Porous Membranes on a Basis of Phase-separated Alkali Borosilicate Glasses That Contain PbO and F Additives

T. Antropova[1], L. Ermakova[2], S. Medvedeva[1], M. Sidorova[2]

Grebenshchikov Institute of Silicate Chemistry, RAS, Russia[1]

Sankt-Petersburg State University, Russia[2]

ABSTRACT. The influence of PbO or F presence in the phase-separated alkali borosilicate glasses on a kinetic of their acid leaching as well on a structure of the porous glasses received have been investigated. The structure parameters of the two-phase glasses and of the porous glasses were studied by electron microscopy and by adsorption methods. The electrochemical characteristics of the porous glass membranes have been done.

INTRODUCTION. Nowadays the membrane processes provide the development of ecologically safe, resource saving and low-expense technologies which contribute the nature protection. One of the most important in the practical attitude nano structural membrane systems, which find expanding applications as adsorbents, catalyst supports, semi permeable membranes for separation of liquid and gas mixtures, etc. are porous glasses (PGs) - the products of through acid leaching of phase-separated alkali borosilicate (ABS) glasses with two-frame structure [1]. Perspectives of use of PGs in membrane technologies are caused by their thermal, chemical and microbiological stability in a combination to adjustable structural characteristics, an opportunity of their regeneration and sterilization, rigidity of the structure, capable to withstanding a high pressure without destruction for a long time. It is well known that PGs can be prepared by acid leaching of the phase-separated glasses with a two-network structure not only in a certain composition region of the ABS system but also by leaching of glasses with a more complex composition. Despite the facts that the leaching mechanism is similar in nature for glasses of different compositions, some specific features of this process are inherent in each composition of the initial glass [2-4]. A process of acid leaching of two-network ABS glass involves few stages that proceed simultaneously [5]. These ones are the dissolution of components of the chemically unstable phase and the

exchange interdiffusion of acid and of dissolved glass components in the leached layer, which is accompanied by a secondary silica gel formation.
In present work an influence of the different factors such as initial ABS glass composition and a regime of its thermal treatment on a kinetic of phase-separated glass leaching in the different acid solutions as well on the structure parameters and electro kinetics characteristics of the PG membranes received has been investigated.

EXPERIMENTAL. The as-analyzed compositions of the phase-separated glasses under study are presented in Table 1. Glass samples in a form of polished plates or disks 2 – 4 mm thick were leached without forced stirring. The ratio between the surface area of a glass sample and a solution volume was (2-4) x 10^{-2} cm^{-1}. The rate of increase in the leached layer thickness h_{exp} was examined with an optical microscope. Extraction kinetics of components from glass into acid solution was studied. The results of chemical analysis of the solutions were used to calculate the number Q of moles of the components passed into the solution in a given time, which was normalized to the sample surface area S_0. By using the values of Q/S_0, the thickness h_{calc} of the layer, from which the components were extracted, was calculated according to procedure described in [4].

Table1. Compositions of the initial phase-separated glasses.

Glass	Glass composition (as-analyzed, mol. %)								Glass thermal treatment
	Na_2O	K_2O	B_2O_3	SiO_2	PbO	Al_2O_3	P_2O_5	F	Temperature T, ^0C /time t, hrs
8B	7.6	-	20.4	71.9	-	0.1	-	-	550/144
NFF(I) NFF(II)	6.8	-	22.1	70.4	-	-	0.19	0.52	550/40 550/142
NK	4.0	3.8	33.2	59.0	-	-	-	-	500/30
NKS	3.3	2.9	33.2	58.5	1.2	0.95	-	-	500/24

PGs obtained were washed with distilled water for 5 days and dried at 120 ^0C for 1 h. The structural characteristics of PGs – the mean radius of pores r, their porosity W and the specific surface area S_{sp} – were determined by BET methods. The composition of PGs prepared was chemically analyzed using standard procedures. The comparative study of equilibrium (structural resistance coefficient β, surface charge σ_0, electro kinetic potential ζ) and transport (ion transport numbers $n_\pm$, membrane conductivity κ_m) characteristics of PG membranes with different chemical composition was made in dependence on pH and background electrolyte concentration (HCl, KCl, 10^{-4} – 1 M) according to procedure described in [6, 7].

RESULTS AND DISCUSSION. Results of the phase-separated glass leaching investigations have shown that a growth rate of the leached layer thickness h_{exp} is mainly determined by Na_2O/B_2O_3 and B_2O_3/SiO_2 molar ratio in glass rather than by the pore dimensions of a leached layer obtained (Figure 1, Table 2).
It is seen that the calculated h_{calc} (B_2O_3) values are less than the experimental thickness h_{exp}. The same results were obtained for other glass components specifically for PbO. The "lag" of the component extraction into solution can be explained by a intermediate precipitation of the hard soluble products inside porous layer [5].

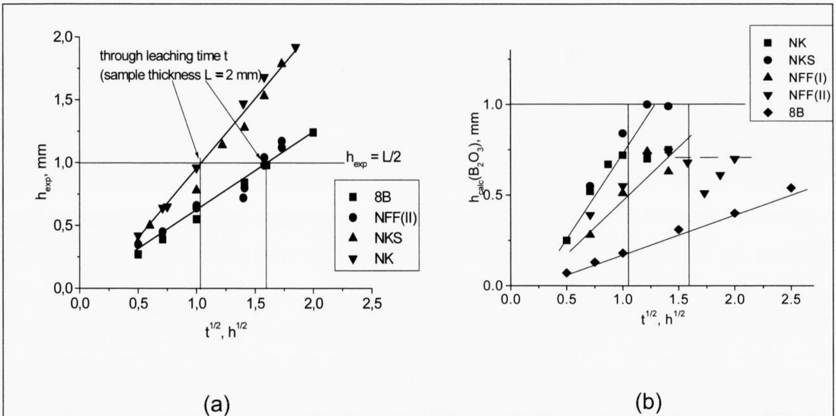


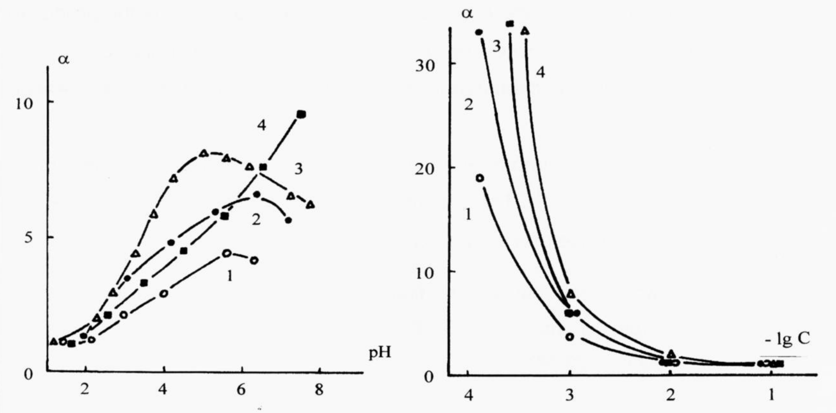
Figure 1. Graphs of the leached layer thickness values - (a) experimental h_{exp} (L = 4 mm) and (b) calculated from the B_2O_3 amount extracted h_{calc} (L = 2 mm), which were determined in the phase-separated glass samples during their leaching in 3 M HCl solutions at 100 °C.

In the case of the lead-containing ABS glass the hetero coagulation of the negatively charged secondary silica particles at interaction with positively charged hydrolytic forms of lead salts in pore solution is likely to take place [4]. Owing to that the PG membranes produced are characterized by considerably smaller radius of pores and their larger specific surface as compared to the membranes which are obtained from the base ABS glass (Table 2). In a case of NFF glass a presence of fluoride - ions in a pore solution can promote dissolution of secondary silica during a glass leaching, thus resulting in formation of the PGs with a large-sized pore structure [3]. This result is promoted by a formation of the $[RO_{3/2}F]^-$ structural elements in NFF glass, which is accompanied by a substantial loosening of the glass network [8].

Table 2. Molar ratio of the components in the phase-separated glasses, time of their through leaching in 3 M HCl at 100 °C and parameters of pore structure of the porous glasses obtained.

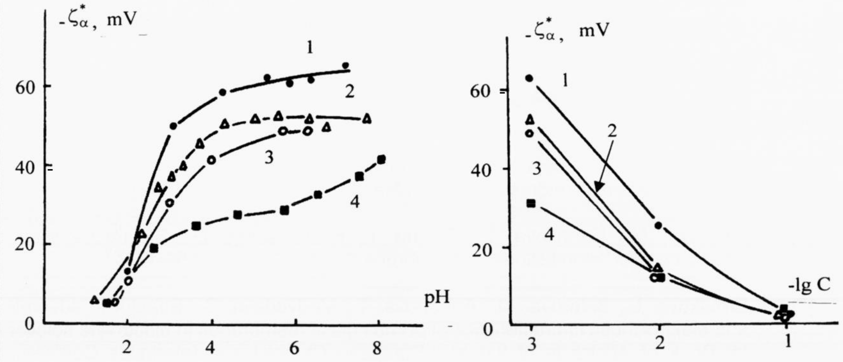
Glass	Molar ratio of the components in a glass		Time of a glass through leaching (h_{exp} = L/2 = 1 mm), hrs	Mean pore radius r, nm	Pore specific surface area S_{sp}, m^2/g	Porosity W, cm^3/cm^3	Structural resistance coefficient β
	$\frac{Na_2O}{B_2O_3}$	$\frac{B_2O_3}{SiO_2}$					
8B	0.37	0.28	2.7	3.3	260	0.26	19.9
NFF(II)	0.31	0.31	2.7	7.3	30	0.23	17.3
NK	0.12	0.56	1.1	5.1	95	0.37	4.9
NKS	0.10	0.57	1.2	2.9	330	0.43	6.2

Results of the measurements of membrane conductivity have shown that the β values of the PG membranes depend on a composition of phase-separated glass (Table 2). During a long contact of PG membranes with dilute electrolyte solutions the β values were practically unchanged (PGs on the base of NK and NKS glasses) or were decreased (PGs based on 8B and NFF glasses). The efficiency coefficients α that characterized the electrical double layer (EDL) ion contribution into membrane conductivity increased with an increase in pH up to pH ≈ 5.8 and decreased with a salt level and pore radius growth (Figure 2). The same dependencies of counter ions (K^+) transport numbers in PG membranes on mentioned factors were observed. The values of adsorption of the potential-determining ions increase with an increase in pH as a result of an increase in the degree of dissociation of surface silanol groups. The |ζ| values, calculated with taking into account the EDL overlapping, increase with the shift to the base pH region and as dilution of an electrolyte solution occurs (Figure 3).



(a) 1 - NFF-1, 2 – NK, 3 - NKS, 4 - 8B (b) 1- NFF-1, 2 - NK, 3 - NKS, 4 - 8B

Figure 2. Dependences of the efficiency coefficient on the (a) pH for PG membranes on the background of the 10^{-3} M KCl solution and (b) concentration of the KCl solutions at pH = 6.



(a) 1 – NK, 2 – NKS, 3 – NFF, 4 – 8B (b) 1 – NK, 2 – NKS, 3 –NFF, 4 – 8B

Figure 3. Dependences of the electro kinetic potential on the (a) pH for the PG membranes on the background of the 10^{-3} M KCl solution and (b) concentration KCl (pH = 6).

SUMMARY. The main feature of leaching process of the phase-separated lead- or fluorine-containing ABS glasses in comparison with the base ones is the production of the porous glasses possessed by different porous structure parameters at the same leaching rate due to chemical processes, which occur in the glass leached layers.

All kinds of PG membranes under study are negatively charged in the investigated pH region (4 - 9). The injection of fluorine or lead oxide into initial ABS glass leads to the increase of a surface charge value.

The work was carried out with the financial support of the Russian Foundation of Basic Research (project no. 04-03-32165) and of Russian Federation Programs "Integration" (project no. 326.48).

REFERENCES

[1] Mazurin, O.; Roskova, G.; Aver'yanov, V.; Antropova T.: Dvukgfaznye Stekla: Structura, Svoistva, Primenenie (Two-phase Glasses: Structure, Properties, Application). Leningrad: Nauka, 1991.

[2] Takusagawa, N.; Yamamoto, K.; Kitajima, K: Structure of porous glass prepared from fluorine-containing sodium borosilicate glasses. J. Non-Crystall. Solids. **95&96** (1987) pt. II, p. 1055-1062.

[3] Exnar, P: Macroporous glass with P_2O_5 and fruorides content. In: Proceeding of the 5th Conference of the European society of Glass Science and Technology, Book of Abstracts, Prague (Crezh Republic) 1999. Prague: Czech Glass Society, 1999, p. 184.

[4] Antropova, T.; Tsyganova, T.; Roskova, G. et.al.: Some features of leaching of two-phase alkali borosilicate glass containing PbO. Glass Phys. Chem. **27** (2001) no. 2, p. 175-181.

[5] Antropova, T.: A model of the porous glass producing process. In: Proceeding of the XVII International Congress on Glass, Madrid (Spain) 1992. **5** (1992), p. 195-199.

[6] Sidorova, M.; Ermakova, L.; Savina, I.; Fridrikhsberg, D.: Electrochemistry of weakly charged membranes. J. Membrane Sci. **79** (1993), p. 159-179.

[7] Ermakova, L.; Sidorova, M.; Antropova, T.; Medvedeva, S.: Structural, adsorption and elektrokinetic characteristics of porous glass membranes in electrolyte solutions. In: Book of Abstracts of the XVI European Chemistry at Interfaces Conference, Vladimir (Russia) 2003. Vladimir, 2003, p. 142.

[8] Kiprianov, A.; Karpukhina, N.: Influence of fluoride additives on the electrical characteristics of alkali silicate electrode glasses. Glass Phys. Chem. **27** (2001) no. 1, p. 74-79.