

NOVEL GLASS-CRYSTALLINE MEMBRANE MATERIALS FOR HELIUM CAPTURE BASED ON FLY ASH CENOSPHERES

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Abstract

The diffusion properties of narrow fractions of cenospheres have been investigated with respect to helium and hydrogen. It has been found that the permeability coefficients for the glass phase of the shells of cenospheres are directly proportional to the content of the glass-forming oxide SiO_2 in it. The calculated values of the permeability coefficients follow the general trend with the calculated and experimental data for silicate glasses over a wide range of compositions. The experimental values of the permeability coefficients for the glass phase of the cenosphere shells at a temperature of 280°C exceed the calculated values for helium and hydrogen by a factor of 3–24 and 12–111, respectively. For helium at a temperature of 25°C , the experimental values of the permeability coefficients are 11–1000 times greater than the corresponding calculated values. The selectivity for the cenospheres reaches a high level $\alpha(\text{He}/\text{H}_2) = 10\text{--}33$.

Key words: cenospheres, microspheres, silicate glasses, membrane, helium, hydrogen

1. INTRODUCTION

Owing to the low energy consumption, the membrane technology for the separation and deep purification of gases, including the production of high-purity helium, has a distinct advantage over the traditional cryogenic method [1]. Low-tonnage production of high-purity gases does not require high performance of the process. Therefore, the main criterion for the choice of membrane materials is the level of their selectivity capable to provide the desired degree of purification. Moreover, there are additional important characteristics of membrane materials, for example, their high permeability, high chemical and thermal stability, high durability, and low cost [2].

Among the promising systems used for the fabrication of highly selective gas separation membranes are materials based on non-porous silicate glasses, which, in contrast to other known membrane materials, such as polymers, carbon molecular sieves, zeolites, and metal–organic framework structures (MOFs), are characterized by high mixture separation factors even in the high-temperature range: $\alpha(\text{He}/\text{CH}_4) = 10^6$, $\alpha(\text{He}/\text{H}_2) = 10^2$, and $\alpha(\text{He}/\text{H}_2) = 10$ at 400°C [3, 4].

The diffusion properties of silicate glasses are determined by their composition and structure. The dependence of the gas permeability on the glass composition was noted for the first time in [5] and confirmed subsequently in the investigations [6] performed on 19 silicate glass samples of different compositions (*Corning Glass Works*) and 2 vitreous silica glass samples (*Amersil, General Electric*). It was shown that an increase in the content of glass-forming oxides ($G = \text{SiO}_2 + \text{B}_2\text{O}_3 + \text{P}_2\text{O}_5$) in the glass composition leads to a significant increase in their permeability to helium. The maximum helium permeability among silicate glass was observed in vitreous silica glasses [3, 6].

The relationship between the composition, structure, and gas permeability of silicate glasses is well explained in the framework of the Zachariasen structural model of the vitreous state [7], according to which the glass structure is a disordered network consisting of multi-membered rings formed by silicon–oxygen (SiO_4) tetrahedra. The diffusion of light noble gases through the glass occurs due to the migration of gas atoms in the free interstitial space. The modifying ions (Al_2O_3 , K_2O , Na_2O , MgO , CaO , Fe_2O_3 , and others) occupy interstitial voids in the structural network, thereby preventing the diffusion. It should be noted that the above-described two-dimensional model of the glass structure proposed more than eight decades ago by Zachariasen [7] was later confirmed experimentally using transmission electron microscopy [8].

A particular direction in membrane materials science is the preparation and use of hollow glass microspheres (HGMS) as membrane elements. For example, in the review [9], where glasses were considered as engineering materials with a wide range of properties for different fields of applications, it was noted that the technology for the fabrication of HGMS was developed by 3M (United States) as far back as the 1960s. However, just recently, there has been observed an increased interest in HGMS as promising systems – containers for storage and transportation of hydrogen. A prerequisite for this was the observed possibility of increasing the diffusion coefficient of hydrogen through the glass shells of HGMS with an increase in the temperature by several orders of magnitude and the ability of microspheres to withstand a high pressure of gaseous hydrogen of up to 150 MPa for a long time [10, 11]. It should also be noted that, in this case, each individual microsphere contains only a small volume of hydrogen and, therefore, is not explosive. The hydrogen storage systems based on HGMS have the following advantages: high efficiency, safety, lightness, low cost, and simplicity of the design [9, 10].

The use of hollow glass microspheres as membrane elements underlies the diffusion–sorption technology for the separation of gas mixtures, which combines pressure swing adsorption (PSA) and membrane separation [12, 13]. Membrane modules based on microspheres are characterized by a large surface per unit volume of 10^4 – 10^5 m²/m³ [4], which corresponds to the level of membrane cells consisting of hollow fibers and exceeds the level of rolling and flat membranes by several orders of magnitude. In addition, they exhibit reliable gas separation properties for a long time, because the efficiency of the process does not depend on the damage of individual globules.

Hollow glass-crystalline aluminosilicate microspheres, namely, cenospheres, can also be used as promising membrane materials. Cenospheres belong to valuable microsphere components of fly ashes [14–17], which represent large-capacity wastes of man-made origin and are formed during industrial pulverized combustion of coals from aluminosilicate mineral precursors. In the field of membrane materials science, cenospheres are convenient objects for studying the diffusion properties of glass-crystalline materials over a wide range of variations in the chemical and phase compositions [4, 18, 19]. According to the data reported in [4], with an increase in the content of the mullite phase in the shells of cenospheres in the range from 4 to 48 wt %, the helium permeability coefficient at a temperature of 25°C increases by almost two orders of magnitude. In this case, the selectivities $\alpha(\text{He}/\text{H}_2)$ and $\alpha(\text{He}/\text{Ne})$ have high values of 10^2 and 10^4 , respectively, which exceed by several orders of magnitude the corresponding values of $\alpha(\text{He}/\text{H}_2) = 1$ –4 [20] and $\alpha(\text{He}/\text{Ne}) = 5$ [21] for polymeric membrane materials.

The purpose of this work was to investigate the diffusion properties of narrow fractions of cenospheres with different compositions and structures with respect to hydrogen and helium, as well as to compare the experimental permeability coefficients for the glass phase of the shells of cenospheres with the calculated values and the relevant data available in the literature for commercial silicate glasses.

2. EXPERIMENTAL

2.1. Materials

The objects of investigation were morphologically homogeneous narrow fractions of non-magnetic non-perforated cenospheres with a low bulk density of less than 0.41 g/cm³, which were separated from concentrates of fly ash cenospheres. The fly ashes were formed as a result of the industrial pulverized combustion of coals from the main Russian coal basins, namely, Kuznetsk coals burnt at the Novosibirsk Heat and Electric Power Plant No. 5 (series *H*) and the Moscow Heat and Electric Power Plant No. 22 (series *M*), as well as Ekibastuz coals burnt at the Reftinsk Hydroelectric Power Station (series *R*). The separation of the narrow fractions of non-magnetic non-perforated cenospheres was performed using the technological scheme, including stages of grain-size classification, magnetic separation, separation in liquids of different densities (water, hexane), and aerodynamic classification in an air vortex flow with the subsequent hydrostatic separation from perforated and broken globules [22–24]. The physical and chemical characteristics of the narrow fractions of the cenospheres are presented in Tables 1–3.

As commercial silicate glass samples, we used hollow synthetic microspheres 3M Scotchlite™ K37 Glass Bubbles (3M™, United States) of the fraction $-0.063 + 0.05$ mm with a bulk density of 0.20 g/cm^3 and an average globule diameter of $57 \text{ }\mu\text{m}$ with a shell thickness of $1.4 \text{ }\mu\text{m}$. The shells of the hollow microspheres have the following chemical composition (wt %): $\text{SiO}_2 - 70.62$, $\text{CaO} - 13.67$, $\text{B}_2\text{O}_3 - 8.90$, $\text{Na}_2\text{O} - 5.40$, $\text{MgO} - 0.63$, $\text{SO}_3 - 0.29$, $\text{Fe}_2\text{O}_3 - 0.12$, $\text{P}_2\text{O}_5 - 0.08$, and $\text{K}_2\text{O} - 0.01$. The phase composition of these shells includes the glass phase (99 wt %) and cristobalite (1 wt %).

2.2 Characterization methods

For each narrow fraction of the cenospheres, we determined the bulk density, particle size distribution, average diameter of globules, thickness of globule shells, chemical composition, and the content of globules of a particular morphological type. The procedures used for the determination of these parameters, including the control of the purity of separated fractions, were described in detail in [22–24]. The composition of the glass phase was calculated from the combined data of the chemical analysis and the quantitative X-ray powder diffraction analysis. The diffusion properties of the shells of the cenospheres were investigated in the temperature ranges from 25 to 350°C for helium and from 280 to 500°C for hydrogen. The procedure used for the determination of the diffusion characteristics, including the permeability coefficients of the glass phase with respect to helium and hydrogen, K_{He} and K_{H_2} , respectively, the selectivities $\alpha(\text{He}/\text{H}_2)$, and the activation energies E_a for the diffusion of helium and hydrogen, was described in [4].

3. RESULTS AND DISCUSSION

The diffusion properties of microsphere membrane materials were investigated on the characterized morphologically homogeneous narrow fractions of non-magnetic non-perforated cenospheres with a low bulk density of less than 0.41 g/cm^3 , in which the vast majority of the globules had a ring structure with solid (Fig. 1a) or porous (Fig. 1b) shells (Table 1). Figure 2 shows, as an example, the scanning electron microscopy (SEM) images of the narrow fraction of cenospheres HM-M-1A $-0.063+0.05$ vg, which contains 85% of the particles with a solid shell (Table 1, Fig. 2a), and the narrow fraction of cenospheres HM-H-1A $-0.16+0.125$, where 95% of the globules have a porous shell (Table 1, Fig. 2b).

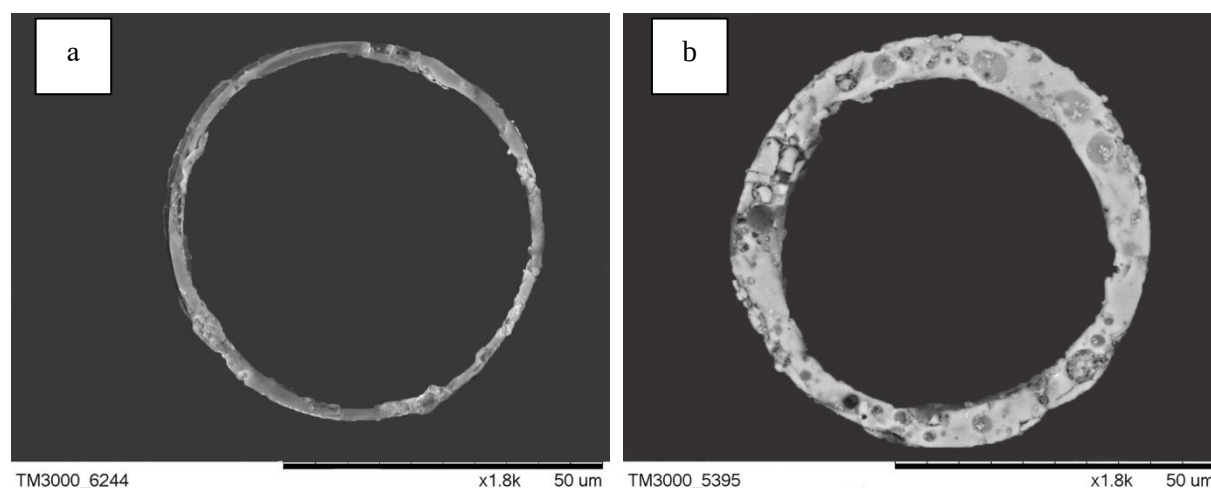


Figure 1. SEM micrographs of polished sections of individual globules with a ring structure: (a) solid shell and (b) porous shell.

Table 1. Contents of globules of different morphological types in narrow fractions of cenospheres

Sample	Content of particles (%)	
	Ring structure with a solid shell	Ring structure with a porous shell
H -0.08 -0.063+0.05 vg	53	47
HM-H-1A -0.16+0.125	5	95
HM-H-1A -0.16+0.125 aero (0.298)	54	46
HM-M-1A -0.063+0.05 vg	85	15
HM-M-5A -0.063+0.05	74	26
HM-M-5A -0.063+0.05 aero (0.321)	70	30
HM-M-5A -0.1+0.08 aero (0.260)	65	35
HM-M-5A -0.1+0.08 aero (0.303)	59	41
HM-M-5A -0.16+0.125	22	78
HM-M-1A -0.16+0.125 aero (0.306)	36	64
HM-R-5A -0.063+0.05	26	74
HM-R-5A vg -0.063+0.05	31	69
HM-R-5A vg -0.071+0.063	30	70

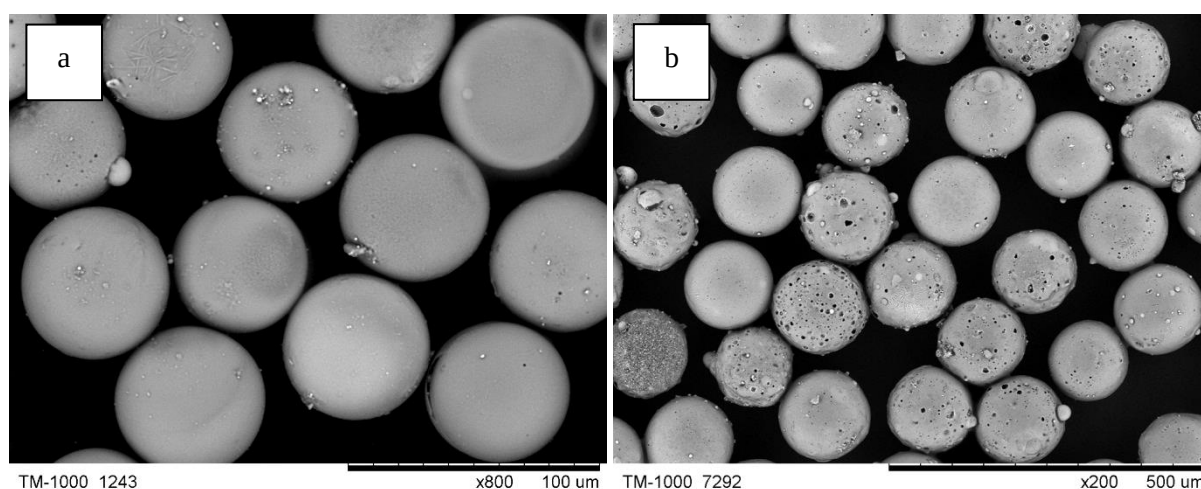


Figure 2. SEM micrographs of narrow fractions of cenospheres: (a) HM-M-1A -0.063+0.05 vg and (b) HM-H-1A -0.16+0.125.

The major component composition of the narrow fractions of cenospheres used in this study varies over wide ranges of 58–68 wt % SiO_2 and 21–37 wt % Al_2O_3 (Table 2), thus covering the entire region of cenosphere compositions known in the literature [22–24]. The Fe_2O_3 content does not exceed 3.5 wt %.

According to the data of the quantitative X-ray powder diffraction analysis (Table 3), the contents of the main crystalline phases, namely, mullite (0) and quartz, are equal to 1–39 and 1–7 wt %, respectively. The content of the calcite phase is at the level of 0.1–0.7 wt %. The content of the amorphous glass phase lies in the range of 60–93 wt %.

Table 2. Chemical composition of narrow fractions of cenospheres (wt %)

Sample	Loss on ignition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	P ₂ O ₅
H -0.08 -0.063+0.05 vg	0.62	60.92	25.92	3.4	1.63	2.31	0.21	1.18	3.55	0.09
HM-H-1A -0.16+0.125	0.20	67.52	21.27	3.46	1.21	1.71	0.17	0.97	3.37	0.10
HM-H-1A -0.16+0.125 aero (0.298)	0.44	62.25	21.75	3.43	1.68	2.10	0.38	0.95	3.42	0.10
HM-M-1A -0.063+0.05 vg	0.96	59.20	32.10	2.30	1.01	0.71	0.19	0.64	2.53	0.08
HM-M-5A -0.063+0.05	0.82	58.26	32.08	2.80	1.27	1.15	0.27	0.72	2.39	0.08
HM-M-5A -0.063+0.05 aero (0.321)	0.56	60.52	30.63	2.16	1.45	1.25	0.25	0.51	2.28	–
HM-M-5A -0.1+0.08 aero (0.260)	0.14	61.12	30.85	1.92	1.52	1.62	0.33	0.40	2.24	0.06
HM-M-5A -0.1+0.08 aero (0.303)	0.12	62.58	28.94	2.14	1.58	1.70	0.30	0.40	2.32	0.08
HM-M-5A -0.16+0.125	0.40	67.16	23.66	2.05	1.92	1.44	0.28	0.43	2.60	–
HM-M-1A -0.16+0.125 aero (0.306)	0.72	65.16	25.34	3.43	0.91	1.35	0.12	0.41	2.38	–
HM-R-5A -0.063+0.05	0.06	58.12	36.63	0.80	1.54	1.22	0.21	0.63	0.56	0.08
HM-R-5A vg -0.063+0.05	0.14	60.80	34.65	1.02	1.02	1.12	0.10	0.31	0.51	0.10
HM-R-5A vg -0.071+0.063	0.20	57.80	36.37	1.25	1.24	0.88	0.08	0.56	0.68	0.08

In order to more accurately calculate the composition of the glass phase of the shells of cenospheres from the combined data of the chemical analysis and the quantitative X-ray powder diffraction analysis, it was necessary to determine the composition of the crystalline phase of mullite. This is associated with the fact that mullite is an aluminosilicate of variable composition with different Al/Si ratios and, in addition of the stoichiometric mullite $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, can be represented by a series of solid solutions $\text{Al}_2[\text{Al}_2 + 2x\text{Si} - 2x]\text{O}_{10-x}$, where $0.18 \leq x \leq 0.88$ [25]. It is known [25–27] that the lattice parameters of mullite depend on the Al/Si ratio in its structure: with an increase in the content of Al_2O_3 in the mullite composition, the lattice parameters a and c increase, whereas the lattice parameter b decreases. For the entire range of compositions known in the literature for mullite solid solutions, the Al_2O_3 content amounts to 57–92 mol % (69–95 wt %). In this case, the lattice parameters of mullite vary within the following wide ranges: $a = 7.5251(4)–7.7616(5)$ Å, $b = 7.6873(5)–7.5969(8)$ Å, and $c = 2.8862(2)–2.9201(2)$ Å [26, 27]. There is a linear relationship between the molar content of Al_2O_3 in mullite m (mol %) and the lattice parameter a (Å) [26]:

$$m = 144.5 \cdot a - 1029.5. \quad (1)$$

According to this relationship, the chemical composition of mullite can be determined from the known value of the lattice parameter a .

A detailed investigation of the structural characteristics of the mullite phase for the narrow fractions of cenospheres, including the determination of the lattice parameters and crystallite sizes, demonstrated that, as compared to the data available in the literature [25–27], the lattice parameters of mullite (0) change only slightly: $a = 7.5611(2)–7.573(3)$ Å, $b = 7.6909(4)–7.699(4)$ Å, and $c = 2.887(1)–2.8887(1)$ Å. The content of Al_2O_3 in the mullite (0) phase for the narrow fractions of cenospheres, according to the calculations from the dependence on the lattice parameter a [26], lies in the range of 63–65 mol % (74–76 wt %). These values are somewhat higher than the content of Al_2O_3 in the stoichiometric mullite $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, which contains 60 mol % (72 wt %) Al_2O_3 [27], and are shifted to the region of Al-rich mullite [26]. The size of crystallites in the mullite (0) phase of the narrow fractions of cenospheres amounts to ~100–200 nm. The content of the modifying oxides ($\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O} + \text{MgO} + \text{K}_2\text{O}$) in the glass phase of the shells of cenospheres varies in the range from 15 to 29 mol %.

Table 3. Physical characteristics and phase composition of narrow fractions of cenospheres

Sample	Physical characteristics			Phase composition (wt %)				
	Bulk density (g/cm ³)	Average diameter (μm)	Shell thickness (μm)	Quartz	Quartz 1	Calcite	Mullite (0)	Glass phase
H -0.08 -0.063+0.05 vg	0.35	59	2.5	1.2	1.8	0.6	3.7	92.7
HM-H-1A -0.16+0.125	0.38	144	6.8	3.2	3.5	0.3	1.5	91.5
HM-H-1A -0.16+0.125 aero (0.298)	0.298	129	4.7	3.0	2.8	0.4	1.3	92.5
HM-M-1A -0.063+0.05 vg	0.29	58	2.1	1.3	–	0.4	8.9	89.4
HM-M-5A -0.063+0.05	0.34	60	2.5	0.2	1.3	0.7	8.4	89.4
HM-M-5A -0.063+0.05 aero (0.321)	0.321	58	2.3	0.8	0.4	0.4	11.7	86.7
HM-M-5A -0.1+0.08 aero (0.260)	0.260	90	2.8	2.0	–	0.5	13.7	83.8
HM-M-5A -0.1+0.08 aero (0.303)	0.303	91	3.4	2.2	–	0.4	11.0	86.4
HM-M-5A -0.16+0.125	0.34	146	6.2	0.4	2.4	0.3	7.0	91.1
HM-M-1A -0.16+0.125 aero (0.306)	0.306	144	5.4	2.4	–	0.4	8.2	89.0
HM-R-5A -0.063+0.05	0.40	58	3.0	1.4	–	0.3	30.1	68.2
HM-R-5A vg -0.063+0.05	0.37	60	2.8	1.2	–	0.1	29.8	68.9
HM-R-5A vg -0.071+0.063	0.37	69	3.2	1.2	–	0.4	38.9	59.5

For the purpose of a change in the composition of the glass phase and its purification from modifying ions, the narrow fractions of cenospheres were subjected to additional high-temperature treatment at temperatures of 1000 and 1100°C in an oxygen atmosphere. Figure 3 shows, as an example, the SEM micrographs of the narrow fraction of cenospheres after the additional heat treatment at a temperature of 1000°C (Fig. 3a), its individual globules (Figs. 3b, 3c), and the inner surface of the shell (Fig. 3d).

The quantitative X-ray powder diffraction analysis revealed that the heat treatment of the narrow fractions of cenospheres leads to the formation of additional crystalline phases, namely, 4–21 wt % mullite (I) and 0.3–14 wt % cristobalite, in the shells of the cenospheres (Table 4). The mullite (I) phase has the following lattice parameters: $a = 7.5667(1)–7.572(3)$ Å, $b = 7.7131(9)–7.718(3)$ Å, and $c = 2.8917(8)–2.8949(9)$ Å. These values are higher than the corresponding lattice parameters for the initial phase, mullite (0), exceed the data available in the literature for the entire range of possible Al/Si ratios in mullite [26, 27], and are at the level of lattice parameters for iron-containing mullites, in which the Fe₂O₃ content can be as high as 12 wt % [27–30]. In particular, according to the data reported in [30], the mullite containing 10.3 wt % Fe₂O₃ has the following lattice parameters: $a = 7.5740(1)$ Å, $b = 7.726(1)$ Å, and $c = 2.9004(5)$ Å.

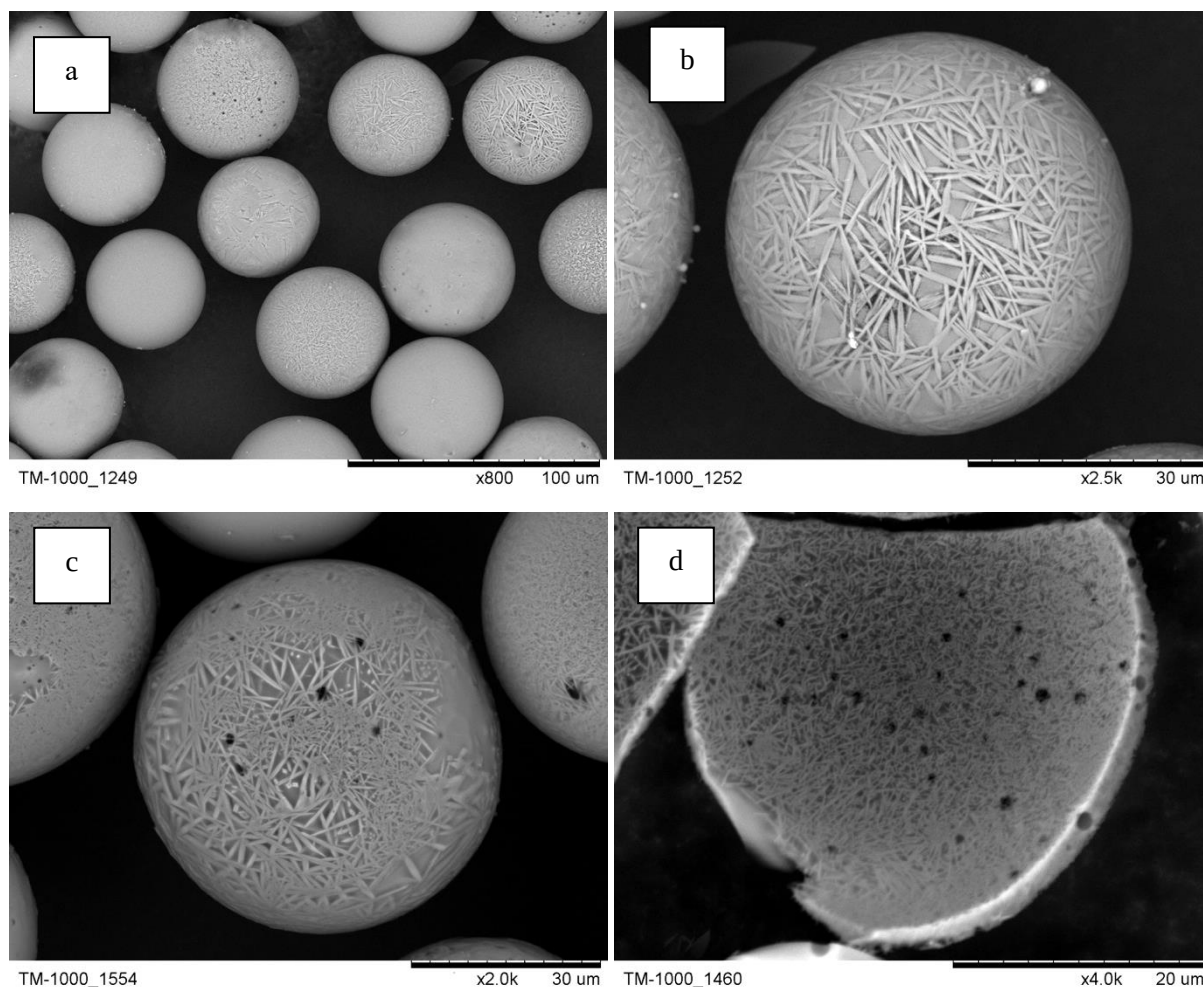


Figure 3. SEM micrographs of (a) narrow fraction of cenospheres after the additional heat treatment at a temperature of 1000°C, (b, c) individual globules, and (d) inner surface of the shell.

During the additional heat treatment of the narrow fractions of cenospheres, the formation of the mullite (I) phase in an oxidizing atmosphere is accompanied by the oxidation of Fe^{2+} ions to Fe^{3+} ions, as well as by their extraction from the glass phase and incorporation into the lattice of the crystallizing mullite in the positions of Al^{3+} ions. This results in the formation of a defective iron-containing phase of mullite (I) in the shells of the cenospheres, which is favorable for additional purification of the glass phase from the modifying ions [4]. The size of crystallites in the mullite (I) phase lies in the range of ~20–30 nm. The content of modifying oxides in the glass phase of the shells of cenospheres after the additional heat treatment varies in the range of 10–17 mol %.

The formation of mullite crystallites is especially pronounced after the treatment of cenospheres with fluorine-containing reagents due to the removal of a 30- to 50-nm-thick surface film. The performed investigations of the structure of individual globules demonstrated that large crystallites of mullite are in-plane localized on the outer and inner surfaces of the cenospheres, whereas small crystallites of the mullite phase are localized inside the shells of the cenospheres, thus forming a specific framework (Fig. 4) and imparting the globules additional strength characteristics.

Table 4. Phase composition of narrow fractions of cenospheres after the additional heat treatment

Sample	Phase composition (wt %)					
	Quartz	Quartz 1	Mullite (0)	Mullite (I)	Cristobalite	Glass phase
HM-M-5A $-0.063+0.05$ 1000°C	0.3	1.4	9.5	20.9	-	67.9
HM-M-5A $-0.1+0.08$ aero (0.260) 1000°C	0.4	1.9	15.8	14.9	0.3	66.7
HM-M-5A $-0.16+0.125$ 1000°C	0.5	2.1	7.2	16.5	-	73.7
HM-R-5A $-0.063+0.05$ 1000°C	2.4	-	31.3	5.9	0.5	59.9
HM-R-5A $-0.063+0.05$ 1100°C	2.1	-	37.0	11.4	14.1	35.4
HM-R-5A vg- $-0.063+0.05$ 1000°C	1.4	-	32.5	4.0	0.4	61.7
HM-R-5A vg- $-0.063+0.05$ 1100°C	2.0	-	33.0	10.3	13.9	40.8

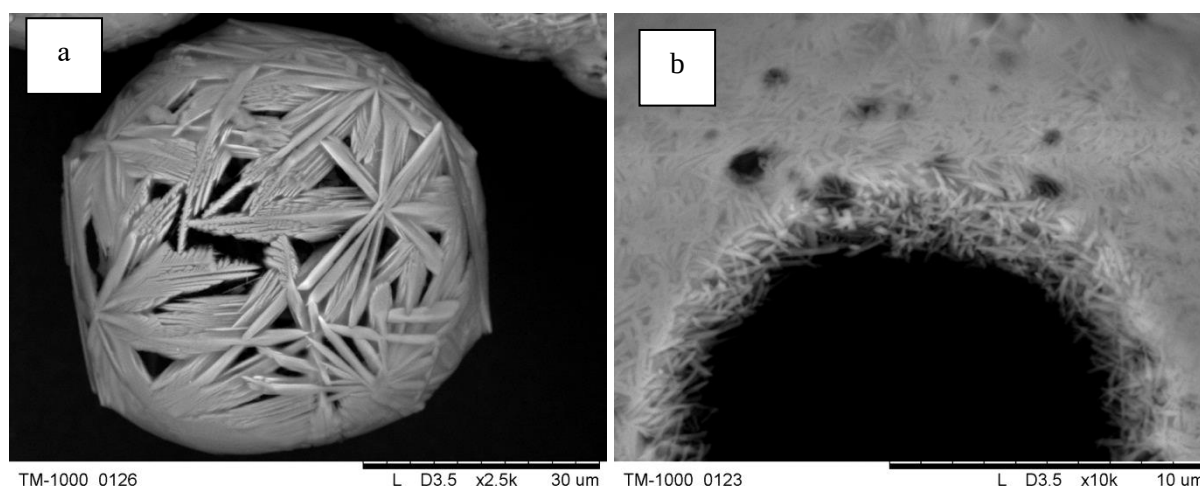


Figure 4. SEM micrographs demonstrating the localization of large and small crystallites after the heat treatment and acid etching of narrow fraction of cenospheres: (a) cenosphere and (b) cleavage of the globule.

The investigations of the diffusion properties of the narrow fractions of cenospheres with respect to He and H₂ showed that the permeability coefficients of the glass phase are directly proportional to the content of the glass-forming oxide SiO₂ (*G*, mol %) in it (Figs. 5, 6). With an increase in the content of SiO₂ in the range from 71 to 90 mol %, the permeability coefficients of the glass phase for these gases, *K*_{He} and *K*_{H₂}, increase over the entire temperature range, whereas the activation energies for their diffusion decrease (Tables 5, 6). For example, the experimental dependences of the permeability coefficient log*K* on the glass-forming oxide content *G* at 280°C are described by the following regression equations with high correlation coefficients: lg*K*_{He}(exp) = $-19.98 + 0.052 \cdot G$ for *r* = 0.96 and lg*K*_{H₂}(exp) = $-20.71 + 0.045 \cdot G$ for *r* = 0.91 (Figs. 5, 6).

The permeability coefficients for the glass phase of the shells of the cenospheres significantly exceed the permeability coefficients for the synthetic glass microspheres 3M K37 (Table 5, 6). For example, for the narrow fraction of cenospheres HM-R-5A $-0.063 + 0.05$ with the minimum content of modifying oxides (10 mol %) after the additional heat treatment at a temperature of 1100°C, the

permeability coefficient K_{He} at 25°C exceeds by more than two orders of magnitude the corresponding value for the synthetic glass microspheres. The selectivity for all the narrow fractions of cenospheres under investigation reaches a high level (Table 5, 6) and, at a temperature of 280°C, lies in the range $\alpha(\text{He}/\text{H}_2) = 10\text{--}33$. These values correspond to the selectivity of the vitreous silica glass $\alpha(\text{He}/\text{H}_2) = 10$ [3, 4] and substantially exceed the selectivity of membrane materials, such as polymers [20], zeolites [31, 32], and carbon molecular sieves [33], which have the selectivity $\alpha(\text{He}/\text{H}_2) = 1\text{--}2$.

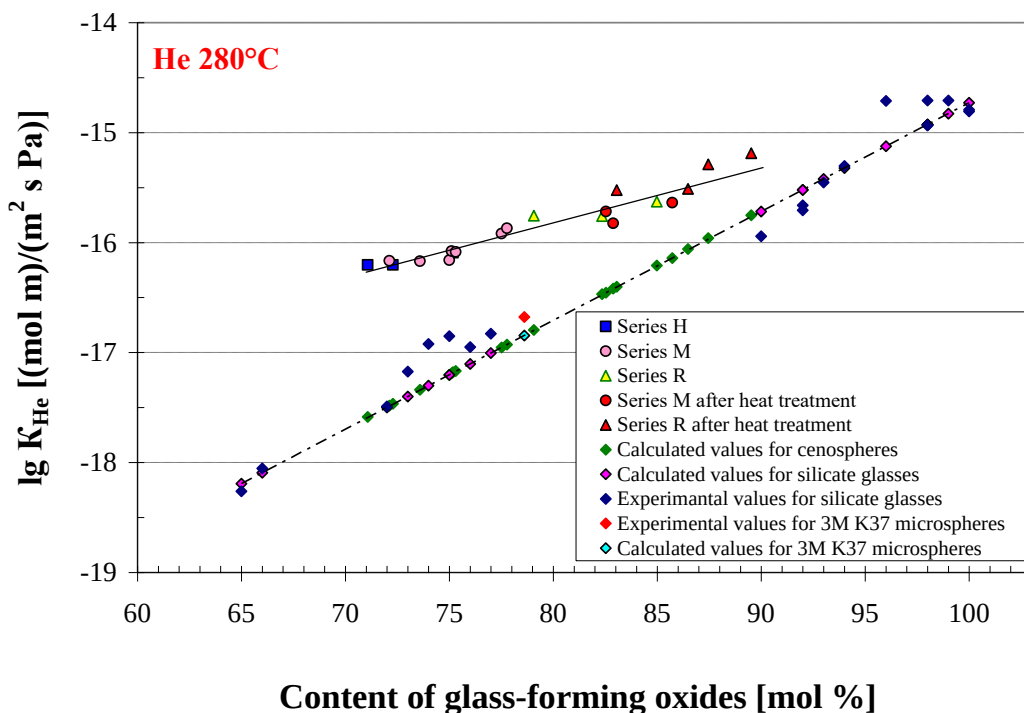


Figure 5. Dependences of the helium permeability coefficients (experimental and calculated values) at a temperature of 280°C for the glass phase of the shells of narrow fractions of cenospheres and hollow glass microspheres 3M K37 on the content of glass-forming oxides in comparison with the data available in the literature (experimental and calculated values) for silicate glasses of different compositions [6].

The analysis of the data available in the literature revealed [6] that, for silicate glasses with different compositions, an increase in the content of glass-forming oxides $G = \text{SiO}_2 + \text{B}_2\text{O}_3 + \text{P}_2\text{O}_5$ in the range from 65 to 100 mol % leads to a significant increase in the helium permeability, which, for example, at a temperature of 280°C, amounts to more than three orders of magnitude (Fig. 5), and is accompanied by a decrease in the activation energy for the diffusion of helium from 50 to 20 kJ/mol. This observation is similar to the dependence established for the narrow fractions of cenospheres. Among silicate glasses, the vitreous silica glass with $G = 100$ mol % has the maximum helium permeability (Fig. 5).

We performed the theoretical evaluation of the helium permeability coefficients for the glass phase of the shells of cenospheres and silicate glasses with different compositions at 280°C. For this purpose, we used the empirical equation [34], according to which the helium permeability of silicate glasses is directly proportional to the content of glass-forming oxides:

$$K_{\text{He}} = 1.54 \cdot 10^{-13} \exp[-(1/T) \cdot (15040 - 126 \cdot G)], \quad (2)$$

where K_{He} is the calculated helium permeability coefficient $[(\text{mol m})/(\text{m}^2 \text{ s Pa})]$, T is the temperature [K], and G is the content of glass-forming oxides ($\text{SiO}_2 + \text{B}_2\text{O}_3 + \text{P}_2\text{O}_5$) [mol %].

Table 5. Characteristics of the diffusion of helium and hydrogen for narrow fractions of cenospheres and hollow synthetic glass microspheres 3M K37

Sample	G^* , mol %	Permeability coefficient of the glass phase (mol m)/(m ² s Pa)			Selectivity	Activation energy, kJ/mol	
		25°C	280°C		280°C		
		K_{He}	K_{He}	K_{H_2}	$\alpha(\text{He}/\text{H}_2)$	He	H ₂
3M K37	78.61	$4.41 \cdot 10^{-20}$	$2.12 \cdot 10^{-17}$	$2.87 \cdot 10^{-19}$	74	33	54
H -0.08 -0.063+0.05 vg	71.07	$2.16 \cdot 10^{-19}$	$6.26 \cdot 10^{-17}$	n. d. [†]	n. d	31	n. d
HM-H-1A -0.16+0.125	75.18	$1.75 \cdot 10^{-19}$	$8.09 \cdot 10^{-17}$	$7.87 \cdot 10^{-18}$	10	33	31
HM-H-1A -0.16+0.125 aero (0.298)	72.29	n. d	$6.27 \cdot 10^{-17}$	n. d	n. d	35	n. d
HM-M-1A -0.063+0.05 vg	73.59	$2.33 \cdot 10^{-19}$	$6.77 \cdot 10^{-17}$	n. d	n. d	30	n. d
HM-M-5A -0.063+0.05	72.12	$2.35 \cdot 10^{-19}$	$6.82 \cdot 10^{-17}$	$2.46 \cdot 10^{-18}$	28	30	40
HM-M-5A -0.063+0.05 aero (0.321)	75.00	$2.31 \cdot 10^{-19}$	$6.92 \cdot 10^{-17}$	n. d	n. d	31	n. d
HM-M-5A -0.1+0.08 aero (0.260)	75.10	$4.42 \cdot 10^{-19}$	$8.35 \cdot 10^{-17}$	$3.82 \cdot 10^{-18}$	22	28	38
HM-M-5A -0.1+0.08 aero (0.303)	75.30	$5.44 \cdot 10^{-19}$	$8.22 \cdot 10^{-17}$	$3.59 \cdot 10^{-18}$	23	27	38
HM-M-5A -0.16+0.125	77.51	$8.78 \cdot 10^{-19}$	$1.21 \cdot 10^{-16}$	$6.70 \cdot 10^{-18}$	18	26	38
HM-M-1A -0.16+0.125 aero (0.306)	77.77	n. d	$1.35 \cdot 10^{-16}$	n. d	n. d	20	n. d
HM-R-5A -0.063+0.05	79.07	$1.38 \cdot 10^{-18}$	$1.76 \cdot 10^{-16}$	$5.28 \cdot 10^{-18}$	33	26	40
HM-R-5A vg -0.063+0.05	82.35	$1.35 \cdot 10^{-18}$	$1.74 \cdot 10^{-16}$	n. d	n. d	26	n. d
HM-R-5A vg -0.071+0.063	84.98	$1.50 \cdot 10^{-18}$	$2.35 \cdot 10^{-16}$	$8.40 \cdot 10^{-18}$	28	27	35

* Content of glass-forming oxides: for 3M K37 cenospheres, it is the content of the sum of oxides ($\text{SiO}_2 + \text{B}_2\text{O}_3 + \text{P}_2\text{O}_5$); for narrow fractions of cenospheres, it is the content of SiO_2 ,

[†] not determined.

For silicate glasses over a wide range of compositions, the calculated and experimental values of K_{He} almost coincide with each other (Fig. 5), follow the similar regression equations with high correlation coefficients $\lg K_{\text{He}}(\text{exp}) = -24.21 + 0.095 \cdot G$ for $r = 0.99$ and $\lg K_{\text{He}}(\text{calc}) = -24.62 + 0.099 \cdot G$ for $r = 1.00$, and demonstrate a good agreement with each other. In few cases, there is only a one- to three-fold discrepancy between the experimental and calculated values of the permeability coefficients.

The calculated values of K_{He} for the glass phase of the shells of cenospheres fit in the general trend with the calculated and experimental data for silicate glasses of different compositions, including the vitreous silica glass with $G = 100$ mol % (Fig. 5), and are described by the general equation $\lg K_{\text{He}}(\text{calc}) = -24.62 + 0.099 \cdot G$ for $r = 1.00$. The experimental values of the helium permeability coefficient $K_{\text{He}}(\text{exp})$ for the glass phase of the shells of cenospheres are described by the relationship $\lg K_{\text{He}}(\text{exp}) = -19.98 + 0.052 \cdot G$ with the high correlation coefficient $r = 0.96$ and, at a temperature of 280°C, exceed the calculated permeability coefficients $K_{\text{He}}(\text{calc})$ by a factor of 3–24. At a temperature of 25°C, the experimental values of $K_{\text{He}}(\text{exp})$ exceed the calculated values by a factor of 11–1000. For the glass microspheres 3M K37 with a thin shell of 1.4 μm in thickness, a similar comparison between the experimental and calculated values of K_{He} at 280°C demonstrated a small 1.5-fold discrepancy.

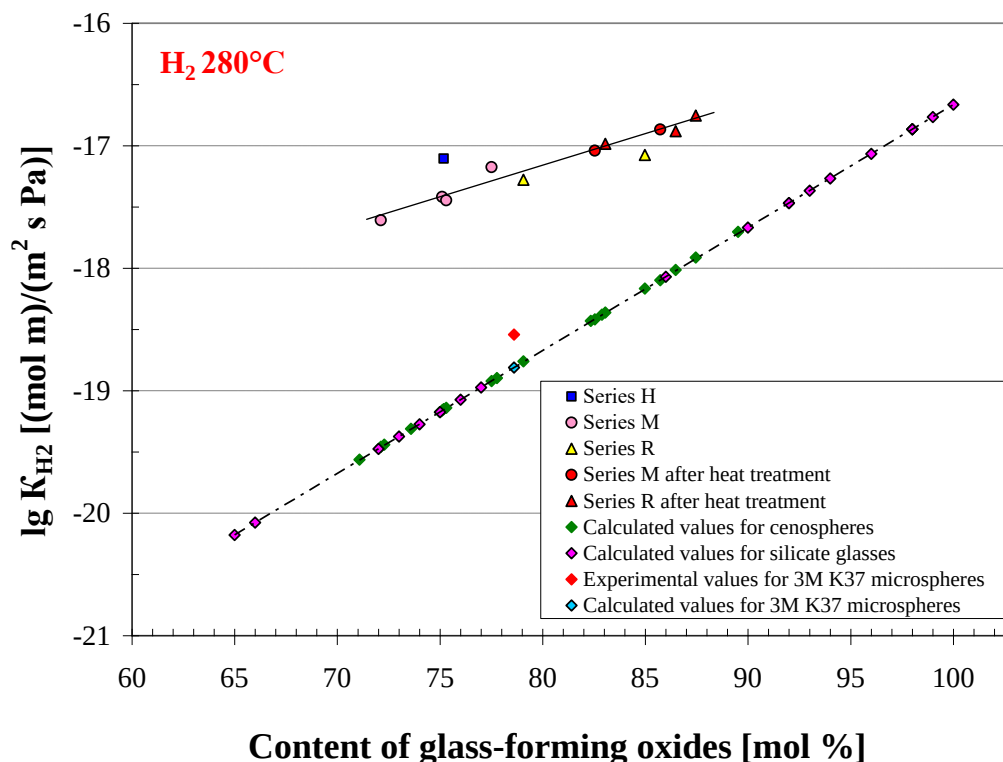


Figure 6. Dependences of the hydrogen permeability coefficients (experimental and calculated values) at a temperature of 280°C for the glass phase of the shells of narrow fractions of cenospheres and hollow glass microspheres 3M K37 on the content of glass-forming oxides in comparison with the calculated values available in the literature for silicate glasses of different compositions [6].

We also performed the theoretical evaluation of the hydrogen permeability coefficients for the glass phase of the shells of cenospheres at a temperature of 280°C and their comparison with the obtained experimental values (Fig. 6). The calculation was carried out using the following empirical equation [34]:

$$K_{H_2} = 8.10 \cdot 10^{-14} \exp[-(1/T) \cdot (17330 - 127.8 \cdot G)]. \quad (3)$$

It was found that, at a temperature of 280°C, the calculated values of $K_{H_2}(\text{calc})$ for the glass phase of the shells of cenospheres fit in the general trend with the calculated data for silicate glasses of different compositions and are described by the general equation $\lg K_{H_2}(\text{calc}) = -26.70 + 0.100 \cdot G$ for $r = 1.00$ (Fig. 6). The experimental values of $K_{H_2}(\text{exp})$ for the glass phase of the shells of cenospheres follow the relationship $\lg K_{H_2}(\text{exp}) = -20.71 + 0.045 \cdot G$ for $r = 0.91$ and exceed the calculated values of $K_{H_2}(\text{calc})$ by a factor of 12–111. A similar comparison between the experimental and calculated values of K_{H_2} for the glass microspheres 3M K37 demonstrated a small 1.8-fold discrepancy.

The observed significant excess of the experimental values of the permeability coefficients for the narrow fractions of cenospheres with respect to helium and hydrogen over the corresponding calculated values indicates that the diffusion properties of silicate glass-crystalline materials exert an influence not only on the composition of the gas-permeable glass phase, but also on the specific features of its structure.

Table 6. Characteristics of the diffusion of helium and hydrogen for narrow fractions of cenospheres after the additional heat treatment

Sample	G^* , mol %	Permeability coefficient of the glass phase (mol m)/(m ² s Pa)			Selectivity	Activation energy, kJ/mol	
		25°C	280°C		280°C	He	H ₂
		K_{He}	K_{He}	K_{H_2}	$\alpha(He/H_2)$		
HM-M-5A -0.063+0.05 1000°C	82.54	$1.62 \cdot 10^{-18}$	$1.91 \cdot 10^{-16}$	$9.13 \cdot 10^{-18}$	21	26	30
HM-M-5A -0.1+0.08 aero (0.260) 1000°C	82.88	$9.15 \cdot 10^{-19}$	$1.50 \cdot 10^{-16}$	n. d. [†]	n. d.	28	n. d.
HM-M-5A -0.16+0.125 1000°C	85.73	$5.97 \cdot 10^{-18}$	$2.31 \cdot 10^{-16}$	$1.36 \cdot 10^{-17}$	17	20	35
HM-R-5A -0.063+0.05 1000°C	83.05	$3.51 \cdot 10^{-18}$	$3.01 \cdot 10^{-16}$	$1.04 \cdot 10^{-17}$	29	24	25
HM-R-5A -0.063+0.05 1100°C	89.52	$6.21 \cdot 10^{-18}$	$6.50 \cdot 10^{-16}$	n. d.	n. d.	25	n. d.
HM-R-5A vg-0.063+0.05 1000°C	86.48	$3.73 \cdot 10^{-18}$	$3.08 \cdot 10^{-16}$	$1.31 \cdot 10^{-17}$	23	24	26
HM-R-5A vg-0.063+0.05 1100°C	87.46	$5.64 \cdot 10^{-18}$	$5.15 \cdot 10^{-16}$	$1.76 \cdot 10^{-17}$	29	24	30

* Content of glass-forming oxides: for narrow fractions of cenospheres, it is the content of SiO₂,

[†] not determined.

It can be assumed that this influence is due to the formation of cenospheres under conditions of rapid melt quenching for contact times of ~1 s [35], which leads to the formation of a glass phase whose structure differs from the structure of glasses prepared from homogeneous melts followed by prolonged annealing for the removal of inhomogeneities. The structure of the glass phase formed in the shells of cenospheres, possibly, is more loosened and defective as compared to commercial glasses. Consequently, the glass phase can significantly facilitate the diffusion of light noble gases, while maintaining the high selectivity, which is also confirmed by the decrease in the activation energy.

4. CONCLUSIONS

The diffusion properties of the narrow fractions of cenospheres over wide ranges of major component compositions (58–68 wt % SiO₂, 21–37 wt % Al₂O₃) and phase compositions (1–48 wt % mullite, 1–7 wt % quartz, 0.3–14 wt % cristobalite, 35–93 wt % glass phase) were investigated with respect to He and H₂. It was found that the permeability coefficients for the glass phase of the shells of cenospheres are directly proportional to the content of the glass-forming oxide SiO₂ in it.

The calculated values of the permeability coefficients $K_{He}(\text{calc})$ and $K_{H_2}(\text{calc})$ for the glass phase of the narrow fractions of cenospheres with the SiO₂ content in the range of 71–90 mol % follow the general trends with the calculated and experimental data for silicate glasses over a wide range of compositions $G = 65$ –100 mol % and, at a temperature of 280°C, are described by the general regression equations: $\lg K_{He}(\text{calc}) = -24.62 + 0.099 \cdot G$ for $r = 1.00$ and $\lg K_{H_2}(\text{calc}) = -26.70 + 0.100 \cdot G$ for $r = 1.00$.

The experimental values of $K_{He}(\text{exp})$ and $K_{H_2}(\text{exp})$ for the cenospheres follow individual trends and, at 280°C, are described by the regression equations with high correlation coefficients: $\lg K_{He}(\text{exp}) = -19.98 + 0.052 \cdot G$ for $r = 0.96$ and $\lg K_{H_2}(\text{exp}) = -20.71 + 0.045 \cdot G$ for $r = 0.91$. It was found that the experimental values of the permeability coefficients for the glass phase of the shells of cenospheres at a temperature of 280°C exceed the calculated values of the helium and hydrogen permeability coefficients by a factor of 3–24 and 12–111, respectively. For helium at a temperature of 25°C, the experimental values of the permeability coefficients are 11–1000 times greater than the corresponding calculated values. An increase in the content of SiO₂ in the glass phase of the cenospheres leads to a decrease in the activation energy of the diffusion of helium and hydrogen.

Narrow fractions of cenospheres correspond in the level of permeability to the vitreous silica glass with the glass-forming oxide phase content $G = 100$ mol %, which significantly exceeds the level of permeability for hollow synthetic glass microspheres 3M K37 with $G = 79$ mol %. The selectivity $\alpha(\text{He}/\text{H}_2)$ for the cenospheres has high values and reaches $\alpha(\text{He}/\text{H}_2) = 10\text{--}33$ at 280°C . These values are not inferior to those for the vitreous silica glass, which, among the known membrane materials, is characterized by the maximum mixture separation factors, and exceed by several orders of magnitude the corresponding values for membrane materials, such as polymers, zeolites, metal–organic framework structures, and carbon molecular sieves.

Based on the fact that the experimental values of the permeability coefficients for the glass phase of the shells of cenospheres significantly exceed the calculated permeability coefficients, it was concluded that the structure of silicate glass-crystalline materials affects their diffusion properties. The formation of cenospheres under conditions of rapid melt quenching, which is accompanied by the crystallization of phases and the displacement of modifying ions from the structural glass network, leads to the formation of the glass phase in the shells of cenospheres. The structure of the glass phase can substantially facilitate the diffusion of gases, which is also confirmed by the decrease in the activation energy for the diffusion of helium and hydrogen.

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REFERENCES

1. Baker, R.W. 2004, *Membrane technology and applications*, 2nd edn, John Wiley & Sons Ltd.
2. Drioli, E. and Romano, M. 2001, “Progress and New Perspectives on integrated Membrane operations for sustainable industrial growth”, *Industrial and Engineering Chemistry Research*, vol. 40, pp. 1277-1300.
3. Stern, S.A., Singlair, T.F. et al. 1965, “Helium recovery by permeation.” *Industrial and Engineering Chemistry*, vol. 57, no. 2, pp. 49-60.
4. Fomenko, E. V., Rogovenko, E. S. et al. 2014, “Gas permeation properties of hollow glass-crystalline microspheres.” *RSC Advances*, vol. 20, no. 4, pp. 9997-10000.
5. Norton, F. J. J. 1953, “Helium diffusion through glass.” *Journal of the American Ceramic Society*, vol. 36, no. 3, pp. 90-96.
6. Altemose, V. O. J. 1961, “Helium diffusion through glass.” *Journal of Applied Physics*, vol. 32, no. 7, pp. 1309-1316.
7. Zachariasen, W. H. 1932, “The atomic arrangement in glass.” *Journal of the American Chemical Society*, vol. 54, pp. 3841-3851.
8. Huang, P. Y., Kurash, S. et al. 2012, “Direct imaging of a two-dimensional silica glass on graphene.” *Nano Letters*, vol. 12, pp. 1081-1086.
9. Axinte, E. 2011, “Glasses as engineering materials: A review.” *Materials and Design*, vol. 32, pp. 1717–1732.
10. Brow, R. K. and Schmitt, M. L. 2009, “A survey of energy and environmental applications of glass” *Journal of the European Ceramic Society*, vol. 29, pp. 1193–1201.
11. Shelby, J.E., Raszewski, F.C. et al. 2009, “Fuels-hydrogen storage: hydrogen storage in glass microspheres, encyclopedia of electrochemical power sources” *Elsevier*; pp. 488-492.
12. Vereshchagin, S. N., Anshits, A. G. et al. 2010, “Features of profound processing of natural gas of Eastern Siberia.” *Chemistry for Sustainable Development*, vol. 18, pp. 229-238.

13. Fomichev, V. P., Fomin, V. M. et al. 2005, *The system and method of separating gas mixtures*, RU Patent 2291740.
14. Fischer, G. L., Chang, D. P. J. et al. 1976, "Fly ash collected from electrostatic precipitators: microcrystalline structures and the mystery of the spheres." *Science*, vol.192, pp. 553-555.
15. Kizil'shtein, L. Ya., Dubov, I. V., Shpitsgluz, A. L. & Parada, S. G. 1995, *Components of ashes and slags of heat power plants*, Energoatomizdat, Moscow.
16. Raask, E. 1985, *Mineral impurities in coal combustion*, Hemisphere, New York.
17. Vassilev, S. V. & Vassileva, C. G. 1996, "Mineralogy of combustion wastes from coal-fired power stations." *Fuel Processing Technology*, vol. 47, pp. 261-280.
18. Fomenko, E. V., Anshits, N. N. et al 2012, "Influence of the composition and structure of the glass-crystalline shell of cenospheres on helium permeability." *Glass Physics and Chemistry*, vol. 38, no. 2, pp. 218-227.
19. Fomenko, E. V., Anshits, N. N. et al. 2010, "Helium permeability of microspherical membranes based on mullitized cenospheres." *Doklady Physical Chemistry*, vol. 435, no. 2, pp. 202-204.
20. Robeson, L. M. 2008, "The upper bound revisited." *Journal of Membrane Science*, vol. 320 pp. 390-400.
21. Kuz'menko, I. F.; Gorokhov, V. A.; Talakin, O. G. 2009, *Device for Neon Concentration in Air Mixtures Containing Neon*. RU Patent 2441693.
22. Anshits, N. N., Mikhailova, O. A., et al. 2010, "Chemical composition and structure of the shell of fly ash non-perforated cenospheres produced from the combustion of the Kuznetsk coal (Russia)." *Fuel*, vol. 89, pp. 1849-1862.
23. Fomenko, E. V.; Anshits, N. N. et al. 2013, "Composition and morphology of fly ash cenospheres produced from the combustion on Kuznetsk coal." *Energy & Fuels*, vol. 27, no. 9, pp. 5440-5448.
24. Fomenko, E. V., Anshits, N. N. et al. 2015, "Characterization of fly ash cenospheres produced from the combustion of Ekibastuz coal." *Energy & Fuels*, vol. 29, no. 8, pp. 5390-5403.
25. Schneider H., Schreuer J. et al. 2008, "Structure and properties of mullite – A review." *Journal of the European Ceramic Society*, vol. 28, pp. 329-344.
26. Fischer, R.X., Schneider, H. et al. 1996, "Formation of Aluminium Rich 9:1 Mnullite and its Transformation to Low Alumina Mullite upon Heating." *Journal of the European Ceramic Society*, vol. 16, pp. 109-113.
27. Schneider, H. & Komarneni, S. 2005, *Mullite*. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
28. Cardile, C. M., Brown, I. W. M. et al. 1987, "Mossbauer spectra and lattice parameters of ion-substituted mullites." *Journal of Materials Science Letters*, vol. 6, no. 3, pp. 357-362.
29. Parmentier, J., Vilminot, S. 1997, "Influence of synthesis and composition on mullite crystallization", *Chemistry of Materials*, vol. 9, no. 5, pp. 1134-1137.
30. Schneider, H. 1990, "Transition metal distribution in mullite." *Ceramic Transaction*, vol. 6, pp.135-158.
31. Tomita, T., Nakayama, K. et al. 2004, "Gas separation characteristics of DDR type zeolite membrane." *Microporous and Mesoporous Materials*, vol. 68, pp. 71-75.
32. Guan, G., Kusakabe, K. et al. 2001, "Gas permeation properties of ion-exchange LTA-type zeolite membranes." *Separation Science and Technology*, vol. 36, no. 10, pp. 2233-2245.

33. Favvas, E. P., Heliopoulos, N. S. et. al. 2015, "Helium and hydrogen selective carbon hollow fiber membranes: The effect of pyrolysis isothermal time." *Separation and Purification Technology*, vol. 142, pp. 176-181.
34. Tsugawa, R. T., Moem, J. et al. 1976, "Permeation of helium and hydrogen from glass-microsphere laser targets." *Journal of Applied Physics*, vol. 47, pp. 1987-1993.
35. Raask, E. 1968, "Cenospheres in pulverized-fuel ash." *Journal of the Institute of Fuel*, vol. 43, pp. 339-344.