Morphological Properties of Microspheres from Combustion of Coal in Thermal Power Plants

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Summary

Ashes – solid wastes from combustion of coal in thermal power plants must be utilized or disposed as a waste. Combustion of coal leads to formation of utilizable components – ash particles with morphology dependent on properties of burned coal, combustion temperature, atmosphere, construction of burning compartment and combustion process control. Temperature has dominant effect affecting morphology. Burning temperature relates to polycomponency of ashes, which tend to partially up to fully melt, individual particles tend to form aggregates up to clinker. Ashes contain particles of organic and inorganic origin.

In this contribution, knowledge about chemical, physical – mainly morphological properties of microspheres from combustion of black coal in fusion boilers, about physical and chemical properties of microspheres from combustion of brown coal in granulation boilers is presented. Unique properties of mainly black coal microspheres allows them to be utilized in a broad range of industrial areas.

Conditions in fluid boilers are not suitable for formation of microspheres as at the temperatures below 1000°C, formed gasses have enough time to escape from melt ash.

Keywords: microspheres, cenospheres, plerospheres, ash, coal, combustion

Introduction

Black and brown coal is combusted in fusion, granulation and fluid boilers of thermal power plants. Products of combustion - ashes from individual combustion devices differ from each other, have different morphology depending on conditions of combustion. This contribution presents different properties of microspheres from individual combustion processes.

Analysis

Following components were identified in inorganic component of ashes from combustion of black coal in fusion boilers: microspheres, mineral novelties of magnetite iron and unburned coal residuals. At combustion temperature 1400 – 1600°C, almost all ash forming components are partially up to fully molten and therefore spherical shape of particles and glass phase prevails after coolEng.

Combustion temperature of brown coal in granulation boilers is controlled to be in the range of 1100 up to 1300 °C. Brown coal ash contains porous particles in which cellular structure prevails. Particles retain the shape of original coal particles, but grains are rounded because of partial meltEng. There are almost no spherical particles.

Fluid ash from black and brown coal has morphology of original coal grains. Presence of glass phase is significantly lower when compared to black coal and brown coal ash from fusion boilers, depends on presence of low-fusing eutectics/components in ash, melting point of which is in the range of temperatures achieved in fluid boiler (800 – 850 °C).

Content of microspheres in ashes from individual combustion devices

Black coal ashes from fusion boilers contain hollow spherical particles denoted as cenospheres, light inert hollow spheres with mainly SiO_2 and Al_2O_3 content (Tab. 1). They are formed during combustion of coal particles as gaseous components escape. It is assumed that gasses (COx, NOx, H_2O and other) are formed as a product of dissociation of carbonates and clay minerals.

Formation of cenospheres is affected by mineral composition of combusted coal, conditions during combustion (temperature and its gradient) and fineness of millEng. Optimum temperature for formation of cenospheres is between 1200 and 1500 °C. At temperatures below 1000 °C the gasses have good conditions for escape from volume of ash particles and microspheres are not formed.

Content of microspheres in ashes is about 5%, their amount depends on carbon and iron content in burned coal (Kolay et al., 2001). Microspheres are formed only in certain areas of boiler and only at certain conditions which can explain different composition of microspheres and ash.

Except for cenospheres, plerospheres were also identified in ashes. These are cenospheres with other particles inside of their volume, which can be hollow or massive (see Fig. 1) (Michalíková et al., 2013). Cenospheres and plerospheres are commonly denoted as microspheres, sometimes in conjunction "light microspheres" (cenospheres) or "heavy microspheres" (plerospheres).

Properties of microspheres

Microspheres can be because of their physical and chemical properties used in a broad range of applications in many areas of industry as well as area of cosmic research. Microspheres can be separated from ashes using gravitational methods. These spherical particles contain carbon and nitrogen oxides inside of their volume. This particular conformation is decisive for their low density 0.3 – 0.6 $g.cm^{-3}$ and low temperature conductivity coefficient – about 0.1 $Wm^{-1}K^{-1}$.

Vasilieva et al., (2004) presented mineral and chemical composition of light thin walled ceramic cenospheres (formed from mullite, quartz, cristoballite, plagioclase, Fe oxides, clay minerals, mica and feldspar). They melt at 1250 – 1450°C. They are "inflated" by gasses formed during combustion of organic components in coal. Deepthi et al. (2009): Cenospheres are naturally occurring by-products of coal combustion in thermal power plants, can be used for decreasing the density of plastics, as fillers, are compatible with special binders and glues. Compatibilation led to significant increase in mechanical properties and thermal resistance of plastic polymer composites.

Kolay and Bhusal (2013) present unique properties of cenospheres – low density, high hardness, excellent thermal isolation, low – almost no absorption of water, chemical inertivity, good thermal resistance. These properties allows for a broad range industrial applications for utilization of cenospheres.

Arizmendi-Morquecho et al., (2012) present such as Kolay et al. (2013) properties of cenospheres with low coefficient of thermal expansivity, low thermal conductivity, thermal diffusivity, thermal effusivity of ash and cenospheres which were measured in a range of 373 to 1173 K. Values of thermal conductivity were low 0.17 W/m and 0.32 W/m.

Arizmendi-Morquecho et al. (2012) and Kolay et al. (2013) presented properties of cenospheres with low coefficient of thermal expansivity, low thermal conductivity, thermal diffusivity, thermal effusivity of ash and cenospheres, that were measured in the temperature range 373 K and 1173 K. Values of thermal conductivity were low 0.17 W/m and 0.32 W/m. These values were measured for fly ash cenospheres and fly ash at 1200 K. These result acknowledge the posiibility of their usage as ultralow-temperature isolators for high temperature applications.

McCarty et al. (2013) describes three studies about the possibilities of separation of unburned coal residuals and inorganic component of ash. Examples of separability include classification process, hydraulic separation, froth flotation and lamel separator. These processes allowed separation of particles rich in LOI and ash. Test results show, that optimization must be oriented towards properties of individual ashes.

Stárková (1983) published results of her research works about morphological properties of brown coal ashes from thermal power plants.

In presence of Fe as alum silicate, cenospheres are more resistant to destructive phenomena.

Physical properties of microspheres are presented in Tab. 5. Behavior of microspheres is similar to be-

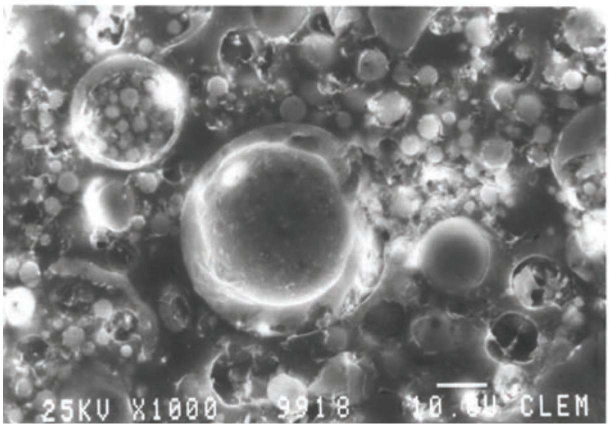

Fig. 1. Microspheres – cenospheres and plerospheres in ash (Michalíková et al., 2013).

Rys. 1 Mikrosfery - Cenosfery i plerospheres w popiele (Michalíková i wsp., 2013)

Tab. 1 Characteristic properties of microspheres (Hycnár 1987)

Tab. 1 Charakterystyczne właściwości mikrosfer (Hycnar 1987)

Chemical element content	Microspheres light [%]	Microspheres heavy [%]
Silica as SiO_2	49,0 – 61,0	54 – 55
Alumina as Al_2O_3	26,0 – 30,0	25 – 31
Iron as Fe_2O_3	4,0 – 10,0	0,5 – 18
Calcium as CaO	0,2 – 4,5	1,5 – 9
Magnesium as MgO	1,1 – 1,6	1,5 – 7
Natrium as Na_2O	0,3 – 1,8	0,8 – 2,8
Potassium as K_2O	0,2 – 4,2	0,2 – 3,5
Content of gas, that fills particles of light microspheres [$cm^3.g^{-1}$]		
CO_2	0,17 – 0,31	
N_2	0,03 – 0,13	
Physical properties		
Apparent density [kg.m-3]	250,0 – 400,0	700 – 1100
Thermal conductivity [$W.m^{-1}.K^{-1}$]	0,07 – 0,10	0,16 – 0,20
Content of size class		
0 – 60 μm [% wt.]	5,0 – 20,0	60,0 – 90,0
60 – 400 μm [% wt.]	80,0 – 95,0	10,0 – 40,0

Tab. 2 Content of heavy metals in ash and in microspheres (Kolářová and Novák 1999)

Tab. 2 Zawartość metali ciężkich w popiele i w mikrosferach (Kolářová i Novák 1999)

Chemical element	Content [ppm = mg/kg]	
	Microspheres	Ash
Pb	80	43 – 78
Cd	20	8 – 20
Cu	-	70 – 180
Zn	-	100 – 186
Cr	120	87 – 170
Ni	62	100 – 116
Co	14	21 – 69
Be	-	16 – 32
As	9,5	10 – 190
Th	-	14 – 18,5
Ra	-	4,3
U	-	3,0 – 9,6
B	330	–

havior of liquids – minimum angle of repose, good fluidity. Thickness of walls is 2 – 5 μm. They are chemically inert, nontoxic, nonflammable and insoluble in water and other chemical solvents. They have exceptional thermal and sound insulation properties, low density. They resist temperatures up to 1250°C.

Important property of microspheres is area of their surface. Following measurements, that were done using Areameter repeatedly validated, that surface area of microspheres is low due to their smooth, near ideal spherical surface. Inner surface of microspheres can only be measured after their destruction.

Tab 6. (Michalíková et al., 2003) shows surface areas of microspheres from brown coal ash from ENO Nováky and black coal ash from TEKO Košice, Skawina power plant in Poland.

Microspheres separated from black coal ash from thermal heating plant with 0.35 – 1.5% wt. yield.

Tab. 3 Chemical composition of ash and microspheres

Tab. 3 Skład chemiczny popiołu i mikrosfer

Chemical composition	Content [wt.%]	
	Microspheres	Ash
SiO_2	87,0 - 93,0	50,4 - 55,3
Al_2O_3	8,0 -11,0	22,2 - 32,5
CaO	0,5 - 0,8	0,9 - 4,2
SO_3 / SO_2	0,8 - 11,0	0,2 - 0,9
Fe_2O	0,6 - 1,5	6,2 - 17,4
Mn_3O_4	-	0,03 - 0,06
MgO	0,3 - 0,7	1,0 - 1,7
Na_2O	-	0,15 - 0,7
K_2O	3,2 - 3, 7	0,8 - 1 ,6
P_2O_2	-	0,1 - 0,5
TiO_2	0,1 - 1,1	0,7 - 3,2
Cl	< 0,3	

Tab. 4 Results of EDX analyses of ash from TEKO heating plant.

Tab. 4 Wyniki analizy EDX popiołów z ciepłowni TEKO

	Content of element [%]									
EDX particle	Al K	Si K	K K	Ca K	Fe K	Ti K	Mn K	Mg K	S K	Na K
121	22,3	46,7	8,8	1,4	16,0	1,8	0,8	1,9	0,0	0,4
122	24,1	53,8	10,3	3,0	6,2	1,5	0,1<	0,9	0,0	2,0<
123	19,8	64,3	6,8	1,6	4,3	1,4	0,5<	1,2	0,0	1,0<
124	20,6	53,7	7,8	3,0	11,1	2,4	0,0	1,3	0,0	1,0<

Tab. 5 Physical properties of microspheres – mean values

Tab. 5 Właściwości fizyczne mikrosfer - wartości średnie

Parameter	Value
Density of microsphere "case" [$kg.m^{-3}$]	2 100 –2 500
Apparent density in dry state [$kg.m^{-3}$]	340 – 350
Thermal conductivity [$W.m^{-1}.K^{-1}$]	0,08 – 0,14
Hardness according to Mohs scale	5 – 6
Fusion temperature [°C]	1 386
Temperature of softening [°C]	1 000 – 1 210
Inner pressure [bar]	0,2
pH of conductive leachate	6,3 - 6,5
Color	light gray

Tab. 6 Surface areas of microspheres from brown coal and black coal ash [$m^2.g^{-1}$]

Tab. 6 Powierzchniach mikrosfer z popiołu z węgla brunatnego i kamiennego [m2/g]

Brown coal ash microspheres	ENO Nováky	light heavy whole	9,4356 7,6109 10,6536
Black coal ash microspheres	TEKO, Košice	I. hopper II. hopper III. hopper cleaned	4,5295 0,9614 2,6952 0,6433
	Skawina, Poland		0,7027

Yield of microspheres separated from EVO Vojany thermal power plant was 1.4 – 2.1%. Separation of microspheres is done using "natural approach" on the settling pit, microspheres are collected at the end of depositing area.

Morphology of black and brown coal microspheres

Measurements of morphology were realized using raster electron microscope JSM 35 CF and Link AN 10.000 analysator.

Samples of microspheres chosen for measurements were:

- black coal ash from PK3 boiler hopper of thermal heating plant in Košice,
- black coal ash from PK3 boiler, hydraulically transferred to settling pit,
- brown coal ash from granulation boilers of ENO Nováky thermal power plant.

Microspheres from black coal ash from PK3 granulation boiler of thermal heating plant in Košice.

Microspheres were obtained as "on water floating particles", which were cleaned in methanol (density 0.788). Two components were obtained:

- Lighter – floating on surface – microspheres – cenospheres hollow or porous.
- Heavier, that sank – composed mainly of unburned residuals and plerospheres (Fig. 1) microspheres denser than the density of methanol.

Fig. 2 shows composition of microspheres from black coal ash from TEKO heating plant, Košice. Microspheres are of almost ideal spherical shape and their surface is mainly smooth.

From Fig. 3 and Fig. 4 it is clear that microspheres from TEKO Košice (Michalíková et al. 2003) ash are mainly hollow with porous shell, causing their low density – from 0,3 g.cm^{-3}.

Microspheres from black coal ash from fusion boiler of Košice heating plant that were hydraulically transferred to settling pit were obtained as on pit surface floating particles. After their removal from settling pit they were cleaned by ultrasound.

Microspheres were during 2.5 – 3.5 km transfer

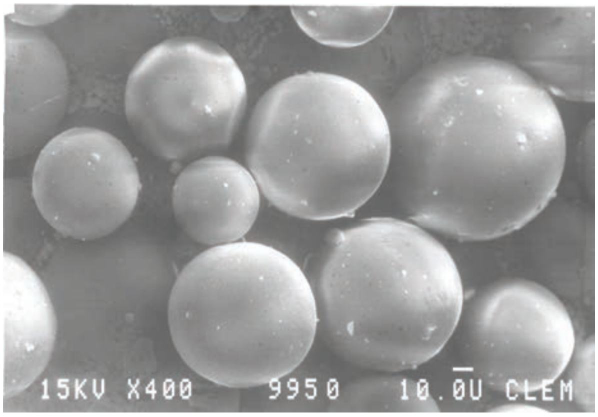

Fig. 2 Composition of microspheres from black coal ash from fusion boiler of TEKO Košice.

Rys. 2. Skład mikrosfer z popiołu z węgla kamiennego z kotła TEKO Košice.

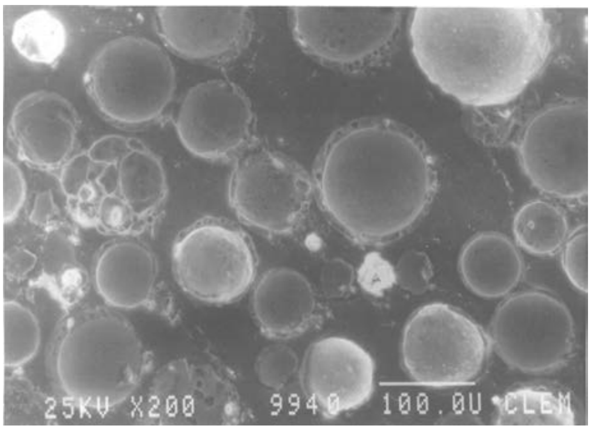

Fig. 3 Composition of whet areas of microspheres from TEKO Košice

Rys. 3 Skład w mikroobszarach obszarach mikrosfer z TEKO w Koszycach

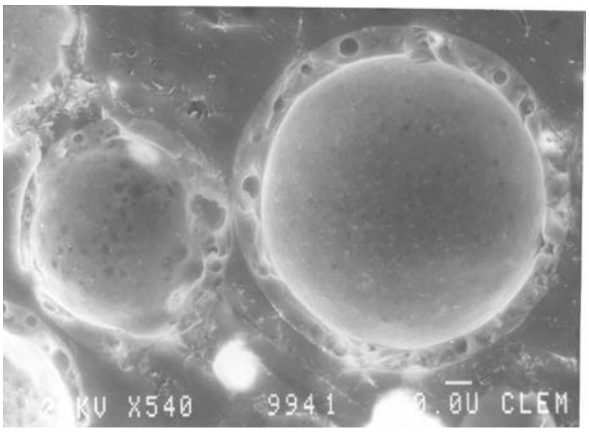

Fig. 4 Whet area of microspheres from fusion boiler of TEKO Košice

Rys. 4 Szlif powierzchni mikrosfer z kotła fluidalnego w TEKO w Koszycach

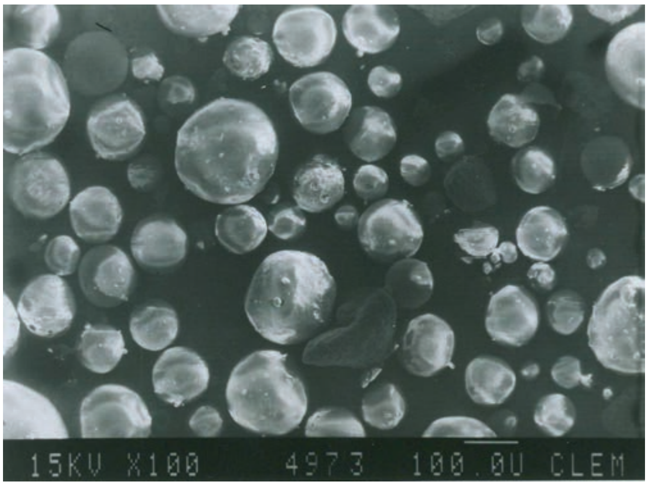

Fig. 5 Composition of microspheres from settling pit of Košice heating plant
Rys. 5 Skład mikrosfer z osadnika w ciepłowni w Koszycach

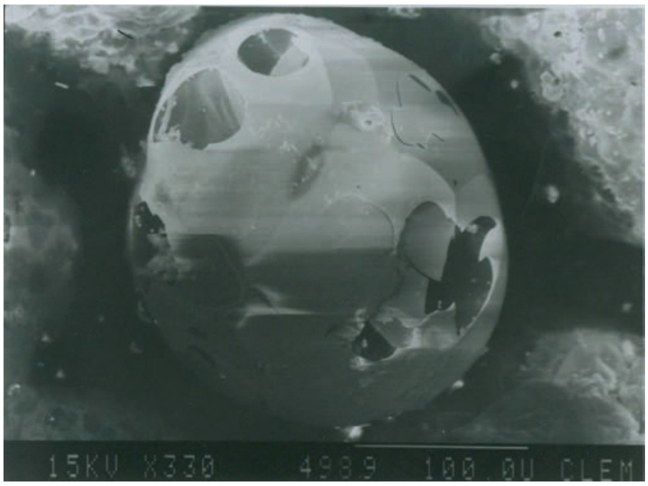

Fig. 6 Particles after hydraulic transport to settling pit
Rys. 6 Ziarna po transporcie hydraulicznym transportu do osadnika

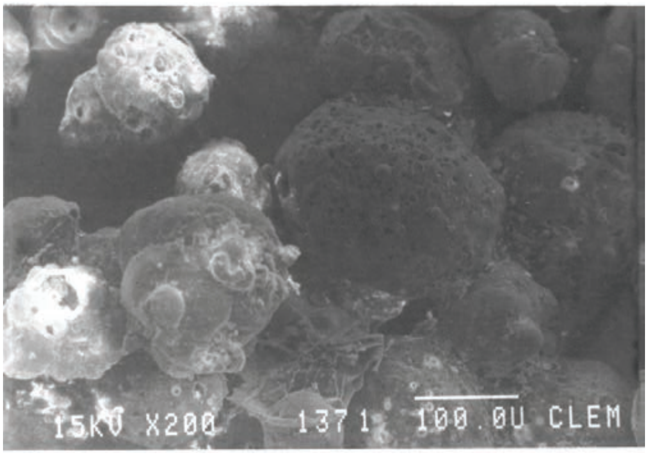

Fig. 7 Morphology of microspheres from brown coal ash from granulation boiler of ENO Nováky
Rys. 7 Morfologia popiołów z mikrosfer z popiołu z węgla brunatnego po granulacji z ciepłowni ENO Nováky AK

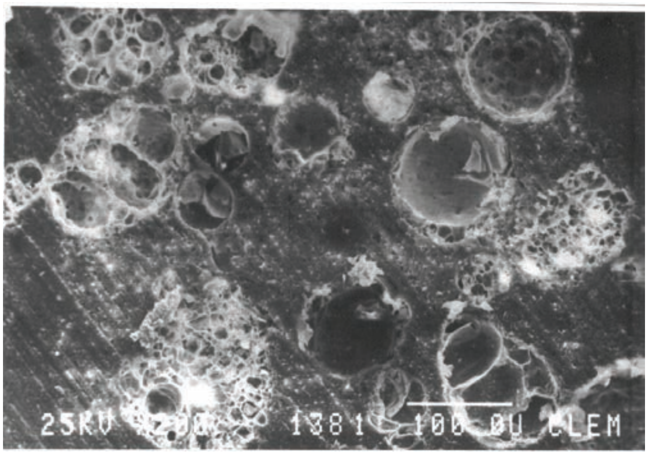

Fig. 8 Whet area of brown coal ash microspheres from granulation boiler of ENO Nováky
Rys. 8 Szlif obszaru mikrosfer z popiołu z węgla brunatnego po granulacji z ciepłowni ENO Nováky

to settling pit exposed to abrasion. Fig. 5 shows their surfaces partially destructed as a result of hydraulic transport.

Brown coal ash microspheres from granulation boilers

Microspheres were obtained by floating in methyl alcohol. Morphology of microspheres from brown coal ash from ENO Nováky is presented on Fig. 7 (Michalíková et al., 2003, Horovčák et al. 2012).

Whet area on Fig. 8 shows oval shape of microspheres and that their pores are noticeably larger when compared to black coal ash microspheres. Ratio of isometric rounding of the ash particles is lower, their porous surface is visible. At lower combustion temperature COx, NOx and possibly also H_2O gases had enough time to "escape" from volume of the particles resulting in larger pores in microspheres.

From comparison of both types of microspheres it is clear that brown coal ash microspheres are round, but their surface is not smooth. Explanation is in conditions of their formation: combustion of black coal takes place at 1400 – 1600°C, combustion of brown coal ta 1100 – 1300°C, where part of the ash matter was not completely melted, as in the case of black coal ash microspheres. Similar to black coal ash microspheres, microspheres from brown coal ash contain mainly following chemical elements: Si, Al, Fe, Ca, K, Ti, Cu.

One of the first informations about properties of microspheres were presented by Stárková (1993) and Hycnár (1985, 1988). In the last years microspheres were mainly used as fillers in plastic compounds: lowering the consumption of plastics and enhancing thermodynamic properties of products.

Use of microspheres allowed increase in heat resistance of vinyl compounds, layered on polyester fabrics. Such isolation compounds can be used for shielding of high voltage cables, for lowering of heat transfer during fire. Produced isolation is light and resistant to fire up to 980°C, because cracking microspheres release gaseous NOx and COx, which slows oxidation processes. Analogically are produced protective clothes for covering of whole cable canals, protective suits (workers in steel works, welders, etc.), thermal and fireproof curtains (Hycnár, 1985). Microspheres are used in space research for production of thermal insulation compounds.

Conclusion

Study of unique properties of black and brown coal ash microspheres is a basis for selection of proper methods of their utilization. Unique properties of cenospheres – low weight, high compressive strength , low, almost zero water absorption, chemical inactivity, good thermal resistivity, allows a broad range of industrial aplications of cenospheres and their use in space research.

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Streszczenie

Uboczne produkty spalania węgla w energetyce cieplnej muszą być wykorzystywane lub unieszkodliwiane jako odpady. Spalanie węgla prowadzi do powstawania składników użytecznych - cząsteczek popiołu, których morfologia zależy od właściwości spalonego węgla, temperatury spalania, atmosfery spalania, konstrukcji komory spalania i kontroli procesu. Temperatura ma dominujący wpływ na morfologię popiołów, w szczególności wieloskładnikowych. Popioły takie mają tendencję do częściowego stapiania się, pojedyncze cząstki mają tendencję do tworzenia agregatów aż do powstania klinkieru . Popiół zawiera cząstki pochodzenia organicznego i nieorganicznego .

Przedstawiono wyniki badania parametrów chemicznych, fizycznych - głównie morfologicznych- mikrosfer ze spalania węgla kamiennego w kotłach fluidalnych, oraz badania właściwości fizycznych i chemicznych mikrosfer ze spalania węgla brunatnego w kotłach rusztowych . Wyjątkowe właściwości mikrosfer, głównie pochodzących ze spalania węgla kamiennego umożliwiają ich wykorzystanie w wielu dziedzinach przemysłu.

Warunki spalania w kotłach fluidalnych nie sprzyjają powstawaniu mikrosfer, w temperaturach poniżej 1000° C, powstałe gazy mają wystarczająco dużo czasu, aby uwolnić się z popiołu.

Słowa kluczowe: mikrosfery, cenosfery, plerosferes, popiół, węgiel, spalanie