

## EXTRACTION OF SODIUM FROM THE SURFACE OF GLASS BY THE PRODUCTS OF DECOMPOSITION OF AMMONIUM SULPHATE

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*Extraction of sodium from the surface of container glass was studied for temperatures of 400° C and 600° C in terms of the time of heating (exposure) and the way of dosing (single dose and repeated doses) of ammonium sulphate. The amount of sodium extracted increases with increasing temperature of heating. At the lower dealcalization temperature, the time dependence exhibits a steady increase in the amount of sodium extracted with both the single a repeated dosage of the reactive agent, and shows a parabolic course. At the higher temperature, the amount of sodium extracted increases uniformly only when the dealcalizing agent is supplied continuously to the glass surface (repeated dosing). The chemical durability of all the dealcalized surfaces is many times higher than that of the original untreated glass. In the case of glass surface dealcalized at the higher temperature with an only limited dose of the reactive agent, the chemical durability of the surface is becoming gradually reduced as a result of the diffusion of sodium from the internal glass layers into the dealcalized surface layer.*

## INTRODUCTION

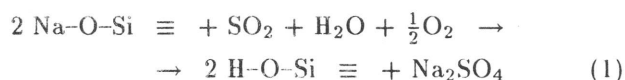
The corrosion of glass surface by aqueous solutions and atmospherical humidity, and the undesirable leaching of glass components into solutions can be suppressed by suitable treatments. The most common ones include application of protective layers or dealcalization of the surface (leaching of the surface layer, ion exchange, extraction of alkalies by reactions with gaseous substances, etc.).

Dealcalization using reactive gases at elevated temperatures is an effective and technologically viable method, which can be introduced either into the manufacturing process directly after forming (prior to annealing), or as a separate additional process after annealing the ware.

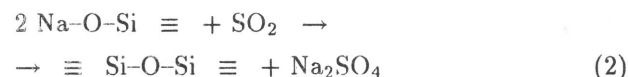
The high-temperature dealcalizing is based on reaction of the alkalies (or possibly also other components) in the glass surface with gaseous substances (sulphur oxides, HCl, HF, etc.) producing a well soluble deposit on the surface, or substances that vaporize from the surface at the temperature of the treatment.

Dealcalization with gaseous substances has been known in glass technology for a long time. Extraction of sodium by producing sodium sulphate in connection with the formation of a white deposit in annealing lehrs was already mentioned e.g. by Williams and Weyl [1]. In addition to these authors, an explanation of the dealcalization mechanism was attempted by Douglas and Isard [2] who studied extraction of sodium from glass with sulphur dioxide in terms of temperature and the presence of water vapours. They concluded that the dealcalization mechanism is temperature-dependent. At lower

temperatures (below approx. 550°C) the reaction proceeds according to the equation



The process involved is an ionic exchange of Na<sup>+</sup> for H<sup>+</sup>. The rate of the counter-diffusion of the ions in the glass depends on temperature and partial pressure of water vapour in the atmosphere. At the standard dealcalization temperatures (400°–700°C), the surface reaction of Na<sup>+</sup> with SO<sub>2</sub> (and generally with other reactive gases) is faster than the diffusion of ions in the glass, so that the diffusion is the controlling process of the extraction. The surface reaction may become the controlling process only during the initial stage of the treatment when the surface is treated with a highly dilute or poorly reactive gas. In the presence of water vapour, a hydrated surface layer rich in SiO<sub>2</sub> is formed on the glass surface. The dealcalization mechanism undergoes a change at the higher temperatures. The alkalies are then removed from the glass according to [2] by unidirectional diffusion of Na<sup>+</sup> and O<sup>-2</sup> ions, while new Si-O-Si bonds are formed in the glass surface:



This reaction, in which water vapour does not participate, yields on the surface an anhydrous high-silicate layer whose character approaches that of silica glass [3].

The effect of water vapour on the dealcalization rate was further investigated by Mochel et al. [4]

Table I

Data on the glass samples employed

Chemical composition of the glass (wt. %)	SiO <sub>2</sub> - 72.60 Na <sub>2</sub> O - 13.42 K <sub>2</sub> O - 0.80 CaO - 6.02 MgO - 4.55 Al <sub>2</sub> O <sub>3</sub> - 1.41
Transformation temperature (T <sub>g</sub> )	530°C
Chemical durability of the surface with respect to water at 121°C (autoclave test to ČSN-ISO 4802-1)	Consumption of 0.01 mol/l HCl : 3.2 ml Durability class: HC 3
Inner bottle capacity	64cm <sup>3</sup>
Inner surface area of the bottle	90 cm <sup>2</sup>

who found that SO<sub>3</sub> had more powerful dealkalization effects than SO<sub>2</sub>, as also proved by Hubert [5].

Apart from sulphur oxides, use can also be made of the vapours of HCl, H<sub>2</sub>SO<sub>4</sub>, HF, (AlCl<sub>3</sub>)<sub>2</sub>, organic fluoroderivatives, and also solid compounds ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, NH<sub>4</sub>NO<sub>3</sub>, K<sub>2</sub>S<sub>2</sub>O<sub>7</sub>, KHS<sub>2</sub>O<sub>8</sub>, etc.) which decompose at the treatment temperature, releasing simple reactive gases (SO<sub>2</sub>, SO<sub>3</sub>, HCl, HF) [6-10].

The mechanism of dealkalization, explained at first on the example of sulphur dioxide, is also applicable to chlorine compounds. Schaeffer [6, 7] points out that if the agent contains hydrogen, such as HCl, dealkalization at the lower temperatures does not so much depend on the presence of water vapour in the mixture, as is the case with SO<sub>2</sub> or SO<sub>3</sub>. However, the water does affect the degree to which the surface layer becomes hydrated. Different explanations of the mechanism of dealkalization by means of fluorine compounds can be found in the literature [9-11]; the main disagreement concerns the presence of fluorine in the dealkalized layer.

High-temperature dealkalization brings about a significantly improved chemical durability of the surface. The ware treated in this way conforms to the requirements for medicinal purposes, where they can replace borosilicate glass. The dealkalized surface retains its satisfactory chemical durability even after repeated autoclave tests or sterilizations, and also resists weathering [12, 13]. Dealkalization will prevent leaching not only of alkalis, but also of other undesirable components from glass, for instance even that of lead from lead crystal ware [14].

The present study summarizes the results obtained in the study of extraction of sodium from the surface of container glass by the products of decomposition of ammonium sulphate. The study was aimed at elucidating the effects of the dealkalization conditions on the resulting chemical durability of the glass surface.

#### EXPERIMENTAL

The experiments were carried out with colourless container glass bottles having the composition listed in Table I.

The dealkalization was carried out at 400°C (<T<sub>g</sub>) and at 600°C (>T<sub>g</sub>). The dealkalization agent employed, ammonium sulphate, was introduced into the bottles heated in advance at the respective temperature, in the form of pellets weighing 0.090 g each. The dosing was effected either once by putting in one pellet, or by repeated charges introduced at predetermined intervals: for 600°C, 1 and 3 minutes, for 400°C, 10 minutes. At 600°C, the results of the measurements were identical for the intervals of 1 and 3 minutes, whereas the interval of 10 minutes did not ensure an adequately continuous supply of the reactive component. At 400°C, the results for the intervals of 3 and 10 minutes were identical. Following the introduction of the agent, the samples were heated on in the furnace at the respective temperature for the period of time selected (0.5 to 240 minutes) and then removed from the furnace. In the case of repeated charging, the samples were always withdrawn from the furnace half a minute after introducing the last charge of the agent.

Both the dealkalized samples and the untreated ones were evaluated by the following procedures:

1. With the dealkalized samples, the deposit of sodium sulphate from the inner surface was rinsed with a defined amount of distilled water, the concentration of sodium in the rinsing solutions was determined by the AAS method, and the amount of  $\text{Na}_2\text{O}$  extracted from the unit area of the inner glass surface calculated.

2. With both the dealkalized and the original samples, the surface chemical durability with respect to water was determined by the autoclave test (temperature  $121^\circ\text{C}$ , 1 hour, total alkalinity of the leachate by titration with 0.01 mol/l HCl solution).

### THE RESULTS AND DISCUSSION

For both temperatures selected ( $400^\circ\text{C}$  and  $600^\circ\text{C}$ ), the extraction of alkalis from the glass surface was determined in terms of the time of heating (exposure) and of the way of dosing the dealkalization agent (single and repeated charging).

Fig. 1 shows the dependence of the amount of sodium extracted ( $\mu\text{g Na}_2\text{O}/\text{cm}^2$ ) on the second root of the time of heating, for both temperatures and both ways of dosing. The amounts of sodium extracted for both single and repeated dosing were higher at  $600^\circ\text{C}$  than at  $400^\circ\text{C}$ . For the temperature of  $400^\circ\text{C}$ , the course of the time dependence was virtually identical with both ways of dosing over the time period examined (up to 60 minutes), and the amount of sodium increases continuously with time. At this temperature, the amount of the sulphur oxides in the gas volume was obviously satisfactory for the reaction with alkalis even after introduction of

the single dose, so that the reaction could proceed for a longer time until the dealkalization agent was spent. After introduction of the single dose at  $600^\circ\text{C}$ , the amount of sodium extracted at first increased and later on remained unchanged. This indicates that the decomposition of the sulphate and the reactions of its decomposition proceed at this temperature substantially faster than at  $400^\circ\text{C}$ , and that the reactive gases at the surface of glass become soon spent, in particular as a result of their rapid escape from the bottle. Out of the dose of the agent employed, only a small fraction is actually utilized for the reaction with the alkalis, as shown by a calculation based on the amount of sodium found in the extract from the glass surface. For example, at  $600^\circ\text{C}$ , of the single dose of 90 mg ammonium sulphate during 10 minutes of heating, only about 3% of the sulphate got used up in the reaction with alkalis (calculated on the assumption of its decomposition to  $\text{SO}_3$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}$ ).

During the experiments, the ammonium sulphate pellets were patently decomposed at temperatures above  $300^\circ\text{C}$ , and the decomposition was vehement at temperatures of  $500^\circ\text{C}$  and higher. In the literature, a comparatively wide temperature interval of  $250^\circ\text{C}$ – $513^\circ\text{C}$  is specified, and the explanations of the decomposition mechanism differ. The decomposition is assumed to take place in several stages yielding intermediate reaction products [15, 16].

The diagram in Fig. 1 also shows that with repeated charging of the agent at intervals of 1 to 3 minutes, where the reactive gas was available at the glass surface for the entire time of heating, the amount of sodium extracted increased continuously during the heating at  $600^\circ\text{C}$ . In this case, the sodium diffusing to the glass surface was continuously consumed by the reaction with the dealkalization agent.

Following the initial faster rise, the dependence of the amount of sodium extracted on the second root of time at  $400^\circ\text{C}$  had a linear course indicating that diffusion of ions through the surface layer of glass was the controlling process.

Using the known amount of sodium extracted ( $m$ ) and the value of initial concentration ( $C_0$ ) it was possible to calculate the effective diffusion coefficient ( $D$ ) for the linear part of the curve by resolving the 2nd Fick's law for diffusion from a constant source ( $m = 2C_0\sqrt{Dt/\pi}$ ). In view of the relatively poor accuracy of diffusion coefficient determinations, the calculated value  $D_{400} = 4.4 \times 10^{-14} \text{ cm}^2\text{s}^{-1}$  is in a relatively good agreement with that given by Douglas and Isard [2] for dealkalization of glass by sulphur dioxide ( $D = 1.1 \times 10^{-13} \text{ cm}^2\text{s}^{-1}$ ). However, the values are lower by several orders of magnitude than the coefficient of self-diffusion of sodium in  $\text{Na}_2\text{O}$ - $\text{CaO}$ - $\text{SiO}_2$  glasses, which should amount to about  $10^{-10}$ – $10^{-9}$

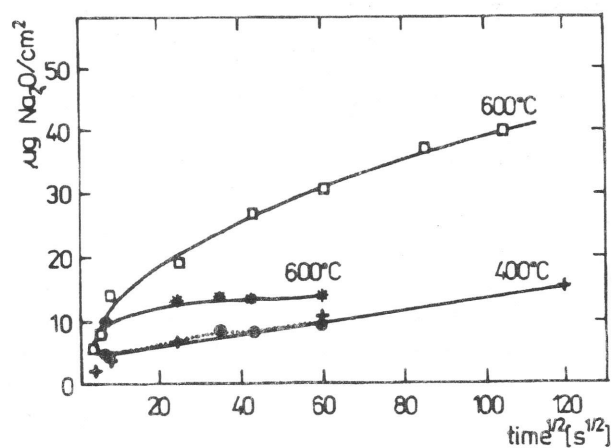


Fig. 1. The amount of sodium extracted vs. the second root of the time of heating

- +  $400^\circ\text{C}$ , single dose of  $(\text{NH}_4)_2\text{SO}_4$
- $400^\circ\text{C}$ , repeated doses of  $(\text{NH}_4)_2\text{SO}_4$
- \*  $600^\circ\text{C}$ , single dose of  $(\text{NH}_4)_2\text{SO}_4$
- $600^\circ\text{C}$ , repeated doses of  $(\text{NH}_4)_2\text{SO}_4$

$\text{cm}^2\text{s}^{-1}$  at  $400^\circ\text{C}$ . There is a difference in the mechanism of the process, and in addition to this, the dealkalized layer becomes gradually dehydrated with a resulting densification of structure and a change in the composition towards a higher content of  $\text{SiO}_2$ .

For the temperature of  $600^\circ\text{C}$ , the course of the dependence of the amount of extracted sodium on  $\sqrt{t}$ , after an initial rapid increase (up to approx 1.5 minute), is not explicitly linear (Fig. 1). It cannot be ruled out that this course may be affected by a slowing down of diffusion caused by densification of the glass surface layer, which is more distinct at this higher temperature than at  $400^\circ\text{C}$ .

The short initial non-linear part of the curve at both temperatures may be affected by an elevated content of alkalis in the surface layer of the original glass surface, formed in consequence of the migration of alkalis to the surface in the course of the manufacture [3]. One should also take into account that the very short times of dealkalization (0.5–1 min.) involve the largest error due to continuing extraction of alkalis during the cooling down of the samples following their removal from the furnace.

The chemical durability of the inner surfaces of the dealkalized samples, assessed by the autoclave test at  $121^\circ\text{C}$  and expressed by the consumption of HCl in titrating 100 ml of the leachate, is plotted in Fig. 2 for both temperatures in terms of the time of heating following introduction of one dose of ammonium sulphate. The consumption of HCl for the original untreated surface is likewise plotted for the sake of comparison. The consumption of HCl for dealkalized surfaces is much lower (approx. 100-times for the short times of dealkalization) than that for the original surface. The chemical durability of the surface, achieved by a single dose of ammonium sulphate at  $400^\circ\text{C}$ , remained virtually unchanged in terms of the time of heating, whereas in the same case at  $600^\circ\text{C}$  it decreased distinctly with the time of heating (the HCl consumption increased) in spite of the fact that the amount of sodium extracted after using one dose of the agent at  $600^\circ\text{C}$  was higher at all the times of heating (Fig. 1) than it was at  $400^\circ\text{C}$ . This result indicates that at  $600^\circ\text{C}$ , when the reactive gaseous component produced from one dose of the agent is quickly spent at the glass surface, the subsequent heating leads to a gradual equalization of the concentration profile of sodium in the surface layer, as a result of its diffusion from the interior glass layers. In consequence of this, the chemical durability of the glass surface is becoming gradually reduced.

The concentration profiles of sodium in the surface layers of the glass were measured in order to explain the differences in the behaviour of surfaces dealkalized under different conditions. The results will be presented in another publication being prepared [17].

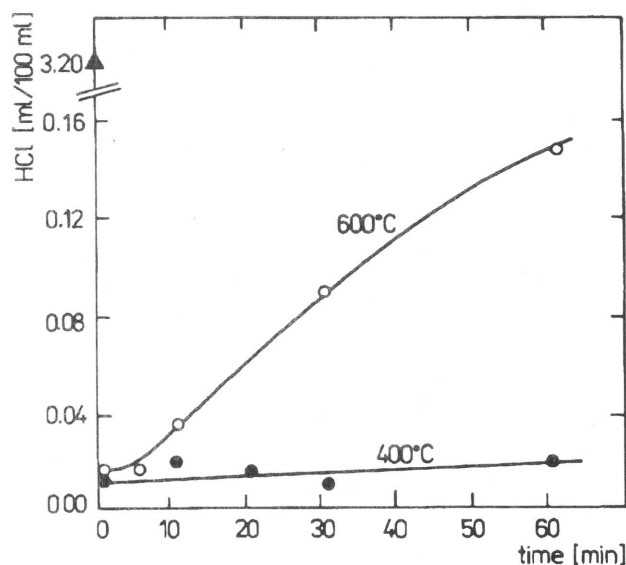


Fig. 2. The effect of the time of heating (exposure) during dealkalization on chemical durability of the surface expressed as consumption of HCl ( $C = 0.01 \text{ mol/l}$ ) on titrating the leachate after the autoclave test.

▲ consumption of HCl for the original non-dealkalized surface

## CONCLUSION

The extraction of sodium from the surface of glass resulting from a reaction with the products of decomposition of ammonium sulphate depends on temperature, the time of heating and the way of charging the dealkalization agent. The amount of sodium extracted increases with the heating temperature. At the lower temperature, the time dependence exhibits a continuous increase in the amount of sodium extracted in terms of time, and shows a parabolic course indicating that diffusion of ions through the surface layer of glass is the controlling process. At the higher temperature, the amount of sodium extracted increases uniformly only when the dealkaling agent is continuously and adequately supplied to the glass surface, and the time dependence is not explicitly parabolic. The extraction of sodium at higher temperatures is associated with a densification of the dealkalized surface layer which may affect the diffusion of the ions.

The chemical durability of dealkalized surfaces is many times higher than that of the original glass. The chemical durability of glass surfaces dealkalized at higher temperatures by a limited amount of the agent tends to decrease in terms of the time of heating, as a result of the diffusion of sodium from the inner glass layers into the dealkalized surface layer. The chemical durability of glass surfaces dealkalized at the lower temperatures is not influenced by the time of heating.

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### EXTRAKCE SODÍKU Z POVRCHU SKLA PRODUKTY ROZKLADU SÍRANU AMONNÉHO

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Vysokoteplotní dezalkalizace působením reaktivních plynů na povrch skla je účinnou úpravou pro zvýšení povrchové chemické odolnosti. Její podstatou je reakce alkálií (event. dalších složek) v povrchu skla s plynnými látkami (oxydy síry, HCl, HF aj.) za vzniku solí, které vytvářejí na povrchu skla snadno rozpustný nálet nebo z povrchu skla vytékají.

Experimentálně byla sledována extrakce sodíku z povrchu obalového skla produkty rozkladu síranu amonného

pro teploty 400°C (<T<sub>g</sub>) a 600°C (>T<sub>g</sub>) v závislosti na čase temperování a způsobu dávkování (jednorázová dávka a opakované dávky) dezalkalizačního činidla. Dezalkalizované i původní povrchy byly hodnoceny následujícími postupy:

1. Stanovením množství sodíku vyextrahovaného ze skla na základě analýzy depozitu vytvořeného při reakci na jeho povrchu.
2. Stanovením chemické odolnosti povrchů proti vodě autoklávovou zkouškou (121°C; 1 h; titrace výluhu HCl o koncentraci 0,01 mol/l).

Závislost množství vyextrahovaného sodíku na čase temperace je pro obě sledované teploty a oba způsoby dávkování dezalkalizačního činidla na obr. 1. Množství vyextrahovaného sodíku roste s teplotou temperace. Časová závislost vykazuje pro nižší použitou teplotu (400°C) plynulý vzrůst vyextrahovaného množství sodíku s dobou temperace a má po počátečním rychlejším nárůstu parabolický tvar (lineární závislost na  $\sqrt{t}$ ) naznačující, že řídicím dějem extrakce je difúze iontů povrchovou vrstvou. Ve sledovaném časovém rozmezí (60 min) je průběh této závislosti stejný pro jednorázové i opakované dávkování činidla. Při této teplotě je ve výrobku po vhození pouze jedné dávky činidla dostatečné množství reaktivní složky pro plynulý průběh reakce i po delší dobu. Při vyšší teplotě (600°C) roste množství vyextrahovaného sodíku s časem plynule pouze při nepřetržitém přísunu reaktivní složky k povrchu skla (opakované dávky). Časová závislost nemá v tomto případě jednoznačně parabolický tvar. Extrakce sodíku při vyšších teplotách je spojena se zhutňováním struktury povrchové dezalkalizované vrstvy skla a touto skutečností může být difúze iontů povrchovou vrstvou ovlivněna.

Chemická odolnost dezalkalizovaných povrchů je ve všech případech mnohonásobně vyšší, než u povrchů původních. U povrchů dezalkalizovaných při vyšší teplotě pouze jednou dávkou reaktivního činidla se s rostoucí dobou temperace výsledná chemická odolnost postupně poněkud zhoršuje v důsledku difúze sodíku z vnitřních vrstev skla do povrchové dezalkalizované vrstvy (obr. 2). U povrchů dezalkalizovaných při nižší teplotě není výsledná chemická odolnost dobou temperace ovlivněna.

Obr. 1 Závislost množství vyextrahovaného sodíku na druhé odmocnině z času temperace

+ 400°C, jedna dávka (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>

● 400°C, opakované dávky (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>

\* 600°C, jedna dávka (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>

□ 600°C, opakované dávky (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>

Obr. 2 Vliv doby temperace při dezalkalizaci na chemickou odolnost povrchu. [Vyjádřeno spotřebou HCl (C=0,01 mol/l) při titraci výluhu po autoklávové zkoušce.]

▲ spotřeba HCl pro původní nedezalkalizovaný povrch