14. Fire-retardant paint with steel structure [Electronic resource]: Patent CN 101857756 A / Shang Zhenguo, Zhang Yongjun, Li Feiyun, Wang Zhe, Wang Xiaomei, Wang Jingbo, Zhiteng Ming, Su Zhongjie, Xie Chenggang, Hao Lin, Han Ping, Ma Zheng, Gao Liang; assignee: Inner Mongolia Xingtai Construction Co., Ltd. – Appl. No. CN 201010221161; Filed July 8, 2010; Published October 13, 2010. – Available at: \www/URL: https://www.google.com/patents/CN101857756A?cl=en
15. Ognestoikii sostav [Electronic resource]: Patent RU 2148605 / Riabov S. V., Matveev S. A. – Appl. No. 99104530/04; Filed March 9, 1999; Published May 10, 2000. – Available at: \www/URL: http://ru-patent.info/21/45-49/2148605.html
16. Method of producing vibration- and noise-attenuating fire-retardant composition [Electronic resource]: Patent RU 2470966 C2 / Ponimatkin V. P., Chernova N. S., Mnatsakanov S. S., Zybina O. A., Zav'jalov D. E.; assignee: Obshchestvo s ograniche nnoj otvetstvennost'ju «FAKTORIJa LS». – Appl. No. 2011113427/05; Filed April 8, 2011; Published December 27, 2012. – Available at: \www/URL: http://www.freepatent.ru/images/patents/147/2470966/patent-2470966.pdf
17. Ognezashchitnaia vspuchivaiushchaiasia kraska [Electronic resource]: Patent RU 2224775 C1 / Zahvatkin S. S., Fasiura V. N., Vladislavleva E. Yu. – Appl. No. 2003110927/04; Filed April 17, 2003; Published February 27, 2004. – Available at: \www/URL: http://bd.patent.su/2224000-2224999/pat/servl/servletbfae.html
18. Fire-resistant coating material adina [Electronic resource]: Patent UA 110236 C2 / Magdina R., Nemecek L. – Appl. No. a201311315; Filed February 7, 2012; Published December 10, 2015. – Available at: \www/URL: http://uapatents.com/6-110236-vognestijjkijj-material-dlya-pokrittiv-adina.html

РАЗРАБОТКА ОГНЕСТОЙКОГО ПОКРЫТИЯ ДЛЯ ЗАЩИТЫ ЭЛЕКТРИЧЕСКИХ КАБЕЛЕЙ ПРИ ПОЖАРЕ В ЗАМКНУТОМ ПРОСТРАНСТВЕ

Приводятся результаты разработки и оптимизации состава огнестойкого покрытия для защиты кабельной изоляции при пожаре в замкнутом пространстве. Компоненты покрытия выбраны по требованиям огнестойкости и токсичности. Обоснован предполагаемый механизм работы огнестойкого покрытия при пожаре. Проведены лабораторные испытания образцов огнестойких покрытий. Получена временная зависимость температуры на обратной стороне огнестойкого покрытия от состава композиции.

Ключевые слова: нетоксичное огнестойкое интумесцентное покрытие для защиты кабельной изоляции, компоненты состава, методика испытаний.

Korostylev Leontiy, *Doctor of Technical Sciences, Professor, Head of the Department of Design and Production of Structures from Composite Materials, Admiral Makarov National University of Shipbuilding, Mykolaiv, Ukraine, e-mail: leontyy.korostilyov@nuos.edu.ua, ORCID: http://orcid.org/0000-0002-4370-3270*

Kochanov Vladimir, *Scientific Researcher, Department of Design and Production of Structures from Composite Materials, Admiral Makarov National University of Shipbuilding, Mykolaiv, Ukraine, e-mail: Kochanov@nuos.edu.ua, ORCID: http://orcid.org/0000-0001-7525-0870*

Geyko Sergey, *PhD, Department of Design and Production of Structures from Composite Materials, Admiral Makarov National University of Shipbuilding, Mykolaiv, Ukraine, ORCID: http://orcid.org/0000-0002-5005-2437*

Yuresko Tetiana, *Assistant, Department of Design and Production of Structures from Composite Materials, Admiral Makarov National University of Shipbuilding, Mykolaiv, Ukraine, e-mail: tyresko@gmail.com, ORCID: http://orcid.org/0000-0002-4197-1677*

UDC 662.613.11
DOI: 10.15587/2312-8372.2017.118958

Demchenko V., Simyachko E., Svidersky V.

RESEARCH OF MINERALOGICAL COMPOSITION, STRUCTURE AND PROPERTIES OF THE SURFACE OF UKRAINIAN ASH MICROSPHERES

Досліджено властивості (мінералогічний склад, змочуваність, пористість, питому поверхню та її енергетичний стан) зольних мікросфер різних ТЕС України, що отримуються в результаті спалювання вугілля Донецького (Трипільська, Курахівська, Криворізька і Придніпровська ТЕС) та Львівсько-Волинського вугільних басейнів (Бурштинська ТЕС). Проаналізовано вплив властивостей поверхні зольних мікросфер на їх потенційну здатність використання в якості наповнювачів для будівельних матеріалів.

Ключові слова: *зольні мікросфери, питома поверхня, мінералогічний склад, порошкоподібний матеріал, аморфна фаза.*

1. Introduction

The development of industry, especially in recent years, requires the creation of new building materials with improved properties. First of all, these materials must have increased strength, heat resistance, reduced thermal conductivity, as well as a lower cost in comparison with analogues present in the construction market of Ukraine.

With the development of scientific and technical progress, systematic identification of factors determining the operational properties and cost of building materials and, as a consequence, the potential possibilities of their regulation become more and more urgent [1].

Significant interest in this direction is represented by ash microspheres. These are hollow ash pellets with an average size of 20 to 500 μm with solid, non-porous walls

2 to 10 μm thick. The ash microspheres are filled with a mixture of nitrogen and carbon dioxide under reduced pressure (about 0.3 atmospheres). Such characteristics may allow them to be used in industry (including construction). Microspheres are formed as a result of high-temperature flaring of solid fuel at TPSs and specific granulation of the melt of the mineral part of the coal by crushing it into individual small droplets and blowing up the latter due to an increase in the volume of gas inclusions. Under the influence of high temperatures during the coal combustion, conditions are created for the formation of a closed structure, the so-called ash microspheres. These materials have low thermal conductivity, density, shrinkage and water absorption, compact particle packing, high fluidity, strength, heat resistance and resistance to environmental factors. It is the above properties that determine the potential ability of microspheres to be used as filler for building materials with increased thermal insulation properties.

2. The object of research and its technological audit

The objects of research are the ash microspheres of Prydniprovska, Kryvyi Rig, Trypillia, Burshtyn and Kurakhove TPSs (Ukraine).

The ash microspheres have found application in almost all spheres of industry, in particular, in construction, oil and gas, and the chemical industry. In 2015, the volume of ash and slag materials (including ash microspheres) amounted to 348.2 thousand tons, and sales revenue – 5 million USD. At the same time, 31.5 thousand tons of ash microspheres were sold to customers in export markets. In recent years, there has been a tendency to increase exports and reduce imports of ash microspheres, which, in general, positively affects the Ukrainian industrial market.

The use of fly ash microspheres for commercial purposes has an environmental effect. At present, ash dumps of Ukrainian TPSs are 50 % full, and in some cases 95 %. Secondary processing and use of ash microspheres allows to reduce the negative influence of existing ash dumps on the environment due to reduction of their storage volumes.

Today, products using ash and slag wastes from thermal power plants have been widely used both in Ukrainian industry and in industry in Europe and the CIS. The use of ash and slag wastes (including ash microspheres) of TPSs in the production of concrete and reinforced concrete products makes it possible to reduce cement consumption by 10.2 %; improve physical, mechanical and operational properties of building materials; reduce the cost of the creation and operation of dumps [2–8].

The composition and properties of ash microspheres obtained from fly ash from TPSs are determined by the type of coal. Therefore, the study of their structure and surface properties is one of the priority tasks, determines the feasibility and possibilities of using the latter as filler with increased thermal insulation properties [7].

Based on the analysis of previous studies and the study of the structure and properties of the surface of ash microspheres, it is necessary to determine the principle of application of these materials in mixtures based on mineral binders.

3. The aim and objectives of research

The aim of research is establishment of the possibility of using the surface of ash microspheres of Prydniprovska, Kryvyi Rig, Trypillia, Burshtyn and Kurakhove TPSs to fill composite construction materials based on mineral binders.

To achieve this aim, the following tasks are accomplished:

1. To analyze the mineralogical composition of the Ukrainian ash microspheres.
2. To investigate the surface properties and structure of ash microspheres.
3. To estimate the level of thermal conductivity of the investigated ash microspheres.
4. To assess the degree of compliance of ash microspheres with the requirements for fillers of heat-insulating building materials.

4. Research of existing solutions of the problem

Recent advances in fill technology, which due to the regulation of the packing density of the filler in the material, make it possible to increase the thermal insulation properties of building materials, have not yet found wide coverage in the literature and use in practice [9–17]. In most cases, the manufacture of construction products without fillers is technically less well founded than innocent. Therefore, it is obvious that with the development of technology for the introduction of the latter will increase the efficiency of the use of fillers in the construction materials [3].

The analysis of literature sources on the properties of fillers of composite materials has shown the possibility of using ash microspheres in building materials to enhance their thermal insulation and operational properties [5, 6].

An experience of the factories of a number of countries has shown that it is economically expedient to introduce ash microspheres into the composition of concrete mixtures. It is known that when the part of cement is replaced with ash microspheres, the convenience of embedding the concrete mix improves. This is due to the smooth surface and the spherical shape of the ash particles, and the thinner these particles, the more they are needed. According to this dependence, the amount of water decreases to obtain the necessary consistency of the concrete mixture and its indices are improved: plasticity, uniformity and density increase. The ash microspheres make it possible to improve the sand granulometry, in which there are no fine fractions. It is particularly advisable to add them to difficult-to-machine concrete mixtures with a small amount of cement. At the same time, the scope of application is limited due to the lack of information regarding the properties of the surface of ash microspheres [9–13].

5. Methods of research

The mineralogical composition of the ash microspheres and the quantitative relationship between the phases are determined by X-ray diffraction analysis (DRON-2diffractometer, Russian Federation) and optical microscopy [8].

The contact angle, porosity, specific surface area, and lyophilicity coefficient are determined using water and xylene, thermal conductivity is determined by the stationary cylinder method [4].

ISSN 2226-3780

6. Research results

The ash microspheres are formed by pulverized coal combustion of solid fuel, after which they are collected by electrostatic precipitators and, in a dry state, are taken away with the help of ash separator for production needs, or, together with water and slag, are sent to the ash dump. Thus, the mineralogical composition of the ash microspheres depends on the type of solid fuel burned at the TPSs.

It is established that the main components of microspheres are glass phases, mullite and quartz. Hematite, feldspar, magnetite, hydrous micas and calcium oxide are also present in the form of impurities.

In the composition of the investigated microspheres, the predominant crystallophase is, with the exception of the Kurakhove TPSs. It is mainly represented by mullite (43–98 % by weight). Its minimum amount (43 % by weight) is detected for the above station, and the maximum (98 % by weight) – Trypillia TPS (Table 1).

Table 1

Mineralogical composition of ash microspheres, wt. %

TPS	Glass phases		Crystal phase		The refractive index of the glass phase
	Glass	Opal cristobalite	Mullite	Quartz	
Burshtyn	2	–	95	3	1.519
Kryvyi Rig	6	–	93	1	1.512
Prydniprovska	3	1	91	5	1.512
Trypillia	1	–	98	1	1.516
Kurakhove	14	37	43	6	1.518

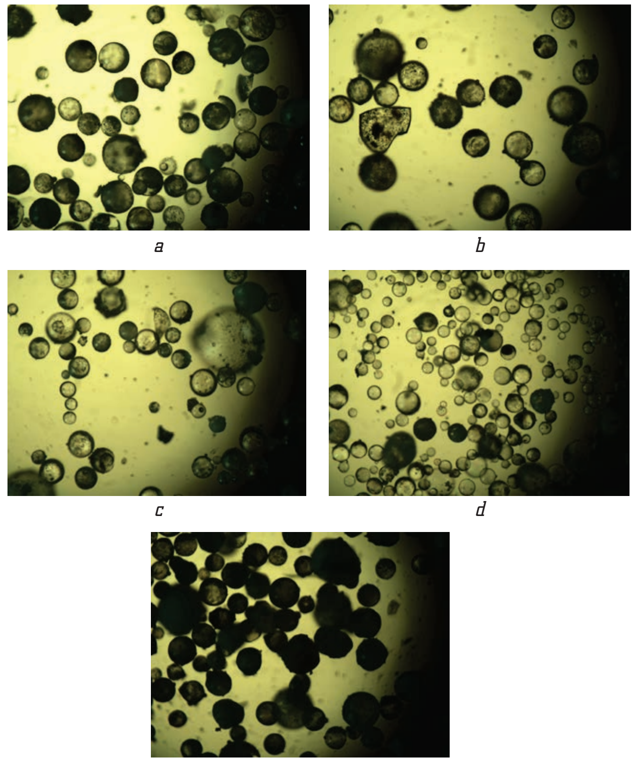
The quartz content in the crystal phase of microspheres is 1–6 wt. %. On the x-ray diffraction patterns, the shift of quartz reflexes towards its curved modification indicates the presence of impurities. The content of the latter in microspheres of different bulk density differs.

The increased content of the glass phase is characteristic for ash microspheres from fly ash of thermal power plants burning Donetsk anthracites (Kryvyi Rig, Prydniprovska, Kurakhove TPS) – 4–51 wt. %. The content of the glass phase in the microspheres formed during the combustion of coal from the Lviv-Volyn Basin (Burshtyn TPS) is only 2 wt. %.

It is established that the refractive index of the glass phase of microspheres is in the range of 1.512–1.519, which corresponds to a glass with a silicon content of 56.8 to 60.2 wt. %.

Studies using optical microscopy show that the ash microspheres have a shape close to spherical and a smooth outer surface, and using the scanning electron microscope revealed irregularities in their external surface of various shapes and sizes. The presence of closed porosity of the shells on the chips in separate microspheres is also established (Fig. 1).

In non-magnetic ash microspheres resulting from a three-stage separation containing both perforated and unperforated microspheres, in addition to the quartz phase, there is also an insignificant (not more than 5 mass %) amount of mullite. The latter is found only in perforated microspheres, while the non-perforated contain only the quartz phase (Fig. 1).



a b c d e

Fig. 1. Microstructure of ash microspheres of Ukrainian TPSs: *a* – Burshtyn; *b* – Kryvyi Rig; *c* – Kurakhove; *d* – Prydniprovska; *e* – Trypillia

The main difference between the magnetic microspheres and the non-magnetic appearance in their composition, along with the quartz, is the magnetite Fe_3O_4 phase. It should also be noted that there are no significant differences in the mineralogical composition of the perforated and non-perforated microspheres, where the phases of quartz, magnetite and mullite are recorded (the latter on the verge of detection). At the same time, mullite does not appear in all ashes with a density of 0.52 g/cm^3.

The use of ash microspheres as a filler is largely determined by the ability of this material to be wetted with various liquids to form stable disperse systems. In these systems, the wetting liquid would act as a dispersion medium, and the ash microspheres would be a dispersed phase [10].

Thus, in order to determine the feasibility of using ash microspheres as a filler of heat-insulating building materials, their wettability is determined by polar and nonpolar liquids: investigated liquid (water) and the reference liquid, the viscosity and surface tension of which is very low – xylene. The results of the study are given in Table 2.

It is established that the ash microspheres are much better wetted by nonpolar liquids (xylene, C_8H_{10}) than polar (water, H_2O). Moreover, the investigated material is not wetted well (the contact angle of the three phases is 50–90°) [11, 12].

The maximum wettability, both in water and in xylene, is characterized by ash microspheres obtained by burning Kurakhove coal (0.0394 in water and 0.5736 in xylene) and at Prydniprovska TPS (0.0523 in water and 0.0334 in water xylene). The lowest wettability is characteristic for ash microspheres for water – Kryvyi Rig TPS (0.1045), for xylene – Trypillia TPS (0.7771) [13, 14].

Table 2

Properties of ash microspheres

Indicator	Burshtyn TPS	Prydnip-rovska TPS	Kryvyi Rig TPS	Trypil-lia TPS	Kurak-hove TPS
Wettability: – water; – xylene	0.0872 0.5878	0.0523 0.6018	0.1045 0.6691	0.0872 0.7771	0.0349 0.5736
Effective specific surface, m^2/g	1.7	1.9	1.5	2.0	2.3
Lyophilicity coefficient (β)	0.148	0.087	0.156	0.112	0.061
The conditional tangent of the dielectric loss angle: – dried up; – incubated in a humid environment	0.021 0.027	0.025 0.040	0.026 0.031	0.024 0.075	0.016 0.018

The coefficient of lyophilicity is the highest in ash microspheres obtained from coal combustion at Burshtyn TPS and is 0.148, and the lowest in ash microspheres of Kurakhove TPS (0.061).

In addition to wettability, no less important characteristic in studying the properties of powdered materials, in this case ash microspheres, is their specific surface area.

The specific surface of the disperse phase determines the nature of its interaction with the matrix and depends on the contact surface and the distribution of particles in the dispersion medium.

The ash microspheres have a relatively low specific surface (Table 2). This is directly related to their granulometric composition: the total size of the fraction, the content of fractions of increased size (300–500 μm), the distribution of particles in the volume; as well as its mineral-phase composition.

Thus, the highest specific surface area is obtained by ash microspheres obtained by burning coal from Trypillia and Kurakhove TPSs (2.0 and 2.3 m^2/g). The lowest value of this indicator is in the samples from the Kryvyi Rig TPS.

The ash microspheres exhibit the properties of a typical dielectric. The dried material is characterized by relatively low values of the conditional tangent of the dielectric loss angle.

However, adsorbed on its surface a certain amount of moisture, tgδ increases by an order of magnitude. This indicates that the dielectric properties of ash microspheres depend on the properties of their surface: potential energy, polarity of uncompensated energy potentials, adsorption capacity of the surface and adsorbed substances. The higher the value of tgδ, the higher the hydrophilicity and the low hydrophobicity the test materials have.

The obtained data shows that the high value of tgδ in the ash microspheres of the Trypillia TPS, also high values for the Kryvyi Rig and Prydniprovska TPSs wastes. The minimum value is for the ash of Burshtyn and Kurakhove TPSs. It follows from the foregoing that the ash microspheres of the last two thermal power plants have, respectively, minimum moisture absorption among the investigated material.

The main properties of thermal insulation materials are determined by their porosity: air pores dramatically reduce the thermal conductivity of the material. In addition, the density, strength, gas permeability of heat-insulating materials depend on porosity.

The uniform distribution of air pores in the microspheres and the nature of the pores, as well as the chemical composition and molecular structure of the framework and the conditions for using this material are very important. Especially it should be taken into account when choosing materials for high-temperature insulation.

Higher thermal insulation properties with the same porosity have materials that have small closed pores due to reduced heat transfer by convection and radiation.

An estimate of the porosity of the ash microspheres by a method using liquids of different polarity is shown in Table 3.

Table 3

Porosity of ash microspheres,%

TPS	Water	Xylene
Burshtyn	43.5	44.2
Prydniprovska	39.4	41.3
Kryvyi Rig	45.2	47.1
Trypillia	50.0	51.8
Kurakhove	38.8	39.6

It is the highest in the case of the Trypillia and Kryvyi Rig TPSs (50 % and 45.2 %, respectively), and the lowest – Kurakhove TPS (38.8 %).

Taking into account that the properties of microspheres are investigated in order to make them useful as a filler for heat-insulating building materials, at this stage it will be important to give the results of the study of the thermal conductivity of ash microspheres of various TPSs in Ukraine [9].

The results of determining the thermal conductivity coefficient (λ) are given in Table 4.

Table 4

Thermal conductivity coefficient of ash microspheres, W/(m·K)

Indicator	Burshtyn TPS	Prydnip-rovska TPS	Kryvyi Rig TPS	Trypillia TPS	Kurak-hove TPS
Thermal conductivity coefficient (λ)	0.184	0.162	0.173	0.190	0.177

The highest coefficient of thermal conductivity is the ash microspheres obtained from the Trypillia and Burshtyn TPSs (0.190 and 0.184 W/(m·K), respectively), and the lowest – Prydniprovska TPS. Since the low coefficient of thermal conductivity leads to less heat exchange of the internal environment with the external one, the ash microspheres of Prydniprovska, Kryvyi Rig and Kurakhove TPSs have higher thermal insulation properties.

Based on the obtained data using independent methods of physical and chemical analysis, it is found that mullite, quartz, glass and opal-cristobalite are in the composition of the investigated ash microspheres. Their number is determined by the features of technological processes for obtaining ash microspheres and coal deposits.

The study of the mineralogical composition of ash microspheres makes it possible to determine the main directions for the realization of their potential capabilities. To obtain a more complete picture, it is necessary to characterize the relationship of the mineralogical composition of the fillers – the surface properties [13].

Water wettability is associated with the crystal-chemical structure of the ash microspheres, the molecular nature of the surface and the presence of such centers or radicals on it, attach water molecules to them through hydrogen bonds. So, the initial properties of the surface of raw components should be taken into account in the practical application of ash microspheres as filler for building materials with increased thermal insulation properties.

The presence of some disagreements in assessing the interaction of ash microspheres with water (based on the wettability index and the conditional tangent of the dielectric loss angle) is due, in addition to differences in the mineralogical composition, and the different degree of development of the specific surface. In this regard, it has been experimentally established (Table 2), the research sample of ash microspheres of the Kryvyi Rig TPS differs from the Kurakhove TPS by its greater wettability by polar (water) and nonpolar (xylene) liquid. As well as the above samples are characterized by a coefficient of lyophilicity (0.156 for Kryvyi Rig TPS versus 0.061 for Kurakhove TPS) with a slightly lower effective specific surface area.

In order to determine the feasibility of using ash microspheres as fillers for building materials with increased thermal insulation properties, it is necessary to characterize the relationship of the mineralogical composition-porosity-thermal conductivity of the investigated domestic microspheres.

In addition to these factors, the physical and chemical properties of the surface of ash microspheres are determined to a certain extent by the parameters of their pore structure.

Its quantitative evaluation using water and xylene shows significant differentiation. Thus, the minimum pore volume for the investigated materials is 38–43 %, depending on the type of liquid (water), and the maximum pore volume 47–51.8 % (xylene). Samples of the ash microspheres of the Burshtyn TPS differ approximately in the same porosity both in water and in xylene. The cause of this phenomenon can be the mineralogical composition of coal, acts as a raw material for obtaining ash microspheres [14].

The amount of porosity greatly influences the strength of the ash microspheres. In this case, with increasing porosity, the mass of the material decreases, its thermal conductivity decreases, the strength, water permeability, frost resistance and the like change significantly.

The wetting phenomenon characterizes the molecular interaction between the liquid and the ash microspheres and significantly affects the prospects of using ash microspheres as filler for building materials with increased thermal insulation properties.

The best wettability during the flow is observed for the ash microspheres of Kryvyi Rig, Burshtyn and Trypillia TPSs, the worst for Kurakhove TPS. Concerning the mineralogical composition, it should be noted that in the first three cases mullite predominates, and in the latter, the components (mullite and opal cristobalite) vary in practically the same ratio.

The relationship between the mineralogical composition of ash, their energy state (the conditional tangent of the dielectric loss angle) and wettability of water is also clearly monitored. The maximum values of $tg\delta$ are observed in case of poor wetting. With improved wetting, the conditional tangent of the dielectric loss angle decreases [15].

The thermal insulation properties of building materials primarily depend on the bulk density of the filler (density). Some influence on the thermal conductivity is also caused by the structure of the pores and the mineralogical composition of this filler (ash microspheres) [16, 17].

The coefficient of thermal conductivity of the investigated ash microspheres ranges from 0.162–0.190 W/(m·K). It follows that the highest thermal insulation properties are found in the samples obtained from the Trypillia TPS, and the lowest – at the Prydniprovska TPS.

7. SWOT analysis of research results

Strengths. Among the strengths of this research, it is necessary to note the reasonable choice of the raw material base for using ash microspheres as a filler for building materials with increased thermal insulation properties: ash and slag waste from solid fuel thermal power stations (Burshtyn, Prydniprovska, Kryvyi Rig, Trypillia and Kurakhove), because today such data are not available.

Investigation of the mineralogical composition, structure and properties of the surface of domestic ash microspheres will expand the scope of use of this material as filler for composite materials (including construction materials). In addition, ash microspheres are alternative raw materials, produced during high-temperature coal combustion at TPSs and does not require additional processing, and, as a result, financial costs in this direction. The ash microspheres have sufficiently high thermal insulation properties, therefore this material has the prospect of being used as a filler for construction materials (in particular, for building mixtures).

Weaknesses. The weak side of this research is that the study of the mineralogical composition, structure and properties of ash microspheres is not sufficient for a full and comprehensive assessment of these materials for the use of the latter as a filler of building materials with increased thermal insulation properties.

Another weakness is that the scientific experiment is conducted over a long period of operation in real time. As a result, unacceptable errors due to the factor of subjectivism can arise. Therefore, in order to prevent this drawback, special attention should be paid to the purity of the procedure itself at all stages of the procedure. To prevent such drawback, it is necessary to strictly follow the methods of research and purity of the experiment.

Opportunities. In the long term, it is advisable to carry out other studies related to the determination of physical and chemical, physical and technical and physical and mechanical properties of ash microspheres. Such properties can be: chemical composition of the material, density, IR spectrometry and others. The study of the above properties of ash microspheres will allow to determine more deeply the expediency of using the latter as a filler for building materials (in particular, dry building mixtures) with increased thermal insulation properties. Research in this direction will expand the possibilities of using ash microspheres.

Threats. The difficulties in implementing the obtained results may be due to the fact that this material is not as well-known as, for example, glass microspheres. The properties of the rest are not fully researched, and their use as a filler for building materials is not as common as others (for example, sand). Due to low strength characteristics in comparison with other fillers, it is necessary to modify and improve them to use ash microspheres in the construction industry.

Thus, SWOT analysis of research results allows to determine the main directions for achieving the research objective, namely:

– to conduct complex studies to determine the influence of individual properties on the potential for use of ash microspheres for building materials with increased thermal insulation properties;
– to develop a methodology for additional studies of the properties of ash microspheres;
– to investigate the individual characteristics of modified ash microspheres in order to further recommend their use in the construction industry.

8. Conclusions

1. Five samples of ash microspheres obtained from various TPSs of Ukraine are studied using X-ray phase analysis and optical microscopy. The presence in their composition of glass, opal-cristobalite, mullite and quartz is recorded.

2. The determining role of the amount of adsorbed water on the wettability of the investigated ash microspheres is revealed. A comparative quantitative assessment of their wettability by water and xylene at a level of 0.0394–0.1045 and 0.5736–0.7771, respectively, and the energy state of the surface is presented.

3. The influence of the specific surface area of various ash microspheres and the nature of their pore structure on the physicochemical properties of the surface is estimated. In particular, the absorbing power of the material under study depends on the specific surface area. Also, the specific surface area characterizes the dispersion of the ash microspheres. Research results (Table 2) confirm the expediency of using ash microspheres as filler for building materials with increased thermal insulation properties.

4. The thermal conductivity is studied and its interrelation with mineralogical composition and porosity of Ukrainian ash microspheres is characterized. The mineralogical composition and porosity of the ash microspheres directly affect the thermal conductivity of the latter. According to the results of the studies (Tables 1, 3) with the same or similar chemical composition, the thermal conductivity of materials having a crystalline structure is higher than that of materials of an amorphous and mixed structure. With the same porosity (Table 3), materials having small closed pores have higher thermal insulation properties due to a decrease in the transfer of heat by convection and radiation.

References

1. Chumakov, L. D. Tehnologiia zapolnitelei betona (praktikum) [Text]: Handbook / L. D. Chumakov. – Moscow: ASV, 2006. – 48 p.
2. Danilovich, I. Yu. Ispol'zovanie toplivnyh shlakov i zol dlia proizvodstva stroitel'nyh materialov [Text] / I. Yu. Danilevich, N. A. Skanavi. – Moscow: Vysshaia shkola, 1988. – 72 p.
3. Haluschak, M. O. Methods of Measuring the Thermal Conductivity of Bulk Solids and Thin Films (Review) [Text] / M. O. Haluschak, V. G. Ralchenko, A. I. Tkachuk, D. M. Freik // Physics and Chemistry of Solid State. – 2013. – Vol. 14, No. 2. – P. 317–345. – Available at: \www/URL: http://www.pu.if.ua/inst/phys_che/start/pcss/vol14/1402-03.pdf
4. Pashchenko, A. A. Gidrofobnyi vspuchennyi perlit [Text] / A. A. Pashchenko, M. G. Voronkov, A. A. Krupa, V. A. Svidersky. – Kyiv: Naukova dumka, 1977. – 204 p.
5. Kochergin, C. M. Betony. Materialy. Tehnologii. Oborudovanie [Text] / S. M. Kochergin. – Moscow: Stroiinform; Rostov na Donu: Feniks, 2006. – 424 p.
6. Kats, G. S. Napolniteli dlia polimernyh kompozitsionnyh materialov [Text] / ed. by G. S. Kats, D. V. Milevski. – Moscow: Khimiia, 1981. – 736 p.
7. Teriaeva, T. N. Fiziko-himicheskie svoistva aliumosilikatnyh polyh mikrosfer [Text] / T. N. Teriaeva, O. V. Kostenko, Z. R. Ismagilov, N. V. Shikina, N. A. Rudina, V. A. Antipova // Vestnik Kuzbasskogo gosudarstvennogo tehnicheskogo universiteta. – 2013. – Vol. 5 (99). – P. 86–90.
8. Landel, R. F. Mechanical Properties of Polymers and Composites, Second Edition [Text] / R. F. Landel, L. E. Nielsen. – CRC Press, 1993. – 580 p.
9. Mironyuk, I. F. The Scientific Principles of Controlled Synthesis of Fumed Silica and its Physico-Chemical Properties [Text]: Thesis for a Doctor's Degree / I. F. Mironyuk. – Kyiv: The Institute for Surface Chemistry of the National Academy of Sciences of Ukraine, 2000. – 46 p.
10. Barthel, H. Fumed Silica – Production, Properties, and Applications [Text] / H. Barthel, L. Rosch, J. Weis // Organosilicon Chemistry II: From Molecules to Materials. – Weinheim: VCH Verlagsgesellschaft mbH, 1996. – P. 761–778. doi:10.1002/9783527619894.ch91
11. Meyer, K. Fiziko-himicheskaia kristallografiia [Text] / K. Meyer, E. D. Shchukin, B. M. Summ. – Moscow: Metallurgiia, 1972. – 480 p.
12. Wang, Q. The role of fly ash microsphere in the microstructure and macroscopic properties of high-strength concrete [Text] / Q. Wang, D. Wang, H. Chen // Cement and Concrete Composites. – 2017. – Vol. 83. – P. 125–137. doi:10.1016/j.cemconcomp.2017.07.021
13. Ivanov, M. G. Sorbtsiia formal'degida i tehnologiia polucheniia opoki, modifitsirovannoi silanom [Text] / M. G. Ivanov, O. B. Lihareva, A. I. Matern, O. V. Stoianov // Vestnik Kazanskogo tehnologicheskogo universiteta. – 2017. – Vol. 20, No. 12. – P. 22–26.
14. Bodnar, R. T. Ekspres-metod vyznachennia kraiovoho kuta zmochuvannia porystykh til [Text] / R. T. Bodnar // Metody ta prylady kontroliu yakosti. – 2016. – Vol. 1 (36). – P. 30–38. – Available at: \www/URL: http://elar.nung.edu.ua/bitstream/123456789/4256/1/5397p.pdf
15. Dai, S. The sources, pathway, and preventive measures for fluorosis in Zhijin County, Guizhou, China [Text] / S. Dai, W. Li, Y. Tang, Y. Zhang, P. Feng // Applied Geochemistry. – 2007. – Vol. 22, No. 5. – P. 1017–1024. doi:10.1016/j.apgeochem.2007.02.011
16. Jow, J. Fly Ash-based Technologies and Value-added Products Based on Materials Science [Text] / J. Jow, Y. Dong, Y. Zhao, S. Ding, Q. Li, X. Wang, S. Lai // 2015 World of Coal Ash (WOCA)

Conference in Nasvhille, May 5–7, 2015. – 26 p. – Available at: \www/URL: http://www.flyash.info/2015/047-jow-2015.pdf
17. Liu, H. Morphology and Composition of Microspheres in Fly Ash from the Luohuang Power Plant, Chongqing, Southwestern China [Text] / H. Liu, Q. Sun, B. Wang, P. Wang, J. Zou // Minerals. – 2016. – Vol. 6, No. 2. – P. 30. doi:10.3390/min6020030

ИССЛЕДОВАНИЕ МИНЕРАЛОГИЧЕСКОГО СОСТАВА, СТРУКТУРЫ И СВОЙСТВ ПОВЕРХНОСТИ ЗОЛЬНЫХ МИКРОСФЕР УКРАИНЫ

Исследованы свойства (минералогический состав, смачиваемость, пористость, удельная поверхность и ее энергетическое состояние) зольных микросфер различных ТЭС Украины, получаемых в результате сжигания угля Донецкого (Трипольская, Кураховская, Криворожская и Приднепровская ТЭС) и Львовско-Волынского угольных бассейнов (Бурштынская ТЭС). Проанализировано влияние свойств поверхности зольных микросфер на их потенциальную способность использования в качестве наполнителей для строительных материалов.

Ключевые слова: зольные микросферы, удельная поверхность, минералогический состав, порошкообразный материал, аморфная фаза.

Demchenko Valentyna, *Postgraduate Student, Department of Commodity and Customs Affairs, Kyiv National University of Trade and Economics, Ukraine, e-mail: tina76748@gmail.com, ORCID: http://orcid.org/0000-0001-7527-2236*

Simyachko Olena, *PhD, Associate Professor, Department of Commodity and Customs Affairs, Kyiv National University of Trade and Economics, Ukraine, e-mail: olesim@ukr.net, ORCID: http://orcid.org/0000-0002-5229-8000*

Svidersky Valentin, *Doctor of Technical Sciences, Professor, Head of the Department of Chemical Technology of Composite Materials, National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute», Ukraine, e-mail: xtkm@kpi.ua, ORCID: http://orcid.org/0000-0002-2246-3896*

UDC 539.26
DOI: 10.15587/2312-8372.2017.119311

Zavodyannyy V.

CRYSTALLINE STRUCTURE ANALYSIS OF Ba_3WO_6 COMPOUND

Показано, що сполука Ba_3WO_6 має три поліморфні модифікації, дифракційні спектри яких розміщенні в базах даних pdf-2 за 2004 р. За спектром згенерованим HiphScorePlus 3.0 під номером 00-033-0182 сполука належить до структури типу $Ba_{11}W_4O_{23}$. Уточнено періоди решітки, мікроструктурні параметри та стехіометричний склад сполуки Ba_3WO_6.

Ключові слова: *рентгеноструктурний аналіз, база даних pdf-2, Ba84.46W31.07O189.08, метод Рітвельда.*

1. Introduction

Metal-porous cathodes are widely used in electric rocket engines of space vehicles, as well as in powerful electric vacuum devices, for example, microwave range. They combine a large number of composite cathodes and are multiphase systems consisting of a metal matrix (sponge), in the pores and on the surface of which an emission-active substance is located. In the process of impregnating the sponge with an emission active substance, Ba_3WO_6 is formed, which explains the presence of barium on the emitter surface [1]. Consequently, studies of the properties of this compound, in particular its crystal structure, are relevant.

2. The object of research and its technological audit

The object of research is Ba_3WO_6 crystal structure. This compound is formed from a mixture of $BaCO_3$ i WO_3, which is heated at 1000–1400 °C for 30 hours, followed by hardening. At 690 °C, polymorphic transformation of Ba_3WO_6 from triclinic crystal system to cubic is observed. Also, this compound can be synthesized from a mixture of oxides at a pressure of 7 kbar, a temperature of 1300 °C and a holding time of 24 hours [2].

One of the most problematic places is the presence of a large number of diffraction spectra captured for this compound, obtained by the Bragg-Bertrand method on copper filtered radiation.

For example, in the pdf-2 database for 2004, there are 7 diffraction spectra of different quality are obtained for the Ba_3WO_6 compound synthesized by various methods.

3. The aim and objectives of research

The aim of this work is studying the crystal structure of Ba_3WO_6 compound, presented in the diffraction data base pdf-2 for 2004 at the number 00-033-0182.

For the set aim the following tasks are solved:

1. To conduct X-ray phase analysis for the presence of compounds indicated in the state diagram (Fig. 1).

2. Taking into account the results of the phase analysis, to propose a model of the microstructure parameters of the spectrum of this compound.

3. To refine the microstructural parameters of this compound by the Rietveld method.