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Influence of the Leaching Process on Adsorption Properties of Porous Glasses

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NOTE

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Abstract

Among numerous material used as ion exchangers, porous glasses show a high affinity toward cesium ions. This affinity depends on the pore diameter and the presence of an alkaliborate phase. Materials exhibiting extremely high selectivity of cesium adsorption are obtained from glass of 62.7% SiO_2, 26.9% B_2O_3, 6.6% Na_2O, and 3.5% Al_2O_3 by fast cooling of a crude glass mixture in water and then by leaching with water at 90°C for 1 to 4 h. The selectivity factor of cesium adsorption in relation to sodium exceeds 50.

INTRODUCTION

Controlled pore glasses (CPG) are materials composed of silica (94–99%) and residual amounts of B_2O_3 and alkaline oxide (*1*). They are prepared mainly from ternary ($Na_2O/B_2O_3/SiO_2$) or quaternary ($Na_2O/B_2O_3/SiO_2/Al_2O_3$) glass systems (Vycor glass) (*2*). These systems are characterized by unlimited miscibility of the components at higher temperatures and limited miscibility in the temperature range 500–700°C. In order to

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prepare the initial material, the melted and well-mixed (at about 1450°C) glass mixture is quickly cooled in air or water. This leads to freezing of the equilibrium established during the melting procedure.

Heating of glasses prepared as described above in the temperature range 500–700°C causes the demixing (liquation) process in the raw material, i.e., the separation of the components contained in the glass. A continuous alkali metal borate phase (alkali borate heterogeneities) is formed in the continuous silica structure. This so-called soluble phase can be removed from the thermally treated glass by means of a leaching process in water or acids. This procedure gives porous materials. The pore diameter in CPG depends on the composition of the initial glass, the duration and temperature of thermal treatment (i.e., the prehistory of the demixing process), and the leaching procedure of the crude material (*2, 3*).

The silica network formed during the liquation process is purified from alkaliborates. Alkali metal atoms and boron atoms diffuse toward the alkaliborate phase, increasing the diameter of the existing heterogeneities and causing their mutual contact. Liquation usually is carried out until the maximum possible purification of siliceous skeleton is achieved.

During the investigation of siliceous ion exchangers it was found that CPG may be used for the determination of metal ions concentration in solution (*4*). Porous glasses containing alumina show especially high specific adsorption properties which may be advantageous for analytical purposes (*5*). They are particularly interesting for determination of radiocesium because γ-radioactivity may be measured directly from the adsorbent bed.

Previous experiments (*4, 5*) revealed that porous glasses from which the alkaliborate phase has not been completely removed during the leaching process show the best adsorption properties in relation to metal ions.

It is noteworthy that the above-mentioned liquation process (causing separation of alkaliborate phase) just occurs during cooling of the initial glass but is quickly stopped due to the high viscosity of glass below 500°C. Leaching of raw glass just after cooling (without further heating) leads to a silica skeleton very rich in alkaliborates, with extremely narrow pores.

The present paper deals with the ion-exchange properties of porous glasses obtained by direct leaching of the initial glass (without typical liquation) at various conditions. Experiments were carried out on two initial materials.

For comparison, artificial systems composed of sodium tetraborate deposited on silica gel were also studied.

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EXPERIMENTAL

Preparation of PG

All the experiments were carried out by using the following two raw glass compositions:

D: 40% SiO_2, 49% B_2O_3, 11% Na_2O

J: 62.7% $Si)_2$, 26.9% B_2O_3, 6.6% Na_2O, 3.5% $A1_2O_3$

The raw glass, after melting, was cooled in water and did not undergo further thermal treatment. Particles of grain size 0.31 to 0.4 mm underwent treatment with 2.5 *N* H_2SO_4 and then with water with a conductivity below 5 μS for different times. A sample of 0.071–0.125 mm grain size of J composition was also studied for comparison. The washing was carried out in a thermostated water bath shaker at 90°C. The solid:liquid w/w ratio was 1:4, and fresh portions of a washing agent (acid or water) were added every 1/2 h (± 10 min). After cooling to room temperature, the conductivity and pH values of the supernatant were measured by using an OK 102/1 conductivity meter and an OP 208/1 pH meter, respectively (both from Radelkis, Budapest). See Table 1. The BET specific surface was measured by a Sorptomat Type 1806 (Carlo Erba, Milan, Italy).

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Determination of the Selectivity Factor

This was described in a previous paper (*5*). Except for CPG, selectivity factors were also measured for silica gel from Merck. Gel 40 (typical pore diameters in angstroms) was impregnated with borax solutions (2.5, 5, and 10% in relation to silica and a blank sample), heated at 530°C for 14 h, and washed with water until there was a decay of conductivity.

Column Experiments (dynamic test)

In order to examine the ion-exchange properties of particular materials, a column of 1 cm^3 cross section was packed with 10 cm^3 of PG and settled with 24 dm^3 of a solution composed of the municipal water of Lublin (conductivity ≃ 1 mS, 60 ppm of calcium) and carrier free ^{137}Cs from OPiDI (Swierk, Poland). The radioactivity of the top and bottom parts of the column was measured by using a Gama Automat NRG 603 (Tesla, Czechoslovakia). These results are presented as the sum of the percent of initial radioactivity (top + bottom) in Tables 1 and 2.

RESULTS AND DISCUSSION

The physicochemical properties of materials obtained from Glass D are summarized in Table 1. The first three lines of Table 1 correspond to materials prepared by leaching the initial glass with water for various time periods. The next part of Table 1 deals with sorbents obtained by leaching the initial material with acid and then with water.

It follows from Table 1 that during the leaching process in water the supernatant conductivity decreases and its pH value increases. The decrease of conductivity follows from the decrease of the amount of components leaving the glass. This is confirmed by the last column of Table 1, which reports the bulk densities of the dry porous glass bed. These values are a measure of reversed pore volume.

It should be emphasized that during leaching with water the conductivity of the last portions of supernatant is far from the conductivity of the washing water. The increase of the supernatant pH value suggests removal of more alkaline substance after a longer period of leaching. This suggestion corresponds to the next column of Table 1 in which the decrease of the equilibrium constant $K_{Cs/Na}$, which defines the selectivity of cesium adsorption in relation to sodium, is observed. At the beginning of the leaching procedure the pores are narrow (in the range of a few angstroms) and higher amounts of sodium atoms remain in the porous glass. The presence of these atoms probably gives convenient properties in relation to cesium adsorption. On the other hand, the increase in the size of pore diameters and the decrease of sodium content occur simultaneously. Therefore, it is difficult to estimate the role of the above-mentioned factors separately.

A more drastic leaching process (i.e., leaching with acid and then in water) causes a significant drop of the Cs/Na ion-exchange equilibrium constant. The results of a dynamic test were also considerably worse for these glasses. This may partially confirm the role of the sodium borates contained in the porous glass on their ion-exchange properties. Alkaliborate components are more soluble in acids and are satisfactorily and quickly removed from a porous skeleton which shows a lower selectivity

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TABLE 1
Properties of CPG Obtained from Raw Material D

Time of treatment (hours and minutes)		Conductivity of supernatant (μS)	pH	$K_{Cs/Na}$	Dynamic test	BET surface (m^2/g)	Bulk density (g/cm^3)
H_2SO_4	H_2O						
0	1 + 40	8700	7.9	22		96	0.695
0	3 + 10	2900	8.37	28		211	0.564
0	8	1500	8.99	15	62 + 15	80	0.528
1 + 40	3	1800	2.45	3.9	6 + 3	885	0.543
1 + 40	13	5	6	4	10 + 6	824	0.54

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TABLE 2
Properties of CPG Obtained from Raw Material J

Time of treatment (hours and minutes)		Conductivity of supernatant	pH	$K_{Cs/Na}$	Dynamic	BET surface	Bulk density
H_2SO_4	H_2O	(µS)			test	(m^2/g)	(g/cm^3)
0	1	700	8.5	62		[a]	1.115
0	1 + 45			59	76 + 30	[a]	1.102
0	7	630	8.5	21	61 + 25	[a]	1.068
0	17	290	8.65		67 + 30	[a]	1.07
24	3	1800	2.37	17	62 + 16	125	0.915
24	5	85	3.65	14	78 + 26	122	0.906
24	6	28	4.47	13	75 + 25	116	0.926
24	9	5	6	22	61 + 34		0.893
48	4	4300	1.88	13	55 + 34	52	0.918
48	5	1500	2.28	14	51 + 29	71	0.914
48	7	210	3.89	13	56 + 28	60	0.893
48	13	5	6	23		91	0.95

[a] Zero within experimental error.

for cesium adsorption. It is noteworthy that the complete removal of H^+ ions from a porous structure after acid treatment leads to an increase of the $K_{Cs/Na}$ value in relation to glasses for which removal was not complete.

Table 2 collects data corresponding to the initial material J. It follows from the top part of Table 2 (corresponding to materials obtained by leaching in water only) that an increase of leaching time leads to a decrease in supernatant conductivity, a small pH decrease, and a significant drop in $K_{Cs/Na}$. The materials obtained by water treatment for 1 to 4 h show favorable adsorption properties in relation to cesium. The pores of these materials are so narrow that the apparent specific surface measured by means of the BET method is zero. A sample of smaller grain size (0.071–0.125 mm) was examined for comparison. For this sample, leaching with water for 4 h gave a material with a selectivity factor of 50.

It is known from the literature that Vycor glass containing alumina shows a higher resistance against leaching then do corresponding materials without alumina (*6*). The values of $K_{Cs/Na}$ show that material J after water leaching shows considerably better ion-exchange properties in relation to cesium in comparison with analogous materials obtained from initial material D. This is also confirmed by dynamic tests.

Similar conclusions may be drawn from the bottom part of Table 2 which presents materials from series J obtained by acid and then water treatment. These sorbents show lower selectivities in relation to materials from the top part of Table 2, but the results of dynamic tests are still positive.

Table 3 presents values of $K_{Cs/Na}$ for artificial systems composed of sodium tetraborate deposited on silica gel. No essential increase of $K_{Cs/Na}$ was achieved. The results of dynamic test for these systems were quite negative. It seems that impregnation of silica with sodium tetraborate does not lead to materials exhibiting high selectivity in relation to cesium.

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TABLE 3

Values of $K_{Cs/Na}$ for Silica Gels 40 Impregnated with Sodium Tetraborate

Sodium tetraborate (w/w %)	Unwashed sample	Washed sample
Blank sample	2.7	2.4
2.5	2.6	2.6
5	2.8	2.7
10	1.6	2.1

CONCLUSION

1. The main factors defining the selectivity of cesium adsorption are narrow pores and the presence of an alkaliborate phase. Especially favorable are materials with extremely narrow pores (of a few angstroms) which are not entered by nitrogen molecules. Their apparent specific surface as determined by the BET method is zero. Cesium adsorption in such materials in highly irreversible.

2. The above sorbents are obtained by fast cooling of the initial glass in water after a melting procedure but without the classical liquation procedure.

3. For the preparation of selective adsorbents (in relation to cesium), a gentle leaching process should be carried out. This may be achieved by using water as the leaching agent. The leaching process may also be moderated by the presence of alumina in the initial glass.

4. The other possibile leaching process modifications are decreasing the temperature and/or using mixed solvents containing organics.

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