Fly Ash Cenospheres: Composition, Morphology, Structure, and Helium Permeability

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ABSTRACT

The interrelation between the composition, morphology, structure, and helium permeability of the shells of narrow fractions of nonmagnetic non-perforated cenospheres has been investigated. The narrow fractions of nonmagnetic non-perforated cenospheres have been separated from concentrates of cenospheres of the sialic fly ash type with the use of the technological scheme, including stages of hydrodynamic gravitational separation, magnetic separation, grain-size separation, and aerodynamic classification.

It has been established that, in the range of variation in the Al_2O_3 content from 20 to 38 wt %, the concentrations of the major components of the chemical composition of the products obtained are related by a linear regression equation with a correlation coefficient of –0.98.

It has been found that, when the Al_2O_3 content changes in the range from 20 to 38 wt %, the content of the mullite (0) phase increases from 1.3 to 42.4 wt %, which leads to an increase in the helium permeability of the glass-crystalline shell of the cenospheres by more than two order of magnitude.

The equilibrium devitrification of the glass phase of the cenosphere shell results in the formation of small (17–33 nm) crystallites of the mullite (I) phase, which, in turn, leads to the formation of additional interfaces for selective diffusion of helium.

INTRODUCTION

At present, membrane technologies used for separating gas mixtures have been intensively developed [1] and, consequently, have required to design and fabricate selective membranes characterized by the high permeability, enhanced mechanical strength, high thermal stability, and increased chemical resistance. Selective membranes have been fabricated from inorganic and polymer materials in the form of planar, tubular, and spiral elements [2]. Damage of these constructions in the course of their operation leads to a drastic decrease in the quality of the separation of gas mixtures.

The efficiency of separation of gas mixtures has been increased using closed hollow membrane elements. For this purpose, it is customary to use expensive synthetic glass microspheres based on borosilicate glass [3, 4], which have been subjected to additional treatment (acid etching, doping with rare-earth and transition metals) for increasing the membrane permeability.

The prospects for the use of silicate glasses as membranes are determined by a combination of their high permeability for helium and hydrogen with a very low diffusion permeability with respect to oxygen, nitrogen, methane; moreover, the selectivity of separation of the helium–nitrogen and helium–methane gas mixtures reaches high values of 10^5–10^6. This is one of the significant technological advantages of silicate glass membranes over polymer membranes [5].

The phase transformations observed in glasses and accompanied by the crystallization of phases exert a profound influence on the diffusion properties. In glass-crystalline materials, the diffusion of helium proceeds in two different paths: (i) through the anion sublattice of the glass phase and (ii) along the "crystal–glass phase" interfaces. The contribution from each path to the overall process of diffusion depends on the temperature. In particular, for samples of quartz glass containing cristobalite crystallites, the lattice diffusion of helium with an activation energy of 24 kJ/mol is more preferential at a temperature above 300 °C, whereas the diffusion of helium along the "cristobalite–glass phase" interfaces with an activation energy of 18 kJ/mol [6] becomes preferential in the low-temperature range 0–110 °C.

For the use in the design of selectively permeable membranes intended for separation of gas mixtures, as well as for sorption and storage of the desired components, for example, helium and hydrogen, hollow microspheres with a thin glass-crystalline shell providing an increased permeability and an enhanced mechanical strength are of special interest. These microspherical membranes can be fabricated from glass-crystalline cenospheres of fly ashes, because the specific features of their morphology and phase-mineral composition determine new prospects for the preparation of modern functional materials based on these cenospheres.

Cenospheres or aluminosilicate hollow microspheres represent one of microspherical components of the sialic fly ashes type [7], which are characterized by a low bulk density (0.2–0.8 g/cm^3) and can be easily separated by the gravitational methods in the form of a concentrate in aqueous media [8, 9]. The content of cenospheres in fly ashes from the combustion of different types of coals varies over a rather wide range from 0.01 to 4.80 wt % and, in the majority of cases, amounts to 0.3–1.5 wt % [9-14].

The formation of cenospheres occurs as a result of thermochemical and phase transformations of the original mineral coal forms in the course of their combustion. The granulometric, chemical, and phase-mineral compositions of the cenospheres depend on the composition of the original coal, the type of furnaces employed, the conditions used for cooling melt droplets, etc. [9, 11-16].

The results presented in the literature on the investigation of the concentrates of fly ash cenospheres from the combustion of different types of coals [9, 11, 14, 16-23] have clearly demonstrated the inhomogeneity of their granulometric, phase-mineral, major component, and minor component compositions. It has been shown that the concentrates of cenospheres are represented by mixtures of hollow spherical particles with sizes ranging from 5 to 500 μm [9, 10] and a shell thickness varying from 2 to 30 μm [9, 11, 13, 19]. According to their chemical composition, the concentrates of cenospheres are the SiO_2–Al_2O_3–Fe_2O_3–CaO–MgO–Na_2O–K_2O–TiO_2 multicomponent systems in which the contents of the major components vary in the following ranges: 50–65 wt % SiO_2, 20–36 wt % Al_2O_3, and 2–10 wt % Fe_2O_3 [9-11, 17]. The glass-crystalline shell of cenospheres is a multiphase system consisting of the glass phase (50–90 wt %) and the crystalline phases of mullite, quartz, cristobalite, calcite, potassium feldspar, hematite, and magnetite[9, 10, 24]. The outer and inner surfaces of the cenospheres are covered by a nanometer-sized film with a thickness ranging from 30 to 50 nm [25].

The different chemical and phase-mineral compositions of the cenospheres determine the diversity of morphological types of globules [16, 17, 19, 22], among which are thin-walled spheres with a continuous shell, spheres with porous shells, spheres containing numerous silicate globules within their volumes, perforated spheres, and spheres with a network structure.

The narrow fractions of cenospheres with certain composition, morphology, thickness, and porosity of the shell can be considered as promising microspherical membranes with a predicted permeability with respect to helium and hydrogen. In this paper, we have presented the results of our investigation of the composition, morphology, structure, and helium permeability of the shells of globules of narrow fractions of nonmagnetic non-perforated cenospheres, as well as the preparation of microspherical membranes based on these cenospheres with a mullitized shell.

EXPERIMENTAL

The methodology developed for producing narrow fractions of nonmagnetic non-perforated cenospheres with a constant composition from concentrates with a variable composition[26] is based on one of the fundamental principles underlying the physicochemical analysis of functional materials, which determines the "composition–morphology–structure–properties" relationship and includes the system for sampling and controlling the quality of products at all stages of the technological process.

The raw materials used for the preparation of narrow fractions of nonmagnetic non-perforated cenospheres were concentrates of cenospheres of the sialic fly ash type taken from the Novosibirsk Heat and Electric Power Plant No. 5 (series N) and the Moscow Heat and Electric Power Plant No. 22 (series M), which have burnt coals from the Kuznetsk Basin (Russia) at temperatures of 1500 and 1650 °C in the core of the flame, respectively, as well as those taken from the Reftinsk Hydroelectric Power Station (series R), which has burnt coals from the Ekibastuz Basin (Russia) at a temperature of 1600 °C. The separation of narrow fractions of nonmagnetic non-perforated cenospheres was performed with the use of the technological scheme [26], including stages of hydrodynamic gravitational separation, magnetic separation, grain-size separation, and aerodynamic classification with the subsequent hydrostatic separation of broken globules.

Each fraction of cenospheres was characterized by a set of physicochemical parameters [27], including the chemical and phase-mineral compositions, the bulk density, the size distribution, the average globule diameter, the shell thickness, and the content of globules of particular morphological types.

The chemical compositions of the initial concentrates and separated narrow fractions of cenospheres, which included the contents of silicon, aluminum, iron, calcium, magnesium, potassium, sodium, titanium, manganese, sulfur, and phosphorus oxides, as well as the weight loss during heating, were determined according to the conventional technique [28] with the standard error in the reproducibility of the results (S_n) for the major components as a function of their content, i.e., S_n = ±0.35–±0.60 for SiO_2; ±0.30–±0.40 for Al_2O_3; ±0.15–±0.30 for Fe_2O_3; and ±0.04–±0.10 for CaO, MgO, Na_2O, K_2O, and TiO_2.

The phase-mineral composition of narrow fractions of cenospheres was determined using the quantitative X-ray powder diffraction analysis within the Rietveld approach [29] with the derivative difference minimization method [30].

The structure of the outer and inner surfaces, the thickness, and the specific features of the shell of cenosphere globules were examined using optical microscopy (AxioImager D1 light microscope, Carl Zeiss, Germany) and scanning electron microscopy (SEM) (JSM-6460 LV electron microscope, JEOL, Japan; accelerating voltage, 25 kV; resolution to 40 nm).

The heat treatment of narrow fractions with the aim of producing cenospheres with a mullitized shell was carried out under conditions of equilibrium devitrification of the glass phase at a temperature of 1000 °C for 3 h.

The permeability of narrow fractions of cenospheres was investigated in a static vacuum chamber under conditions of helium diffusion from the bulk of the reactor into the globules in the temperature range from 23 to 350 °C and at a pressure varying from 3.0 to $9.5\cdot10^4$ Pa. The determination of the permeability (Q) is based on the measurement of the pressure drop in time after the gas was delivered into the reactor filled with cenospheres. The permeability was calculated from the equation describing the absorption of gases by cenospheres in the following form: $dn/dt=KS_{sp}m(\Delta P/d)=Q(P_{out}-P_{in})$, where K is the permeability coefficient [mol·m/(s·m^2·Pa)]; S_{sp} is the specific diffusion surface area of the sample [m^2/g]; m is the weight of the sample [g]; d is the thickness of the shell [m]; Q is the permeability of the cenospheres [mol/(s·g·Pa)]; and

P_{out} and P_{in} are the gas pressures [Pa] outside and inside of the particles at the instant of time *t* [s], respectively.

RESULTS AND DISCUSSION

Investigation of the Composition, Morphology, and Structure of Narrow Fractions of Cenospheres

The use of the technological scheme, including stages of hydrodynamic gravitational separation, magnetic separation, grain-size separation, and aerodynamic classification, made it possible to separate fractions of nonmagnetic non-perforated cenospheres with a narrow size distribution of globules with certain composition, morphology, thickness, and porosity of the glass-crystalline shell from three concentrates. As an example, Table 1 presents the physicochemical characteristics of narrow fractions of cenospheres –0.063+0.05 and –0.16+0.125 of the series N, M, and R.

According to their chemical composition, the separated narrow fractions of cenospheres are multicomponent systems containing 20–38 wt % Al_2O_3 and 56–68 wt % SiO_2, which corresponds to the known compositions of cenospheres [9, 11, 17] formed from aluminosilicate melts. All the separated fractions are characterized by a stable low Fe_2O_3 content (1–5 wt %) and a nearly constant content of alkali and alkaline-earth metals within each series.

It has been established that the concentrations of the major components of the chemical composition for all three series of narrow fractions of cenospheres are related by a linear regression equation (Fig. 1) with a correlation coefficient of –0.98. The ratio SiO_2/Al_2O_3 is a geochemical indicator of the mineral coal forms, from which the cenospheres are formed [10]. For the separated narrow fractions of cenospheres, this ratio varies in the range from 1.5 to 3.4.

In the fractions under examination, the optical microscopy investigation has revealed the following main morphological types of cenospheres (Fig. 2): (a) cenospheres with a thin continuous shell; (b) cenospheres with a thick porous shell; (c) cenospheres with a porous shell and a relief surface; (d, e) cenospheres with a thin or porous shell containing mullite crystallites; and (f) cenospheres with a network structure, which are characteristic of only the narrow fractions of fly ash cenospheres produced from the combustion of coals from the Ekibastuz Basin (series R).

The analysis of the relationship between the chemical composition and morphology of cenosphere globules has demonstrated that, for the globules of narrow fractions of the N and M series separated from the concentrate of cenospheres of fly ash produced from the combustion of coals from the Kuznetsk Basin, an increase in the Al_2O_3 content leads to a decrease in the diameter of globules, as well as in the thickness and porosity of the shell of cenospheres. For the globules of narrow fractions separated from the concentrate of cenospheres of fly ash produced from the combustion of coals from the Ekibastuz Basin, the inverse relationship has been observed.

Table 1. Physicochemical characteristics of narrow fractions of cenospheres

Sample	Physical characteristics			Morphological types, vol %			Chemical composition, wt %									Phase-mineral composition, wt %			
	Bulk density, g/cm^3	Average diameter, μm	Average thickness of the shell, μm	Spheres with a continuous shell	Spheres with a porous shell	Spheres with a porous shell and a relief surface	LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Quartz	Calcite	Mullite (0)	Glass phase
N-0.08 -0.063+0.05	0.34	59	2.5	62	28	10	0.20	64.75	24.67	3.20	1.01	1.64	0.16	0.88	3.09	3.0	0.6	3.7	92.7
NM-M-5A -0.063+0.05	0.30	58	2.1	77	21	2	0.62	60.30	31.16	2.08	1.72	1.88	0.22	0.42	2.08	2.0	0.8	8.8	88.4
NM-R-5A -0.063+0.05	0.40	58	2.9	20	55	25	0.32	61.24	33.55	1.12	0.97	0.96	0.30	0.50	0.60	1.3	0.2	30.1	68.4
NM-N-1A -0.16+0.125	0.30	129	4.7	54	31	15	0.44	62.25	21.75	3.43	1.68	2.10	0.38	0.95	3.42	5.8	0.4	1.3	92.5
NM-M-1A -0.16+0.125	0.31	144	5.4	36	63	1	0.72	65.16	25.34	3.43	0.91	1.35	0.12	0.41	2.38	2.4	0.4	8.2	89.0
NM-R-5A -0.16+0.125	0.45	143	8.2	0	99	1	0.16	58.60	35.20	2.30	1.62	1.28	0.20	0.32	0.36	1.6	0.1	38.4	59.9

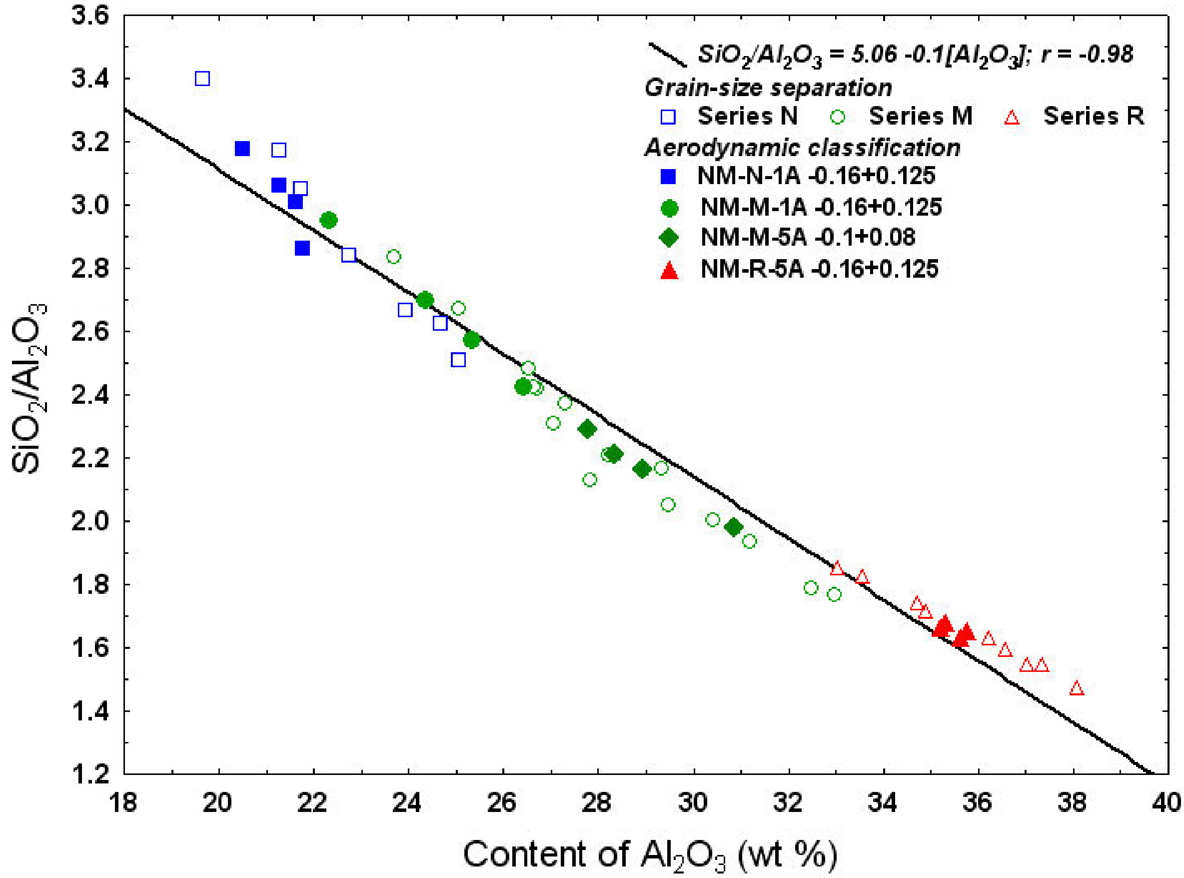

Fig. 1. Dependences of the SiO_2/Al_2O_3 ratio on the Al_2O_3 content in narrow fractions of cenospheres

The shell of cenospheres has a complex layered structure. The outer and inner surfaces of the cenosphere globules are covered by a nanometer-sized (30–50 nm) film [25]. It has been found that, after the film was removed by etching with a fluorine-containing agent[31], the surface of the glass matrix contained plane-oriented mullite crystallites (Fig. 3) formed during crystallization of the aluminosilicate melt of the shell.

The quantitative X-ray powder diffraction analysis has demonstrated (Table 1) that the phase-mineral composition of the narrow fractions of cenospheres of the N and M series includes the glass phase (from 84 to 93 wt %) and the crystalline phases of quartz (1.3–7.0 wt %) and mullite (1.3–11.0 wt %). For the narrow fractions of cenospheres of the R series, the content of the glass phase varies from 56 to 73 wt % and the content of mullite ranges from 25.3 to 42.4 wt %. It has been established that, for the narrow fractions of cenospheres of the N and M series, a decrease in the particle size leads to an increase in the content of the mullite phase, whereas for the narrow fractions of cenospheres of the R series, the maximum content of the mullite phase is observed in large fractions. The content of the quartz phase in the narrow fractions of cenospheres of the M and R series remains almost unchanged with variations in the particle size, whereas for samples of the N series, an increase in the particle diameter leads to an increase in the content of the quartz phase. It should be noted that, apart from the quartz phase, the products obtained do not contain phases that are characteristic of the original coals.

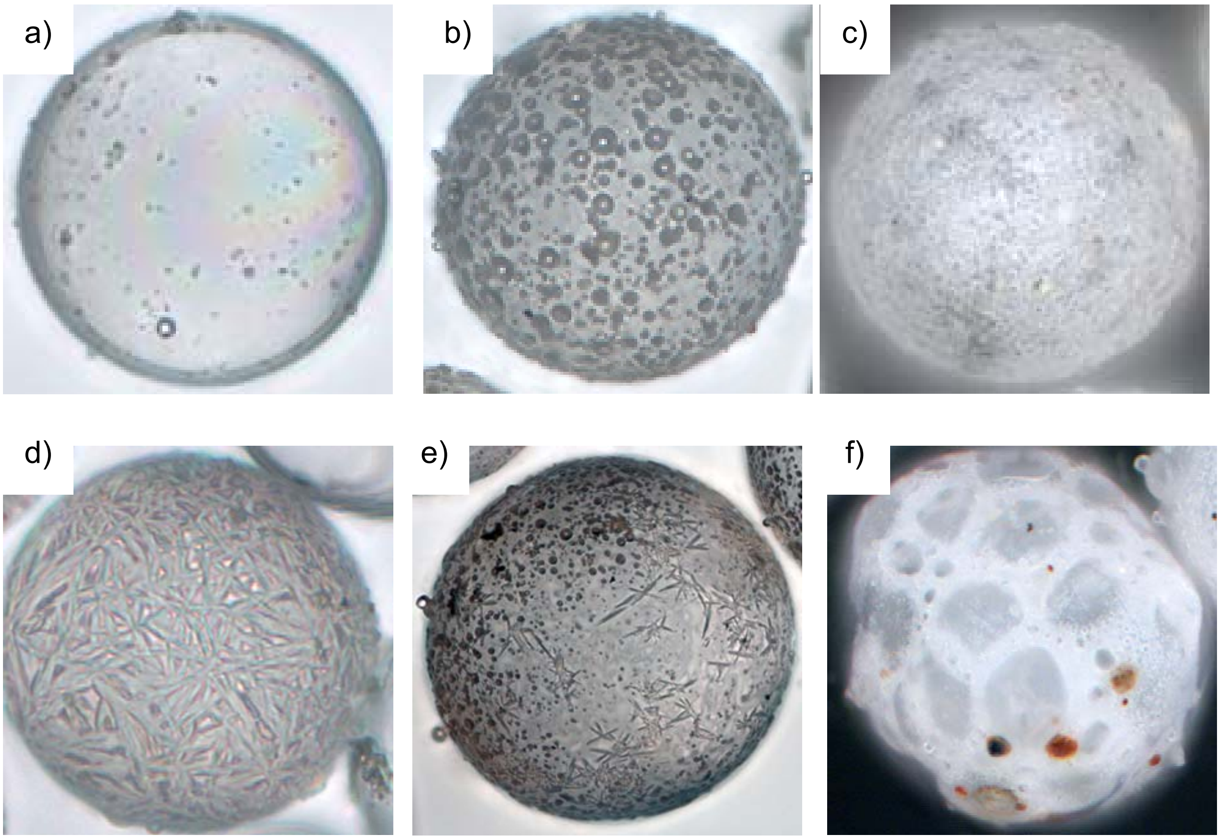

Fig. 2. Morphological types of cenospheres according to the optical microscopy data

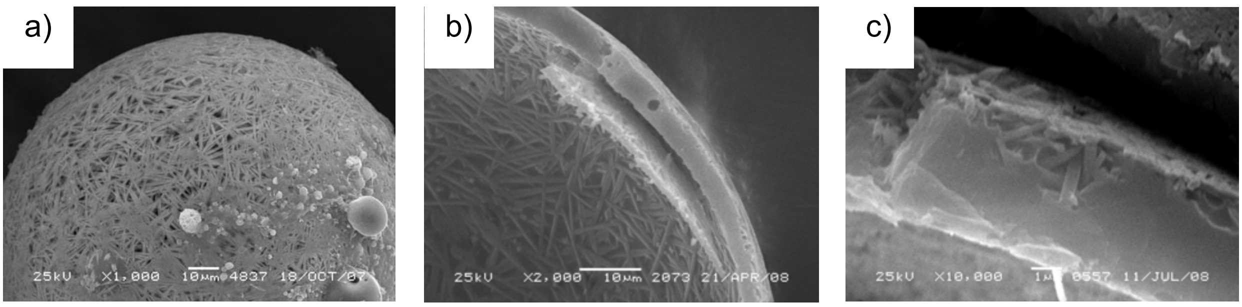

Fig. 3. SEM micrographs of (a) the outer surface and (b) the inner surface and (c) the shell of globules of the narrow fraction NM-M-1A –0.16+0.125

Thus, narrow fractions of nonmagnetic non-perforated cenospheres with specific composition, morphology, thickness, and porosity of the shells were separated from concentrates of fly ash cenospheres from the combustion of different types of coals and then were thoroughly characterized. The chemical composition of narrow fractions of nonmagnetic non-perforated cenospheres (20–38 wt % Al_2O_3 and 56–68 wt % SiO_2)

suggests that the cenospheres subjected to heat treatment resulting in the devitrification of the glass phase can be used in the preparation of microspherical materials with a high content of the mullite phase, which is able to reinforce the cenosphere shell by needle-shaped crystals, thus forming interfaces, and, hence, to increase the gas permeability of the shell with respect to helium and hydrogen. This will make it possible to use narrow fractions of cenospheres as microspherical gas-permeable membranes for selective separation of helium and hydrogen.

Investigation of the Helium Permeability of Narrow Fractions of Cenospheres

A detailed investigation of the composition, morphology, and structure of the shells of narrow fractions of nonmagnetic non-perforated cenospheres over a wide concentration range from 20 to 38 wt % Al_2O_3 makes it possible to analyze the possibility of designing and producing modern functional materials based on these cenospheres with controlled properties, including selective membranes intended for diffusion separation of helium from helium-containing mixtures.

In order to prepare microspherical membranes with a high gas permeability, we have chosen narrow fractions of cenospheres (Table 1) corresponding to the following criteria: the morphological homogeneity, which is determined by a predominant number of globules of particular morphological types; the average thicknesses of the continuous and porous shells of the cenospheres, which are equal to 2–3 and 5–8 μm, respectively; and the chemical composition of the shells of the cenospheres (the Al_2O_3 content in the range 20–38 wt %), which indicates that the high content of the mullite phase can be achieved under the conditions of devitrification of the glass phase.

The differential thermal analysis has revealed that the crystallization of mullite in the shell of cenospheres proceeds in the temperature range from 980 to 1000 °C. For the purpose of producing the cenospheres with a mullitized shell, the narrow fractions were subjected to heat treatment at a temperature of 1000°C for 3 h, which resulted in the devitrification of the glass phase.

The quantitative X-ray powder diffraction analysis has demonstrated that the content of the glass phase in the devitrified cenospheres decreases as a result of the formation of an additional phase of mullite (I) (Table 2). According to their microstructural characteristics, the mullite (I) phase differs from the original mullite (0) phase by a smaller crystallite size and a larger unit cell volume. The lattice parameters of the mullite (I) phase systematically exceed not only the lattice parameters of the original mullite (0) phase but also the corresponding data available in the literature for the entire range of possible ratios Al/Si in mullite [32]. The observed increase in the lattice parameters of the mullite (I) phase can be associated with the incorporation of the Fe^{3+} ions into the mullite lattice [33].

The investigation of the diffusion properties of initial cenospheres of different series with both continuous and porous shells with respect to the helium permeability has demonstrated that their diffusion properties are determined by the composition and structure of the shell of globules. In particular, the best values of the helium permeability (*Q*) of the shell of globules (Figs. 4, 5) are obtained for cenospheres of the R series, which are characterized by an increased Al_2O_3 content and a high content of the crystalline mullite phase. At a temperature of 25 °C, the helium permeability of the narrow fraction of cenospheres NM-R-5A –0.063+0.05 with a continuous shell 2.9 μm thick and a mullite content of 30.1 wt % reaches $6.2 \cdot 10^{-14}$ mol/(s·g·Pa), which is 3–10 times higher than the helium permeability of the narrow fractions of cenospheres of the M and N series –0.063+0.05 (Fig. 4), which are characterized by thinner shells 2.1 and 2.5 μm in thickness but with lower mullite contents of 8.8 and 3.7 wt %, respectively.

Table 2. Characterization of the modifications of the mullite phase in the initial and devitrified cenospheres

Sample	Content of the class phase, wt %	Mullite (0)			Mullite (I)		
		Content, wt %	Unit cell volume, Å^3	Crystallite size, nm	Content, wt %	Unit cell volume, Å^3	Crystallite size, nm
N-0.08 -0.063+0.05	92.7	3.7	168.06	196	–	–	–
N-0.08 -0.063+0.05 1000 ºC	84.5	3.1	168.06	196	9.7	169.33	–
NM-M-5A -0.063+0.05	88.4	8.8	168.09	136	–	–	–
NM-M-5A -0.063+0.05 1000 ºC	64.5	9.7	168.09	136	24.1	169.18	22
NM-R-5A -0.063+0.05	68.4	30.1	167.99	100	–	–	–
NM-R-5A -0.063+0.05 1000 ºC	54.9	33.7	167.99	100	10.3	168.66	17
NM-N-1A -0.16+0.125	92.5	1.3	168.33	–	–	–	–
NM-N-1A -0.16+0.125 1000 ºC	86.1	1.2	168.33	–	7.7	169.13	–
NM-M-1A -0.16+0.125	89.0	8.2	168.07	227	–	–	–
NM-M-1A -0.16+0.125 1000 ºC	74.1	7.0	168.07	227	16.0	169.07	33
NM-R-5A -0.16+0.125	59.9	38.4	167.98	113	–	–	–
NM-R-5A -0.16+0.125 1000 ºC	49.1	44.9	167.98	113	2.6	170.22	–

The helium permeability of the narrow fraction of cenospheres NM-R-5A –0.16+0.125 (Fig. 5) with a porous shell 8.2 μm thick and a high content of the mullite phase (38.4 wt %) in the temperature range from 25 to 350 °C does not differ from the helium permeability of the narrow fraction of cenospheres NM-M-5A –0.16+0.125 with a porous shell 5.4 μm thick and a mullite content of 8.2 wt % and, at a temperature of 25 °C, is more than two order of magnitude higher than the helium permeability of the narrow fraction of cenospheres NM-N-1A –0.16+0.125 with a porous shell 4.7 μm thick and a mullite content of 1.3 wt %.

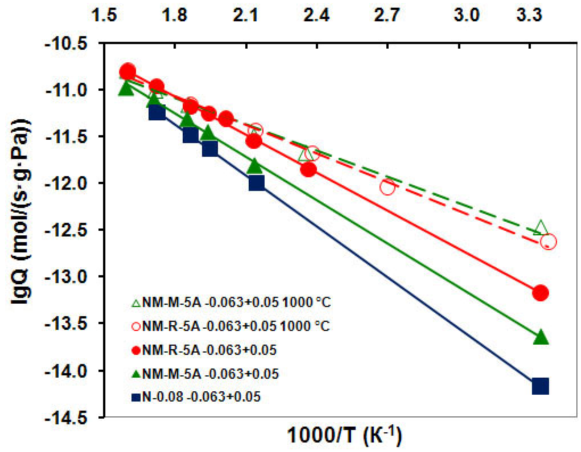

Fig. 4. Helium permeability of the narrow fractions of cenospheres –0.063+0.05 mm of the series N, M, and R

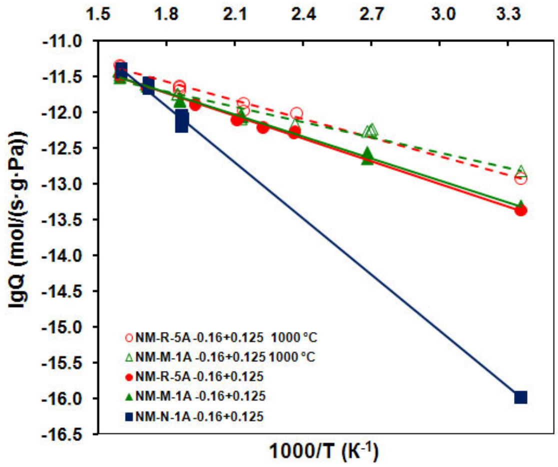

Fig. 5. Helium permeability of the narrow fractions of cenospheres –0.16+0.125 mm of the series N, M, and R

The low values of the activation energy (E_a = 20–29 kJ/mol) obtained for samples with a high content of the crystalline mullite phase indicate that the diffusion of helium along the "mullite–glass phase" interfaces dominates.

The diffusion of helium in devitrified samples of the M and R series is characterized by lower values of the activation energy E_a = 14–19 kJ/mol (for the initial cenospheres, E_a = 20–29 kJ/mol) and increased values of the helium permeability (*Q*) of the shell of globules at low temperatures (Figs. 4, 5). In particular, at a temperature of 25 °C, the helium permeability of the cenospheres increases by a factor of 10–13 for globules with a continuous shell and by a factor of 3 for globules with a porous shell.

By analogy with the devitrified quartz glass containing cristobalite crystallites [6], it can be concluded that the low activation energy obtained for the mullitized cenospheres and the observed increase in the helium permeability of the cenosphere shell are associated with the formation of small crystallites of the mullite (I) phase (Table 2), which provide the development of interfaces for selective diffusion of helium.

CONCLUSIONS

Thus, we have investigated the macrocomponent and phase-mineral compositions, the bulk density, the average diameter, the shell thickness, and the content of particular morphological types of globules in narrow fractions of nonmagnetic non-perforated cenospheres in the concentration range 20–38 wt % Al_2O_3, which were separated from concentrates of cenospheres of the sialic fly ash type with the use of the technological scheme, including stages of hydrodynamic gravitational separation, magnetic separation, grain-size separation, and aerodynamic classification.

It has been established that the concentrations of the major components of the chemical composition of the products obtained are related by a linear regression equation with a correlation coefficient of –0.98.

The relationship between the chemical composition and morphology of the globules of narrow fractions of nonmagnetic non-perforated cenospheres has been investigated. It has been found that, for the globules of narrow fractions separated from concentrates of cenospheres of fly ash produced from the combustion of coals from the Kuznetsk Basin, an increase in the Al_2O_3 content leads to a decrease in the diameter of cenospheres, as well as in the thickness and porosity of the shell of globules. For the globules of narrow fractions separated from concentrate of cenospheres of fly ash produced from the combustion of coals from the Ekibastuz Basin, the inverse relationship has been observed.

At high Al_2O_3 concentrations, regions of the plane-devitrified mullite (0) phase with a crystallite size ranging from 100 to 227 nm have been revealed under the surface film on the outer and inner surfaces of the cenosphere shell.

It has been found that, when the Al_2O_3 content changes in the range from 20 to 38 wt %, the content of the mullite (0) phase increases from 1.3 to 42.4 wt %, which leads to an increase in the helium permeability of the glass-crystalline shell of the cenospheres by more than two order of magnitude.

It has been demonstrated that the devitrification of the glass phase of the cenosphere shell results in the formation of small (17–33 nm) crystallites of the mullite (I) phase with the lattice in which Al^{3+} ions are substituted for by Fe^{3+} ions. Owing to the formation of additional interfaces in the bulk of the glass phase, the helium permeability of the glass-crystalline shell of the mullitized cenospheres increases by a factor of 3–13.

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