The Influence of Acidic Treatment and Mechanical Grinding on the Structural Characteristics and Morphology of Pores in Iron-Containing Sodium-Borosilicate Porous Glasses

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Abstract—The method of low-temperature equilibrium nitrogen adsorption and desorption has been employed to study the porous structure and morphology of porous glass (PG) with a composition of (wt %) 1.54Na₂O·6.02B₂O₃·82.24SiO₂·10.20Fe₂O₃ as depending on the acidic treatment of initial two-phase glass and mechanical grinding of PG obtained by the through acidic leaching of liquation glass with a two-matrix structure. It has been found that all studied PG samples have a polymodal mesopore size distribution and contain micropores. Judging by the desorption isotherms, the main modes of the mouth sizes of the mesopores correspond to 3.6–3.8 and 23–25 nm. The micropores have sizes of 1.1–1.4 nm. The calculated structural coefficient indicates that the mesopores have predominantly cylindrical shapes. The comparison between the modes in the distribution curves obtained from the data on adsorption and desorption has indicated the presence of bottle-shaped and conical pores. Mechanical grinding of PGs to the powdered state does not changes the general pattern of the adsorption-desorption isotherms but enhances the volume of mesopores due to the opening of internal dead-end pores and widens the mode of 24-nm liquation channels. An increase in the duration of the acidic leaching under boiling from 7 to 14 h leads to a rise in the mesopore volume and average mesopore diameter by 35 and 25%, respectively. At the same time, the fraction of the micropores in the total pore volume decreases by nearly 10%, while the 8.0-nm mode increases. The results obtained may be useful for improving the synthesis conditions and widening the application fields of PGs exhibiting magnetic properties.

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INTRODUCTION

The practical and scientific interest in porous glasses (PGs), which permanently grows in 21th century, is due to their unique properties and widening fields of application [1]. PGs exhibit valuable properties, such as the chemical, thermal, and microbiological stability; optical transparency in the visible spectral region; and the possibility of varying mesopore sizes in wide ranges. PGs are used as membranes, adsorbents, catalyst carriers, and nanocomposites, as well for the production of microfluid chips, biochemisensors, and optical and laser systems [2-7].

High-silica PGs are obtained by the through selective chemical leaching of two-phase alkali borosilicate glasses. For successful PG synthesis, it is necessary to have a two-matrix structure of liquation phases, which is obtained by a special thermal treatment of glasses after melting. Upon acidic leaching, alkali borate components of the chemically unstable phase are removed, whereas the silica phase forms a PG matrix with a through porosity. The unstable phase also contains a certain fraction of silica, which, after the acidic leaching, remains preserved as colloidal formations (globules of so-called "secondary silica") in the pore space [8, 9].

In recent years, iron-containing sodium-borosilicate (ISBS) glasses attract especial attention. Such glasses are prone to crystallization of magnetite (Fe_3O_4) , which possesses ferromagnetic properties, thereby determining their potential application in medicine [10] and spintronics [11-13], as components of electric ovens for induction heating [14], etc. In particular, two-phase ISBS glasses containing magnetite in the silica matrix were used to obtain magnetic PGs by acidic leaching [11, 15, 16]. Such PGs are promising matrices for creating composite materials of the "carrier-dopant" type. For example, the filling of the pore space in magnetic PGs with ferroelectrics makes it possible to obtain materials possessing simultaneously ferroelectric and magnetic orders. Such composites with multiferroid properties are of interest from the viewpoint of their use for creating various

sensors, detectors, elements of energy-independent memory, durable record media possessing high stability and reliability (FeRAM and FLESH memory), etc. [17].

For successful synthesis and subsequent application of PG-based materials, it is necessary to have information on the parameters of their pore space as depending on various factors, such as the production conditions of PGs, their subsequent mechanical treatment, etc. Previously, the chemical stability of ISBS glasses with a constant silica content (70 mol % SiO₂) was studied, PG samples were prepared as plates, and some of their structural parameters were determined [17–19]. However, the fine structure of the pore space in the ISBS glasses and the morphology of their pores remain to be investigated. The pore structure predetermines the most important properties of PGs, i.e., diffusion, sorption, optical, adhesion, capillary, catalytic, and other characteristics [1, 8, 20–23].

The goal of this work is the detailed study of the porous structure and pore morphology of iron-containing PGs by the example of magnetite-containing glass of the following composition (wt %): $1.54Na_2O.6.02B_2O_3.82.24SiO_2.10.20Fe_2O_3$ [17] and the influence of mechanical grinding and the duration of acidic leaching of a two-phase glass on its pore structure. The results obtained may be useful for improving the synthesis conditions and widening the application fields of magnetic PGs.

OBJECTS AND METHODS OF INVESTIGATION

The objects of the study were three iron-containing PG samples prepared by through acidic leaching of liquation ISBS glass with a two-matrix structure. Initial one-phase glass was synthesized by melting of an initial batch mixture followed by annealing, which removed internal stresses, by the procedure described in [17, 19]. The glass samples were prepared as blocks. According to analysis data, unleached initial glass (denoted as K12) had the following composition (mol %): $5.80Na_2O \cdot 13.63B_2O_3 \cdot 70.84SiO_2 \cdot 9.72Fe_2O_3$ To form the two-phase (two-matrix) liquation structure with interpenetrating phases, the glass was subjected to thermal treatment at 550°C for 144 h. Then, the blocks were mechanically treated to obtain samples as plates of desired sizes. Polished samples with sizes of 10×10 \times 1 mm³ were obtained from these plates. Before the chemical leaching, the polished samples of the twophase glass had no through porosity.

Using X-ray energy-dispersive spectroscopy, it was previously revealed that the components were uniformly distributed over the thickness of the initial sodium borosilicate glasses (including iron-oxidedoped glasses with a composition close to that of glass K12) and the PGs based thereon (see, e.g., [24]). Thus, the chemical composition of the PG surface

COLLOID JOURNAL Vol. 84 No. 1 2022

corresponded to the chemical composition of the PG bulk.

The conditions for the preparation of PG samples studied in the work are presented in Table 1. To create the through porosity, two-phase glass K12 was subjected to acidic leaching by boiling it in an aqueous 3 M HCl solution (Table 1). Among the three studied samples, two samples (K12-7_{pl} and K12-14_{pl}) were prepared as polished plates with sizes $10 \times 10 \times 1 \text{ mm}^3$ at different durations of leaching with HCl (7 and 14 h, respectively, Table 1). A ground sample (K12-7_{pow}) was obtained from sample K12-7_{pl} by attriting in a mortar into a powder with an average particle size of about 20 µm. The particle size was measured using a MIN-8 optical microscope.

The structure of the unleached two-phase glass was studied by transmission electron microscopy (TEM) with an EM-125 instrument (OAO SELMI, Russia) operating at an accelerating voltage of 75 kV and a resolution of ~ 10 nm using platinum/carbon replica method by the procedure described elsewhere [8, p. 68].

The structural characteristics and morphology of pores in the iron-containing PGs were studied by analyzing the equilibrium nitrogen adsorption/desorption isotherms obtained with a NOVA 1200e analyzer (Quantachrome Instruments, United States) at liquid nitrogen temperature (77 K). The isotherms were measured within relative pressure range $p/p^0 = 0.005-0.988$, where mesopores (sizes of 2 - 50 nm, according to the IUPAC nomenclature [26]) and large micropores (1–2 nm) were recorded.

As the relative pressure is elevated, micropores are filled in the range of low pressures, monolayer adsorption occurs in the BET region, and mesopores are filled by the capillary condensation mechanism at moderate and high relative pressures [27].

The mesopores were analyzed on the basis of the isotherms of nitrogen adsorption and desorption at 77 K in the range of moderate and high relative pressures in accordance with the capillary condensation mechanism using the modified Barrett–Joyner–Halenda (BJH) method. The micropores were diagnosed in accordance with the volume filling mechanism at low relative pressures of nitrogen using the dependence of the partial pressure on the micropore diameter, with the dependence being found in terms of the density functional theory [28, 29].

Experimental equilibrium isotherms of nitrogen adsorption and desorption at 77 K that combine both the range of moderate and high relative pressures and the range of low pressures were approximated by the following pentamodal equation comprising the Boltzmann functions [28–30]:

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Sample no.	Sample 1	Sample 2	Sample 3	
Sample denotation	K12-7 _{pl}	K12-7 _{pow}	K12-14 _{pl}	
Sample geometry	Plate	Powder	Plate	
Sizes	$10 \times 10 \times 1 \text{ mm}^3$	≈20 µm	$10 \times 10 \times 1 \text{ mm}^3$	
Chemical composition (wt %)	$1.54 Na_2 O \cdot 6.02 B_2 O_3 \cdot 82.24 Si O_2 \cdot 10.20 Fe_2 O_3$		Analysis was not performed	
Synthesis conditions	Leaching in an aqueous 3 M HCl solution under boiling (7 h) followed by washing with distilled water (5 days) and drying at 120°C in a drying oven (1 h)		Leaching in an aqueous 3 M HCl solution under boiling (7 h), followed by exposure in the acid at room temperature (16.5 h) and sequent boiling (7 h) followed by washing in distilled water (5 days) and dry- ing at 120°C (1 h); total chemical etching duration of 30.5 h, including 14 h under boiling*	
Mechanical treatment after leaching	No	Attrition in a jasper mortar	No	

Table 1. Formation conditions of PG samples studied in the work

* Previously, the leaching of sodium-borosilicate glass with a close composition has shown that, after the stationary regime of leaching at a constant temperature is established, an increase in the duration of the acidic treatment of the glass has no effect on the leaching rate [24].

$$a(p) = \sum_{i=1}^{5} \frac{a_i^0}{1 + \left(\frac{d_i}{d(p)}\right)^{1/\ln s_i}} + a_s + a_0,$$

where *a* is the adsorption value at pressure *p*, a_i^0 is the maximum adsorption value upon volume filling for each type of pores, d_i is the effective pore diameter of each mode, d(p) is the dependence of the diameter of pores on the partial pressure at which their volume filling occurs, s is the Boltzmann function parameter that characterizes the peak width in the differential distribution curve, a_s is the adsorption on the internal pore surface, and a_0 is the adsorption on the external surface of a PG sample. According to the ideology of the BJH method, a decrease in the internal surface area of pores upon their volume filling was taken into account in the calculations. In addition, a rise in the adsorption on the small external surface of PGs and new data on the pressure dependence of the adsorbed film thickness [31] were taken into account.

Corresponding differential pore diameter distribution curves obtained from integral equilibrium adsorption isotherms are described by the following equation:

$$\frac{\partial(a)}{\partial(\lg d)} = \sum_{i=1}^{5} \frac{a_i^0 \left(\frac{d_i}{d}\right)^{1/\ln s_i}}{\log s_i \left[1 + \left(\frac{d_i}{d}\right)^{1/\ln s_i}\right]^2}.$$

RESULTS AND DISCUSSION

Sample K12-7_{pl}

According to the IUPAC classification [32], adsorption–desorption isotherms of the K12-7_{pl} sample (Fig. 1) are most likely attributed to type-IV isotherms, which are characterized by the capillary condensation and hysteresis loops. The desorption branch indicates that the pore mouths have a polymodal size distribution with two main modes. The steep rise of the isotherm in the range of low relative pressures attests to the presence of micropores.

According to the ideology of the BJH method, having known the density of liquid nitrogen at 77 K (34.67 cm³/mol), differential curves for pore volume V distribution over pore diameters d (Fig. 2) were calculated by approximating the isotherms of adsorption and desorption by a polymodal equation with five modes [29]. The regression coefficient for the approximation by the polymodal equation was 0.9997-0.9999.

The pore distribution curve obtained from the desorption branch show two main modes in the region of mesopores with sizes of 3.6 and 25 nm and one mode in the region of micropores with a size of 1.1 nm. Moreover, small wide modes of mesopores are present at 2.3 and 7.0 nm. In addition, the two main modes of mesopores (3.6 and 25 nm) have been diagnosed by the classical BJH method. The calculation performed by the Dubinin–Astakhov method also confirmed the presence of micropores with sizes of 1–2 nm, although this method can be correctly used only for predominantly microporous samples.

COLLOID JOURNAL Vol. 84 No. 1 2022



Fig. 1. Isotherms of nitrogen adsorption and desorption measured at 77 K for ISBS PG K12 in the forms of a plate and a powder after acidic leaching for 7 h; samples K12- 7_{pl} and K12- 7_{pow} .

According to the TEM data (Fig. 3), the thermal treatment of glass K12 leads to the formation of a distinct two-matrix structure containing inclusions of crystalline magnetite, with this circumstance being the necessary condition for obtaining PGs as a result of subsequent chemical etching. According to the TEM data, the average diameter of liquation channels formed in the places of the chemically unstable phase is 25–35 nm. The maximum pore size determined from the adsorption–desorption isotherms (Fig. 1) agrees with this value.

The pore distribution curve, obtained from the adsorption branch somewhat differs from the distribution curve for the desorption branch (Fig. 2), thus indicating the presence of pores with more complex shapes than those represented by the simple geometric models. The pore diameters determined from the desorption data (1.1 and 3.6 nm) are smaller than those obtained from the adsorption data (1.2 and 9.5 nm), which is commonly inherent in bottleshaped pores. At the same time, the maximum-size pores, which correspond to the liquation channels (Fig. 3), seem to have some conicity; therefore, adsorption begins in the pore regions with smaller diameters, while desorption starts from the regions with larger diameters. Accordingly, the adsorption and desorption data have attested to maximum pore diameters of 18.5 and 25.0 nm, respectively.

The structural characteristics calculated for PGs from the low-temperature isotherms of nitrogen adsorption and desorption on sample K12- 7_{pl} are presented in Table 2.

The total pore volume corresponding to the final value of the nitrogen adsorption isotherm at $p/p^0 = 0.988$, i.e., pores with diameters below 161 nm, is

COLLOID JOURNAL Vol. 84 No. 1 2022



Fig. 2. Pores diameter distribution curves for ISBS PG K12 plate after leaching for 7 h; sample $K12-7_{pl}$.

 $0.102 \text{ cm}^3/\text{g}$. The same total volume of micro- and mesopores was obtained by summing the volumes corresponding to the five modes of the adsorption iso-therm.

The micropore volume determined from the first mode of the distribution curve for the adsorption isotherm amounted to 13.3% of the total pore volume. For determining the micropore volume, the adsorption branch is preferable, because all micropores are filled with an increase in p/p^0 during the adsorption, whereas the desorption experiments come to the end at $p/p^0 = 0.005$, when the adsorbate still remains in some pores.



Fig. 3. TEM micrograph of ISBS two-phase glass K12.

Table 2. Structural characteristics of iron-containing PGs

PG sample	K12-7 _{pl}	K12-7 _{pow}	K12-14 _{pl}
Total pore volume, cm ³ /g (from equilibrium nitrogen adsorption isotherm)	0.1020	0.111	0.135
Total volume of micro- and mesopores, cm^3/g (as the sum of pore volumes in the modes according to adsorption data)	0.102	0.111	0.135
Total volume of micro- and mesopores, cm^3/g (as the sum of pore volumes in the modes according to desorption data)	0.101	0.110	0.135
Micropore volume, cm^3/g (data on adsorption mode, per- centage of the total volume is given in parentheses)	0.0136 (13.3%)	0.0104 (9.4%)	0.0163 (12.1%)
Micropore volume, cm^3/g (data on desorption mode, per- centage of the total volume is given in parentheses)	0.0121 (12.0%)	0.0130 (11.9%)	0.0141 (10.5%)
Mesopore volume, cm ³ /g (from adsorption isotherm)	0.088	0.100	0.119
Mesopore volume, cm ³ /g (from desorption isotherm)	0.089	0.097	0.121
BET specific surface area, m^2/g (nonlinear regression of adsorption isotherm at $p/p^0 = 0.05-0.2$)	110	104	114
Constant <i>C</i> of BET equation at $p/p^0 = 0.05 - 0.2$	381	300	247
BET specific surface area of mesopores, m^2/g (nonlinear regression of adsorption isotherm at $p/p^0 = 0.05-0.2$ taking into account micropore filling and constant $C = 70$)	72	70	80
BET specific surface area of mesopores, m^2/g (nonlinear regression of desorption isotherm at $p/p^0 = 0.05-0.2$ taking into account micropore filling and constant $C = 70$)	82	75	85
Specific surface area of micropores, m^2/g (difference between the total BET surface area and specific surface area of mesopores)	38	34	34
Micropore volume, cm^3/g (BET nonlinear regression and constant $C = 70$)	0.0175	0.0158	0.0157
Effective mesopore diameters, nm (adsorption isotherm,	2.30 (28.2%)	2.51 (29.2%)	3.41 (10.4%)
volume fraction of the mode in mesopore volume is given in	5.67 (18.4%)	4.11 (1.6%)	3.80 (29.7%)
parentineses)	9.45 (20.5%)	7.20 (25.7%)	7.47 (10.0%)
	18.5 (32.9%)	18.1 (43.5%)	18.1 (49.9%)
Effective mesopore diameters, nm (desorption isotherm,	2.27 (22.6%)	2.07 (8.2%)	3.23 (20.5%)
volume fraction of the mode in mesopore volume is given in	3.63 (38.1%)	3.82 (53.6%)	3.63 (30.3%)
parentineses)	6.95 (10.0%)	5.75 (5.1%)	8.02 (18.9%)
	25.0 (29.3%)	23.6 (30.0%)	23.1 (30.3%)
Average mesopore diameter, nm (adsorption)	5.13	5.56	6.43
Average mesopore diameter, nm (desorption)	4.33	4.92	5.44
Micropore diameter, nm (adsorption)	1.21	1.08	1.42
Micropore diameter, nm (desorption)	1.08	1.18	1.22
Structural coefficient of mesopores (adsorption)	4.20	3.89	4.34
Structural coefficient of mesopores (desorption)	4.00	3.81	3.82
Structural coefficient of micropores (adsorption)	3.76	2.82	3.37
Structural coefficient of micropores (desorption)	3.36	3.08	2.90

COLLOID JOURNAL Vol. 84 No. 1 2022



Fig. 4. Pore diameter distribution curves for ISBS PG K12 powder after leaching for 7 h; sample K12-7_{pow}.

The mesopore volume was calculated as the difference between the total pore volume and the volume of micropores.

The BET method is adequately applicable for determining specific surface area of only mesoporous samples [27]; therefore, processing of the data on samples containing micropores by this method is not correct, because not only the monolayer filling of mesopores, but also the volume filling of micropores, is taken into account in this case. At the same time, constant C in the equation acquires a value above 100, thereby indicating the presence of micropores with a high adsorption capacity (Table 2). Therefore, the specific surface area of namely mesopores was determined by the BET method with the nonlinear regression from the isotherms of adsorption and desorption at relative pressures $p/p^0 = 0.05 - 0.20$ taking into account micropore filling and using constant C in the BET equation equal to 70, which is characteristic of micropore-free silica adsorbents.

The difference between the total BET specific surface area and the specific surface area of mesopores may be conventionally considered to be the specific surface area of micropores. On the basis of the adsorption isotherm, it amounts to 37.6 m²/g for sample K12-7_{pl.}

Effective diameters obtained for mesopores using the approximation of the equilibrium adsorption and desorption isotherms by the polymodal dependence are presented in Table 2. The volume fractions of all modes in the total mesopore volume are presented in parentheses.

The average mesopore diameters for the equilibrium adsorption and desorption were calculated taking

COLLOID JOURNAL Vol. 84 No. 1 2022

into account the weight of each mode in the mesopore size distribution curve.

Having known the average diameter, specific surface area, and volume of mesopores, one can calculate structural coefficient K, which characterizes the prevailing shape of mesopores. For slitlike, cylindrical, and spherical pores, this coefficient is equal to 2, 4, and 6, respectively. For interglobular pores resulting from regular packing of spherical globules of secondary silica with coordination numbers (i.e., the numbers of their contacts) ranging from 4 to 12, structural coefficient K is 2.8 ± 0.2 [28].

For sample K12- 7_{pl} , structural coefficient *K* is equal to 4.0–4.2, thus predominantly corresponding to cylindrical mesopores.

For micropores, structural coefficient K is, on average, equal to 3.6, thereby indicating a contribution of interglobular pores.

Effect of Mechanical Grinding. Sample K12-7_{pow}

For sample K12-7_{pow}, the isotherms of low-temperature nitrogen adsorption and desorption (Fig. 1) were measured using the same equipment and under the same conditions as those for sample K12-7_{pl}. The pore size distribution for sample K12-7_{pow} (Fig. 4) was calculated as was done for the first (basic) sample.

The patterns of adsorption and desorption isotherms, as well as the pore size distribution curves, are, in many respects, similar for these two samples. Only for the desorption branch (pore mouths), the mode at 3.8 nm (interglobular channels) has become narrower, while the mode at 24 nm (liquation channels) has become wider. Moreover, some differences can be seen when comparing the quantitative characteristics obtained for the porous structure from experimental isotherms (Table 1).

The total pore volume and the volume of mesopores have grown by, on average, 8.8 and 10.5%, respectively, owing to an increase in the external surface of PG and the opening of dead-end pores. For the same reason, the fraction of micropores has, on average slightly decreased from 12.7 to 10.7%. The specific surface area of mesopores has decreased, whereas the average diameter of mesopores has grown by, on average, 11%. The recorded maximum micropore size (1.1-1.2 nm) has remained unchanged. The structural coefficient of mesopores has somewhat decreased possibly due to the opening interglobular pores.

Effect of Acidic Leaching Duration. Sample K12-14_{pl}

As has been shown previously, a leaching duration of 7 h is insufficient for the complete extraction of the alkali borate components of the chemically unstable phase from glass K12 [17, 18]: the degree of sodium and boron extraction is nearly 70%. The extrapolation of approximating kinetic curves for the extraction of



Fig. 5. Isotherms of nitrogen adsorption and desorption measured at 77 K for ISBS PG K12 plate after acidic leaching for 7 and 14 h; samples K12- 7_{pl} and K12- 14_{pl} .

the components to the region of long durations has indicated that the leaching duration must be doubled to reach the theoretically possible extraction of Na and B. Therefore, the total time of sample K12 leaching under boiling has amounted to 14 h.

The influence of an increase in the acidic leaching duration on the structure and morphology of pores in iron-containing PG K12 was studied using a sample prepared as a plate. The isotherms of low-temperature nitrogen adsorption and desorption (Fig. 5) were measured with the same equipment and under analogous conditions. The pore size distribution (Fig. 6) was calculated in the way the same as was used for the aforementioned samples.

A rise in the acidic leaching duration increased the total pore volume and the volume of mesopores by 32 and 35%, respectively (Table. 2). The fraction of micropores in the total pore volume decreased by nearly 10%. The specific surface area of mesopores calculated by the BET method from the adsorption isotherm increased by 10.6%. Micropore diameters slightly grew from 1.1-1.2 to 1.2-1.4 nm. The position of the maximum of the largest peak for mesopores at 3.6 nm in the distribution curve plotted from the desorption data remained unchanged; however the peak at 18.1 nm in this curve became wider as compared with the peak for sample K12-7_{pl}. The modes recorded at 7.5 and 8.0 nm upon adsorption and desorption, respectively, became more distinct. The average mesopore diameter increased by 25%.

The structural coefficient for sample K12-14_{pl} remained unchanged, i.e., equal to 4.1 ± 0.2 , thus indicating the prevalence of a cylindrical shape of mesopores in this glass. The structural coefficient for micropores decreased to 3.1 ± 0.2 , thereby witnessing a rise in the contribution of interglobular pores.



Fig. 6. Pore diameter distribution curves for ISBS PG K12 plate after leaching for 14 h; sample $K12-14_{pl}$.

Thus, the detailed analysis of the low-temperature adsorption and desorption isotherms yields definitive information on the structure and morphology of the pore space in PGs and on the influence of the treatment conditions of the initial glass on them, with the duration of the acidic leaching of two-phase glass and its mechanical grinding after the leaching being among these conditions.

CONCLUSIONS

The detailed analysis of equilibrium isotherms for low-temperature nitrogen adsorption and desorption has, for the first time, been employed to characterize the structural characteristics and morphology of pores in samples of iron-containing sodium-borosilicate PGs obtained by the through acidic leaching of corresponding liquation glasses with a two-matrix structure. The study has been carried out using two plateshaped PG samples prepared at different times of leaching in an aqueous 3 M HCl solution (7 and 14 h) and one powdered sample prepared by mechanical grinding of the plate leached for 7 h. Experimental equilibrium isotherms of nitrogen adsorption and desorption at 77 K, which covered both the range of moderate and high relative pressures and the range of low pressures, were approximated by a pentamodal equation comprising the Boltzmann functions. All studied PG samples had polymodal mesopore size distributions and contained micropores. According to the desorption isotherms, the main modes of mesopore mouths lie in the ranges of 3.6-3.8 and 23-25 nm. The sizes of micropores are 1.1–1.4 nm. The structural characteristics, including volumes and specific surface areas of meso- and micropores, pore diameters corresponding to different modes in the dis-

COLLOID JOURNAL Vol. 84 No. 1 2022

tribution curves, and mesopore diameters, have been calculated for the pores in the PG samples. The structural coefficient equal to 4 corresponds, predominantly, to cylindrical mesopores. The difference between the pore size distribution curves obtained from the adsorption and desorption branches of the isotherms has indicated a more complex pore shape, i.e., bottle-shaped and conical pores have been found.

Mechanical grinding of a PG plate to a powdered state causes no changes in the general pattern of the adsorption–desorption isotherms. It increases the mesopore volume by nearly 10% via the opening of internal dead-end pores and widens the peak of the mode for 24-nm liquation channels. Therewith, the specific surface area of mesopores decreases, while their average diameter grows by 11%. The recorded maximum of micropores (1.1-1.2 nm) remains unchanged. The structural coefficient of mesopores somewhat decreases possibly due to the opening of interglobular pores.

The prolongation of the acidic leaching under boiling from 7 to 14 h leads to a rise in the volume and average diameter of mesopores by 35 and 25%, respectively. At the same time, the fraction of micropores in the total pore volume decreases by nearly 10%. The mesopore mode at 8.0 nm becomes more pronounced. The position of the maximum of the largest peak of mesopores at 3.6 nm in the distribution curve derived from the desorption isotherm remains unchanged. The peak at 18.1 nm in the distribution curve calculated from the adsorption isotherm widens.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

COLLOID JOURNAL Vol. 84 No. 1 2022

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