Original Paper

Some physical and chemical properties of a massive 96 % SiO_2 glass block

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Sections cut from a thick block of porous 96 % SiO_2 glass were subjected to surface area and pore size evaluation. Some also were consolidated to clear impervious glass, and then checked for water content (OH groups) or analyzed for Na_2O and B_2O_3 in efforts to determine whether structural and compositional gradients result on leaching thick blocks of heat-treated alkaliborosilicate glass.

The study shows that small systematic changes in surface area, pore size, and soda content exist. However, none of them are attributable to the leachant. Arguments are set forth that they simply are caused by longer heat retention in the interior of the block and the temperature gradient that will exist between the inside and the outside surface.

The dewatering characteristics (removal of OH groups) of the porous glass remain unaffected by the thickness of the base glass. However, the hydroxyl content in the final 96 % SiO_2 glass increases with distance from its external surface, reaching a maximum at the center of the block. A plausible explanation for the hydroxyl gradient is given.

Einige physikalische und chemische Eigenschaften eines 96-%-SiO_2-Glasblockes

Dünne, von einem dicken Block aus porösem 96-%-SiO_2-Glas stammende Scheiben wurden der Bestimmung der spezifischen Oberfläche und der Porengröße unterworfen. Einige Scheiben wurden zu dichtem klarem Glas zusammengesintert und dann auf ihren Wassergehalt (OH-Gruppen) oder Na_2O- und B_2O_3-Gehalt hin untersucht. Mit Hilfe der Messungen sollte ermittelt werden, ob durch das Auslaugen dicker Blöcke aus wärmebehandeltem Alkali-Borosilicatglas strukturelle Änderungen und Konzentrationsgradienten entstehen.

Die Untersuchung zeigt, daß geringe systematische Veränderungen der spezifischen Oberfläche, der Porengröße und des Sodagehaltes auftreten. Jedoch kann keine von ihnen dem Auslaugungsmedium zugeschrieben werden. Es wird dargelegt, daß sie auf der längeren Wärmespeicherung im Inneren des Blockes sowie auf dem Temperaturunterschied, der sich während der Wärmebehandlung zwischen der inneren und äußeren Oberfläche ausbildet, beruhen.

Die Entwässerungseigenschaften (Abspaltung von OH-Gruppen) des porösen Glases werden nicht von der Dicke des Grundglases beeinflußt. Aber der OH-Gehalt des gesinterten 96-%-SiO_2-Glasblockes steigt mit der Entfernung von seiner äußeren Oberfläche an und erreicht in seinem Zentrum ein Maximum. Eine überzeugende Erklärung für den OH-Gradienten wird gegeben.

1. Introduction

High-silica reconstructed glass has found major commercial applications since its inception over a half century ago. Its uses in the laboratory and in various industries stem from the fact that 96 % SiO_2 glass, like fused quartz glass, possesses excellent thermal shock resistance and high deformation temperatures in addition to excellent chemical resistance, low contamination, and special tailored visible, infrared and ultraviolet transmittance. Most of the commercial applications involve objects ranging in thickness from about 1 to 10 mm. However, massive optical-grade windows of 96 % SiO_2 glass have been made in thicknesses up to about 25 mm. All of these objects are made from a special alkaliborosilicate glass by heat treating, acid leaching, and subsequently sintering into impervious clear or colored glass. Since the removal of the nonsiliceous constituents from the base glass by the hot acid solution is diffusion-controlled, and involves also restructuring of the silica-rich phase, it was of special interest to determine whether the physical or chemical properties of the resulting porous structure are in any way thickness-related.

The purpose of this paper is to present physical and chemical data obtained on thin sections removed from a leached massive glass block. It includes information on surface area, pore size and dewatering characteristics of the porous glass, Na_2O and B_2O_3 contents and β_{OH} values of the fired glass. Plausible explanations for small systematic variations in some of these parameters are given.

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2. Experimental part

2.1. Samples

Porous glass, a high-silica body with continuous pore structure was used in this study in the form of a block and a flat sheet. The block was 25 cm long by 20 cm wide with 29 mm thickness. The sheet was of similar size but only about 12 mm thick.

The composition of the porous block on the basis of its ignited weight (in wt%) is: 96 SiO_2, 4 B_2O_3, and

Table 1. Physical properties of sections cut from a 28.32 mm thick porous glass block

section no.	distance[1]) in mm	surface area in $m^2\ g^{-1}$	average pore size in nm	pore volume in $cm^3\ g^{-1}$
1	1.72	63.5	12.8	0.204
2	6.42	63.5	13.3	0.211
3	10.28	62.7	13.4	0.209
4	13.92	61.5	13.6	0.209

[1]) Measured from external surface of porous glass block to center of porous section.

traces of Na_2O; and that of the sheet is 96 SiO_2, 3 B_2O_3, 0.4 R_2O_3 + RO_2 (chiefly Al_2O_3 + ZrO_2) and traces of Na_2O. Their pore size was about 13 and 5 nm, respectively.

The samples used in this study were cut parallel to the leach plane at various distances from both the external surface of the porous glass block and the consolidated flat sheets. The thickness of the cut sections was about 3 and 2 mm. Their location from the external surface was determined with a vernier caliper, taking into account the thickness of glass removed on cutting.

2.2. Surface area and pore size measurements

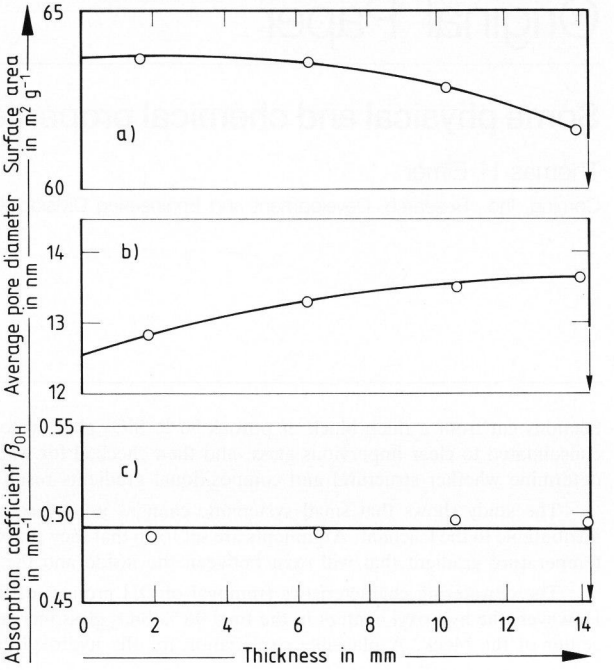
All measurements of the porous glass sections were made with the Quantachrome Autosorb-6 instrument (Quantachrome Corp., Syosset, NY (USA)) using nitrogen as the adsorbate. The samples were comminuted to pass through a 12 mesh US Standard Sieve and were outgassed at 300 °C prior to making the measurements. The surface area was obtained from the BET values, and the average pore diameter (pore size) was determined from data that had been generated by means of a computer from the desorption isotherms.

2.3. Firing of porous glass samples

The porous glass sections from the block were fired in air at 100 K/h from room temperature to 1225 °C and held for 30 min to consolidate the porous structure into a clear impervious glass. Two large pieces from the porous glass sheet were slowly heated to about 120 °C and then further heated in air at 150 K/h to about 900 °C. Each was degassed in vacuum for 2 d, one at 930 and the other at 975 °C prior to consolidation at 1225 °C.

2.4. Infrared measurements and chemical analysis

Spectrographic measurements were made of the fired samples with a recording infrared spectrometer (Model 221, Perkin-Elmer Corp., Norwalk, CT (USA)). The absorption coefficients β_{OH} were calculated using equation (1):



Figures 1a to c. Surface area (figure a), average pore size (figure b), and absorption coefficient β_{OH} (figure c) of consolidated glass as a function of distance from the external surface of a 28.3 mm thick porous glass block. The arrow indicates the center of the block.

$$\beta_{OH} = \frac{1}{t} \lg T_{2.6} / T_{2.72} \qquad (1)$$

where t = sample thickness in mm, $T_{2.6}$ = transmittance in percent at 2.6 μm, and $T_{2.72}$ = transmittance at the peak of the OH band at 2.72 μm.

The chemical composition across the entire thickness of the glass block was determined by wet chemical analysis. Such analysis, however, was not made on samples from the glass sheet since earlier work had shown that its composition remains essentially constant with thickness.

3. Results

The surface area and average pore size of the porous samples from the 28.32 mm thick porous glass block are summarized in table 1 and shown graphically in figures 1a to c. The surface area decreases while the pore size increases with distance from the external surface of the block. However, the amount of change in these two parameters is only slight.

The β_{OH} values of the consolidated glass sections from the porous glass block are given in table 2. The values for the sections cut from the two fired glass sheets are shown in table 3. The data for the block are included in figure 1, but those for the two sheets are shown in figure 2.

The Na_2O and B_2O_3 contents in the fired samples taken from the porous glass block are summarized in table 4 and shown graphically in figures 3a and b.

Table 2. Absorption coefficient β_{OH} of 2 mm thick fired sections from a 28.32 mm thick porous glass block

section no.	distance in mm[2])	β_{OH} in mm^{-1}
1	1.72	0.487
2	6.42	0.490
3	10.28	0.499
4	13.92	0.499

[2]) see [1]) of table 1.

Table 3. Absorption coefficient β_{OH} of 2 mm thick fired sections from a 10 mm thick 96 % SiO_2 glass sheet

distance in mm from external surface to middle of sections	β_{OH} in mm^{-1}	remarks
1	0.169	
3	0.509	porous glass sections
5	0.544	were outgassed in
7	0.507	vacuum at 975 °C
9	0.182	(sample 2)
1	0.049	
3	0.092	porous glass sections
5	0.101	were outgassed in
7	0.088	vacuum at 930 °C
9	0.044	(sample 1)

Table 4. Chemical analysis of fired samples from a 28.32 mm thick porous glass block

section no.	distance[3]) in mm	Na_2O content in wt%	B_2O_3 content in wt%
1	1.72	0.025	3.94
2	6.42	0.029	3.97
3	10.82	0.030	3.93
4	13.92	0.030	3.91
5	18.23	0.029	3.93
6	22.96	0.027	3.99
7	27.23	0.022	3.87

[3]) Measured from external surface of porous glass block to center of a ≈ 3 mm thick porous glass section.

4. Discussion

Figures 1a to c show that the porous glass from the interior of the glass block has a somewhat lower surface area than that from the external surface. Since interior glass is less subject to loss of silica than surface glass during exposure to the hot acid solutions it must be concluded that the systematic decrease shown in figure 1a is not caused by the interaction of such solutions during leaching and washing. One must look for other possible causes to explain the decrease. The temperature gradient and heat retention that exist in the base glass block during thermal processing can play a role, as will be seen later.

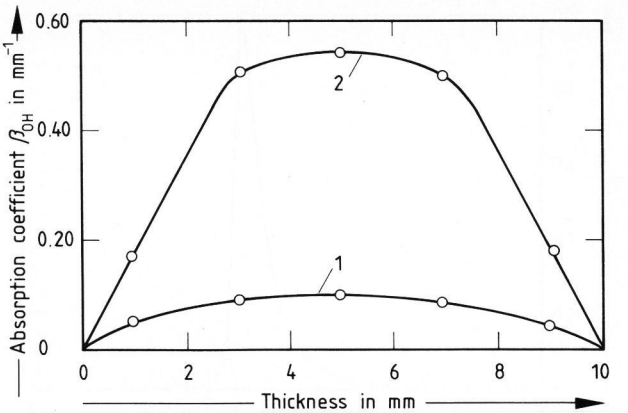
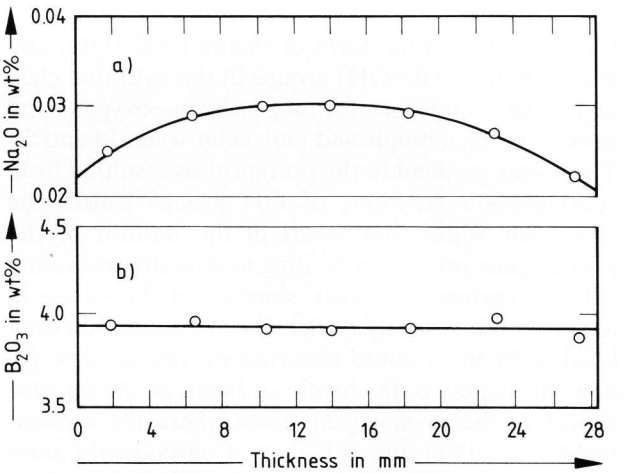


Figure 2. OH gradient in terms of β_{OH} values in a porous 96 % SiO_2 glass block: sample 1 outgassed at 930, and sample 2 at 975 °C prior to consolidation at 1225 °C.



Figures 3a and b. Soda (figure a) and boron oxide (figure b) contents in a 28.3 mm thick 96 % SiO_2 glass block.

The degree of coarsening of the microdisperse phases in alkaliborosilicate glasses is known to increase with temperature and/or time [1 to 3]. Since the core in a thick block of glass retains heat for a considerably longer time than the glass near its external surface it is not surprising that the pore size shows a slight increase with distance as shown in figure 1b. Such increase is in keeping with the decrease in surface area shown in figure 1a.

The β_{OH} values of the consolidated sections in table 2 and in figure 1c are remarkably constant. Thus one can conclude that the dewatering characteristics of the individual sections of porous glass do not change along the thickness of the leached block. However, it should be pointed out that a consolidated glass block contains a notable water gradient, not unlike that shown in figure 2 for the 10 mm thick glass sheets. This comes about in the following manner: Molecular water in the pores begins to vaporize on heating, and the vapor flows through the porous glass to the surface and to the surrounding air from where it is carried away by the air stream. At about 180 °C

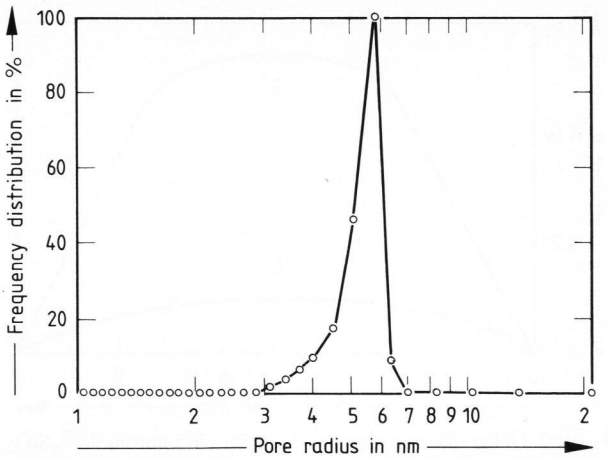


Figure 4. Pore size distribution of porous glass from the interior of a 28.3 mm thick glass block.

the hydroxyls in the form of silanol (≡Si−OH) and also boranol (=B−OH) groups in the hydrated glass begin to condense forming silicon−oxygen and boron−oxygen bonds and molecular water [4 and 5]. The water gradient in the porous glass resulting from condensation reactions of OH groups causes the molecular water that forms in the interior of the porous glass on further heating to migrate toward the external surface. However, since water plays a role in lowering the viscosity of the silica-rich skeleton on a local level to promote sintering by viscous flow [6] one can expect pore closure to begin at the interior center of the thick porous glass where the concentration of OH groups is highest. Consequently, pore closure proceeds from the interior toward the surface of the porous glass at temperatures above 900 °C, where viscous flow becomes significant [7].

The consolidated glass contains a permanent record of the hydroxyl content that existed at the time pore closure was initiated in the interior of the porous glass and gradually completed at its outside surface. The OH gradient that results depends on the firing conditions, as illustrated in figure 2 for sheets of 96 % SiO_2 glass that had been outgassed at 930 or 975 °C prior to consolidation into clear impervious glass. It should be pointed out that such OH gradients can be eliminated by chlorine treatment of the porous glass at elevated temperatures prior to consolidation [8].

Figures 3a and b show that the B_2O_3 content in the thick glass block is essentially constant across its entire thickness, whereas the Na_2O content goes through a maximum at the center of the block. Unlike boron oxide, the soda content in reconstructed 96 % SiO_2 glass is strongly dependent on the thermal history of the base glass. Since a relatively thick piece of glass retains heat longer in its interior than near its outside surface it is not surprising that there exists a Na_2O gradient. Additional washing of a sample from the interior center of the block did not lower the alkali level, indicating that the Na_2O gradient is indeed associated with thermal processing rather than leaching and washing. The pore size distribution of porous glass from the interior of a massive glass block is shown in figure 4.

5. Summary

A block of porous glass prepared from 28.3 mm thick alkaliborosilicate glass shows small systematic variations in physical and chemical properties along its thickness. The slight decrease in surface area and corresponding slight increase in pore size of the porous glass as a function of distance from the external surface of the glass block, as well as the maximum in Na_2O content at its center, are all related to subtle changes in the microdisperse phases of the base glass. Such changes are chiefly due to longer retention of heat in the interior of thick blocks of glass encountered on thermal treatment such as is necessary to avoid fracture during leaching.

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