

## CONCENTRATION PROFILES OF SODIUM IN THE SURFACE OF DEALKALIZED GLASSES

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*Concentration profiles of sodium in the surface layer of glasses dealkalized with ammonium sulphate were measured by the stepwise etching method and subsequent chemical analysis of the solutions obtained, as well as by the ESCA method. The results allow to conclude that the difference in hydrolytical resistance of glass surfaces dealkalized by different procedures can be explained by the parallel effects of the chemical dealkaling reaction, and of the diffusion processes involved. At the lower temperatures (of approx. 400 °C) the concentration profiles formed are stable in character, whereas at the higher temperature (800 °C), following exhaustion of the reaction agent, the difference in the concentration of sodium will be gradually eliminated by diffusion within the concentration gradient zone formed.*

### INTRODUCTION

Dealkalization of surface layers of glass by the effect of reactive gases at elevated temperatures is an efficient method for upgrading chemical durability of glasses. Its principle is based on reactions of alkalis (and possibly also other components) at the surface of glass with gaseous substances (sulphur oxides, HCl, HF and others) producing salts which form efflorescence on the surface of glass, or vaporize.

A previous study by the present authors [1] was concerned with extraction of sodium from the surface of container glass by the products of decomposition of ammonium sulphate. The results showed that the extraction of sodium depends on temperature, the time of tempering and the way the dealkaling agent is introduced (by a single dose, or by repeated ones). The amount of sodium extracted increased with increasing dealkaling temperature. At the lower temperature ( $<T_g$ ), the time dependence exhibited a continuous growth of the amount of sodium extracted, both with single and repeated dosages of the dealkaling agent. At the higher temperature ( $>T_g$ ), the amount of extracted sodium showed a continuous increase in terms of the time of tempering only when sufficient amounts of the dealkaling agent were continuously supplied to the surface of glass (repeated dosage).

As expected, the chemical durability of the dealkalized surfaces was in all instances much superior

to that of the original glass. However, in the case of glasses dealkalized at the higher temperature by a single dose of the dealkaling agent only, the chemical durability showed a certain deterioration following the initial improvement. In the case of glasses dealkalized at the lower temperature, the final durability was not affected by the time of tempering.

In order to explain the differences in the behaviour of glass surfaces dealkalized under various conditions, the concentration profiles of sodium in the surface layer of the glasses were measured. The results of the measurements are described in the present paper.

### EXPERIMENTAL PART

Small bottles of white container glass having the same composition as those used in the previous study [1] were employed as experimental specimens. The dealkaling procedure was likewise identical with that used in the respective study. Ammonium sulphate as dealkaling agent was introduced into the preheated bottles (tempered for 30 minutes at the dealkaling temperature) in the form of pellets 0.09 g in weight. Either a single pellet was introduced, or the dosing was repeated at intervals of 3 minutes. Following the dosing, the specimens were further heated at the given temperature for a chosen period of time (0.5 to 240 minutes), and then removed from the furnace.

With both dealkalized and original specimens the concentration profiles of sodium were determined by the method of stepwise etching off the surface layers of glass with a solution of hydrofluoric acid (0.5 %) and nitric acid (1 %). The solutions obtained by etching were analyzed for sodium content by the AAS method, and for  $\text{SiO}_2$  by the photometric method [2]. The approximate thickness of the etched-off layer  $h$  (nm) was calculated for each time period of etching from the amount of  $\text{SiO}_2$  that has passed into solution, using the equation

$$h = \frac{c_{\text{SiO}_2} V 10}{w_{\text{SiO}_2} \rho_{\text{gl}} A},$$

where  $c_{\text{SiO}_2}$  is the concentration of  $\text{SiO}_2$  in solution ( $\mu\text{g ml}^{-1}$ ),  $V$  is the volume of the solution (ml),  $w_{\text{SiO}_2}$  is the weight ratio of  $\text{SiO}_2$  in the glass,  $\rho_{\text{gl}} = 2.5 \text{ g cm}^{-3}$ ,  $A$  is the surface area of the glass ( $\text{cm}^2$ ).

The experimentally established values of sodium concentrations served to calculate the total amount of  $\text{Na}_2\text{O}$  in the individual layers removed by etching. Using the total loss in weight of the specimen due to etching, the total thickness of the etched-off layer was calculated.

On selected parts of the surfaces, concentration profiles of sodium were measured by the ESCA method [3].

## RESULTS AND DISCUSSION

The concentration profiles of sodium (expressed as  $\text{Na}_2\text{O}$ ) in the surface layer of the glass, measured by the stepwise etching method, are plotted in Figures 1 through 3.

An elevated sodium content was found in the surface layer of the original untreated glass down to a depth of approx. 50 nm, as compared with the glass interior (Figure 1). A surface layer enriched with alkalis which had migrated to the surface during the manufacture, is characteristic of the original surfaces of this type of glass [4]. The specimens employed had therefore obviously retained their original, non-leached surface. The higher concentration of sodium in the surface layer of the original glass may be responsible for the rapid increase in the amount of sodium extracted during the initial stages of dealkalinizing established in the previous study from the time course of the extraction [1]. These alkalis in the surface layer can be eliminated by leaching. For example, a one-hour leaching of the surface in distilled water at 121 °C in an autoclave (a standard test to [5]) brings about a significant decrease of sodium concentration in the surface layer (Figure 1) and produces an alkali-depleted layer about 180 nm in thickness. The leaching will at the same time bring into solution a certain amount of  $\text{SiO}_2$ , corresponding to the dissolving

of a surface layer approx. 60 nm thick (dashed line in Figure 1).

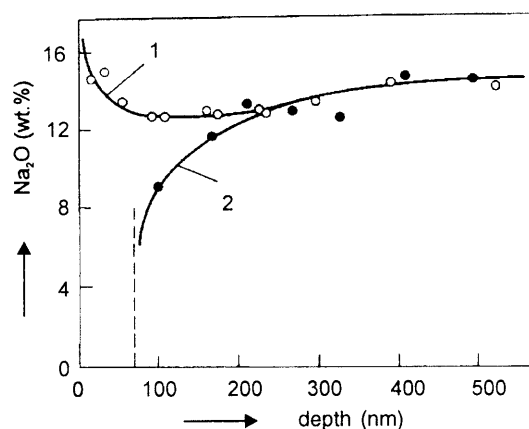


Figure 1. Concentration profiles of  $\text{Na}_2\text{O}$  in non-dealkalized glass (measured by the surface etching method) 1 - original surface; 2 - surface following the autoclave test ( $\text{H}_2\text{O}$ , 121 °C, 1 hr.)

The concentration profiles of sodium in non-dealkalized surfaces (Figures 2 and 3) differ mutually in dependence on the dealkalinizing temperature, the time of tempering following introduction of the dealkalinizing agent, and the way of introducing the agent (one dose or multiple repeated ones). Figure 2 shows the concentration profiles of sodium in glass dealkalinized at 400 °C using short (0.5 min.) and long (60 min.) times of tempering after introduction of a single dose of the dealkalinizing agent. A comparison of the two concentration profiles indicates that at this temperature, the amount of sodium extracted from the surface increases with the duration of tempering.

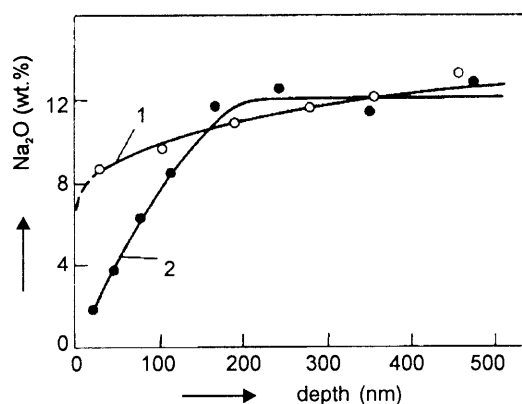


Figure 2. Concentration profiles of  $\text{Na}_2\text{O}$  in glass dealkalinized at 400 °C (measured by the surface etching method). 1 - time of tempering 0.5 min; 2 - time of tempering 60 min

A comparison of the concentration profiles of specimens tempered for a short (0.5 min.) and a long (60 min.) period of time after introduction of a single dose of the dealkalizing agent at 600 °C (Figure 3) gives a result which is quite opposite to that obtained for 400 °C: the specimen tempered for 0.5 minute has a lower concentration of sodium in the surface layer, and the sodium-depleted layer reaches to a greater depth than was the case with specimens tempered for 60 minutes. The extraction of sodium will obviously take place very quickly at the higher temperature, and as soon as the reactive components in the glass surface are spent, diffusion from the glass interior will gradually tend to reestablish the concentration equilibrium of sodium in the internal and surface layers of the glass. This is in agreement with the finding that the chemical durability of glass dealkalized by a single dose of the agent at 600 °C is gradually impaired in terms of the time of tempering [1].

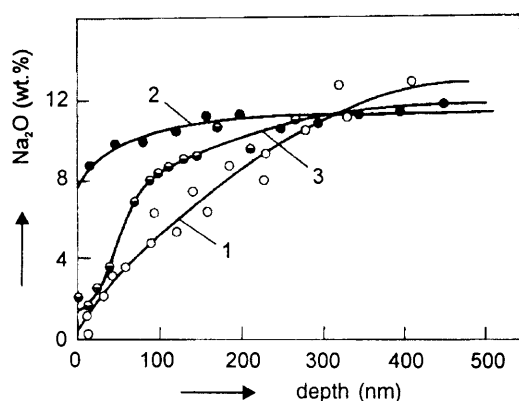


Figure 3. Concentration profiles of  $\text{Na}_2\text{O}$  in glass dealkalized at 600 °C (measured by the surface etching method). 1 - single dose of  $(\text{NH}_4)_2\text{SO}_4$ , tempering for 0.5 min; 2 - single dose of  $(\text{NH}_4)_2\text{SO}_4$ , tempering for 60 min; 3 - repeated doses, total time of tempering 240 min

A different concentration profile was found (Figure 3) with a specimen dealkalized at 600 °C by continuous introduction of ammonium sulphate pellets for 240 minutes (at 3-minute intervals). This profile lies between the two profiles described above. The sodium content in the surface layer is comparable to that of a specimen dealkalized by a single dose of the agent and tempered for a short period of time (0.5 minute). The subsurface layer of the glass to a depth of about 30-100 nm showed a steeper increase in sodium concentration, which then levelled off distinctly in the deeper layers (above 100 nm). This may be the consequence of a change in the surface structure of glass taking place simultaneously with the extraction of

sodium, and influencing the rate of diffusion of sodium from the deeper layers towards the surface.

A difference in the structure of surface layers dealkalized at the higher temperature in comparison with the original structure is also indicated by the results of measuring the concentration of  $\text{SiO}_2$  in the solutions obtained by gradual etching off of surface layers by means of hydrofluoric acid. The rate of dissolution of non-dealkalized surface layers and that of internal non-dealkalized layers calculated from these values varied around 60 to 70  $\text{nm min}^{-1}$  (Figure 4). The original low rate of dissolution of dealkalized layers (approx. 10  $\text{nm min}^{-1}$ .) increased in terms of the distance from the surface, and increased jointly with increasing sodium content over the range of 10 to 60  $\text{nm min}^{-1}$ . In contrast to this, the rate of dissolution in HF of alkali-depleted glass surfaces obtained by autoclaving in distilled water at 121 °C for 1 hour (the standard test) increased up to approx. 100  $\text{nm min}^{-1}$ . The dealkalized layers produced by the reaction of alkalis with reactive gases at higher temperatures have obviously a structure resisting better the dissolution in HF than the layer of hydrated  $\text{SiO}_2$  formed by autoclaving in distilled water.

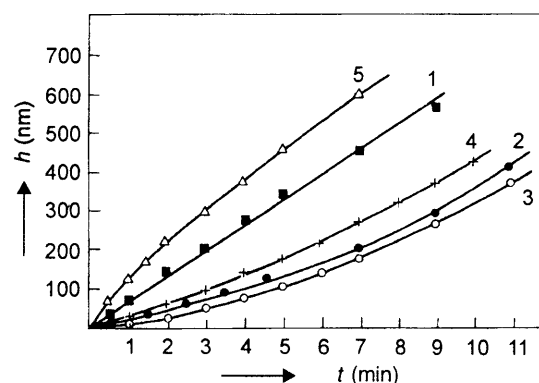


Figure 4. Thickness of the etched-off layer vs. the time of etching

1 - original surface; 2 - dealkalized surface (400 °C, tempered for 60 min); 3 - dealkalized surface (600 °C, tempered for 0.5 min); 4 - dealkalized surface (600 °C, tempered for 60 min); 5 - surface leached with  $\text{H}_2\text{O}$  (autoclave, 121 °C)

On assessing the concentration profiles of sodium in dealkalized specimens one should also take into account the fact that the specimens had first been heated in the furnace for 30 minutes at the dealkalizing temperature before the agent was actually introduced. It may be assumed that at the dealkalizing temperatures employed (400 °C and 600 °C), sodium can already diffuse from

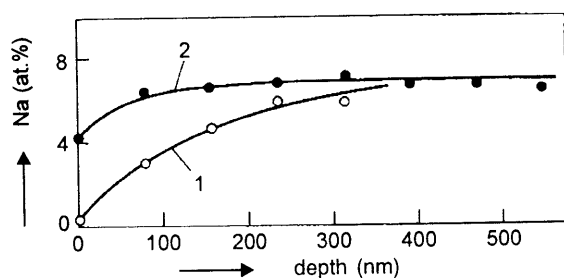


Figure 5. Concentration profiles of  $\text{Na}_2\text{O}$  in glass dealkalized at  $600^\circ\text{C}$  by a single dose of  $(\text{NH}_4)_2\text{SO}_4$ , measured by the ESCA method

1 - time of tempering 0.5 min; 2 - time of tempering 60 min;

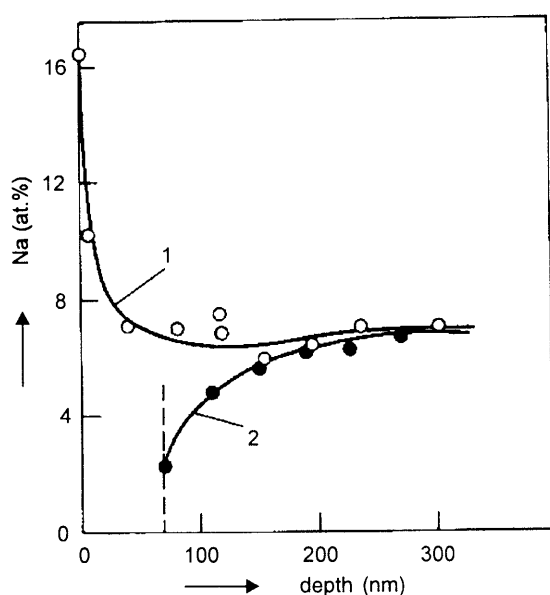


Figure 6. Concentration profiles of  $\text{Na}_2\text{O}$  for non-dealkalized glass, measured by the ESCA method

1 - original surface; 2 - surface after the autoclave test

the interior and enrich the surface layers. The concentration profiles of such specimens may thus differ from those of the original specimens, and moreover may differ in terms of the tempering temperature. The initial concentration profiles of sodium in specimens prior to dealkaling thus need not be quite identical for the tempering temperatures of  $400^\circ\text{C}$  and  $600^\circ\text{C}$ .

The concentration profiles of sodium determined by stepwise etching off the surface layers were successfully verified by the ESCA method. Figure 5 shows the concentration profiles of specimens dealkalized at  $600^\circ\text{C}$  by a single dose of ammonium sulphate and by tempering for 0.5 min. and 60 min. respectively. A comparison with the curves in Figure 3 indicates that the character of the profiles and the differences between

them are similar to those of the curves obtained by the stepwise etching method. The same applies to concentration profiles of the original non-dealkalized surface and those of specimens leached in distilled water, shown in Figure 6 (See also Figure 1).

## CONCLUSION

The results obtained provide an explanation of the different response to corrosive effects of water of glasses dealkalized under different conditions. The concentration profiles of sodium established in the surface layers exhibit differences which are in a satisfactory agreement with the hydrolytical resistance of the surfaces.

With specimens dealkalized at the lower temperature ( $400^\circ\text{C}$ ) by single dosage of the dealkaling agent, the concentration profile is not markedly affected by the secondary diffusion processes. The concentration of alkalis at the surface remains low even following longer periods of tempering. On the other hand, at  $600^\circ\text{C}$ , as soon as the reaction agent has become spent, one can observe a comparatively fast diffusion of  $\text{Na}_2\text{O}$  from the glass interior towards the surface, and gradual establishing of an equilibril concentration of sodium. At the higher temperature, the diffusion processes lead to impairing the desired effect of dealkalization. This is the reason why the glass dealkalized with a single dose of the agent at the higher temperature and exposed to prolonged tempering shows a poorer chemical durability.

## References

1. Plešingerová B., Rybaříková L., Hlaváč J.: *Ceram-Silik* 38, 137 (1994)
2. ČSN 70 0527
3. Maryška M., Matoušek J.: *Sklář a keramik* 39, 113 (1989)
4. Clark D.E., Pantano C.G., Hench L.L.: *Corrosion of Glass*, in Magazine for Industry, New York 1979
5. ČSN ISO 4802

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## KONCENTRAČNÍ PROFILY SODÍKU V POVRCHU DEZALKALIZOVANÝCH SKEL

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Práce navazuje na výsledky uvedené v předchozí publikaci [1]. Byly měřeny koncentrační profily sodíku v povrchové vrstvě

obalového skla dezalkalizovaného síranem amonným při teplotách 400 a 600 °C. Byl sledován vliv způsobu dávkování dezalkalizačního činidla (jednorázová dávka a opakované dávky) a času temperace na obsah sodíku v povrchové vrstvě. Koncentrační profily byly měřeny jednak metodou postupného odleptávání vrstev (HF) a následnou analýzou získaných roztoků, jednak metodou ESCA. Obě metody dávaly shodný charakter koncentračních profilů, jak je patrné z obrázků 1, 6 a 3, 5.

V povrchové vrstvě původního nedezalkalizovaného povrchu byl nalezen zvýšený obsah alkálií (obrázek 1). Při dezalkalizaci za teploty 400 °C jednou dávkou síranu amonného

(obrázek 2) se koncentrace sodíku v povrchové vrstvě snižuje s rostoucím časem temperace. Naproti tomu při teplotě 600 °C (obrázek 3 a 4) se výrazně projevuje rozdíl jednorázového a opakovaného dávkování dezalkalizačního činidla. Při jedné dávce se s dobou temperace již vytvořený koncentrační profil opět vyrovnává následkem poměrně rychlé difúze sodíku z vnitřních vrstev skla v koncentračním spádu, jenž se v krátkém čase vytvořil reakcí se síranem amonným. Důsledkem pak je postupné zhoršování hydrolytické odolnosti s dobou tepelné expozice [1], pokud není reakční činidlo opakovaně dávkováno.