer" experimental data by following equation:

$$\frac{\Delta W}{\Delta \tau} = \beta \cdot F \cdot \left( x_{sat.} - \frac{x_{sat.} + x_0}{2} \right) \cdot \rho , \qquad (1)$$

where  $\beta$  is the mass transfer coefficient from the heat agent to wet CS particles, m<sup>2</sup>/s;  $x_0$ ,  $x_{sat}$  is the moisture content of the heat agent is initial and in the state of saturation, correspondingly.

Calculated values of the mass transfer coefficients at differerent heat agent velocities are presented in Table 1.

 $w^c$ , kg  $H_2O/kg$  dry. SCs.



**Fig. 3.** Kinetics of the filtration drying of CSs at different velocities of the drying agent:  $(T=353K, H_{CSs} = 12 \cdot 10^{-3}m)$ 

Table. 1

Calculated values of the mass transfer coefficients at differerent heat agent velocities

w, <i>m</i> / <sub>s</sub>	1.34	2.05	2.75	3.41	4.11
$\beta, m/s$	0.038	0.048	0.056	0.064	0.075

Using the methods of similarity theory, the generalization of mass transfer results can be presented in the form:

$$Sh = f$$
 Re,  $Sc$ ; (2)

$$Sh = A \cdot \operatorname{Re}^n \cdot Sc^m,$$
 (3)

where  $Sh = \beta \cdot d_e / D$ ,  $\text{Re} = w \cdot d_e / \nu$ ,  $Sc = \nu / D$  – Sherwood, Reynolds and Schmidt numbers, respectively,

where  $d_e$  is the equivalent diameter of channels in the CSs fixed bed, m; *D* is the mass diffusivity of the water waper to the heat agent, m<sup>2</sup>/s;  $\nu$  is the kinematic viscosity of the heat agent, m<sup>2</sup>/s.

The values of the coefficient "A" and exponents "*n*" and "*m*" should be experimentally determined for using the Eq. (5). So, the exponent m = 0.33. According to the recommendations, we assume Sh ~  $Sc^{0.33}$ , and to determine the coefficient A and exponent "*n*" in Eq. (3), the experimental data were plotted as the dependence  $\frac{Sh}{Sc^{0.33}} = f$  Re in the logarithmic coordinates (Fig. 4).

The value of the coefficient A equals to 0.059 and exponent "*n*" equals to 0.65.

$$Sh = 0.059 \cdot \operatorname{Re}_{e}^{0.65} \cdot Sc^{0.33}$$
. (4)



Fig. 4. Generalization of the experimental results:  $Sh / Sc^{0.33}$  versus Reynolds number

Since the Sherwood number includes the value of the mass transfer coefficient, the Eq. (4) may be represented as:

$$\beta = 0.059 \cdot \left(\frac{w \cdot d_e}{\nu}\right)^{0.65} \cdot \left(\frac{\nu}{D}\right)^{0.33} \cdot \frac{D}{d_e} \,. \tag{5}$$

Therefore, the deduced Eq. (5) makes it possible to calculate theoretically with sufficient accuracy the mass transfer coefficients during the filtration of the heat agent through the fixed bed of CSs within Reynolds number  $20 \le \text{Re} \le 100$ .

## 4. Conclussion

Scanning electron microscopy (SEM) was used to study the morphology of CFA and it was suggested that the use potential of CFA is high due to the presence of a large number of cenospheres (CSs), that can be recovered mostly by wet methods and can be used in rational way only after drying.

The filtration method as less energy-consuming for the drying of cenospheres was proposed, and the effect of the increasing drying agent velocity on the mass transfer intensity has been established by conducting thin-layer experiments. The values of mass transfer coefficients have been calculated on the basis of the thin-layer experimental data and equation  $\Delta W / \Delta \tau = \beta \cdot F \cdot x_{sat.} - (x_{sat.} + x_0) / 2 \cdot \rho$ .

Calculated mass transfer coefficients for cenospheres have been correlated by the dimensionless expression  $Sh = 0.059 \cdot \text{Re}_e^{0.65} \cdot Sc^{0.33}$ .

The deduced Eq.  

$$\beta = 0.059 \cdot \left(\frac{w \cdot d_e}{\nu}\right)^{0.65} \cdot \left(\frac{\nu}{D}\right)^{0.33} \cdot \frac{D}{d_e} \text{ makes it possible}$$

to calculate theoretically with sufficient accuracy the mass transfer coefficients during the filtration of the heat agent through the fixed bed of cenospheres (CSs) within Reynolds number  $20 \le \text{Re} \le 100$ .

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