

PERMEABILITY OF HOLLOW MICROSPHERICAL MEMBRANES TO HELIUM

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UDC 539.217.5

This work is devoted to the study of the sorption characteristics of various hollow microspherical membranes to reveal particles most suitable for application in the membrane-sorption technologies of helium extraction from a natural gas. The permeability of the investigated sorbents to helium and their impermeability to air and methane are shown experimentally. The sorption-desorption dependences of the studied sorbents have been obtained, from which the parameters of their specific permeability to helium are calculated. It has been established that the physicochemical modification of the original particles exerts a great influence on the coefficient of the permeability of a sorbent to helium. Specially treated cenospheres have displayed high efficiency as membranes for selective extraction of helium.

Keywords: microspheres, cenospheres, membranes, permeability, helium, separation of gases, membrane-sorption method.

Introduction. The gas fields of East Siberia have enormous resources of helium-containing hydrocarbons, in the first place of methane, and provide an ideal basis for creating a gas-chemical cluster in accordance with the power-engineering strategy of Russia. The development of these fields will make it possible for Russia to become the world's biggest producer and supplier of helium at domestic and external markets.

At the present time, helium is extracted commercially from natural gas by means of a cryogenic technology the physical basis of which is the condensation of hydrocarbon fractions that constitute the principal components of the natural gas. For the extraction of small amounts of helium from the natural gas, this technology requires significant power and capital expenditures [1], which impedes putting the East Siberian gas fields into operation. An alternative to the cryogenic technology of extracting helium from the natural gas is the membrane-sorption technology that is being developed by the present authors and that combines short-cycle adsorption and membrane separation [2, 3]. The fundamental possibility of combining these two methods as a column installation containing hollow spherical particles was shown in [4, 5]. In this case, the process of helium extraction from a gaseous mixture may follow the adsorption-cyclic scheme due to the selective penetration of helium into the interior cavity of spherical particles through the walls that play the role of membrane elements [6].

In the present work, we carried out an investigation of the sorption characteristics of various hollow microspherical membranes to reveal the particles with the greatest permeability and selectivity, elevated mechanical strength, thermal stability, and so on for the potential application in the membrane-sorption technologies of helium extraction from the natural gas.

Experimental Equipment and Materials. To carry out experiments on studying the dynamics of the processes of helium sorption and desorption by various types of sorbents, a special test rig was made. The construction of the rig allows one to promptly replace the test material. In studying the permeability of sorbents, the following gases were used as a working medium: air, methane, helium, and their mixtures. Figure 1 presents the scheme of the test rig used to measure the dynamics of sorption and desorption of helium by different types of sorbents.

The basis of the rig is an adsorber, which is a stainless steel container 1, of volume $0.55 \cdot 10^{-3} \text{ m}^3$, into which a test sorbent is charged. Air, helium, methane, or their mixtures are supplied to the adsorber through a route 3 and valves B3 and B1. The pressure is relieved through an exhaust system consisting of route 2 and valve B2. If it is required to evacuate the adsorber, a vacuum pump is connected to route 2. The pressure in the adsorber is measured by a FESTO pressure transducer of SDET-22T model, with a measurement range of up to 1.6 MPa and accuracy $\pm 100 \text{ Pa}$, connected with the rig by route 4

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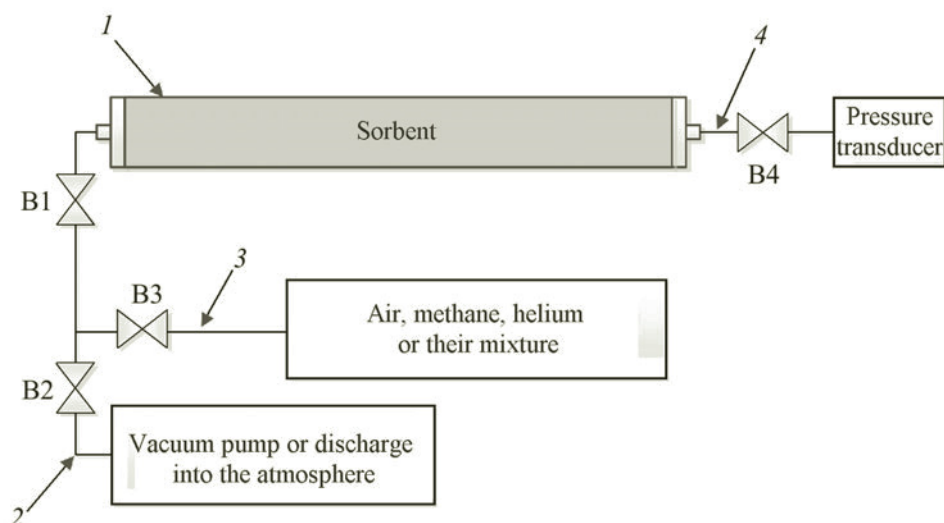


Fig. 1. Schematic of the experimental rig.

and valve B4. Special multilayer filters made from a nonwoven material are installed at the end faces of the adsorber to prevent the sorbent particles from getting into the supplying routes, valves, and measuring devices.

In the absence of an adsorbent in the adsorber, a checking of the airtightness of the rig carried out at a pressure of 1 MPa showed that the rate of change in the pressure did not exceed 50 Pa/h. Thus, the available nontightness can be considered insignificant as compared with the change of pressure in the adsorber in the processes of sorption and desorption.

To carry out experiments with methane as a working gas, the rig was modified to conform to the requirements of safety when operating with dangerously explosive gases: a block for gas utilization and a system for blasting the rig with nitrogen were added.

To determine the structure and composition of the objects, we used a Zeiss EVO MA 15 scanning emission electron microscope with a maximum spatial resolution of 2 nm at magnification of 10^6 times and range of accelerating voltages of up to 30 kV. The images of particles make it possible to obtain information on the surface relief, phase difference, and on the crystal structure of the near-surface layers. An analysis of gas samples was made by means of a Kristall-4000 chromatograph.

Microspheres. Hollow glass microspheres represent a white-colored light loose powder consisting of separate spherical particles of size from 10 to 200 μm with thickness of their walls from 1 to 30 μm . The microspheres are obtained from previously milled multicomponent glass in gas-fired furnaces with subsequent segregation of the product of sphering by density and surface finishing. At a temperature of about 1600°C (depending on the material used), the microdroplets of the molten mineral component expand due to the surface tension of the glass melt and excess pressure of the gases formed inside the molten particles and form hollow microspheres. The regulated regimes of operation of gas-fired furnaces with subsequent segregation of the products of sphering by density make it possible to obtain particles with given compression strength parameters. The chemical composition and physical parameters of the microspheres may differ greatly depending on the type of raw material used and the modes of operation of furnaces.

From the physical properties of the microspheres, we can single out the spherical shape of particles, low density, thermal stability, and chemical inertness. Note should be taken separately of their high hydrostatic strength. Of interest is the thin structure of the microsphere wall, which is an extremely little studied region but whose chemical composition has been investigated fairly thoroughly. The selective permeability of the wall material together with the cavity inside the particle allow one to use microspheres in the processes of separation of gaseous mixtures.

In the present work we used synthetic hollow microspheres of MS-V-1L type made from soda borosilicate glass produced at the Stock Corporation “Research-and-Production Association (RPA) Stekloplastik.” The main parameters of the applied microspheres are: chemical composition 76–78% SiO_2 , 11–13% Na_2O , 4–5% CaO , 4–5% B_2O_3 , 1–2% ZnO_2 ; bulk density 0.18–0.22 g/cm^3 ; particle size 10–90 μm ; wall thickness $\sim 1 \mu\text{m}$. Investigation of the granulometric composition of the microspheres by the laser diffraction method has shown (Fig. 2) that the size distribution of particles for the given type of microspheres is monomodal, the size of particles varies from 5 to 240 μm with a maximum at 55–60 μm .

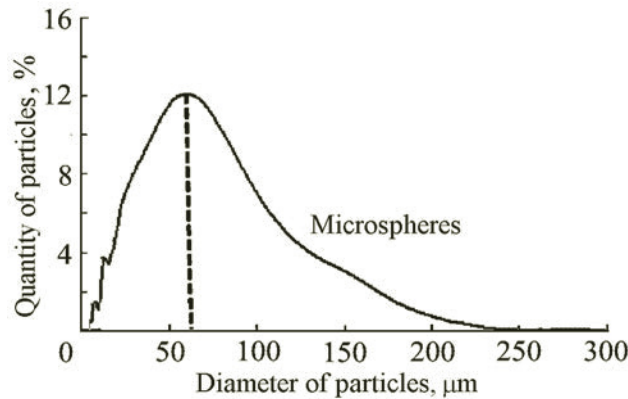


Fig. 2. Size distribution of the MS-V-1L microspheres in conformity with the data of laser diffraction.

Figure 3 presents the MS-V-1L microsphere images obtained by means of an electronic microscope. The particles have a practically ideal spherical shape and a smooth surface (Fig. 3a). It is seen in the picture that the envelope of some particles is fractured, which allows one to see the spalling of the microsphere walls (Fig. 3b). The thickness of the walls is about $1\ \mu\text{m}$, which corresponds to that declared by the producer (Fig. 3c).

We also investigated another type of synthetic MS-VP-A9 microspheres of the 5th group produced by «RPA Stekloplastik» and finished with γ -aminopropyl-triethoxylan. The MS-VP-A9 microspheres have the highest hydrostatic strength, the value of the pressure at which 10% of particles can be destroyed is $177\ \text{kgs/cm}^2$ for a test sample (10% level of destruction of particles in water, the method of the Scientific-Industrial Corporation "Term," Specs. 6-48-91-92), and the bulk density of microspheres is $0.383\ \text{g/cm}^3$.

Photographs of the MS-VP-A9 microspheres of the 5th group obtained on a scanning electron microscope are presented in Fig. 4. The microspheres have a spherical shape and a homogeneous smooth surface externally similar to the MS-V-1L microspheres.

Silica microspheres manufactured by the "RPA Stekloplastik" constitute the next type of tested particles. The distinguishing feature of this type of microspheres is their chemical composition — the content of $\text{SiO}_2 > 80\%$ and a small amount of admixtures. The bulk density of a sample is $0.2\ \text{g/m}^3$, the size of particles varies in the range from 12 to $240\ \mu\text{m}$, and the average diameter is equal to $52\ \mu\text{m}$. Figure 5 presents the photographs of silica microspheres taken by an electron scanning microscope. The particles also have a smooth homogeneous surface.

Cenospheres. Aluminosilicate hollow cenospheres are formed on burning coals at thermal power plants (TPP); they enter into the composition of entrainment ash [7]. As to their properties, cenospheres extracted from power ashes are close to hollow microspheres obtained by commercial methods from a melt. It is important to note that the cost of hollow cenospheres isolated from the entrainment ashes obtained at thermal power plants is several times lower than those obtained artificially by commercial methods.

Samples of the cenospheres investigated in the present work were prepared at the Institute of Chemistry and Chemical Technologies of the Siberian Branch of the Russian Academy of Sciences in Krasnoyarsk. As a raw material for obtaining cenospheres we used concentrates of ashes from the Reftin Water-Power Hydroelectric Station (series R) fired with coals from the Ékibastuz coal basin. The separation of the narrow fractions of cenospheres was made following a technological scheme that involves the following stages: aerodynamic separation of particles, separations through a system of sieves, and also the hydrodynamic, magnetic, and granulometric separations [8–10]. In the final outcome we obtained specimens of original HM-R-5A-0.16-mm cenospheres characterized by the diameter limited from above by about $160\ \mu\text{m}$ and with an average wall thickness of about $8\ \mu\text{m}$, with the bulk density of a sample being $0.43\ \text{g/m}^3$. The size of the particles varied within the limits from 35 to $155\ \mu\text{m}$, with an average value of about $70\ \mu\text{m}$. As to their chemical composition, isolated cenospheres represent multicomponent $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--F}_2\text{O}_3\text{--CaO--MgO--Na}_2\text{O--K}_2\text{O--P}_2\text{O}_5\text{--MnO}$ systems with the content of glass phase and mullite phase of about 62.8 and 35.5 wt.%, respectively, and of $\text{Al}_2\text{O}_3 \sim 39\ \text{wt.}\%$. According to the data of electron microscopy, a sample of cenospheres contains both smooth spherical particles and a large number of particles with a porous envelope of irregular shape (Fig. 6).

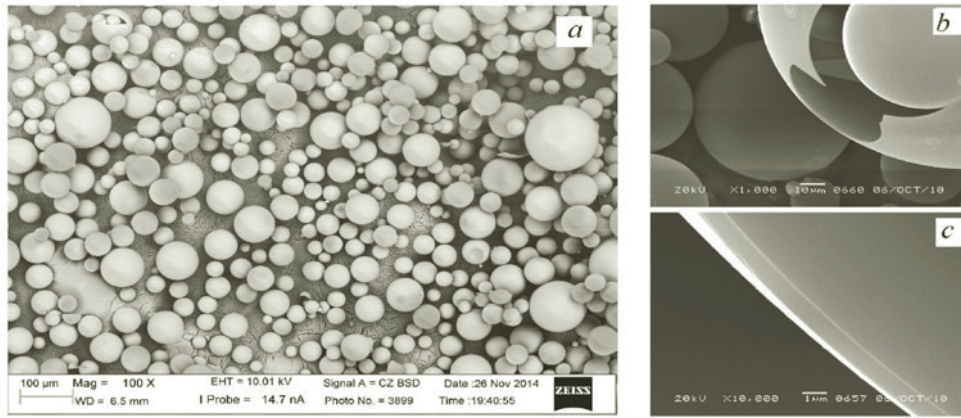


Fig. 3. Photographs of MS-V-1L microspheres.

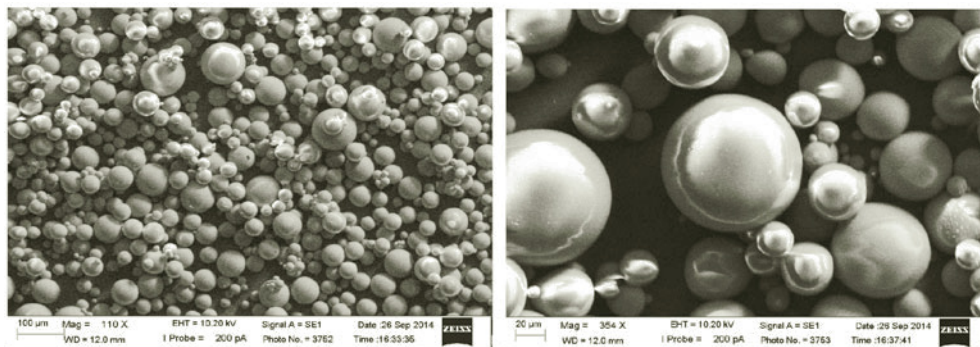


Fig. 4. Photographs of MS-VP-A9 microspheres.

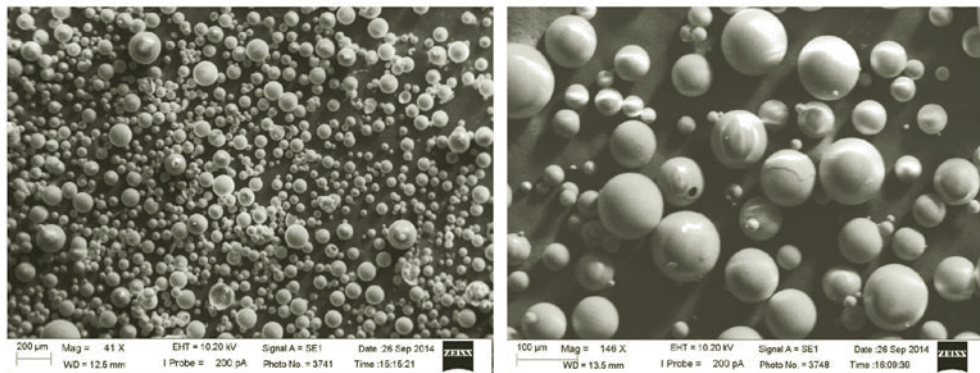


Fig. 5. Photographs of silica microspheres.

To obtain a sorbent with enlarged permeability to helium, original HM-R-5A cenospheres were subjected to additional sizing and treatment including the decrystallization of the particle envelopes. A narrow fraction of nonperforated NM-R-5A-0.063+0.5-mm cenospheres of smaller size was obtained (the particles were shifted through a system of sieves with meshes of size 63 and 50 μm , with the average diameter of particles 57 μm , envelope thickness $\sim 3 \mu\text{m}$), with the bulk density of the sample 0.41 g/m^3 . To increase the fraction of the crystalline phase and reduce the content of oxides-modifiers, the cenospheres were subjected in the glass phase to additional thermal treatment at 1000 $^\circ\text{C}$ with air or methane as a working medium. In this case, in the envelope of the particles an additional phase of mullite is formed that differs from the original one by the smaller size of crystals, which may lead to an increase in the permeability of the vitrocrySTALLINE envelope to helium along the "mullite-glass" interfaces.

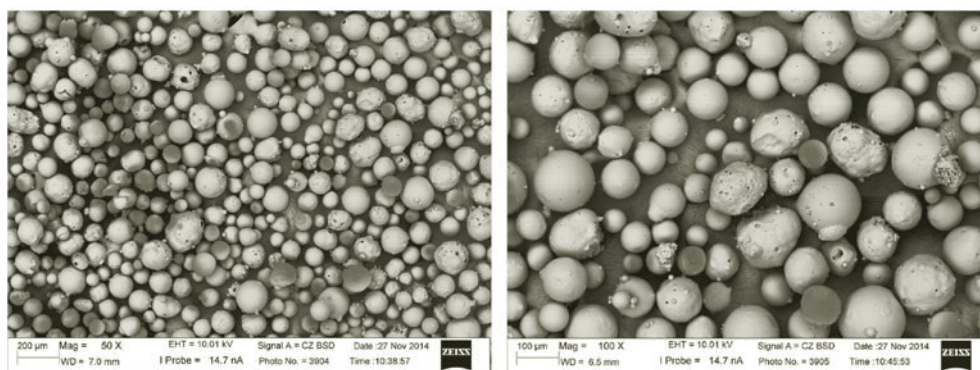


Fig. 6. Photographs of HM-R-5A-0.16-mm cenospheres.

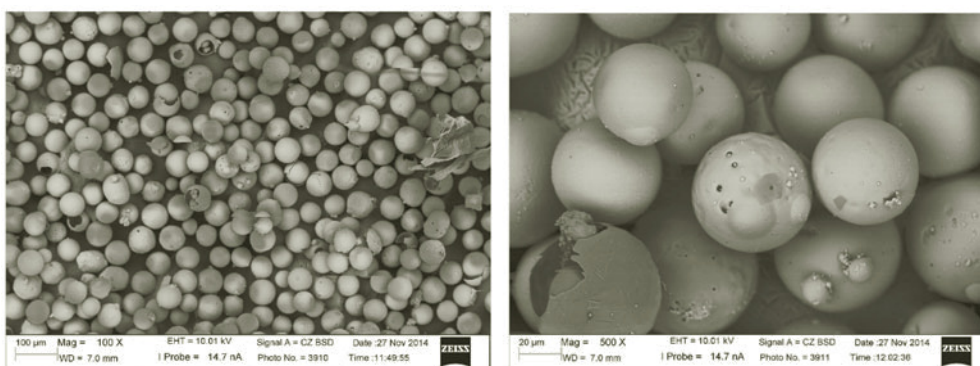


Fig. 7. Photographs of HM-R-5A-0.063+0.05-mm cenospheres thermally treated at a temperature of 1000°C.

The electron scanning microscope images of the cenospheres that were thermally treated additionally are presented in Fig. 7. The picture shows that the majority of particles have a spherical shape and a smooth surface.

Checking of the Impermeability of Sorbents to Air and Methane. Prior to carrying out experiments to investigate the sorption and desorption of helium by cenospheres and microspheres, experiments were run with air and methane as working gases. Figure 8 presents a graph of the pressure variation in the adsorber depending on time for various sorbents (with air or methane as a working medium). It is seen from the figure that the pressure remains practically invariable over a long period of time and that some pressure fluctuations are connected with temperature changes inside the room where the rig was located. This points to the impermeability of the tested sorbents to air and methane.

Experimental Procedure. Experiments on sorption and desorption of helium by different types of sorbents were carried out on a test rig (Fig. 1) by the technique the essence of which is shown schematically in Fig. 9.

Preliminarily the adsorber filled with a test sorbent is evacuated and then it is filled with a working gas (helium or its mixture with air, methane, etc.) up to a certain initial pressure — stage 1. The time for gas admission, usually taking several seconds, changes insignificantly depending on the magnitude of the initial working pressure. After the gas admission, all of the stop valves are closed, and the value of the pressure in the adsorber is recorded. Due to the difference between the partial pressures of helium outside and inside the particles, the process of sorption takes place by means of diffusion through the envelopes of the microspherical membranes — stage 2. Next, directly after the process of sorption, the residual gas is removed from the adsorber by relieving the pressure to atmospheric pressure with subsequent evacuation by a vacuum pump — stage 3 on the diagram. After the evacuation, the stop valves are closed and the pressure inside the vessel is recorded. In this case, due to the reverse pressure drop of gases outside and inside the particles, the gas is desorbed from the inside of the particles into the free volume of the adsorber — stage 4.

The pressure variation in the adsorber with time is recorded onto the hard disk of a computer with a certain interval that varies from 1 s to 1 min depending on the intensity of the sorption/desorption rates. Experiments were run at a temperature in the adsorber $20 \pm 3^\circ\text{C}$.

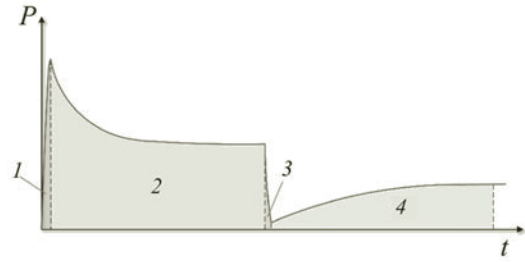
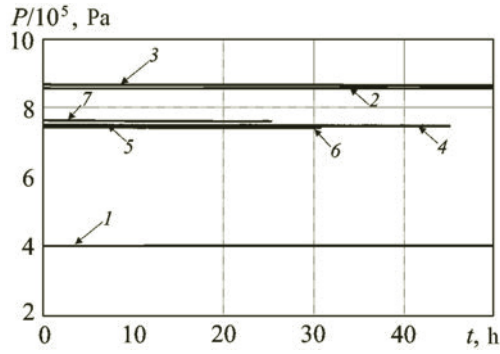


Fig. 8. Change of pressure in the adsorber with different types of sorbent with time, with air as a working medium: 1) MS-V-1L microspheres; 2) MS-VP-A9 microspheres; 3) silica microspheres; 4) HM-R-5A-0.16-mm cenospheres; 5) HM-R-5A-0.16-mm cenospheres (1000°C), with methane as a working medium; 6) MS-V-1L; 7) HM-R-5A-0.16-mm.

Fig. 9. Schematic diagram of an experiment: 1) admission of the working gas into the adsorber with a sorbent; 2) process of gas sorption by a sorbent; 3) pressure drop/evacuation; 4) process of desorption

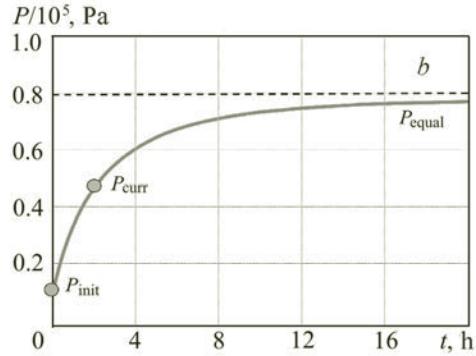
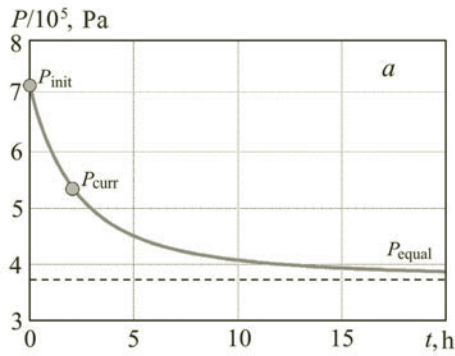


Fig. 10. Characteristic graphs of pressure variation in the processes of sorption (a) and desorption of helium (b) in dimensional form.

Experimental Results. To compare the experimental results obtained at different initial gas pressures, it turned out to be convenient to represent experimental data in the form normalized by the technique described below. Figure 10 shows the experimentally obtained typical graphs in a dimensional form for helium sorption and desorption in the form of pressure variation in time in the free volume of the adsorber. It is seen from the graphs that the process of sorption is characterized by the pressure drop due to the helium absorption by the sorbent, whereas the process of desorption is characterized by the increase of pressure as a result of helium liberation from the sorbent.

Thereafter we normalize the experimental data on pressure basis by the following formula:

$$P_{\text{norm}} = \frac{P_{\text{curr}} - P_{\text{equal}}}{P_{\text{init}} - P_{\text{equal}}}, \quad (1)$$

where P_{norm} , P_{curr} , and P_{init} are the normalized, current, and initial pressures; P_{equal} is the equilibrium pressure of the helium-carrying mixture at the equality of the partial pressures of helium in the outer volume of the reactor and in the inner volume of the microspherical objects. In those cases where it was difficult or impossible to reach the equilibrium pressure P_{equal} , its value was calculated theoretically with account for the relationship between the free and interior volumes. As a result, after carrying out such transformation, the sorption/desorption graphs practically coincided and took the characteristic form shown in Fig. 11, which reveals the universal character of the change in the normalized pressure independently of the initial working pressure and of the process considered.

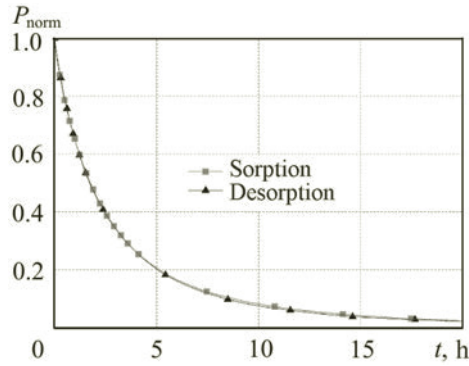


Fig. 11. Graphs of normalized pressure variation in the processes of sorption/desorption.

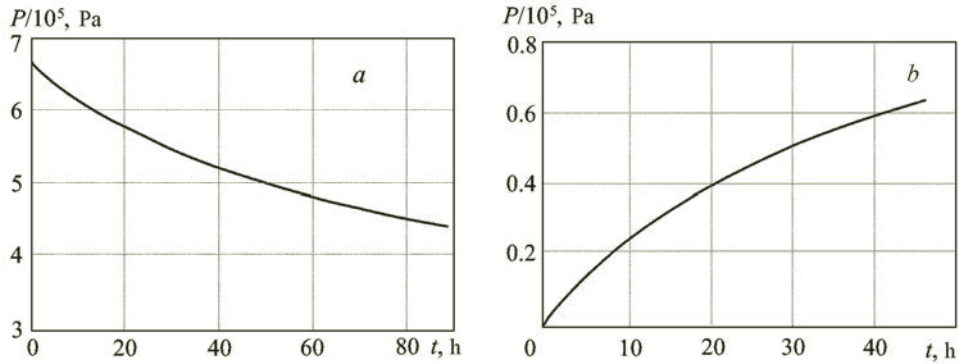


Fig. 12. Helium pressure variation in the adsorber with MS-V-1L microspheres at the initial pressure $P_{\text{init}} = 0.67$ MPa in processes of sorption (a) and desorption of helium (b).

Sorption and Desorption of Helium by Various Sorbents. Next, we consider the results of a series of experiments on sorption and desorption of helium by different types of sorbents. The experiments were carried out with pure helium and with air–helium or methane–helium mixtures at different initial working pressures of the gas in the adsorber. Figures 12–16 present characteristic dimensional curves of the change in the current pressure of helium P_{curr} in the adsorber: the drop in the processes of sorption (the left graphs) and of growth in the processes of desorption (the right graphs).

It is seen from the graphs of Fig. 12 that the pressure in the adsorber with MS-V-1L microspheres changes substantially with time. As the vessel is practically hermetically sealed, the observed drop in the pressure is explained by the penetration of helium inside the particles, i.e., the process of helium sorption by microspheres takes place. The substantial decrease in the rate of pressure variation in the free volume of the adsorber with time is also observed. This occurs because the difference between the partial pressures of helium inside the vessel and inside the microspheres decreases in the course of the process of sorption, which leads as a result to a decrease in the rate of sorption. From this it follows that the process of sorption is a long one and theoretically must continue until the complete equalization of the pressures in the adsorber and inside the microspheres. After the process of sorption, the gas that was left in the adsorber is removed by relieving the pressure to the atmospheric one with subsequent evacuation to a pressure of the order of 0.01 MPa. As a result, the reverse differential pressure of helium is achieved outside and inside the particles, which provides conditions for the progress of the process of desorption. The subsequent increase of the pressure in the adsorber is a consequence of the helium desorption from the microspheres. It should be noted here that the absolute rates of the process of helium desorption by microspheres are substantially lower as compared with the rates of the sorption process. This is explained by the different pressure drops in the adsorber and inside the microspheres in both cases. Thus, a more complete extraction of helium from the microspheres can be achieved by means of multiple successive repetition of the above-described procedure of desorption or in the case of constant pumping out of helium liberated from the particles in order to attain a maximum possible difference of the partial pressures of helium outside and inside the particles. It should be noted here that for the MS-V-1L sorbent the rates of the investigated processes are low enough, namely, the processes of sorption/desorption take several days.

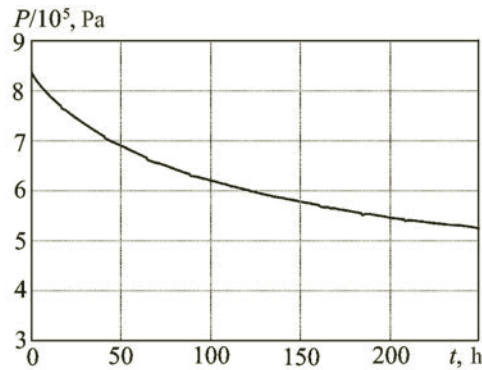


Fig. 13. Sorption of helium in the adsorber with MS-VP-A9 microspheres at the initial pressure $P_{\text{init}} = 0.84$ MPa.

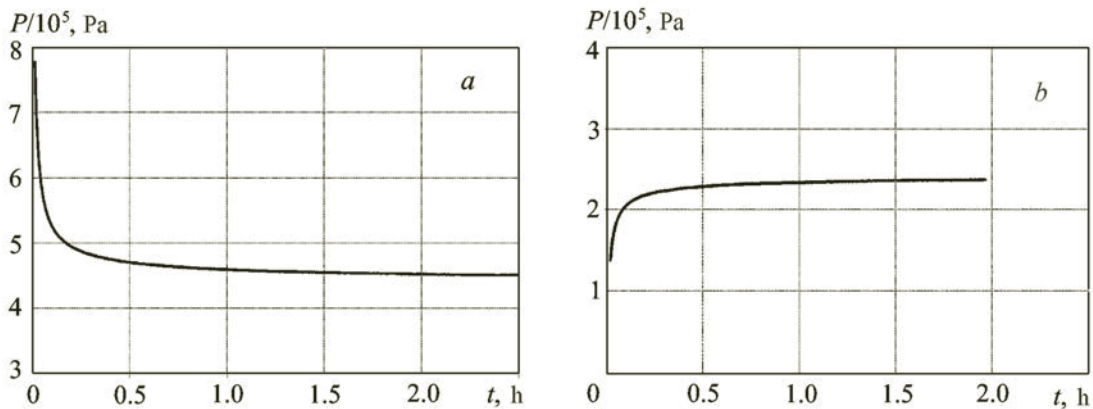


Fig. 14. Variation of helium pressure in the adsorber with silica microspheres at the initial pressure $P_{\text{init}} = 0.78$ MPa in the processes of sorption (a) and desorption (b).

Analogous experiments were carried out for MS-VP-A9 microspheres at the initial helium pressure in the adsorber $P_{\text{init}} = 0.84$ MPa. The character of the pressure drop of helium in the adsorber as a result of its sorption by MS-VP-A9 microspheres is the same as in the case of MS-V-1L microspheres, i.e., with very low pressure drop rates. As follows from Fig. 13, the equilibrium value of helium pressure in the adsorber was not reached even in 250 h.

The next test sample consisted of silica microspheres that displayed a considerable increase in the rate of the processes investigated (Fig. 14). The high rate of absorption and liberation of helium required some correction of the experimental procedure. Namely, it was necessary to accelerate the process of helium admission into the adsorber, and second, to provide for the reverse pressure differential of helium outside and inside the particles in the course of desorption, the pressure was dropped to atmospheric bypassing the stage of evacuation. This was done because the duration of the processes of sorption/desorption for silica microspheres becomes commensurable with the time of admission/discharge of the gas and evacuation of the setup. In this case, qualitatively the character of the sorption and desorption dependences is similar to the available dependences for the MS-V-1L and MS-VP-A9 microspheres: the pressure of helium changes monotonically due to its penetration through the particle walls. However, due to the higher rates of absorption and liberation of helium by the sorbent, it was possible in the experiment to follow the processes of sorption/desorption up to the complete equalization of pressures inside and outside of particles within the accuracy of the pressures measured. Actually for the silica microspheres the equilibrium value of the pressure was achieved during 1 h.

When the cenospheres obtained from the entrainment ashes of the Reftinsk thermal power plant are used as a sorbent, this also made it possible to substantially accelerate the processes of sorption/desorption of helium as compared with soda borosilicate microspheres. As follows from Fig. 15, the character of the sorption and desorption dependences for the HM-R-5A-0.16-mm cenospheres is qualitatively similar to the corresponding dependences for microspheres. Here, just as in the case of silica microspheres, for the HM-R-5A cenospheres we managed to follow the processes of sorption/desorption up to the complete equalization of the pressures inside and outside of particles, which required about 20 h for the given type of sorbent.

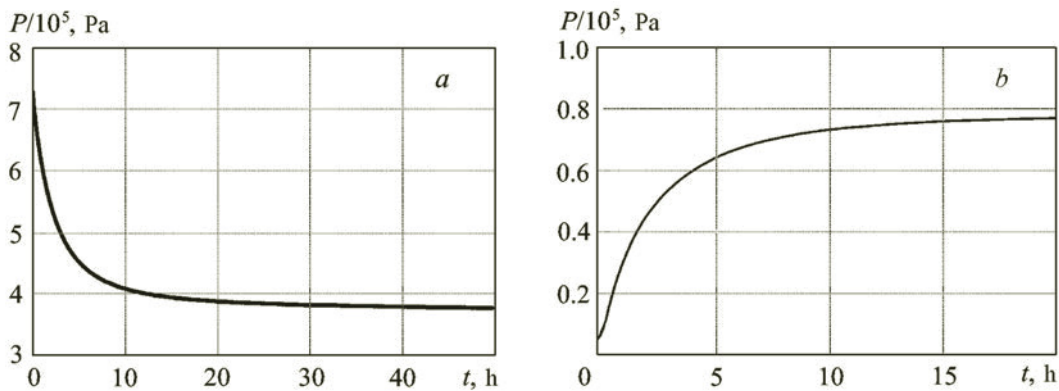


Fig. 15. Variation of helium pressure in the adsorber with HM-R-5A-0.16-mm cenospheres at the initial pressure $P_{\text{init}} = 0.72$ MPa in the processes of sorption (a) and desorption (b).

It is not necessary that an equilibrium pressure of helium in the adsorber be reached in the course of one cycle of sorption or desorption. Thus, for example, as follows from Fig. 15, for the particles to absorb 80% of helium of the maximally attainable value at equal partial pressures, only 5 h are needed. After which one may discharge the remaining gas or the depleted helium-containing mixture into another adsorber, evacuate the free volume in the initial adsorber, and to go over in it to the stage of desorption. Here too it is not necessary in principle to bring the desorption to an equilibrium state. If in the course of desorption the liberated helium is constantly pumped out of the adsorber, then for the time of sorption it is possible to extract practically entire absorbed helium from the sorbent, because the partial pressure of helium inside the microparticles will always be higher than in the free volume of the adsorber.

As a result, for the time needed to reach an equilibrium pressure only in the course of one stage of sorption/desorption of helium (about 40 h), it is possible to carry out eight incomplete (up to 80%) cycles of sorption and seven cycles of desorption and in the final outcome to extract a much greater amount of helium for the same time. If in the first case, when half the helium is absorbed in the course of sorption and it is completely extracted in the course of desorption (with pumping), 50% of the entire amount of helium can be extracted, then in the second case the amount of extracted helium may exceed 97%.

In addition to the above-described results of investigation of the processes of sorption/desorption of pure helium for HM-R-5A-0.16-mm cenospheres, we obtain data on the sorption of helium with the same sorbent for a mixture consisting of 25% helium and 75% air at the initial working pressure of mixture 0.74 MPa and for a mixture of 25% helium and 75% methane at the initial working pressure of mixture 0.33 MPa. The sorption dependences for both mixtures have a character similar to that for pure helium, with a characteristic time of achieving the equilibrium partial pressure of helium inside and outside of the cenospheres of about 20 h.

Using cenospheres of the same series but with a lower value of the mean diameter, i.e., HM-R-5A-0.063+0.05 mm, which were subjected to the procedure of thermal modification for three hours at a temperature of about 1000°C, we managed to additionally intensify the processes of sorption/desorption (Fig. 16). Ultimately, for the complete equalization of the helium pressure in the adsorber with the thermally modified cenospheres, 6 h were required and a little more than 1 h for absorbing 80% of helium.

To correctly compare the rates of helium absorption by microspheres and cenospheres, we represent all of the above-considered dimensional graphs of the processes of sorption in a normalized form.

Figure 17 presents a comparison of the rates of the processes of sorption for all the types of sorbents investigated in the present work. The graph is presented in a normalized form. The MS-V-1L and MS-VP-A9 microspheres displayed practically identical rates of the processes studied, with the rates of the processes themselves being considerably lower than in other samples. The HM-R-5A cenospheres displayed a considerable (more than by an order of magnitude) increase in the rates of the processes of helium absorption in comparison with the MS-V-1L and MS-VP-A9 microspheres. Here, it should be taken into account that the thickness of the cenosphere walls is much larger than in artificially prepared microspheres.

We managed to attain a considerable increase in the permeability of helium for HM-R-5A cenospheres by treating them thermally. A comparison of the dependences given in the graph for the original (line 3) and thermally modified cenospheres (line 6) shows that the sorption rates for the second type of particles increase practically by four times.

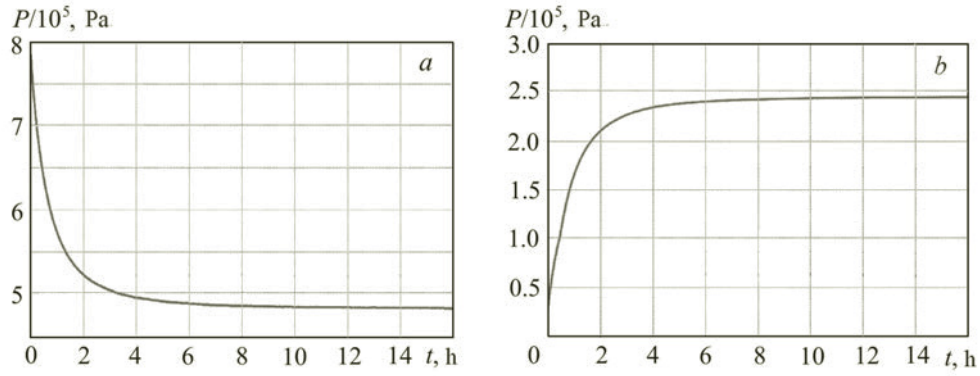


Fig. 16. Variation of helium pressure in the adsorber with HM-R-5A-0.063+0.05-mm cenospheres thermally treated additionally at 1000°C for 3 h at the initial pressure $P_{\text{init}} = 0.77$ MPa in the processes of sorption (a) and desorption (b).

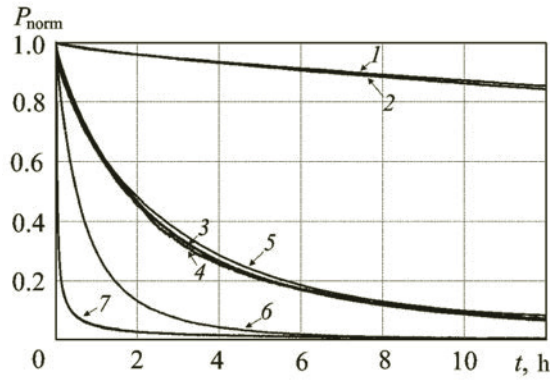


Fig. 17. Graphs of helium sorption by various sorbents in normalized form: 1) MS-V-1L microspheres; 2) MS-VP-A9 microspheres; 3) HM-R-5A-0.16-mm cenospheres; 4) HM-R-5A-0.16-mm cenospheres, air–helium mixture with 25% of helium; 5) HM-R-5A-0.16-mm cenospheres, methane–helium mixture with 25% of helium; 6) HM-R-5A-0.063+0.05-mm cenospheres (1000°C); 7) silica microspheres.

As a result, the process of the equalization of pressures for the modified cenospheres terminates in 6–8 h, whereas about 20 h was needed for the original cenospheres. In this case, the main part of helium (80% of the maximum possible value) is absorbed by the sorbent for about 1.5 h, whereas 5–6 h were required for the original cenospheres.

Among all the sorbents investigated, silica microspheres displayed the highest permeability to helium. The complete equalization of pressures outside and inside the silica microspheres required less than an hour and only 10–12 min for the possible absorption of 80% of helium.

Using the results of experimental investigations of helium sorption by different types of microparticles, we calculated the values of their permeability to helium. The technique for the quantitative estimation of the permeability of hollow microspherical particles to helium is given in works [11, 12] where, to describe the process of the penetration of the gas inside the particles, use was made of the equation of the diffusion of gases through a membrane:

$$J = \frac{dM}{dt} = \frac{KS}{d} (P_{\text{out}} - P_{\text{in}}) = Q (P_{\text{out}} - P_{\text{in}}) = Q_{\text{sp}} m (P_{\text{out}} - P_{\text{in}}). \quad (2)$$

Since hollow spherical particles with a complex diffusion surface S and variable wall thickness d are used as a membrane, it seemed difficult to directly calculate the permeability coefficient K from experiment. Therefore, usually use is made of the value of specific permeability Q_{sp} , by means of which it is possible to estimate the value of K under certain assumptions. Table 1 lists the mass and calculated values of the absolute and specific permeabilities of the test sorbents to helium.

TABLE 1. Values of Helium Permeability

Sorbent	Sorbent mass, g	Q , mole/(Pa·s)	Q_{sp} , mole/(Pa·s·g)
MS-V-1L microspheres	109	$2.1 \cdot 10^{-13}$	$1.9 \cdot 10^{-15}$
MS-VP-A9 microspheres	114	$2.3 \cdot 10^{-13}$	$2.1 \cdot 10^{-15}$
Silica microspheres	110	$4.5 \cdot 10^{-10}$	$4.1 \cdot 10^{-12}$
HM-R-5A-0.16-mm cenospheres	236	$7.8 \cdot 10^{-12}$	$3.3 \cdot 10^{-14}$
HM-R-5A-0.063+0.05-mm cenospheres	211	$1.5 \cdot 10^{-11}$	$7.2 \cdot 10^{-13}$

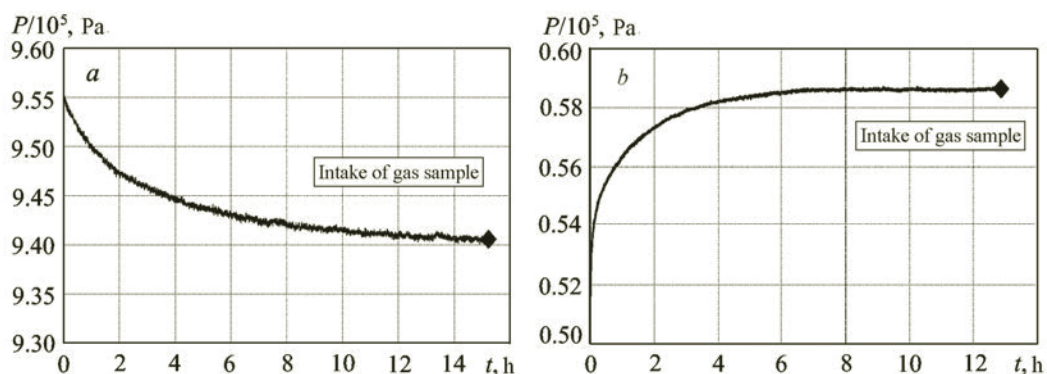


Fig. 18. Variation of helium pressure in the adsorber with HM-R-5A-0.16-mm cenospheres in consecutive processes of sorption (a) and desorption (b).

It should be noted that the above-described mathematical model of the process of sorption is simplified, so that it ignores a number of factors such as the inhomogeneity of a real sorbent in its size, wall thickness, etc. The method of calculation of the permeability of hollow spherical particles to helium with account for their dispersion size distribution is outlined in [13, 14].

Enrichment of an Air–Helium Mixture. Bearing in mind the results of experimental investigations of the permeability of microspherical membranes to helium, we considered a certain feasible procedure of the process of enrichment of a helium-containing mixture with helium. The process of the enrichment of the original mixture with helium is carried out in three stages: 1) pumping of the mixture at a high pressure into the adsorber and sorption of helium by hollow particles; 2) rapid lowering of pressure in the adsorber with subsequent desorption of helium from the particles at a low external partial pressure of helium; 3) pumping-out of the gas enriched with helium.

Experiments on modeling the process of the enrichment of an original mixture with helium were carried out on the experimental rig filled with HM-R-5A-0.16-mm cenospheres. An air–helium mixture with helium concentration of 2.25 vol.% was used as a helium-containing mixture. The original mixture was admitted into the adsorber up to the pressure $P_{init} = 0.95$ MPa. The process of helium sorption by cenospheres is shown in Fig. 18a. After a lapse of the time needed for the equalization of the partial pressures of helium inside and outside the cenospheres, the lean mixture (sample No. 1) was taken from the adsorber to determine the helium concentration on a chromatograph. Next, the depleted gaseous mixture was evacuated from the adsorber by means of rapid discharge with subsequent pumping out to a pressure of 0.05 MPa. This value of the pressure was chosen based on the possibilities of the equipment to extract samples for chromatographic analysis. Figure 18b presents the graph of the variation of pressure in the adsorber in the process of helium desorption from the cenospheres.

At the end of the process of desorption from the adsorber, a sample of the gas (sample No. 2) is again extracted from the adsorber. As a result of the measurement of helium concentration in the course of the experiment on helium enrichment, the following data were obtained: helium concentration in the original mixture 2.25 vol.%; 1.17 in sample No. 1, and 8.6 in sample No. 2. The data show that the helium concentration in the mixture depleted after the sorption decreased by about two times and increased almost by four times in the enriched mixture. In principle, on the basis of the proposed procedure a much

greater degree of enrichment of the mixture with helium can be obtained. Thus, in the course of desorption from particles into the free volume of the adsorber, pure helium is liberated from the particles and the main limiting factor of the enrichment is the presence of a residual depleted mixture in it. Consequently, to increase the degree of enrichment of the mixture with helium, the adsorber must be more fully freed from the depleted mixture.

Conclusions. In order to determine the basic characteristic parameters of microparticles for their possible application in the membrane-sorption technologies of extraction of helium from a natural gas, we carried out experimental investigations of helium sorption and desorption by different hollow microparticles: MS-V-1L and MS-VP-A9 glass microspheres; silica microspheres; HM-R-5A-0.16-mm cenospheres; thermally modified HM-R-5A-0.063+0.05 mm cenospheres. It has been established that these types of sorbents are impermeable to air and methane and permeable to helium and that they possess a high selectivity in relation to these gases.

The similarity between the sorption and desorption processes, the rates of which are mainly determined by the pressure difference outside and inside hollow particles, has been demonstrated. It is shown here that the presence of an accompanying gas in the external volume of the adsorber does not in practice exert its influence on the processes of helium sorption.

The coefficient of permeability of helium and correspondingly the times of permeability of helium and the times of sorption–desorption processes for the investigated sorbents, vary in wide ranges. Synthetic aluminosilicate microspheres have displayed the lowest rates of the investigated processes, with the permeability of MS-V-1L and MS-VP-A9 microspheres being actually identical despite the substantial difference between the wall thicknesses of particles. The cenospheres, i.e., the particles separated from the entrainment ashes of thermal power plants, displayed a higher permeability to helium provided they were purified and processed adequately. The rates of the processes of absorption for HM-R-5A-0.16-mm cenospheres are higher than analogous ones for aluminosilicate microspheres by about 40 times, and for thermally modified HM-R-5A-0.063+0.05 mm cenospheres, by about 70 times. Silica microspheres have displayed the highest coefficient of permeability to helium.

It is shown that by modifying the original material of particles one can substantially alter the permeability of a material to helium. Thereby, depending on the type of a sorbent, the characteristic times of sorption can change from several minutes to several days, which provides wide possibilities of varying the operation regimes of membrane-sorption installations depending on the technological scheme of the process and required efficiency.

This work was carried out with financial support from the integration project of the Siberian Branch of the Russian Academy of Sciences No. 91, the program II.3.5 of the Russian Academy of Sciences in the strategic directions of science development, the grant NSh-679.2014.1 from the President of the Russian Federation for supporting the leading scientific schools, and from the grant No. MK-6657.2012.1 of the President for supporting young scientists.

NOTATION

d , envelope thickness, m; J , mass flux, mole/s; K , coefficient of material permeability, mole·m/(Pa·g·m²); m , mass of a sorbent, g; P_{out} and P_{in} , helium pressure outside and inside particles, respectively, Pa; Q ; permeability, mole/(Pa·s); Q_{sp} , specific permeability, mole/(Pa·g·s); S , diffusion surface, m².

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