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## COMPARATIVE ASSESSMENT OF THE SURFACE PROPERTIES OF UKRAINIAN ASH MICROSOPHERES

The object of research is ash microspheres from the burning of hard coal in Donetsk, Lviv-Volyn (Ukraine) and foreign (South Africa) basins, power plants of various regions. The chemical and mineralogical composition of Ukrainian ash microspheres was analyzed in comparison with foreign counterparts (South Africa, Great Britain, etc.), other types of microspheres (glass, ceramic) and expanded perlite. The advantages of aluminosilicate microspheres of technogenic origin (ASM) over other lightweight fillers are noted.

One of the most problematic areas is the lack of an objective comparative assessment of Ukrainian ash microspheres in terms of the influence of the structure-forming bonds Si–O, Si–O–Si and Si–O–Al on the physicochemical properties and energy and reactivity of their surface. It was established that the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio in their composition is within 1.46–1.87 against 1.53–1.64 in South African ASM and 4.81–5.61 in swollen pearlites, which ensures the content of crystalline phases (mullite, quartz) from 36 wt. % in Trypil microspheres to 53 wt. % in Kurakhove microspheres. The latter have a minimal content of Si–O–Si bonds (the I<sub>0</sub>/I ratio in the 1029 cm<sup>-1</sup> band is 1.25 versus 6.71 in Burstyn ASM).

The revealed features of changes in the chemical and mineralogical composition of microspheres, as well as structure-forming bonds, are fully correlated with the content of adsorbed water and OH and CH groups in the surface layer of the latter and, as a result, the energy state and reactivity of ASM. A quantitative assessment of their wettability with water (0.32–0.106) and under the condition of tgδ (0.196–0.4490) is given. The availability of such information makes it possible to clearly classify Ukrainian ash microspheres according to the degree of efficiency of use, taking into account their advantages in the composition of composite materials on various types of binders and to assess the presence of interchangeability in the context of a special situation in Ukraine.

**Keywords:** aluminosilicate (ash) microspheres, chemical and mineralogical composition, structure-forming bonds, IR spectroscopy, wettability, specific surface area.

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### 1. Introduction

The burning of hard coal is associated with the formation of a significant amount of dispersed mineral waste, ash and slag. To date, 358.8 million tons of ash and slag have accumulated in the dumps of fourteen TPPs of Ukraine on an area of 3,710 hectares [1]. Their average annual output reaches 14 million tons, and in connection with the deterioration of coal quality, it has a tendency to increase. Landfills occupy large areas of land and are sources of unfavorable environmental conditions in the regions. Over time, the cost of transporting TPP ash and slag to landfills increases, as well as the cost of construction of ash dumps and their reconstruction [2].

The level of processing and use of ash and slag waste over the last 10 years varies from 3 to 13 % of their annual output. At the same time, mainly traditional technologies are used (collapse of dams, planning of the territory, production of small construction products, etc.). The share of the use of these wastes in the USA is 22 %, China – 25 %, and EU countries – 90 % [3].

Due to their unique physical and chemical properties, microspheres deserve special attention in the composition of ash and slag waste [4]. Aluminosilicate microspheres (ASM) (cenospheres, light fraction of fly ash, ash microspheres, energy ash microspheres, aluminosilicate microspheres, cenospheres, cenosphere fly ash) are hollow glass crystal microspheres with sizes from 20–50 to 400–500 μm with a predominant content of particles with a diameter of 100–200 μm, wall thickness from 2 to 30 μm. Their bulk density in a compacted state is 350–400 kg/cm<sup>3</sup>, and the true density of the substance of the walls is on average 2.5 g/cm<sup>3</sup> [5].

A comparative analysis of properties shows that ASM has a number of advantages over well-known industrial lightweight materials that are used as ingredients of composites (asbestos, pumice, expanded clay, glass microspheres, expanded perlite). They are manifested in the following [6]:

- high dispersion ensures the formation of homogeneous structures even in thin layers of polymers;
- the possibility of formation of closed pores in the structures;

- low bulk density;
- high isotropic compressive strength;
- increased thermal stability and stability in aggressive environments.

The presence of the specified advantages of ash microspheres, based on the set of features, gives every reason for their use in various industries as part of mineral and organic composites and as an element of organic binders [7].

However, ensuring the necessary and stable efficiency of ASM application requires an objective assessment of their chemical and mineralogical compositions in the context of comparison with the mentioned lightweight materials and the possibility of interchangeability of microspheres of various Ukrainian TPPs. In addition, it is necessary to evaluate the degree of influence of structure-forming bonds in the composition of ash microspheres (Si–O, Si–O–Si, Si–O–Al) on the processes of their surface layer and its energy state. The presence of a reliable analysis of the composition of ASM and their reactivity due to OH, CH groups and adsorbed water will allow predicting the behavior of the latter in the composition of composites at the stages of production and operation.

The presence of a reliable assessment of the specified features will allow to provide a comparative selection of ash microspheres as lightweight fillers for optimal composition of composites on various types of binders, will allow their interchangeability in part of Ukrainian ASM and a comparative assessment of the effectiveness of using foreign analogues.

*The aim of research* is a comparative analysis of the chemical and mineralogical composition of Ukrainian ash microspheres in comparison with foreign analogues (South Africa, Great Britain, russia) and other types of low-weight fillers. This will contribute to identifying features and assessing the state of their surface layer in order to substantiate the effective use of ASM in composites.

## 2. Materials and Methods

*The object of research* is ash microspheres from the burning of hard coal in Donetsk, Lviv-Volyn (Ukraine) and foreign (South Africa) basins, power plants of various regions. A comparative assessment of the physicochemical properties of Ukrainian ASMs is carried out using foreign analogues (South Africa, Great Britain, russia) and lightweight fillers (glass and ceramic microspheres and expanded perlite).

The chemical and mineralogical composition of ash microspheres was investigated using generally accepted

methods. Comparison of ASM, its wettability and energy state were studied by methods based on physical principles (quantitative IR spectroscopy, wettability by polar and nonpolar liquids, conditional tg of the angle of dielectric losses) [8].

## 3. Results and Discussion

A comparative assessment of the composition of ash microspheres with other fillers of a similar class, in particular expanded perlite, was performed. With regard to the chemical composition of aluminosilicate microspheres from different countries (Ukraine, Great Britain, South Africa, russia), it was found that their main components are oxides of silicon (up to 75 wt. %) and aluminum (up to 40 wt. %). Iron, titanium, calcium, magnesium, potassium, and sodium oxides are present in much lower concentrations (up to 5 wt. %).

The ratio between SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> ranges from 1.53–1.64 for South African microspheres to 1.32–5.00 for russian ones. In expanded perlite, for comparison, this indicator is at the level of 4.81–5.62 with a relatively lower content of aluminum oxides (up to 15 wt. %) and magnesium (up to 0.15 wt. %), Table 1 [9].

The noted characteristics make it possible to use ash microspheres in various industries, and to use them to reduce the area of ash slag waste dumps in Ukraine.

Silicate and ceramic microspheres are characterized by a ratio of SiO<sub>2</sub> to Al<sub>2</sub>O<sub>3</sub> of 1.67–2.60 and 1.79–2.83, respectively, with slight differences in the amount of other component oxides [10].

Glass spheres occupy a special place among the studied microspheres. Their chemical composition is characterized by a high content of SiO<sub>2</sub> (up to 80 wt. %), CaO (up to 25 wt. %), B<sub>2</sub>O<sub>3</sub> (up to 20 wt. %) and MgO, K<sub>2</sub>O and Na<sub>2</sub>O (up to 16 wt. %) in the absence of aluminum and iron oxides [11]. In addition to the noted features, small amounts (up to 1 wt. %) of P<sub>2</sub>O<sub>5</sub>, SO<sub>3</sub>, MnO may be present in the composition of microspheres of different composition.

The given data will allow a more objective assessment of Ukrainian ash microspheres in terms of their chemical composition. Its analysis of producers from different regions of Ukraine and hard coal deposits (Donetsk (Prydniprovka, Kryvyi Rih and Kurakhove TPP), Lviv-Volyn (Burshtyn TPP) coal basins and Trypillia TPP) will testify to a high degree of identity with the composition of ash microspheres of other countries.

**Table 1**

Chemical composition of microspheres and expanded perlite, wt. %

Material	Location	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	TiO <sub>2</sub>
Aluminosilicate microspheres	South Africa*	49–51	31–32	3–4	4.5–6.5	1–1.5	0.6–0.7	0.10	1.4–1.7
	russia	50–75	15–38	0.2–5.0	0.2–4.0	0.5–4.0	0.2–4.0	0.3–2.0	0.5–2.0
	Great Britain	55–61	26–30	4–10	0.2–0.6	1–2	–	0.5–4.0	–
	Ukraine	52–69	20–40	–	–	–	–	–	–
Glass microspheres	–	55–65	25–33	1–6	0.2–0.6	1–2	0.2–4.0	0.3–2.0	0.5–1.0
Glass spheres**	–	60–80	–	–	5–25	0–1.5	5–16	5–16	–
Ceramic microspheres***	–	52–65	23–29	6–10	0.1–6.0	1.0–2.0	1.0–2.3	0.3–1.0	0.6–1.0
Swollen perlite	–	73.1–75.9	15.2–13.5	1.2	1.4–2.2	0.02–0.14	3.4–4.2	1.7–3.3	0.04–0.05

**Note:** \* – microspheres additionally contain (wt. %): P<sub>2</sub>O<sub>5</sub> – 0.5–0.7; SO<sub>2</sub> – 0.2–0.25; MnO<sub>2</sub> – up to 0.02; \*\* – (wt. %): MnO<sub>2</sub> – 0–10; B<sub>2</sub>O<sub>3</sub> – 0–20; P<sub>2</sub>O<sub>5</sub> – 0–0.5; \*\*\* – (wt. %): P<sub>2</sub>O<sub>5</sub> – 0.2–1.0

Ukrainian materials are characterized by a somewhat lower level of the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio (1.46–1.87). It is worth noting the fact that there is a minimum content of iron oxides (1.7 wt. %) and potassium (up to 1 wt. %) in the Trypillia microspheres, as well as a reduced amount (up to 3.4 wt. %) of calcium oxide for the Kurakhove microspheres.

It was established that the noted features of the chemical composition of Ukrainian ash microspheres are realized in a certain way during the formation of amorphous and crystalline phases (Table 3). The maximum amount of the glass phase (up to 40 wt. %) was recorded by X-ray phase analysis of ashes for the microspheres of Burshtyn TPP, and the minimum (24 wt. %) – Trypillia. In relation to opal – crystalobalite, the inverse relationship is observed (respectively 12 and 40 wt. %).

The total content of crystalline phases (mullite and quartz) ranges from 36 wt. % (Trypillia TPP) to 53 wt. % (Kurakhove TPP). The mentioned microspheres are characterized by polar differences in the ratios between mullite and quartz. The latter varies from 1.5 for Kurakhove microspheres to 2.6 for Trypillia microspheres (Table 2).

Table 2

Chemical composition of Ukrainian ash microspheres, wt. %

Manufacturer, TPP	Oxide						
	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{TiO}_2$	$\text{SO}_2$	CaO	$\text{K}_2\text{O}$
Burshtyn	56.4	32.5	5.5	1.1	0.1	–	5.2
Prydniprovskaya	52.9	36.1	3.0	0.7	–	0.6	6.4
Kryvyi Rih	57.1	30.5	5.0	1.0	0.1	–	6.1
Kurakhove	56.2	30.0	4.1	1.0	0.3	3.4	5.1
Trypillia	60.7	34.2	1.7	1.2	0.3	1.0	1.0

Note: the composition of microspheres contains 0.04–0.05 wt. %  $\text{MnO}_2$

The obtained data regarding the mineralogical composition of microspheres from Ukrainian coal are qualitatively and quantitatively slightly different from South African ones. The amorphous phase in the latter is 41.5–58.2, mullite – 24.8–34.6; quartz – 13.6–21.4 wt. %. Minor admixtures of magnetite (up to 3.9 wt. %) and hematite (up to 1.4 wt. %) are also possible [6]. The mentioned iron-bearing minerals can be present in small concentrations in the composition of Ukrainian ASMs, with the exception of Trypillia (Table 3).

Table 3

Mineralogical composition of Ukrainian ash microspheres

Manufacturer, TPP	Content of component phases, wt. %			
	Glass phase	Opal-crystalobalite	Mullite	Quartz
Burshtyn	40	12	28	20
Prydniprovskaya	28	22	36	14
Kryvyi Rih	35	20	33	12
Kurakhove	34	13	32	21
Trypillia	24	40	26	10

A more detailed analysis of the structure-forming bonds present and the surface composition of the microspheres was carried out using the methods of quantitative IR spectroscopy.

Infrared spectra of ash microspheres of thermal power plants in different regions of Ukraine have a general configuration characteristic of aluminosilicates (Fig. 1).

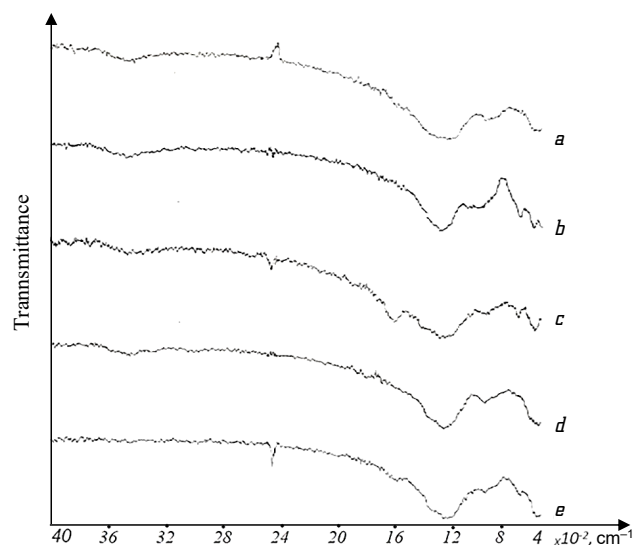


Fig. 1. IR spectra of the microsphere: a – Zuiv; b – Trypillia; c – Vuhlehirsk; d – Kryvyi Rih; e – Chernihiv

With regard to structure-forming bonds in the range of wave numbers 444–461  $\text{cm}^{-1}$ , absorption bands responsible for deformational vibrations of Si–O were recorded. Their maximum shifts towards low frequencies are characteristic of Burshtyn microspheres, and their minimum shifts are typical of Trypillia microspheres. The difference in the position of the maxima of the absorption bands reaches the limit of 20  $\text{cm}^{-1}$ .

Deformation vibrations of Si–O–Al bonds are observed at frequencies of 513 (Chernihiv TPP) – 589 (Prydniprovskaya)  $\text{cm}^{-1}$ . That is, the difference reaches 76  $\text{cm}^{-1}$ . It should also be noted the absence of absorption bands of these bonds in the IR spectra of the Kryvyi Rih and Zuiv microspheres. Valence fluctuations of the observed bonds are recorded at frequencies of 772 (Chernihiv, Kryvyi Rih and Vuhlehirsk TPPs) – 829 (Trypillia, Burshtyn TPPs)  $\text{cm}^{-1}$ . The displacement is 57  $\text{cm}^{-1}$ .

In the range from 1029  $\text{cm}^{-1}$  (Burshtyn TPP) with a difference of 78  $\text{cm}^{-1}$  towards higher frequencies (Trypillia TPP), the valence vibrations of Si–O–(Si) bonds were noted.

In addition to the mentioned absorption bands characteristic of the structure-forming bonds of aluminosilicates, the IR spectra of ash microspheres contain a number of others. Among them, it is possible to note the bands at 873  $\text{cm}^{-1}$  in Trypillia and 900  $\text{cm}^{-1}$  in Chernihiv, which can be attributed to deformation vibrations of the Al–OH bond.

Quite intense absorption bands at 1373 (Trypillia), 1380 and 1453 (Zuiv), 1426 (Vuhlehirsk)  $\text{cm}^{-1}$  were also recorded, which may be associated with deformational vibrations of hydroxyl groups. And the absorption band at 1666  $\text{cm}^{-1}$  (Kryvyi Rih) is responsible for valence vibrations of the C=O bond [12].

The high-frequency part of the IR spectra of ash microspheres has a rather different appearance. Fluctuations of C–H groups are observed at wavelengths of 2840–3083  $\text{cm}^{-1}$  in Kryvyi Rih, Zuiv, and Trypillia microspheres.

Absorbed water with maximum absorption in the frequency range of 3373  $\text{cm}^{-1}$  (Kryvyi Rih TPP) – 3439  $\text{cm}^{-1}$  (Trypillia TPP) was noted for all studied ASMs, except for Chernihiv.

Hydroxyl groups are present in the microspheres of Trypillia (3893  $\text{cm}^{-1}$ ), Chernihiv (3773  $\text{cm}^{-1}$ ), Kryvyi Rih (3693  $\text{cm}^{-1}$ ), Zuiv (3793  $\text{cm}^{-1}$ ), and Vuhlehirsk (3680, 3760, 3932  $\text{cm}^{-1}$ ) TPP. The range of shifts in the position of the maxima of the characteristic absorption bands can reach up to 239  $\text{cm}^{-1}$ .

The researched microspheres also look ambiguous in the context of quantitative assessment of the content of the above-mentioned functional groups and structure-forming bonds, as well as the distribution of their energy state. It was found that the maximum content of Si–O bonds, based on the ratio of the intensities of the absorption bands caused by their deformation fluctuations, is in the composition of the Prydniprovsk microsphere ( $I_0/I=1.72$ ), and the minimum is in the Zuiv microspheres (0.32). The positions of the maxima of the absorption bands do not differ significantly (by 5  $\text{cm}^{-1}$ ). The energy spectrum of the observed bands is characteristic only for Kryvyi Rih ASM ( $\Delta\nu_{1/2}=71.4 \text{ cm}^{-1}$  at values of  $I_0/I=1.11$ ), Table 4.

The number of Si–O–Al bonds is estimated by the intensity of the absorption bands of their deformation vibrations, which is somewhat less compared to Si–O. The maximum values of  $I_0/I$  were observed in Trypillia microspheres (1.14), and the minimum in Kurakhove microspheres (0.10), while they were completely absent for Zuiv and Kryvyi Rih microspheres. The position of the characteristic absorption bands differs by 7  $\text{cm}^{-1}$ .

The intensity of valence vibrations of the mentioned bonds is slightly higher. The ratio  $I_0/I$  in Burstyn microspheres is equal to 1.74, and 0.22 in curved microspheres when the position of the bands is shifted from 829 to 772  $\text{cm}^{-1}$ , respectively. This fact can serve as proof of the formation of stronger bonds in the Si–O–Al system at a much lower concentration. At the same time, the energy spectrum of these connections is the widest at ASM of Trypillia, Chernihiv and Prydniprovsk TPPs.

According to the data of quantitative IR spectroscopy, the concentration of structure-forming bonds Si–O–(Si) was found to be the highest in the composition of the studied ash materials. The maximum ratios of the intensities of their characteristic absorption bands at 1029  $\text{cm}^{-1}$  were noted in the Burstyn ASM (6.71), and the minimum (1.25) in the Kurakhove ones when the absorption extremum was shifted by 51  $\text{cm}^{-1}$  to higher frequencies. Attention should also be paid to the rather wide energy spectrum of the mentioned bonds in the first case ( $\Delta\nu_{1/2}=929 \text{ cm}^{-1}$ ).

The identified features of the chemical and mineralogical composition of ash microspheres, as well as the formation of structure-forming bonds in the  $\text{SiO}_2\text{--Al}_2\text{O}_3$  system, were used to study the composition and physical and chemical properties of the latter's surface. Thus, with regard to adsorbed water, the presence of its maximum concentration in the composition of Burstyn microspheres was established ( $I_0/I$  at 3403  $\text{cm}^{-1}=0.38$ ). For all other materials, with the exception of Chernihiv TPP, this indicator is in a fairly consistent correlation with the content of Si–O–(Si) and Si–O–Al structure-forming bonds in the studied ash materials. The deviation of the position of the characteristic absorption band (at 3373  $\text{cm}^{-1}$  by 27–64  $\text{cm}^{-1}$  in the high-frequency part of the spectrum) and, as a result, the relatively higher binding strength of adsorbed water in the composition of the Kryvyi Rih ASMs, and the latter being completely absent for the Chernihiv ones, deserve attention.

Table 4

Parameters of absorption bands in the IR spectra of ash microspheres

TPP	The position of the absorption band maximum, $\text{cm}^{-1}$	The absorption band intensity, $I_0/I$	The half-width of the absorption band, $\Delta\nu_{1/2}$ , $\text{cm}^{-1}$
Trypillia	463	0.77	–
	546	1.14	–
	829	0.79	–
	873	0.83	665
	1106	3.45	2.0
	1373	0.32	–
	2906	0.04	–
	3083	0.05	–
	3439	0.17	–
Chernihiv	3893	0.32	–
	447	0.50	–
	513	0.17	–
	613	0.04	–
	772	0.50	27
	900	0.60	718
	1046	1.81	53
	1420	0.25	–
	3773	0.06	–
Kryvyi Rih	447	0.4	–
	772	0.22	–
	1053	2.15	–
	1666	0.13	–
	2840	0.04	–
	2893	0.05	–
	2946	0.05	–
	3373	0.17	–
	3693	0.04	–
Prydniprovsk	448	1.72	–
	589	0.24	–
	731	1.12	726
	1041	5.70	–
	3403	0.38	–
Zuiv	453	0.32	–
	798	0.43	–
	1046	5.86	–
	1380	0.46	–
	1453	0.41	–
	2853	0.07	–
	2906	0.07	–
	3426	0.17	–
	3793	0.11	–
Vuhlehirsk	446	0.79	–
	573	0.37	–
	772	0.23	–
	1079	3.58	–
	1426	1.16	–
	3400	0.13	–
	3610	0.07	–
	3680	0.09	–
	3760	0.07	–
3932	0.08	–	
Kurakhove	452	1.11	714
	553	0.10	–
	798	1.06	–
	1080	1.25	–
	3430	0.08	–
Burshtyn	444	0.76	–
	554	0.45	–
	829	1.74	–
	1029	6.71	929
	3437	0.52	–

The presence of OH groups was not detected for the ash microspheres of Burshtyn, Prydniprovsk and Kurakhove TPPs. And their concentration is much lower compared to adsorbed water for all others (max  $I_0/I=0.11$ , for Zuiv).

With regard to Vuhlehirsk ASM, it is advisable to note the presence of a whole series of characteristic absorption bands in the frequency range from 3610 to 3932  $\text{cm}^{-1}$  with an indicator of intensity ratios at the level of 0.07–0.09.

Valence oscillations of CH groups are observed for the materials of the Trypillia, Kryvyi Rih, and ZuiivTPPs in the frequency range of 2840–3083  $\text{cm}^{-1}$ . Based on the position of the maxima of the characteristic absorption bands, the least strongly bound organic groups in the composition of Trypillia microspheres (the shift to the high-frequency region of the spectrum reaches 66–189  $\text{cm}^{-1}$ ). The sum of the  $I_0/I$  ratios is also minimal for the mentioned ASM (0.09), which is 0.05 less compared to other studied materials.

The noted features in terms of the presence of structure-forming bonds in the composition of ash microspheres, as well as OH, CH and adsorbed water groups, their content and energy state significantly affect the wettability of the ASM surface with water and polar liquids (Table 5).

It has been established that the microspheres from Kryvyi Rih have the best wettability with water (0.106), and those from Kurakhove have the worst wettability by more than three times. All other studied materials occupy an intermediate position. Similar regularities were noted when evaluating the lyophilicity coefficient, when the level of wettability by a nonpolar liquid is also taken into account. The  $\beta$  values are 0.62 and 0.24, respectively.

Estimation of the energy state of the surface of ash microspheres using the method of determining the conditional  $\text{tg}$  angle of dielectric losses after exposure of the material in a humid environment is in good agreement with the wettability data.

Compared to the swollen pearlites of the Arahatskyi and Berehivskyi deposits, the studied ash microspheres are characterized by poorer wettability and lower surface energy.

Estimation of the marginal angle of wetting of the ASM surface by water and benzene by different methods (Washburne, sitting drop, B. V. Deriahin) show the presence of minor differences in the first case ( $\theta$  varies within 80–86°).

This difference in the case of benzene can reach 37 degrees (from 73° in the Prydniprovska microspheres to 36° in the Trypillia microspheres). This fact can be explained by the complete absence of OH and CH groups in the composition of the surface layer of the latter and more than twice the amount of adsorbed water.

A more detailed analysis of the components of the surface energy of ash microspheres showed the minimum level of its polar part in the Burshtyn ASMs (0.007  $\text{mN}\cdot\text{m}$ ), and the highest by almost an order of magnitude in the Kurakhove ASMs. The dispersion component ranges from 0.169  $\text{mN}\cdot\text{m}$  in Trypil microspheres to 0.328  $\text{mN}\cdot\text{m}$  in Kryvyi Rih microspheres (Table 6).

**Table 6**  
Surface energy of ash microspheres ( $\text{mN}\cdot\text{m}$ )

TPP	Polar component	Dispersion component
Burshtyn	0.007	0.175
Kryvyi Rih	0.030	0.322
Prydniprovska	0.027	0.322
Kurakhove	0.065	0.278
Trypillia	0.060	0.169

The presence of significant differences in the levels of the polar and dispersive components of the surface energy for Burstyn and Trypillia ash microspheres can be explained by the complete absence of OH and CH groups on the surface of the former. It should be noted that the content of Si–O–Al structure-forming bonds is almost the same for the noted materials, and Si–O–Si and Si–O are almost 1.8 times smaller for the latter.

Thus, the obtained results of the study of the physico-chemical properties of Ukrainian ash microspheres make it possible to determine a significant part of the chemical and mineralogical compositions and their surfaces and the energy state of the latter in the context of specific TPPs and hard coal deposits. These data make it possible to specify the scope of ASM application in the production of a wide range of composite materials on different types of binder.

At the same time, these recommendations may have certain limitations in terms of ensuring a certain level of stability of the studied properties. This is evidenced by a significant range of variations in the wettability and energy state of the ASM surface and their mineralogical composition and the number of structure-forming bonds. Such restrictions can be taken into account based on the results of the performed studies.

In the course of research, the analysis of the properties of ash microspheres, based on a set of features, provides grounds for the use in various industries of such as:

**Table 5**

Surface properties of aluminosilicate dispersed materials

Material	Wettability when infused with water	Coefficient of lyophilicity, $\beta$	Conditional $\text{tg}\delta$	Marginal wetting angle, degrees, (water) benzene; defined by the material		
				Washburn	Sessile drop	B. V. Deriahin
ASM (TPP)						
Kryvyi Rih	0.106	0.62	0.4490	84/54	85/50	86/53
Burshtyn	0.087	0.53	0.3721	84/53	85/56	85/54
Trypillia	0.082	0.44	0.2863	82/41	84/36	85/39
Prydniprovska	0.040	0.26	0.2041	84/73	84/40	88/55
Kurakhove	0.032	0.24	0.1966	84/47	84/48	84/48
Swollen perlite						
Arahatskyi	0.189	1.48	0.2479	–	–	–
Berehivskyi	0.086	0.67	0.5340	–	–	–

– *Oil and gas industry*: lightweight plugging cements for well construction.

– *Construction*: ultra-light concrete, heat-insulating plasters and masonry mixes, other types of dry construction mixes, heat- and sound-insulating coatings for the installation of roof and facade structures, floor coverings, as well as heat-insulating preparations for floors.

– *Ceramic products*: lightweight fire-resistant wall materials and coatings, lightweight materials for aviation and space applications.

- *Paint materials*: thin-layer energy-saving and fire-retardant paints.
- *Polymeric materials*: production of various watercraft (boats, buoys, life jackets, buoyancy modules of submarines and bathyscaphes), radio-transparent heat-insulating screens of radio technical equipment, insulation of heat paths, forming materials for dentistry.
- *Chemical industry*: catalysts for wastewater treatment, sensitizers for emulsion explosives, production of soundproof composites in the automotive industry, production of tires, putties and primers, high-performance abrasive tools, non-slip compounds for shoe soles.

In the conditions of martial law, a comparison of the properties of microspheres from different coal basins of Ukraine, namely Donetsk (Prydniprovsk, Kryvyi Rih and Kurakhove TPP) and Lviv-Volyn (Burshtyn TPP) coal basins and Trypillia TPP was carried out for the possibility of their replacement.

Further research is promising for expanding the possibilities of using ash microspheres as a filler. It is necessary to investigate the effectiveness of using Ukrainian ash microspheres on different types of binders: organic, elemental-organic, and mineral.

#### 4. Conclusions

Using independent methods of analysis based on different physical principles, a comparative assessment of chemical mineralogical compositions and surface properties of Ukrainian ash microspheres has been performed.

It has been established that the ratio of structure-forming oxides  $\text{SiO}_2/\text{Al}_2\text{O}_3$  in Ukrainian ASM is 1.46–1.87 compared to 1.53–1.64 in South African and 4.81–5.62 swollen pearlites, with a minimal content of iron oxides (1.2 wt. %) and potassium (up to 1 wt. %).

In total, the content of crystalline phases (mullite and quartz) ranges from 36 wt. % in the microspheres of the Trypillia TPP to 53 wt. % of the Kurakhove, which is little different from the South African ones. Among the structure-forming bonds, a significant place belongs to Si–O–Si ( $I_0/I$  at the  $1029\text{ cm}^{-1}$  band is 1.25 in Kurakhove microspheres, and the maximum is 6.71 in Burshtyn microspheres).

Adsorbed water, OH and CH groups are recorded in the composition of the surface layer of ASM. Their quantitative indicators are characterized by  $I_0/I$  in the range of 0.05–0.38. Taking into account the noted features, a comparative assessment of the energy state of the surface of ash microspheres with swollen perlite is given (wettability upon inflow 0.032 (Kurakhove TPP) – 0.106 (Kryvyi Rih) vs. 0.086–0.189, and  $\text{tg}\delta$ , respectively, 0.1966–0.4490 vs. 0.2478–0.5340).

A detailed analysis of the components of the surface energy of ash microspheres (0.007–0.060 – polar and 0.169–0.322 dispersive) was performed and the influence of OH and CH groups and structure-forming bonds on the formation of the latter was shown.

The obtained results can be of practical importance in various branches of industry: oil and gas, construction, ceramic, paint, polymer and chemical industries.

#### Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal,

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#### Data availability

The manuscript has no associated data.

#### Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

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