VITRIFICATION OF SIMULATED INTERMEDIATE-LEVEL WASTE FROM NUCLEAR POWER PLANTS

II. CHEMICAL STABILITY OF VITRIFIED PRODUCTS IN ACIDIC SOLUTIONS

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Leaching of glasses of the basic system SiO_2-B_2O_3-Al_2O_3-Na_2O in water and in solutions of mineral acids was studied. All of the tests were carried out on ground samples (0.315-0.50mm). The solutions were analyzed for SiO_2 and Na_2O content and their pH was measured. The static tests showed that the intensity of leaching was raised in acidic solutions having pH=2 compared to leaching in water. More detailed investigations using the flow method and acidic solutions of pH 2, 3 and 4 demonstrated a substantial increase in the leaching rate of alkalies with decreasing pH of the solution; at the same time, the SiO_2:Na_2O ratio in the solution changed. With weakly acidic solutions, their pH is shifted to the alkaline region by the extracted alkalies. A significant decrease of resistance to acidic solutions occurs at pH < 4; at pH $= 2$, the extracted amounts of Na_2O are much higher than those in water.

INTRODUCTION

Tests of chemical durability of the products of fixation of simulated medium-activity waste indicated that even at relatively low melting temperatures it was possible to produce borosilicate glasses with a satisfactory resistance to long-term corrosion by water; however, the durability of the glasses was also shown to decrease in acidic solutions [1]. It was therefore deemed useful to study in more detail the effect of pH on the rate of their leaching or dissolution.

The standard tests for determining the chemical durability of current glasses to acidic media employ either weak organic acids or strong solutions of mineral acids, whereas for vitrified products, also the region of medium-acidity solutions is significant. It was therefore necessary to develop new or modified methods. Apart from the modified static tests, the method using continuous flow of the extracting liquid through the specimen was proved suitable [2, 3]. the method provides regular and reproducible conditions for the leaching, similar to those considered in the derivation of mathematical models of the leaching process.

Silicate glasses are rightly regarded as materials resisting well the effects of acidic solutions. This is probably why the effect of pH on the corrosion of glass in the acidic region has so far been paid comparatively little attention in the literature. The effect of alkaline solutions, where the process of dissolution of the leached surface layer is strongly accelerated from pH 9-11 upwards, has been considered much more significant compared to the effect of an acidic medium on current silicate glasses, which is usually less distinct. However, even in such instances the effect of the chemical composition of glass may be quite strong. Scholze [4] points out a comparison of the corrosion of several types of glass in water and in HCl (0.1 mol l^{-1}). Compared to the effects of water on types NCS glasses (Na_2O-CaO-SiO_2), i.e. container and sheet glasses, and to Pyrex-type glasses, the SiO_2 dissolution in acidic solutions decreases (with NCS by a factor of 20) while the Na_2O extract mildly increases. In contrast to this, with type E-glass (for fibres), the amount of SiO_2 dissolved in HCl of 0.1 mol l^{-1} concentration is higher by a factor of 4 compared to that in water, while the extracted amount of B_2O_3 and Al_2O_3 is higher by an order of magnitude. With NCS and E glasses, there is an extraordinary increase in the amount of extracted CaO.

A detailed study of the effect of pH over the 0-13 range on the leaching and dissolution of a number of glasses was published by El Shamy et al. [5]. With binary alkali silicate glasses and ternary Na_2O-CaO-SiO_2 ones, both alkalies and SiO_2 were leached in the acidic region independently of pH, except for the glass with a high CaO and Na_2O content (both of 20 mol % each). In the latter case, extraction of CaO and Na_2O increased rapidly at pH lower than 3 (at 70°C); at the same time, the rate of dissolution of SiO_2 remained unchanged. This anomaly, similarly to the case of type E glass, indicates a strong effect of the structure of glass on the leaching phenomena if the content of modifiers is high and that of SiO_2 is reduced so as to impair the continuity of the silica network.

A significant decrease of chemical durability in an acidic medium has already long been known to occur with high-alumina container glasses if the Al_2O_3 content exceeds the limit of 14-15 wt.%, and/or the SiO_2 content simultaneously falls below 56% [6]. According to another older study [7], SiO_2-B_2O_3 substitution in borosilicate glasses brings about significant changes in the durability with respect to 20% HCl. A rapid increase in the leaching rate was observed at B_2O_3 content exceeding 13% and SiO_2 content lower than 62 wt.%. This observation likewise implies a relationship between chemical durability and the character of the silicate network of the given glass.

The actual solubility of SiO_2 alone (both crystalline and amorphous) in the acidic region is virtually independent of pH; however, the rate of SiO_2 dissolution increases at pH > 3 [8]. A discrepancy between the data on the solubility of SiO_2 and the behaviour of leached layers formed on the surface of glass by extraction is also pointed out by a recent paper [9]. Long-term tests in buffered solutions showed that with soda-lime-silica glasses (of the sheet-glass type), as well as with Pyrex-type glass, the overall rate of dissolution (in $cm\ s^{-1}$) increases with pH from 4 to 9, whereas the solubility of pure SiO_2 rises only at pH > 8. The results make the authors to assume that the rate of dissolution of silicate glasses is affected by the "openness" of the surface layer.

Part I of the study [1] presented results indicating a reduced chemical durability of glasses in the basic system $SiO_2-Al_2O_3-B_2O_3-Na_2O$ in strongly acidic solutions. The present paper is concerned with a more detailed investigation of the subject matter.

EXPERIMENTAL

Glasses designated in Part I as KL 30, KL 40 and P 40 were used in the experiments (Table I). The former two glasses were prepared in the laboratory, the latter was obtained from a pilot-plant melting and its composition is very close to that of glass KL 40 (the numerals designate the percent of model waste in mixture with clinoptilolite). Following its melting, glass P 40 was rapidly quenched while KL 40 was slowly anneled; the two glasses thus differ in their thermal history.

Table I

Composition of the glasses studied in wt.%

Oxide	KL 30	KL 40	P 40
SiO_2	54.00	45.70	46.24
B_2O_3	12.00	15.80	16.40
Al_2O_3	9.20	8.10	7.48
Fe_2O_3	1.20	1.10	0.98
CaO	2.39	2.00	2.07
MgO	0.80	0.60	0.62
Na_2O	15.80	22.00	21.78
K_2O	4.00	4.10	4.21
MnO_2	0.10	0.10	0.21

Note: The compositions of KL 30 and KL 40 were determined analytically, that of P 40 was calculated from the composition of the raw materials employed.

All of the glasses were ground to the standard particle size of 0.315 – 0.50mm. The finer particles were removed by washing in ethanol. After drying, the samples were placed in a desiccator. The mean specific surface area of the specimens was 110 $cm^2\ g^{-1}$.

Orientation static tests of resistance to highly dilute acids showed that alkalies were extracted in such amounts as to shift rapidly the original acidic solution to the alkaline region. Only an initial solution of pH = 2 yielded results corresponding to actually acidic extraction.

The following method was employed in the static tests: 1g of the standard sample was leached with 100ml of the liquid at 98°C for 1 hour in a measuring flask (without agitation, but a certain amount of free convection could not be ruled out). The SiO_2 concentration in the extracts was determined by the standard silicomolybdate method, that of alkalies by flame photometry. Control analyses by the AAS method were carried out in several instances. The results were expressed as the amount of the respective oxide extracted from 1 cm^2 or 1 m^2 of the glass surface. The pH was measured with a conventional pH-meter using a glass electrode. All of the pH values are given for 25°C.

The results of static tests in solutions of mineral acids and in water are listed in Table II. The values show that the amounts extracted in acids are somewhat higher than those extracted in water, and that the initial pH = 2 of the solution changes considerably during extraction of both P 40 and KL 30 glasses. The

Table II

The amount of oxides extracted in water and in dilute acids with initial pH = 2 (static test)

Glass type	Leachant	Amount extracted [$g\ m^{-2}$] SiO_2	Na_2O	pH	SiO_2/ Na_2O
P 40	H_2SO_4 solut.	0.163	0.432	3.6	0.38
	HCl solut.	0.146	0.298	–	0.49
	HNO_3 solut.	0.141	0.295	3.3	0.48
	dist. H_2O	0.107	0.227	9.8	0.47
KL 30	H_2SO_4 solut.	0.04	0.08	3.0	0.5
	dist. H_2O	0.02	0.02	6.5	*

Note * : The concentrations measured are at the sensitivity limit of the method, so that the ratio is inaccurate and not given.

release of both oxides is higher in H_2SO_4 solution, and the SiO_2/Na_2O ratio is somewhat lower than in the case of the other two acids; extraction of alkalies is therefore more extensive in the H_2SO_4 solution than the dissolution of SiO_2. The content of the two oxides in the extract is substantially lower with glass KL 30.

A more detailed study of the behaviour in acidic solutions was carried out by means of a flow apparatus whose schematic diagram is shown in Fig. 1. The ground sample is placed in a leaching cell prepared from an injection syringe; the cell is provided at both ends with polyethylene tubes and immersed in water in the thermostat. The leachant is supplied to the leaching cell by a peristaltic pump, and the extract is passed into collecting bottles. The leaching thus proceeds under the conditions of a continuous and controlled flow of the liquid. The extract collected in the bottles after a certain time interval (usually 1 hour) was analyzed for the content of SiO_2 and Na_2O and its pH was measured.

The original aim was to carry out long-term measurements at a very low rate of flow of the leachant. In view of a rapid rise of pH and the necessity of concentrating the extracts for chemical analyses, and with regard to the usefulness of determining the initial rates of dissolution, the method was modified to a medium-term measuring cycle, with a maximum time of exposure of 7 hours. All of the results described below were obtained at 85°C at a leachant flow rate of 1.6 ml min^{-1}. Distilled water with an initial pH of 6, and H_2SO_4 solutions of pH 4, 3 and 2 were used as the leachants.

The cumulated amounts of SiO_2 in extracts from P 40 and KL 40 glasses are plotted in Figs. 2 and 3. The amounts of SiO_2 passing into solution from the two glasses are roughly identical, but with glass KL 40 one can observe a mild dependence on the pH of the solution. The time dependences are close to linear ones, except that with glass Kl 40 at pH = 4 and in water, where the process is distinctly slowing down in terms of the time of leaching. With the KL 30 glass (Fig. 3), the SiO_2 concentration in the extracts was always lower, close to the accuracy limit of the determination.

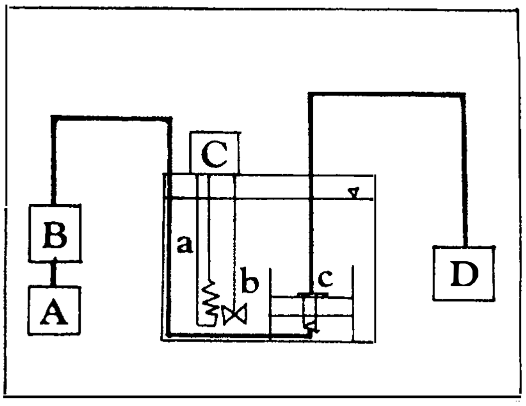

Fig. 1. Arrangement of the flow test. A – stock bottle for the leachant, B – pump, C – thermostat, D – collecting bottle, a – heating element, b – agitator, c – leaching cell.

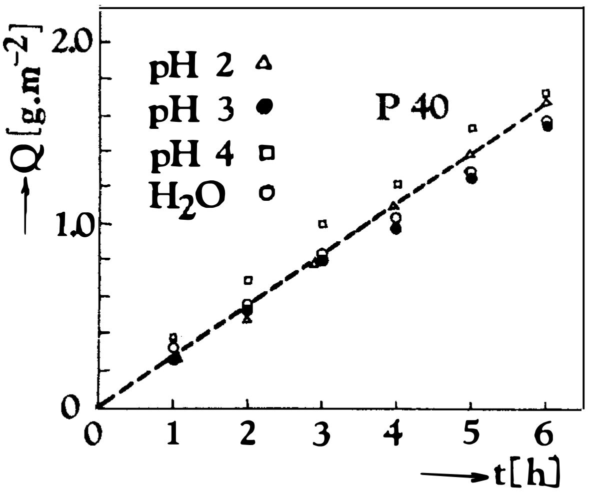

Fig. 2. The amount of SiO_2 dissolved from P 40 glass at various pH of the initial solution (85° C).

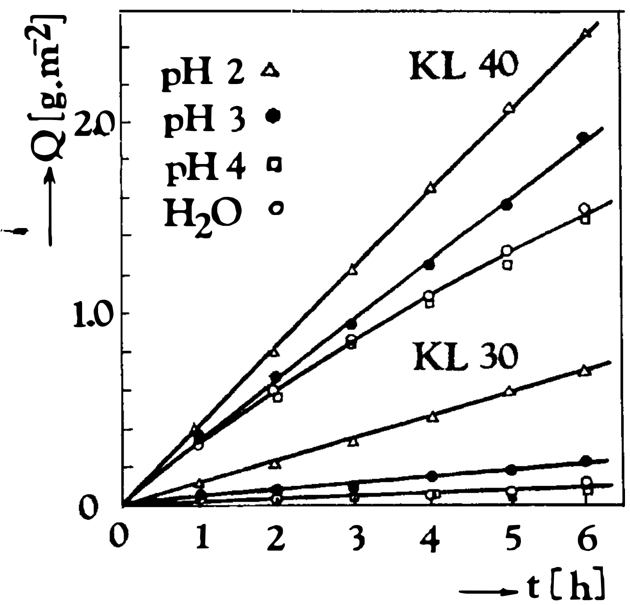

Fig. 3. The amount of SiO_2 dissolved from KL 40 glass (top curves) and KL 30 glass (bottom curves) at various pH of the initial colution (85° C).

Similarly, the cumulated amounts of extracted Na_2O for all three glasses are plotted in Figs. 4 through 6. The behaviour of glasses KL 40 and P 40 is

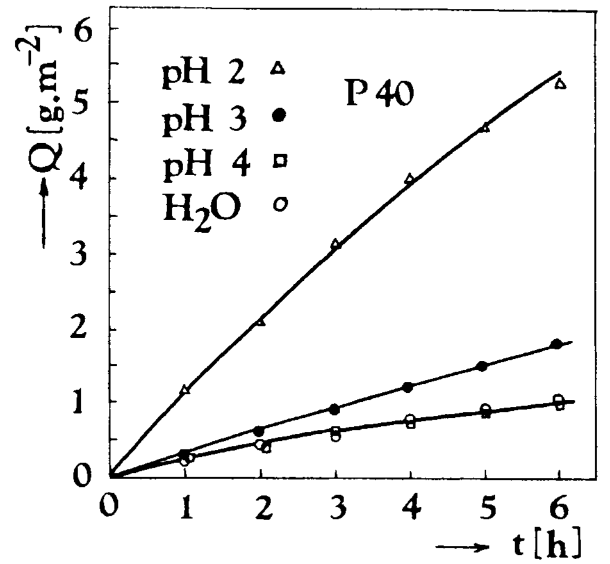

Fig. 4. The amount of Na_2O extracted from glass P 40 at various pH of the initial solution (85° C).

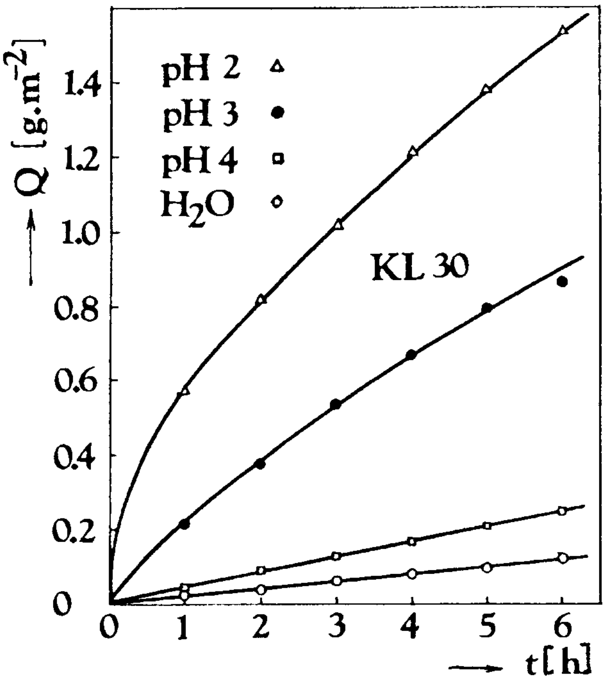

Fig. 6. The amount of Na_2O extracted from glass KL 30 at various pH of the initial solution (85° C).

again very similar; there appears a distinct non-linear time dependence and a strong effect of solution acidity on the amount of extracted Na_2O. Glass KL 30 releases into solution amounts of alkalies lower several times compared to KL 40 and P 40.

Figs. 7 through 9 show the time dependence of pH, established in the solution collected at 1-hour intervals. As a result of a rapid passage of alkalies into solution at the beginning of the process, the pH at first rises steeply and then remains at a virtually constant value. With P 40 and KL 40 glass samples (Figs. 7 and 8), the extracts remain in the alkaline region for all the solutions, except for the most acidic one (pH = 2), where the pH equalizes at a value close to 2.5, showing a mildly decreasing trend. On the other hand, with KL 30 glass (Fig. 9), the amount of leached

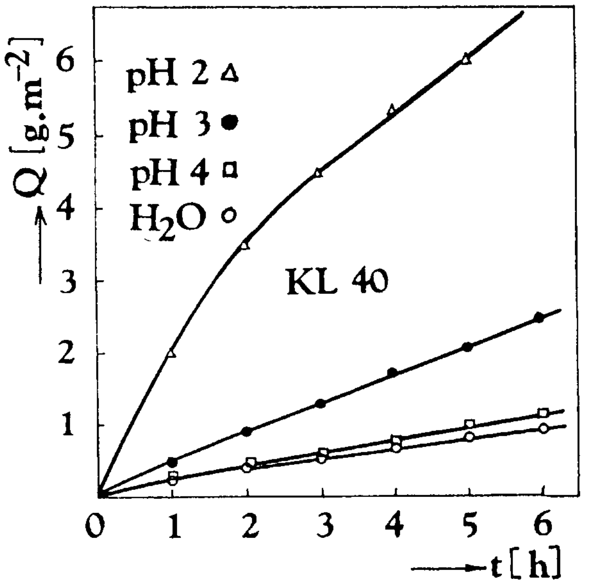

Fig. 5. The amount of Na_2O extracted from glass KL 40 at various pH of the initial solution (85° C).

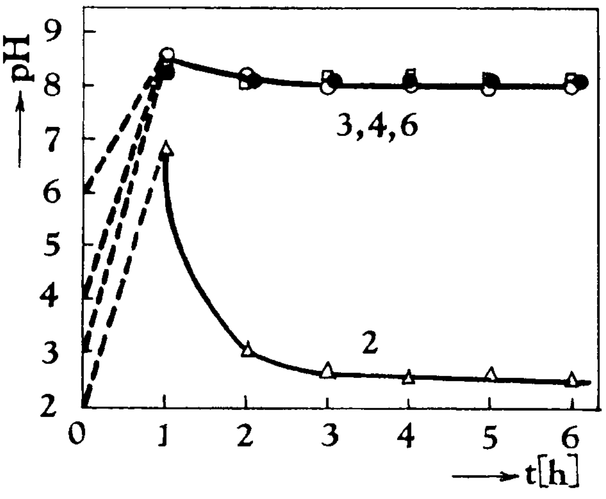

Fig. 7. Time dependence of the pH of solutions after leaching of glass P 40 (the numbers at the curves signify the pH of the initial solution).

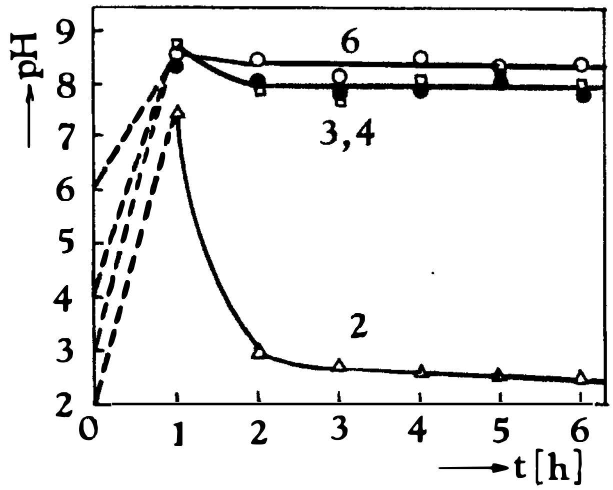

Fig. 8. Time dependence of the pH of solutions after leaching of glass KL 40 (the numbers at the curves signify the pH of the initial solution).

alkalies is considerably smaller, so that all the solutions remain in the acidic region during the leaching, even though to various degrees. At pH = 3, a pronounced peak still occurs on the curve, while at pH = 2 the pH no longer changes in terms of the time of leaching.

The character of the P 40 glass surface following its exposure to a pH = 3 solution is demonstrated in Fig. 10. The thickness of the impaired surface layer is of the order of μm; the layer is composed of gel-type products inclined to forming cracks.

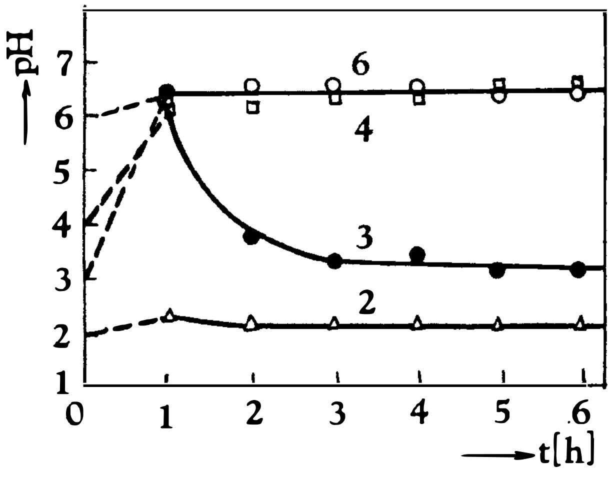

Fig. 9. Time dependence of the pH of solutions after leaching of glass KL 30 (the numbers at the curves signify the pH of the initial solution).

DISCUSSION

The static tests (Table II) showed that with glasses P 40 and KL 30, acidic solutions of pH = 2 increased the amount of extracted Na_2O and SiO_2 by a factor not higher than 1.5 to 2 compared to leaching with water. With the same glasses, the flow tests resulted in substantially greater differences in the amounts of extracted Na_2O. With the KL 30 glass, the amount of both Na_2O and SiO_2 extracted was raised significantly at the lowest pH.

The results of flow tests plotted in Fig. 2 show a good agreement of the behaviour of glasses KL 40 and P 40, which have a similar composition. The minor differences may be due to to the dissimilar thermal history, which affects the degree of stabilization and possibly even metastable separation. In contrast to glass P 40, pH has a distinct effect on the dissolution of SiO_2 from glass KL 40.

Even at a considerable rate of flow, the leachant becomes enriched with extracted alkalies, so that with glasses KL 40 and P 40, the extract exhibited an alkaline reaction till the end of the experiment, if the original solution had pH > 2 (Figs. 7 and 8). It would therefore appear that leaching with a solution having the original pH = 3 or 4 does not in fact proceed in an acidic region. However, it may be assumed that a continuous supply of the leachant to the sample will cause gradual saturation with the corrosion products, so that the acidic character of the extracting liquid will be effective at least at the inlet to the leaching cell. This is also indicated by the processing of results summarized in Fig. 11; although the pH of solutions

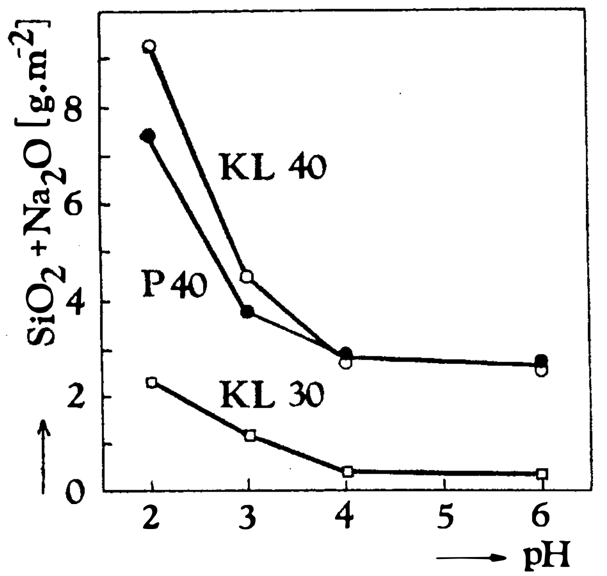

Fig. 11. Total amount extracted (SiO_2+Na_2O) during 6 hours vs. the pH of the initial solution.

after leaching of P 40 and KL 40 for the initial pH = 3 and 4 does not show any substantial difference (pH = 8), the total amount of extracted oxides increases distinctly on reducing the pH of the original solution from 4 to 3. With the KL 30 glass, this increase is already in agreement with the change in the pH value of the solution (Fig. 9).

The summarized amount of $SiO_2 + Na_2O$ in Fig. 11 represents the behaviour of glass as a whole, because it includes the poorly soluble component (SiO_2) as well as the weakly bound alkali oxide, which is extracted from conventional silicate glasses by the diffusion mechanism. The durabitily of the given type of glasses obviously decreases with acidity of the solution only at $pH < 4$. Over the entire pH range, the KL 30 glass shows a substantially greater durability than the other two glasses, as also corresponds to its higher SiO_2 content and a lower content of alkalies.

The increase in the amount of extract due to lowering pH is to a growing degree contributed to by alkalies, as shown for the KL 40 glass by Fig. 12; a similar rule applies to the other two glasses. Evidence for this is also provided by Fig. 13 showing the changes in the SiO_2/Na_2O ratio in the extract in terms of the pH of the initial solution. The ratio of the components in the initial glasses amounts to 2.08 for KL 40 and 3.42 for KL 30. A substantially lower value of the ratio in all extracts indicates that a layer enriched with SiO_2 arises on the surface of the glasses in the course of leaching; its appearance is shown in Fig. 10.

The results described above are in agreement with the general concepts of the leaching of silicate glasses with water and aqueous solutions [10]. According to these concepts, based on many experiments, two parallel basic processes are involved: 1. surface dissolution of glass or that of the impaired surface layer enriched with SiO_2, and 2. diffusive transport of the alkali and other weakly bound cations through this layer by an exchange mechanism of the $Na^+ \rightleftharpoons (H_3O)^+$ type. The results of the present study show the two processes to be affected by the acidity of the solution. A considerable acceleration of the transfer of Na_2O into solution in an acidic medium indicates that the structure of the impaired surface layer depends on the pH of the leachant. The more extensive extraction of Na_2O may be explained by a more permeable structure of the surface layer, probably associated with its gel-type character and porous structure. In addition to this, the faster extraction of Na_2O is contributed to by higher concentration of hydroxonium ions taking part in the exchange mechanism.

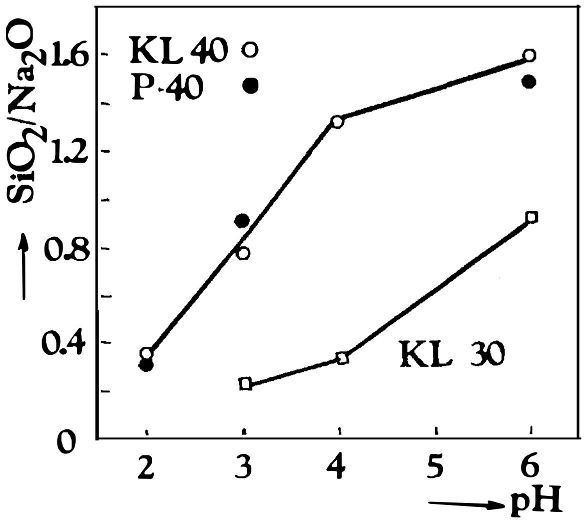

Fig. 13. Dependence of the $SiO2/Na_2O$ wt. ratio in extract on the pH of the initial solution.

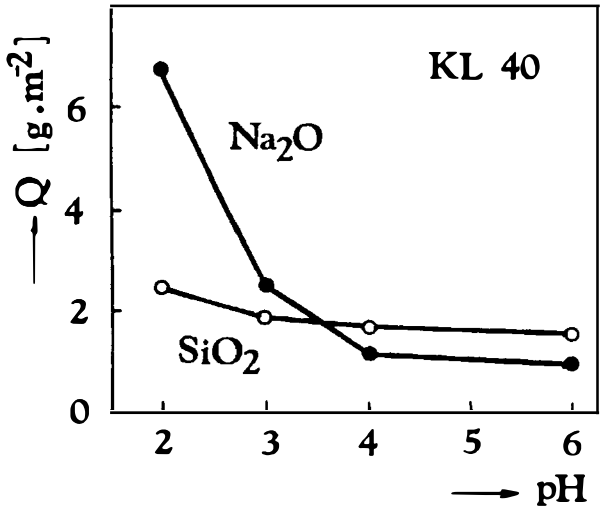

Fig. 12. The effect of pH on the amount of extracted Na_2O and SiO_2 after 6 hours, for glass KL 40.

CONCLUSION

The studied glasses of the basic system SiO_2–B_2O_3–Al_2O_3–Na_2O exhibit a significant increase in the rate of extraction and dissolution in an acidic medium. This phenomenon is mainly contributed to by increased extraction of Na_2O, indicating a dependence of the structure of the impaired surface layer on the pH of the respective solution. A strong decrease of chemical durability of these glasses must be considered at $pH < 4$.

Submitted in English by the authors

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VITRIFIKACE SIMULOVANÝCH RADIOAKTIVNÍCH ODPADŮ STŘEDNÍ AKTIVITY Z JADERNÝCH ELEKTRÁREN

II. CHEMICKÁ STABILITA PRODUKTŮ VITRIFIKACE V KYSELÝCH ROZTOCÍCH

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K experimentální práci byla použita skla základní soustavy $SiO_2 - B_2O_3 - Al_2O_3 - Na_2O$ označená KL 30, KL 40 a P 40; jejich složení je uvedeno v Tab. I. Orientační statické testy loužení ukázaly, že ve srovnání s působením destilované vody přechází z těchto skel do roztoků minerálních kyselin o pH = 2 zvýšené množství Na_2O i SiO_2 (Tab. II). K podrobnějšímu studiu koroze kyselými roztoky bylo použito průtokové metody, jejíž schéma je v obr. 1; sloupcem drtě skla prochází kontinuální loužící kapalina o pH = 2, 3, 4 a 6 (destil. voda), jež se po výstupu z reakční nádoby analyzuje a určí se její pH. Výsledky měření jsou uvedeny v obr. 2–6. S klesajícím pH loužícího roztoku se zvyšuje zejména množství uvolněného Na_2O, což lze interpretovat jako doklad zvýšení propustnosti narušené povrchové vrstvy pro difúzní transport kationtů modifikátorů. Vyloužené alkalické oxidy zvyšují pH loužícího roztoku, takže u slabě kyselých roztoků má výluh v řadě případů alkalickou reakci (obr. 7–9). Výrazné zvýšení množství SiO_2 a Na_2O převedených do kyselých roztoků ukazují obr. 11 a 12, současně se mění i poměr SiO_2/Na_2O ve výluhu (obr. 13). Výsledky jsou v souladu s představami o korozi skel vodou a vodnými roztoky za tvorby narušené povrchové vrstvy, jejíž vzhled je patrný na obr. 10.

Obr. 1. Uspořádání průtokového testu. (A – zásobní láhev na loužící kapalinu, B – čerpadlo, C – termostat, D – jímací láhev, a – topné těleso, b – míchadlo, c – reakční nádobka).

Obr. 2. Množství SiO_2 ve výluhu ze skla P 40 při různém pH výchozího roztoku (85° C).

Obr. 3. Množství SiO_2 ve výluhu ze skla KL 40 (horní křivky) a KL 30 (dolní křivky) při různém pH výchozího roztoku (85° C).

Obr. 4. Množství vylouženého Na_2O ze skla P 40 při různém pH výchozího roztoku (85° C).

Obr. 5. Množství vylouženého Na_2O ze skla KL 40 při různém pH výchozího roztoku (85° C).

Obr. 6. Množství vylouřeného Na_2O ze skla KL 30 při různém pH výchozího roztoku (85° C).

Obr. 7. Časová závislost pH výluhů pro sklo P 40 (číslice u křivek značí pH výchozího roztoku).

Obr. 8. Časová závislot pH výluhů pro sklo KL 40 (číslice u křivek značí pH výchozího roztoku).

Obr. 9. Časová závislost pH výluhů pro sklo KL 30 (číslice u křivek značí pH výchozího roztoku).

Obr. 10. Povrch drtě skla P 40 po 6 h působení roztoku H_2SO_4 o pH = 3 (SEM).

Obr. 11. Závislost celkového vylouženého množství (SiO_2 + Na_2O) po 6 h na pH výchozího roztoku.

Obr. 12. Vliv pH na množství vylouženého Na_2O a SiO_2 po 6 h u skla KL 40.

Obr. 13. Závislost hmotnostního poměru SiO_2/Na_2O ve výluhu na pH výchozího roztoku.

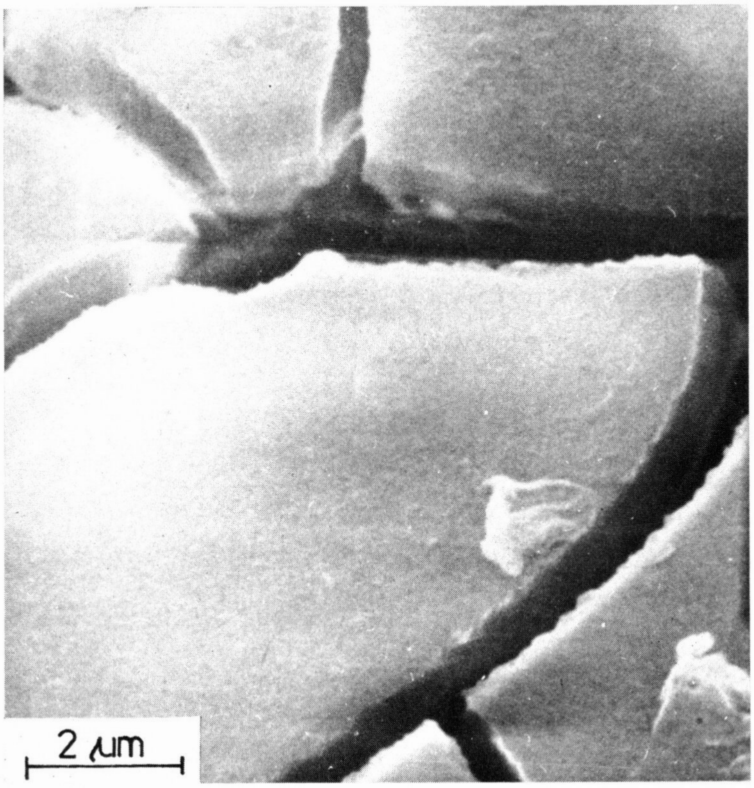

Fig. 10. The surface of glass P 40 after 6 hours of exposure to H_2SO_4 solution of pH = 3 (SEM).