Porous glass for ecology

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Abstract. The intensive development of information, optical, laser, microanalytical, and other modern technologies stimulates the creation of materials with nanostructuring elements that provide their unique physicochemical properties. Porous glass, being a product of through chemical etching of two-phase oxide alkali-borosilicate glasses, has advantages when used as adsorbents and separation membranes, and are promising matrices for the creation of high-silica composite functional materials, including for solving environmental problems (water purification, radioactive waste, etc.).

Modern industrial ecology is connected with the study of technogenic influence of human activity on the state of the environment, and uses the latest achievements of science and technology to reduce anthropogenic influence by improving technologies and treatment facilities.

The interest of researchers in porous glasses (PGs) exists practically from the moment of their discovery due to the fact that they possess adjustable characteristics of the pore space structure; excellent adsorption properties due to a large pore volume with a branched surface capable of active chemisorption of a variety of substances; thermal, chemical, as well as microbiological resistance, providing the possibility of regeneration and sterilization; radiation resistance, unique optical properties (transparency or anomalous light scattering in the visible part of the spectrum).

Porous glass is obtained as a result of through chemical etching (leaching) of a two-phase glass with interpenetrating phases, the composition and structure of which are caused by liquid phase separation (liquation) processes in oxide glass-forming alkali-borosilicate (ABS) systems [1-5] (figures 1-2). As a rule, such PGs consist of (wt. %): 93-95 SiO₂, 2-5 B₂O₃, 0.05-0.5 R₂O and 0.2-0.7 Al₂O₃. For PGs, polymodal porosity is due to the sponge-corpuscular structure, which is formed by particles of finely dispersed secondary silica, distributed in the liberated liquation channels (macropores) in the glassy framework of the high-silica glass phase [6].

Figure 1. Schematic drawing of the structure of phase-separated (right side) and porous (left side) glasses according to the classical notions. D is "diameter" [3].
Porous glass is a promising base material (in the form of matrices/substrates) for the production of functional, including composite materials. Due to a unique complex of properties, porous glasses are widely used in various fields of science and technology [1, 2, 5].

Porous glasses are in many cases more effective sorbents than widespread organic and inorganic sorbents, such as silica gels, activated carbon, cellulose acetate, etc. The homogeneity of the structure, especially for PG with macropores (up to 2000 nm), expressed in a narrower distribution of pore volumes with respect to diameters in comparison with other adsorbents, ensures the completeness and depth of separation of mixtures. All these properties of PG open wide prospects for the use of this unique material in modern materials science, which faces the challenge of creating new materials that meet the needs of modern society.

The scientific school of investigation of processes of liquid phase separation in glass-forming oxide ABS systems and the practical use of this phenomenon has been established at Institute of Silicate Chemistry RAS, new multicomponent glasses have been successfully synthesized by modifying the base ABS glasses with various additives, such as, for example, Al₂O₃, K₂O, Fe₂O₃, PbO, P₂O₅, F (which is due to the tasks of practical use of the received PGs) for a long time [5]. The researches are carried out both in the field of studying the laws of chemical behavior of such multicomponent glasses in aqueous acid-salt solutions and in the field of creating of various composite materials based on porous glasses that are promising for use in modern technologies, including for solving environmental problems.

One of the aspects of use of PG is the synthesis of semipermeable membranes for desalination of water, purification of sanitary water, regeneration of water from the products of human activity in space, etc. Using the reverse osmosis method [7], which consists of pushing the solution through a porous membrane that passes molecules of the solvent (in our case, water) and delays the molecules or ions of the solute (salt included in the sea water), it is quite cheap in terms of economy (as compared to the distillation method) of electricity to obtain fresh water in regions of the country that do not have sufficient drinking water resources. The initial glasses for the synthesis of porous membranes are the basic two-phase sodium borosilicate and sodium alumina borosilicate glasses.

PG with a pore size of 2-4 nm is more preferable for desalination, than organic membranes (acetate, cellulose, nylon, etc.) due to their chemical and thermal stability, which allows regeneration and sterilization of membranes without breaking their structure even under high pressure.

A unique set of properties allows the use of PG in biomedicine as carriers for the immobilization of microorganisms. So, for example, porous material “Siran” (Schott Engineering) in the form of porous silicate glass beads with granule dimensions of 2-3 mm and pores of 60-300 μm is used to immobilize microorganisms [8]. Comparison of the sizes of some microorganisms with the structural characteristics of the PG demonstrate the possibility of synthesizing porous membranes capable of purifying water from harmful pathogens (table 1).

### Table 1.

| Parameters                          | Porous glass | Escherichia coli | Listeria monocytogenes | Candida albicans | Hepatovirus |
|-------------------------------------|--------------|------------------|------------------------|------------------|-------------|
| The size of the pore or the microorganism | 1÷2000 nm    | 400÷3000 nm      | 400÷500 nm             | 6000÷10000 nm   | 2÷50 nm     |

**Figure 2.** Typical TEM micrograph of the porous glass [4].
Recent works have shown the prospects for the synthesis of composites based on PG with polyoxometallate (POM) embedded in the porous space [9-11]. An important feature of POMs is their biological activity. In biochemistry, POMs are used as precipitators of proteins, alkaloids and purines. In work [10] it was shown that the formation of silicon polyoxomolybdate occurs due to the interaction of the ion with the "secondary" silica gel both in the porous space and on the surface of the PG:

$$\text{Si(OH)}_4 + 12(\text{NH}_3)_2\text{MoO}_4 + 20\text{H}^+ \rightarrow \beta\cdot[\text{SiMo}_{12}\text{O}_{40}]^{5-} + 24\text{NH}_3^+ + 12\text{H}_2\text{O}$$

The incorporation of POM into a nanoporous silicate matrix with a high specific surface area increases the catalytic properties of the final materials by increasing the number of active sites, allowing modification of the silica framework and porous base structure. The introduction of POM into a high-silica porous matrix will solve the problem of POM resistance to destruction in aqueous and organic solvents and opens the possibility of their application in medicine and industrial ecology as membranes for purification of water from microorganisms [11] (figure 3).

The study of fungicidal properties of synthesized samples: 1 – initial porous glass, 2 – porous glass with a silver salt of silicomolybdenic acid deposited on the surface; 3 – porous glass with salt of ammonium polyoxomolybdenum

Porous glass has long proven itself as a reliable material for the disposal of radioactive waste. The method of immobilization of hazardous wastes consists of sequential impregnation of the PS with a suitable solution and subsequent sintering before the pores are closed. The final product is covered with a protective layer of metal, glass or synthetics, and is resistant to high temperatures and chemical corrosion [1].

The Institute of Silicate Chemistry RAS conducts research aimed at creating new selective membranes on the basis of silicate porous glasses, which can be used as functional elements of 1) microfluidic analytical systems with optical detection (fields of application: biology, genetic engineering, medicine, ecology, immuno- and biochemical express analysis, sensorics [12], 2) fully dielectric fiber-optic temperature sensors intended for use in monitoring devices for powerful energy systems under the influence of external strong electric and magnetic fields [13]; 3) photochromic quartzoid materials with plasmon structures - quasimetallic silver nanoparticles distributed in a dielectric PG matrix (fields of application: optics, sensorics, ecology) [14]; 4) compact nanoporous containers for disposal of liquid radioactive waste [15].

The above examples of the use of high-silica porous glasses do not reflect the entire range of possible applications for solving environmental problems.

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References

[1] Mazurin O, Roskova G, Aver’yanov V and Antropova T 1991 Dvukhfaznye steкла: Struktura, svoistva, primenenie (Leningrad: Nauka)
[2] Enke D, Janowski F, Schwieger W 2003 Microporous and Mesoporous Materials 60(1) 19
[3] Antropova T 2012 Fizika I Khimia Stekla 38(6) 806
[4] Drozdova I, Vasilievskaya T, Antropova T 2007 Phys.Chem.Glasses: Eur.J.Glass Sci.Technol. B 48(3) 142
[5] Antropova T 2015 Tekhnologiya poristykh ctekol i perspektivy ih primenenny dlya biokhimicheskogo analiza Issledovany, tekhnologia i ispolzovanie nano-poristykh nositeley lekarstv v medicine ed V Shevchenko (Saint-Petersburg: Khimizdat) p 285
[6] Kreisberg V and Antropova T 2014 Microporous and Mesoporous Materials 190(1) 128
[7] Dytnersky U Obratny osmos i ultrafiltracija 1978 (Moscow: Khimia)
[8] Kryakunova E, Kanarsky A 2012 Herald of Kazan Technological University 17 189
[9] Bayanov V, Shevchenko D, Romanov R, Rakhimova O 2014 Proc. Int. Conf. Actual problems of biochemistry and bionanotechnology. V International Scientific Internet Conference (Kazan) (Kazan: IP Synyaev D N) p 31
[10] Tsyganova T, Bayanov V, Shevchenko D, Rakhimova O 2016 Glass Physics and Chemistry 42(4) 426
[11] Pat.178126 (Russia) Bioactive osmosis membrane for water treatment 2018
[12] Esikova N, Evstrapov F, Bulyanitsa A, Antropova T 2015 Glass Physics and Chemistry 41(1) 89
[13] Pat. 2527308 (Russia) 2014 Fiber Optic Temperature Meter pub 27.08.2014
[14] Antropova T, Girsova M, Anfimova I, Drozdova I et all, 2014 Journal of Non-Crystalline Solids 401 139
[15] Tsyganova T, Stolyar S 2016 Glass Physics and Chemistry 42(3) 325