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CENOSPHERES AS AN INNOVATIVE FLUIDISED BED MATERIAL

CENOSFERY JAKO INNOWACYJNY MATERIAŁ ZŁOŻA FLUIDALNEGO

Abstract

In this paper, the possibility of achieving a stable fluidised bed made of the cenospheres was examined. Cenospheres are the waste material from hard coal power plants. This material is perfectly spherical, and it is thin-walled and filled with gases (mainly CO_2, N_2). Because of their low density, particle size and sphericity, cenospheres can be easily fluidised even at low flow rates of the fluidising medium. Moreover, the application of acoustic waves during the fluidisation of cenospheres removes the apparent effect of double stationary states and moves the minimum fluidisation velocity into lower gas flow rates.

Keywords: cenospheres, fluidised bed, minimum fluidization velocity

Streszczenie

W niniejszej pracy zbadano możliwość stworzenia złoża fluidalnego z materiału cenosfer. Cenosfery są materiałem odpadowym z elektorciepłowni. Idealnie kuliste, o cienkich ściankach, wypełnione w środku gazami (CO_2, N_2) są materiałem niezwykle lekkim. Ze względu na niewielkie wartości gęstości, sferyczny kształt oraz rozmiary ziaren cenosfery dają się łatwo sfluidyzować już przy niewielkich przepływach czynnika fluidyzującego. Zastosowanie fal akustycznych podczas fluidyzacji cenosfer niweluje pozorny efekt podwójnej stacjonarności oraz przesuwa początek fluidyzacji w kierunku niższych wartości przepływu gazu przez złoże.

Słowa kluczowe: cenosfery, złoże fluidalne, prędkość minimum fluidyzacji

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1. Introduction

The fluidisation phenomenon is based on the suspension of solid particles in a stream of liquid or gas flowing from the bottom of the reactor [1]. In this way, solid particles take the form of pseudo-liquid, thereby gaining properties that are advantageous from the technological point of view. The most important benefits of a fluidised bed are good temperature equalisation, good mass and heat transfer as well as a low pressure drop [2]. These features allow for the fluidisation to be applied in many industrial applications, including coating [3], combustion [4] and heterogeneous synthesis [5–7]. Not every type of powder is able to achieve stable fluidisation, due to the fact that it depends on the individual characteristics of the powder, such as shape, particle size and density of the material. The ability of the powder to fluidise can be assessed on the basis of the classification created in 1973 by the Geldart [8]. Material density and the average grain size are the main criteria for this powder classification. Geldart's powder classification is shown in Figure 1.
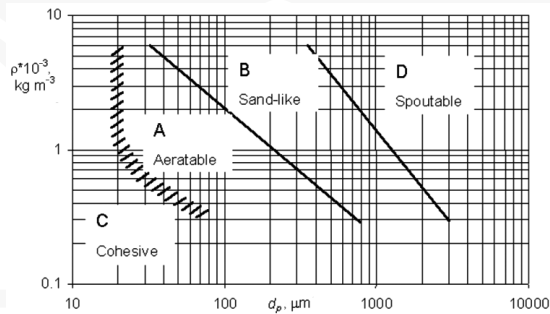

Fig. 1. Geldart's powder classification

Class C powders have the smallest size, which typically does not exceed 30 microns. Such small grains have maximum cohesiveness, hence, they tend to stick together. A large interaction force between particles makes the formation of a stable fluidisation for this type of material difficult, and it often results in channelling. Examples of Group C powders include powder, flour and starch [9]. Group A powders are materials that can be easily fluidised. Such particles have a relatively small average particle size (30–100 μm) and a low apparent density, below 1.4 g/cm^3. Fluidisation of Group A powders is relatively mild and is characterised by small bubbles, high bed expansion and good circulation of the grains [10]. The gas velocity at which bubbles are observed is significantly higher than the minimum fluidisation velocity. The catalyst for fluid catalytic cracking (FCC) is an example of a Class A material. Geldart assigned powders with a particle size of 0.1–1 mm to class B. These powders readily form a bubbling fluidised bed (the minimum fluidisation velocity is equal to the minimum bubbling velocity). The bubbling fluidised beds are classified as heterogeneous beds because a large part of the gas is enclosed in bubbles. Quartz sand with a diameter of approx. 0.5 mm is the most typical representative of group B [11]. Grains greater than 1 mm and with high density (Class D) can be fluidised only at a large momentum value. The bed made out of this material is characterised by large bubbles, whose velocity is lower than the velocity of remaining gas in the emulsion. The low level of mixing also makes the transport of mass and heat is low.

In this paper, the possibility of achieving a stable fluidised bed made of the cenospheres was examined. Cenospheres are the waste material from hard coal power plants equipped with pulverised boilers. It is estimated that cenospheres constitute up to 5% mass of fly ash [12]. This material is perfectly spherical, and it is thin-walled and filled with gases (mainly CO_2, N_2). In addition, cenospheres have low density (ca. 0.7 g cm^{-3}) and they are characterised by high temperature resistance (up to 1300°C), mechanical strength (up to 6 on the Mohs scale) and a low thermal conductivity (about 0.07 Wm^{-1}K^{-1}) [13, 14]. The physical properties of cenospheres indicate that this material could be easily introduced in the fluidised state. The application of the cenosphere material as a carrier for the catalyst grains may be very beneficial in the processes occurring in a catalytic fluidised bed. Covering cenospheres with a catalyst powder allows to obtain catalyst particles with a much lower density compared to the original material grains, so that it will be possible to lower the minimum fluidisation velocity and the carrying processes at low gas flows, and therefore, cause a longer contact time of the reactants with the catalyst.

2. Experimental Methods

Cenospheres were supplied by the Połaniec Power Plant, where its acquisition is based on the wet method. Raw microspheres were subjected to initial drying at 105°C for 12 h, followed by purification in boiling water according to the procedure described before [15]. Furthermore, the cenospheric material was sieved and divided into four fractions: with a particle size less than 45 microns, 45–71 microns, 71–100 microns, 100–125 microns. The processes of fluidisation of the separated fractions of cenospheres were examined by passing a gas through the bed of each fraction of the material. In order to measure the pressure drop caused by the bed of cenospheres, a laboratory installation was built. A transparent flow tubular reactor, having an inner diameter of 3.6 cm and a height of about 25 cm, was used. The pressure sensor was placed under the bottom sieve. Nitrogen was used as the fluidising medium. The measuring system scheme is shown in Figure 2.
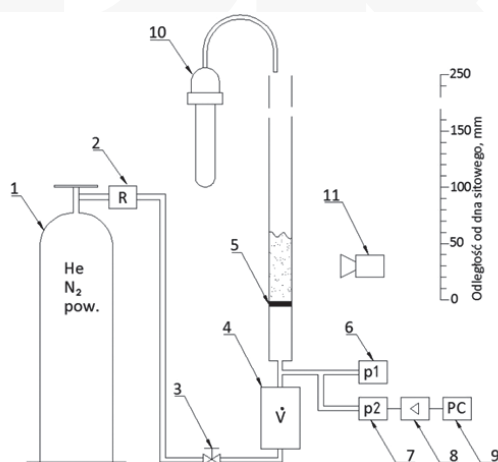

Fig. 2. Installation diagram for measuring the pressure drop: 1 – compressed gas, 2 – reducer, 3 – valve, 4 – flow meter, 5 – bottom sieve, 6, 7 – pressure sensors, 8 – converter, 9 – computer, 10 – dedusting system, 11 – camera

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At first, the pressure drop that occurred during gas flow through an empty reactor was determined. The measured dependence of the pressure drop, caused only by the bottom sieve and the filter with a pore size of 10–20 microns, was linear. Thus, it was possible to calculate an arbitrary pressure drop caused only by one layer of cenospheres.

3. Results and Discussion

The plots of the pressure drop versus the velocity of the fluidising gas were calculated on an empty cross-section of the reactor, which is shown in Figure 3a. Fluidisation is characterised by a constant level of pressure drop, despite increasing the nitrogen velocity, and the beginning of this stabilisation indicates the minimum fluidisation velocity. The value of the minimum fluidisation velocity for each fraction of material was determined from the curve by extrapolating linear lines within the ranges of the lowest and the highest gas flow rates. The abscissa of the intersection point of these lines represents the minimum gas velocity at which fluidisation occurs (Fig. 3b). The coefficients of regression equations for the range of lower and higher flow rate of the gas through the bed, and the minimum fluidisation velocity calculated based on them, were shown in Table 1.
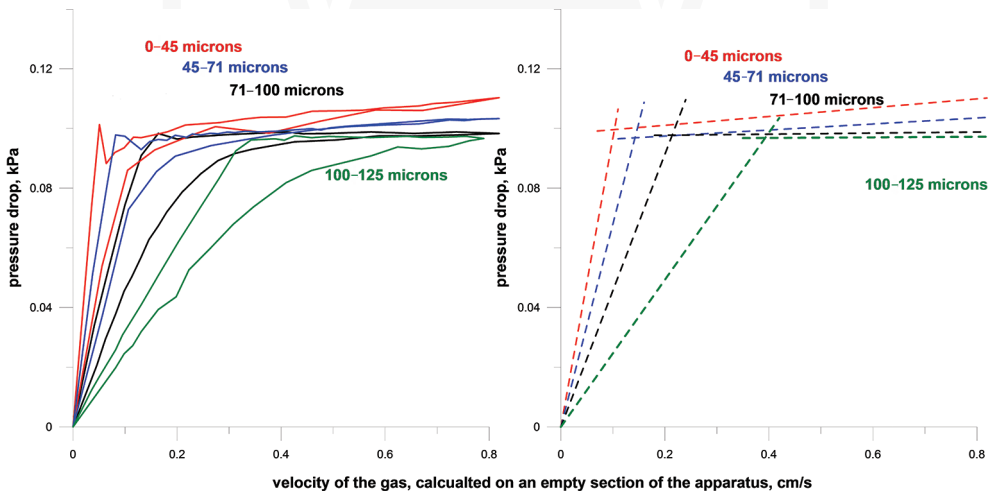

Fig. 3. The dependence of the pressure drop in the layer of cenospheres with a different grain size versus the flow rate of nitrogen: a) actual course of the curves b) extrapolation within ranges of the lowest and the highest flow rates of gas

All of the examined fractions of cenospheres can be easily introduced in the fluidised state. The stable fluidised states of the tested materials were achieved at low flow rate of the fluidising gas (from 0.1 to 0.4 cm s^{-1}). The process of fluidisation was mild because the layers were characterised by a large expansion of the bed and a high degree of mixing.

Coefficients of regression equations for the lower and higher flow rate of the gas through the bed and the minimum fluidisation velocity

Cenospheres fraction	Bed mass	Lower range of flow rate of the gas, $\Delta p = a*u$		Higher range of flow rate of the gas, $\Delta p = a*u + b$			Minimum fluidisation velocity, U_{mf}
μm	g	a	R^2	a	b	R^2	cm/s
0–45	10	0.9679	1.000	0.0148	0.0981	0.986	0.103
45–71	10	0.6797	1.000	0.0101	0.0954	0.973	0.143
71–100	10	0.4568	1.000	0.0018	0.0974	0.439	0.214
100–125	10	0.2465	1.000	0.0010	0.0964	0.132	0.393

In the following study, the fraction of 71–100 μm was purified by heating in water at a temperature of 90°C. Therefore, broken and perforated cenospheres sank to the bottom. The purified fraction of cenospheres is labelled as IMS (intact microspheres). The fluidisation processes of fraction 71–100 microns before and after purification are summarised in Fig. 4. The results of the coefficients of linear regression equations derived from data, obtained in the low and the high value of the fluidising gas flow, are presented in Table 2.
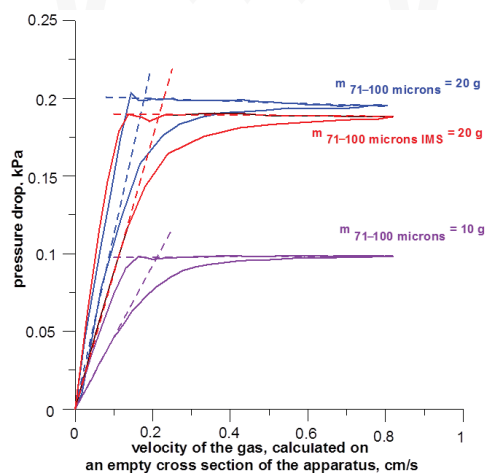

Fig. 4. The dependence of the pressure drop in the layer of cenospheres with a particle size of 71–100 μm versus the flow rate of nitrogen

The pressure drop in a layer of cenospheres is directly related to the weight of the bed. The ratio of pressure drop for fraction 71–100 microns with masses of 10 and 20 grams is the same as the ratio of their masses. It is known that the minimum fluidisation velocity does not depend on the weight of the bed. Minimal difference between minimum fluidisation velocities of fraction 71–100 microns, calculated for 10 g and 20 g of bed mass, can be

explained by a greater stability of the heavier bed and, thereby, the greater accuracy of U_{mf} determination. The minimum fluidisation velocities of raw and purified cenospheres slightly differ from each other (0.214 and 0.220 respectively). However, this difference is not the result of purification because the weight loss after heating was less than 2%, and thus it can be neglected.

Table 2

Coefficients of regression equations for the lower and higher flow rate of the gas through the bed and the minimum fluidisation velocity for raw and purified cenospheres of 71–100 µm

Cenosphere fraction	Bed mass	Lower range of flow rate of gas, $\Delta p = a*u$		Higher range of flow rate of gas, $\Delta p = a*u + b$			Minimum fluidization velocity, U_{mf}
µm	g	a	R^2	a	b	R^2	cm/s
71–100	10	0.4568	1.000	0.0018	0.0974	0.439	0.214
71–100	20	1.1235	0.983	−0.0081	0.2015	0.892	0.178
71–100 IMS	20	0.8628	0.999	−0.0030	0.1907	0.559	0.220

Furthermore, the characteristic hysteresis loop after decreasing of fluidising gas flow rate was observed. The phenomenon of the occurrence of the local maximum, which is the result of large interaction between small grains, is known. Dispersion of the hysteresis is large, which suggests the simultaneous existence of two steady states. For example, fluidisation of 20 g of 71–100 microns IMS could be carried out at a gas velocity of 0.3 cm/s and with a pressure drop equal to approx. 0.17 and 0.19 kPa, respectively. In order to exclude the existence of two stationary states, experiments for fractions 45–71 and 71–100 were repeated with the additional presence of acoustic waves with different frequencies. An example plot for a fraction of cenospheres with a grain size 45–71 µm was shown in Figure 5. The minimum fluidisation velocities were determined on the basis of extrapolation and are summarised in Table 3.
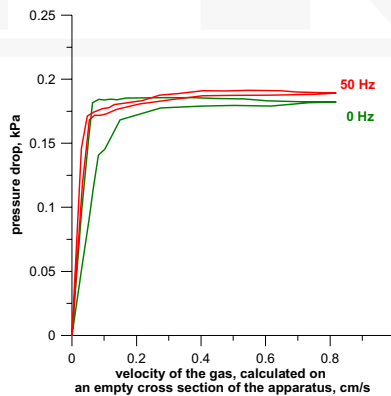

Fig. 5. Changes in pressure drop during the fluidisation of cenospheres with a particle size 45–71 µm in the presence of sound waves of 50 Hz

Table 3

**Minimum fluidisation velocity of cenospheres with a grain size of 45–71 μm
and 71–100 μm in the presence of the acoustic waves**

Particle Size Distribution μm	Frequency of a acoustic Wave Hz	Minimum Fluidisation Velocity cm/s
45–71	0	0.107
	50	0.052
	100	0.072
71–100	0	0.220
	25	0.100
	50	0.108
	75	0.105
	100	0.107
	150	0.131

The application of acoustic waves during fluidisation of cenospheres removes the apparent effect of double stationary states and moves the minimum fluidisation velocity into lower gas flow rates.

The application of sound waves from the 20–100 Hz range makes the minimum fluidisation velocity of cenospheres fraction with a grain size of 71–100 reduced from 0.220 cm/s (for an experiment without vibroacoustics) to the range of 0,100–0,108 cm/s. After a certain level of the impact of sound waves from the range of 20–100 Hz, the efficiency of the influence of lower sound waves on the minimum fluidisation velocity is decreased, and for waves of 150 Hz, this difference in velocities is smaller. It can be stated that the damping of waves with higher frequencies occurs because of the inertia of the individual grains, and it is greater than for the lower waves.

4. Conclusions

Because of their low density, particle size and sphericity, cenospheres can be easily fluidised even at low flow rates of the fluidising medium. For example, the minimum fluidisation velocity of cenospheres with a grain size of 45–71 microns is 0.107 cm/s. Moreover, acoustic waves of 50 Hz may reduce this value to 0.052 cm/s. The physical properties of cenospheres and the easiness of its fluidisation process allow to classify this material to group A in the Geldart's classification.

R e f e r e n c e s

[1] Orzechowski Z., *Przepływy dwufazowe jednowymiarowe ustalone adiabatyczne*, PWN, Warszawa 1990.

[2] Kunii D., Levenspiel O., Brenner H., *Fluidization Engineering*, Second edition, Butterworth-Heinemann, Newton 1991.

[3] Dewettinck K., Huyghebaert A., *Fluidized bed coating in food technology*, Trends in Food Science & Technology, 10(4–5), 1999, 163–168.

[4] Wielgosiński G., *Przegląd technologii termicznego przekształcania odpadów*, Nowa Energia, 1, 55, 2011.

[5] Adlhoch W., Sato H., Wolff J., *High-Temperature Winkler Gasification of Municipal Solid Waste*, 2000 Gasification Technologies Conference, San Francisco 2000, https://www.netl.doe.gov/File%20Library/Research/Coal/energy%20systems/gasification/gasifipedia/5-ASADAL_BOARD_bbs02.pdf (access: 13.04.2016).

[6] Contractor R.M., Garnett D.I., Horowitz H.S., Bergna H.E., Patience G.S., Schwartz J.T., Sisler G.M., *A New Commercial Scale Process for n-Butane Oxidation to Maleic Anhydride Using a Circulating Fluidized Bed Reactor*, Studies in Surface Science and Catalysis, 82, 1994, 233–242.

[7] Zhou J., *Fluidization Technology and its Applications*, http://www.ispe.org/great-lakes/zhou-fluidization-basics-2010-presentation.pdf, 2010 (access: 13.04.2016).

[8] Geldart D., *Types of Gas Fluidization*, Powder Technology, 7, 1973, 285–292.

[9] Thomas B., Mason M.O., Squires A. M., *Some behaviors of shallow vibrated beds across a wide range in particle size and their implications for powder classification*, Powder Technology, 111, 2000, 34–49.

[10] Lii-Ping Leu, Fu-Chien Tsai, *Hydrodynamics of Geldart group A particles in gas-solid fluidized beds*, Korean J. Chem. Eng., 26(2), 2009, 513–517.

[11] Hariprasad J. Subramani, M.B. Mothivel Balaiyya , Lima Rose Miranda, *Minimum fluidization velocity at elevated temperatures for Geldart's group-B powders* Experimental Thermal and Fluid Science, 32, 2007, 166–173.

[12] Anshits N.N., Mikhailova O.A., Salanov A.N., Anshits A.G., *Chemical composition and structure of the shell of fly ash non-perforated cenospheres produced from the combustion of the Kuznetsk coal (Russia)*, Fuel, 89(8), 2010, 1849–1862.

[13] Kruger R.A., *The Use of Cenospheres in Refractories,* Energeia, Center for Applied Energy Research, 7, 4, 1996.

[14] Elpologistyka Sp. z o.o. homepage: *Raport z badań mikrosfery*, http://www.elpologistyka.pl/wp-content/uploads/2015/11/Raport-z-badan-mikrosfery1.pdf (access: 13.04.2016).

[15] Bradło D., Żukowski W., Czupryński P., Witkowski K., *Pozyskiwanie oraz dobór metody frakcjonowania cenosfer z popiołów lotnych/Acquisition and choice of method for fractionation of cenospheres from fly ashes*, Przemysł Chemiczny, 93(7), 2014.