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COMPOSITES THEORY AND PRACTICE

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# THE SELECTED PHYSICO-CHEMICAL PROPERTIES OF MICROSPHERES AND POSSIBILITY OF THEIR USE IN CEMENT COMPOSITES

**Microspheres are formed during the mineral transformation stage in coal combustion. Their content in fly ashes from the combustion of different types of coals varies over a rather wide range from 0.01 to 4.8 wt.%. The microspheres have three main elements, silicon, aluminum and iron, the oxides of which account for about 89.0 wt.% of the material. Mineralogical analysis using XRD shows that microspheres mainly contain mullite and quartz as the main crystalline phases. The size of microspheres varies between 5 and 500 μm and the most common dimension is 20÷300 μm. Microspheres are characterized by a low bulk density (0.2÷0.8 g/cm$^3$) and can be easily separated by gravitational methods in the form of a concentrate in aqueous media or collected from the water surface of lagoons intended for storing of fly ash and slag. The unique properties of microspheres suggest the wide range of their use. They are currently used as lightweight filler which improves the thermal insulation properties of mortars and concretes based on mineral binders.**

**Keywords:** microspheres, properties of physico-chemical, cement composites

## WYBRANE WŁAŚCIWOŚCI FIZYCZNO-CHEMICZNE MIKROSFER I MOŻLIWOŚĆ ICH WYKORZYSTANIA W KOMPOZYTACH CEMENTOWYCH

**Mikrosfery - drobna frakcja popiołów lotnych - powstają w procesie konwencjonalnego spalania węgli kamiennych. Ich zawartość w popiołach lotnych ze spalania różnych gatunków węgla zmieniać się może w szerokim zakresie: od 0,01 do 4,8 wag.%. Pod względem składu chemicznego głównymi składnikami mikrosfer w formie tlenkowej są krzem, glin i żelazo, stanowiące około 89% ich masy. Ich skład mineralny to głównie: kwarc i mulit. Wielkość cząstek sferycznych waha się od 5 do 500 μm, jednak rozmiar większości cząstek mieści się w granicach od 20 do 300 μm. Mikrosfery charakteryzują się niską gęstością w zakresie 0,2÷0,8 g/cm$^3$. Na tej podstawie mogą być łatwo oddzielone metodą flotacji w środowisku wodnym, z powierzchni lagun lub bezpośrednio z basenów osadniczych. Wyjątkowe właściwości mikrosfer sugerują szerokie możliwości wykorzystania. Dzięki właściwościom pucolanowym mikrosfery wykorzystywane są jako lekki wypełniacz poprawiający własności termoizolacyjne zapraw i betonów na bazie spoiw mineralnych.**

**Słowa kluczowe:** mikrosfery, właściwości fizyczno-chemiczne, kompozyty cementowe

## INTRODUCTION

Power stations all over the world have problems with combustion wastes. The progressive development of technology in energy and environmental protection generate new types of waste including changes in the composition and properties of waste already known. The Polish energy industry produces annually more than 15 million tones per year of combustion waste [1]. For the most part, it is fly ash and its mixtures. At the moment, they are valuable by-products of the energy industry and are widely used in the production of building material. Despite the economic growth in the use of combustion waste, a significant part of its mass is still landfilled.

Porous spherical aluminosilicate particles defined as microspheres or cenospheres, are among the most valuable fly ash components. The term cenospheres comes from the Greek *kenos* (hollow) + *sphere*, and reflects their most important feature - the presence of a cavity surrounded by a solid or perforated mineral shell [2-4]. Their content in fly ashes from the combustion of different types of coals varies over a rather wide range from 0.01 wt.% to 4.8 wt.%, in the majority of cases it amounts to 0.3÷1.5 wt.% [5-7].

The formation of microspheres occurs as a result of thermochemical and phase transformations of the mineral forms in coal in the process of its combustion. Coal-fired power plants produce abundant quantities of these spheres (as much as 40 million tons per plant per year), which are normally disposed of in landfills [8]. In Poland, despite the inclusion of microspheres to the register of the waste catalogue [9], their amount is not included in the national statistics.

Microspheres have special properties of great importance to environmental protection. They are hollow spheres, filled with air or gases ($CO_2$ and $N_2$). Microspheres have low densities (0.2÷0.8 g/cm$^3$), low thermal conductivities (about 0.065 W·m$^{-1}$K$^{-1}$), and excellent stability in an alkali solution and at high temperatures [10-12]. Microspheres can be easily separated by gravitational methods in aqueous media or collected from the water surface of lagoons intended for storing fly ash and slag [13].

Taking into account their specific characteristics, microspheres can find great use in various industries. They are currently used as a lightweight filler which improves the thermal insulation properties of mortars and concretes based on mineral binders. They have also found extensive applications in manufacturing lightweight composites [14]. Microspheres with a hollow core-shell structure might be a kind of more attractive raw material for morphology-controlled zeolite synthesis [15]. However, before using microspheres for any of these applications, their properties should be studied in detail.

This paper presents the results of the main properties of microspheres (chemical, physical and mineralogical) obtained from slag, and a mixture of fly ash and slag - by-products of coal combustion in Polish power stations.

## MATERIAL AND METHODS

The microspheres used in this study were collected from two Polish power stations - "Opole" and "Dolna Odra". The microspheres from "Opole" were obtained from ash pools where the slags were hydraulically disposed. The microspheres from the power station "Dolna Odra" were collected from the lagoon, where a mixture of fly ash and slag is stored. Before the study, the microspheres, due to the wet method of extracting from the waste, were dried at a temperature of 20 ±5°C.

Identification of the mineral composition of the determined microspheres was based on the results of the chemical analysis and testing phase composition.

The morphology of the microspheres samples was observed by a scanning electron microscope (SEM, Philips XL30) equipped with energy dispersive X-ray detectors (EDX) for chemical analyses. The heavy metals of the microspheres were determined by atomic absorption spectroscopy (AAS, Analytik Jena AG, type Vario 6).

The mineral composition of the microspheres was determined by an X-ray diffraction (XRD) spectrometer (Phillips X'Pert), with graphite monochromatic and Cu *Kα* radiation. Scans were performed between 2*θ* values of 10$^o$ to 90$^o$ with a step size of 0.02$^o$. The final quantitative XRD analysis was performed using the Reference Intensity Method.

The particle size distributions of the microspheres were determined by means of laser diffraction particle size analysis (Malvern Mastersizer).

The loss on ignition (LOI) contents were determined at 1050$^o$C, respectively.

The density of the microspheres was determined using the pycnometer method, employing kerosene as the immersion liquid. The specific surface area of the sample was determined with the help of Blaine's air permeability apparatus. For standardization, Portland cement was selected as the reference material, according to [16].

All the tests were performed at the Faculty of Civil and Environmental Engineering, Gdansk University of Technology.

## RESULTS AND DISCUSSION

### Mineralogical characterization

Figure 1a and 1b show SEM images of the microspheres, clearly showing their size and porosity. Microscopic examination (SEM) revealed microspheres of varying particle morphology. The visible shape of the microspheres is diverse - from almost perfectly spherical to highly irregular (Fig. 1a). The structure of microspheres is not homogeneous, and it is composed of closed pores and many open pores, as depicted in Figure 1b.

a)

b)

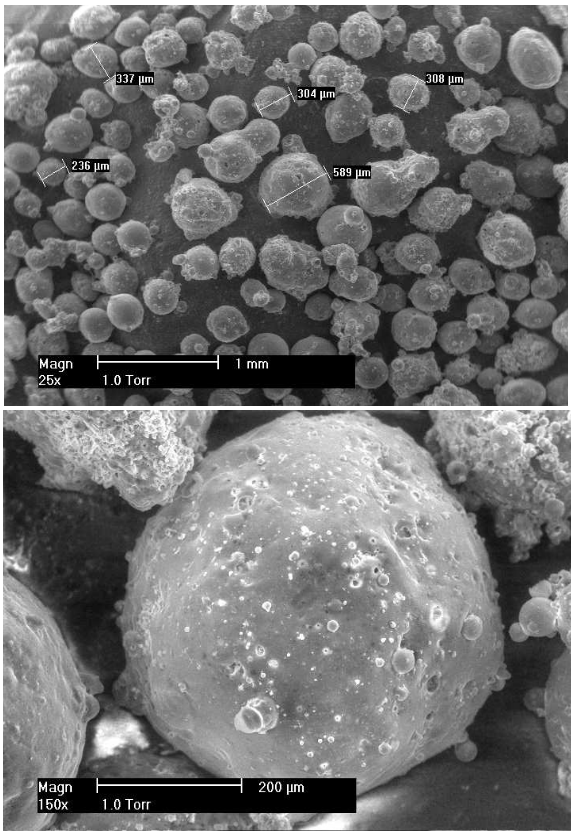


Fig. 1. SEM. Microscopic images of microspheres grain structure: a) general view (magnification 25x) b) single grain (magnification 150x), author E. Haustein

Rys. 1. SEM. Obrazy mikroskopowe struktury ziaren mikrosfer: a) widok ogólny (pow. 25x), b) pojedyncze ziarno (pow. 150x), aut. E. Haustein

 

The outer surface of the microspheres has a spongy or rough form. The microspheres of smaller sizes have a compact smooth wall surface and closed pores. The large microspheres have irregular shapes and a deformed surface structure with open visible pores.

The variety of morphological changes observed in the microspheres is related to the combustion of coal. The wide range of temperatures during its combustion leads to decomposition of the mineral substances contained in them.

## Chemical composition

The analysis results of the chemical composition (by % weight) and physical properties of the microspheres obtained from the slags and mixture of fly ash with the slag are presented in Table 1. The concentrations of heavy metals in the microspheres are illustrated in Table 2.

TABLE 1. **Chemical composition of microspheres in slag (power station "Opole") and mixture of fly ash and slag (power station "Dolna Odra"**

TABELA 1. **Skład chemiczny mikrosfer z żużla (elektrownia „Opole") oraz z mieszanki popiołowo-żużlowej (elektrownia „Dolna Odra")**

| Chemical composition | Power station | | Admissible content acc. to PN-EN 450-1:2009 [18] |
|---|---|---|---|
| | Opole | Dolna Odra | |
| | [% by weight] | | |
| $SiO_2$ | 52.3 | 51.5 | ≥ 70% mass |
| $Al_2O_3$ | 29.8 | 30.3 | |
| $Fe_2O_3$ | 5.6 | 4.8 | |
| CaO | 3.3 | 4.3 | ≤ 10% mass[1)] |
| MgO | 2.8 | 2.4 | ≤ 4.0% mass |
| $K_2O$ | 4.0 | 3.8 | Total content of alkali based on $Na_2O_{eq}$ ($Na_2O$+0.658$K_2O$) ≤ 5.0% by weight |
| $Na_2O$ | 1.1 | 1.0 | |
| $TiO_2$ | 1.2 | 1.8 | - |
| Physical properties | | | |
| LOI (loss of ignition) [%] | 0,9 | 1,1 | Category A ≤ 5.0% mass<br>Category B 2.0÷7.0% mass<br>Category C 4.0÷9.0% mass |
| Specific surface area [$cm^2/g$] | 386 | 457 | - |

1) if the total content of CaO in the fly ash his lower than 10% mass of The requirement for reactive CaO is deemed to be fulfilled

The chemical analysis showed that the microspheres consist mainly of silica oxides (51.9 wt.%), aluminum (30.1 wt.%), iron (5.2 wt.%) with lower amounts of calcium (3.8 wt.%), magnesium (2.6 wt.%), sodium (3.9 wt.%), potassium (1.0 wt.%) and titanium (1.5 wt.%) oxides. The results indicate that microspheres - based on the content of $SiO_2$ (> 40%), $Al_2O_3$ (< 30%), CaO (< 10%) and $SO_3$ (< 4%) - can be accepted by the classification on Polish fly ash to the class of silica (F), according to [17]. The chemical composition of the microspheres is compared with the composition of the fly ash used in concrete or cement composites [18].

The diverse composition of the microspheres results from the different nature of waste from which they were obtained. Additionally, the different types of coal which produce the waste, can change the type and amount of mineral substances present in the form of silicates, carbonates, sulfides or sulfates.

The microspheres are characterized by a relatively low loss on ignition. The LOI results (from 0.9 to 1.1%) give values below the unburned carbon content in fly ash, according to [18]. The differences are most probably due to the dehydration or decomposition of minerals in the slag and mixture of fly ash and slag.

TABLE 2. **General content of selected heavy metals in microspheres from power stations in Poland**

TABELA 2. **Ogólna zawartość wybranych metali ciężkich w mikrosferach pochodzących z polskich elektrowni**

| Type of heavy metal | Power station | | Admissible content of heavy metals in soils [mg/kg] by [19] | |
|---|---|---|---|---|
| | Opole | Dolna Odra | Class A | Class C |
| | Microspheres $\frac{\%}{mg/kg}$ dry weight | | | |
| Copper (Cu) | $\frac{0.012}{120}$ | $\frac{0.0109}{109}$ | 30 | 200÷300 |
| Nickel (Ni) | $\frac{0.013}{130}$ | $\frac{0.0146}{146}$ | 35 | 300÷500 |
| Lead (Pb) | $\frac{0.005}{50}$ | $\frac{0.0102}{102}$ | 50 | 600÷1000 |
| Zinc (Zn) | $\frac{0.0160}{160}$ | $\frac{0.0163}{163}$ | 100 | 1000÷3000 |
| Chromium (Cr) | $\frac{0.0250}{250}$ | $\frac{0.0157}{157}$ | 50 | 500÷800 |
| Cadmium (Cd) | $< \frac{0.0001}{1}$ | | 1 | 6÷20 |

The analysis of heavy metals in the microspheres shows that the content does not exceed 1% of the total weight. For example, the copper (Cu) content in the microspheres ranges between 0.0109 to 0.0120 wt.%, the lead (Pb) content ranges between 0.005 to 0.0102 wt.% and the chromium (Cr) is in the range 0.0157 to 0.0250% by weight (Table 2).

Due to the high content of glassy phase in their compositions, the microspheres only slightly release the heavy metals contained in them. They are permanently embedded in the structure of the microspheres, so there may be an insignificant percentage of leaching of their content.

According to [19], the Regulation of the Minister of the Environment (in Poland) on the quality standards of soil and soil quality standards the investigated microspheres can be used for some agricultural areas (from class A to class C). The microspheres do not contain heavy metals (Zn, Cu, Pb, Cr, Ni and Cd) in amounts that could be considered as hazardous waste which prevent their use in cement composites.

## Mineralogical composition

Figure 2 shows the X-ray diffraction pattern of the microspheres. Due to the very short dwell time of coal combustion at high temperature (> 1000°C), the resulting combustion products may be at different stages of phase transformations. The microspheres formed as a result of thermal action can be a composition of amorphous and crystalline phases.

The common crystalline phases observed on the example of the microspheres obtained from the "Dolna Odra" power station are: mullite ($3Al_2O_3{\cdot}2SiO_2$), iron oxides (magnetite, hematite - $Fe_3O_4$ and $Fe_2O_3$) and quartz ($SiO_2$) - the final product of the transformation of organic carbon. The visible peak of calcium oxide (CaO) present in the microspheres is related to decomposition of the mineral compounds ($CaCO_3$) during coal combustion. The same type of crystalline phases was obtained for the microspheres from the power station "Opole".

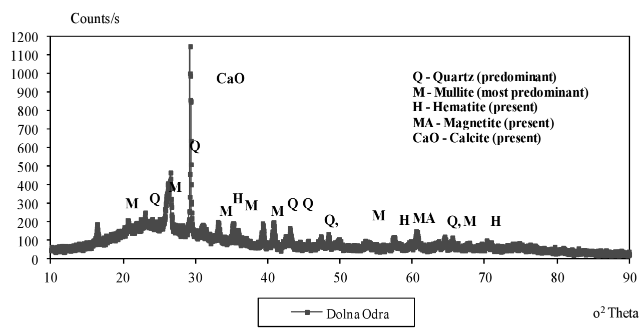


Fig. 2. The X-ray diffraction mineralogy (phases of crystalline) of microspheres from power station "Dolna Odra"

Rys. 2. Dyfraktogram mikrosfer (faz krystalicznych) pochodzących z elektrowni „Dolna Odra"

The microspheres have different proportions of the various mineral and amorphous components. The phase-mineral composition of the microspheres includes mainly the glass phase (from 74.3 to 74.9 wt.%) and the crystalline phases of mullite (17.0÷19.2 wt.%) as well as quartz (3.8÷5.7 wt.%).

Amorphous material (or glass) is the main inorganic component of the microspheres. The glass was probably derived from the melting and recrystallisation of residues from the thermal decomposition of the minerals and non-mineral inorganics in the feed coal at high temperatures. Mullite, derived mainly from kaolinite and other clay minerals, is present in the combusted coal. The Fe-oxides, magnetite and hematite, probably resulted from the oxidation of pyrite and other minerals produced from coal.

## Particle size analysis

The granulometric distribution of the microspheres from the power stations "Opole" and "Dolna Odra" is presented in Figure 3. One can see that the maximal distribution is observed for the fractions: 0.063÷0.125 mm ("Dolna Odra") and 0.150÷0.250 mm ("Opole"): 40.3 and 55.2% respectively. The second largest (34%) for the microspheres from both power stations is the distribution of particle sizes from 0.150 to 0.250 mm.

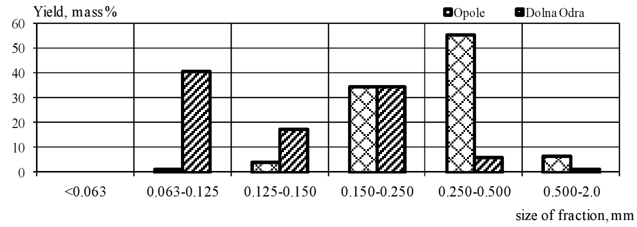


Fig. 3. Particle size distribution of the microspheres [% by mass] from power stations in Poland

Rys. 3. Graficzny rozkład uziarnienia mikrosfer [% wag.] pochodzących z polskich elektrowni

For the microspheres from the power station "Opole" the distribution is also relatively high of the fractions: 0.125÷0.150 mm (3.7%) and 0.500÷2.0 mm (6.2%). The lowest yield is observed for the two smallest fractions: 0.063-0.125 mm and < 0.063 mm: 0.9 and 0.1% respectively.

For the power station "Dolna Odra", the distribution of the fraction 0.125÷0.150 mm is substantially higher (17%), while the yield of fractions > 0.063 mm does not exceed 2.4% as a total and decreases with an increase in particle size (5.5% for size particles 0.250÷0.500 mm and 0.9% for size particles 0.500÷2.0 mm), see Figure 3.

In accordance with [20], microspheres can be compared to medium and fine sands. The obtained results are all more important in the case of the use of microspheres in cement composites.

## Specific surface area and apparent density

The specific surface area of the microspheres is presented in Table 1. The obtained data varies between 386 to 479 $cm^2/g$. It is definitely less than the surface area, for example of fly ash (about 2600 $cm^2/g$).

The density of microspheres ranges from 0.65 ("Dolna Odra") to 0.75 $kg/dm^3$ ("Opole"). Due to their low density, microspheres can be used to produce composites of low weight. The low specific surface area of the microspheres could have a significant impact on their pozzolanic activity in cement composites.

## SUMMARY

The presented results of the studies are designed to characterize the microspheres to provide more detailed information on their properties. In view of these results, the chemical composition and mineralogy, microspheres can be compared to the fly ash produced by the combustion of conventional coals. Due to the desire to minimize the negative impact of combustion waste on the environment, the removal of microspheres from landfills may result in some degree of reduction in the fine fractions in the total waste mass.

From the results and discussion mentioned above, the following generalized conclusions can be drawn:

1. The chemical analysis of the microspheres showed that the surface of the wall is comprised primarily of elements such as silica and aluminum (> 80 wt.%).
2. The main phase present in the microspheres is amorphous aluminosilicate material precipitates mainly of mullite and quartz.
3. The microspheres do not contain heavy metals (Zn, Cu, Pb, Cr, Ni and Cd) in amounts that could be considered as hazardous waste.
4. The microspheres obtained from the slag and mixture of fly ash and slag can be compared to medium and fine sands.
5. The microspheres are characterized by a low specific surface area of particles (< 500 $cm^2/g$), and this suggests low activity in an environment of pozzolanic cement.

These data suggest that microspheres separated from slags or a mixture of fly ash and slag may be used as part of the fine aggregate in cement composites.

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