

REDUCTION OF LEAD LEACHING FROM LEAD CRYSTAL GLASS

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The surfaces of lead crystal glass ware containing 24 wt.% PbO were dealkalized with products of decomposition of ammonium chloride at temperatures of 250 – 500° C. The deposit formed on the glass surface was found to contain also lead, apart from potassium and sodium. The lead content was low compared to that of the alkalis. Tests of surface chemical durability with respect to water by the autoclave method as well as long-term surface leaching with acetic acid solution showed that dealkalization reduced considerably the leaching of alkalis as well as that of lead. The efficiency of the treatment increased with temperature, but even the glass surfaces dealkalized at the lowest temperatures, far below the T_g of the glass, exhibited a very satisfactory durability also on the long-term basis.

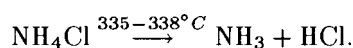
INTRODUCTION

A low extraction of lead from the surface is requested in the case of lead crystal ware coming into contact with foodstuffs. Although most of the current glasses so far conform to the existing standard specifications, extensive research aimed at reducing the leaching of lead has been under way. The research had been instigated by the publications of American authors [1] who studied the leaching of lead from crystal decanters and glasses into various alcoholic beverages, in particular wine. For example, they found that the concentration of lead in wine kept for approximately 4 months in decanters of lead crystal containing 24% PbO increased from the original value of 89 µg/l to 2162 µg/l, and in a decanter with 32% PbO, to 5331 µg/l. In short-term tests with wine glasses, the original lead concentration of 33 µg/l rose up to 68 µg already within one hour.

The research aimed at reducing the leaching of lead is conducted in two directions:

- (1) modification of the glass composition
- (2) surface treatment of the ware.

Dealkalization at elevated temperatures (400 to 600°C) is one of the surface treatment methods generally used to improve the chemical durability of the glass surface [2–6]. It is based on interaction of alkalis in the glass surface with reactive gaseous substances, producing compounds which either volatilize at the treatment temperature, or form a well soluble deposit on the glass surface. The gaseous dealkalization agents employed include SO₂, SO₃ and HCl; the solid ones, such as NH₄Cl, (NH₄)₂SO₄ and KHSO₄, are decomposed at higher temperatures, producing simple gases capable of reacting with the components in the glass surface [5]. For example, ammonium chloride is sublimed at elevated temperature, while some of the molecules are dissociated according to the equation



The dissociation degree depends on temperature. Both HCl and NH₄Cl may take part in the dealkalization.

It is assumed that apart from other alkalis, also other components are extracted from the glass surface to a lesser degree, mostly calcium in the case of soda-lime-silicate glasses [3]. According to some authors, Fe, Al, Mn, Pb, B are likewise extracted [6, 7]. Schaeffer et al. [7] studied dealkalization of lead glass in the system K₂O-Na₂O-PbO-SiO₂ by means of HCl. Although no lead was found in the deposit on the glass surface, according to HCl consumption in the reaction they assumed formation of lead chloride which, however, had probably volatilized at the temperature of the treatment.

Dealkalization leads to an effective suppression of surface corrosion of glass by aqueous solutions as well as by air humidity [8, 9] as a result of changes in the chemical composition and structure of the glass surface layer. Study of the surface layers of glass dealkalized at elevated temperatures shows that a thin compact layer rich in SiO₂, similar in its structure to silica glass, is formed on the surface [3].

High-temperature dealkalization is used above all in the surface treatment of container glasses [8, 9], particularly containers for the pharmaceutical industry [10] as well as as that of sheet glasses. Dealkalization of lead glasses has so far been only sparsely dealt with in available literature [7], and only very recently, it has been paid attention within the framework of efforts aimed at suppression of leaching of lead from lead crystal glass.

The present study deals with the effect of dealkaling the surface of lead crystal on leaching of lead into solutions.

EXPERIMENTAL

In the experiments, use was made of unpolished lead crystal products (glasses of 300 ml capacity and 203 cm² inner surface area, and glass cups of

180 ml capacity and 171 cm² inner surface area). The ware was dealkalized in a laboratory furnace at temperatures ranging from 200 to 500°C using a single dose of 0.1 g ammonium chloride. The dealkaling agent in powder form was introduced into the cold glasses before placing in the furnace. Following attainment of the respective temperature and cooling down, the deposit of dealkalization products was rinsed off with 25 ml of distilled water, and the concentration of potassium in the rinsing solution was determined by flame photometry, and that of lead by AAS. The rinsed dealkalized samples, together with the untreated ones, were evaluated by the following methods:

(1) By leaching the inner surfaces with distilled water under the conditions of the autoclave test to ISO 4802 [11] (temperature 121°C, 1 hour) and by multiple repeating of these cycles. The total alkalinity of the leachates was determined by titration with dilute HCl ($c = 0.01$ mol/l), the concentration of lead by AAS and that of SiO₂ photometrically.

(2) By leaching the inner surfaces with a solution of acetic acid (4% by vol.) at room and elevated temperature (60°C), and by determining the lead concentration in the leachates by AAS. The dilute acetic acid is stipulated as a standard leaching medium by ISO 7086 [12] for the purpose of determining lead and cadmium leached from glass and ceramic containers coming into contact with foodstuffs.

RESULTS AND DISCUSSION

The efficiency of dealkalization was first assessed on the basis of components determined in the deposit on the glass surface. In the case of lead crystal, the components subject to leaching are first of all potassium, then sodium and extraction of lead is also assumed to take place [7]. Although it cannot be ruled out that some of the dealkalization products may volatilize particularly at higher treatment temperatures [4, 7] and the amounts of components determined in the deposit need not correspond fully to the actual amounts extracted from the glass surface, the value is regarded as a convenient approximate measure of the efficiency of dealkalization.

Fig. 1 shows the amount of potassium found in the deposit and expressed as extract from a unit area of the glass surface in terms of the dealkalization temperature. The diagram indicates a distinct increase in the amount of extracted potassium with increasing temperature. In addition to potassium, also a substantially lower amount of sodium, corresponding to its content in glass (the glass contained 11.7 wt.% K₂O and 1.9 wt.% Na₂O) was determined. In contrast to the literature [7], also lead was found in the deposit. However, its content was poorly reproducible and unlike that of potassium, showed no explicit de-

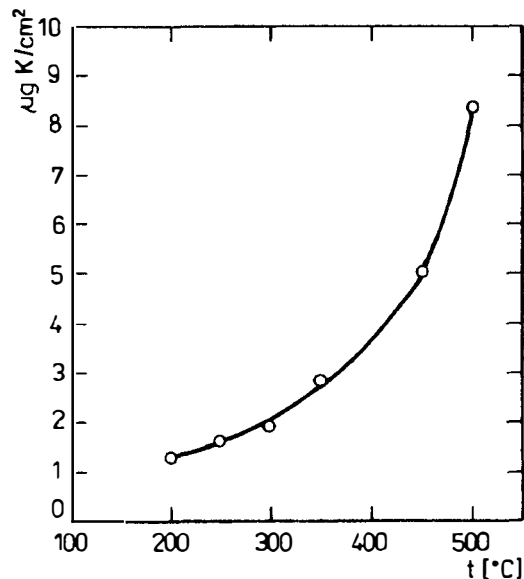


Fig. 1. The amount of potassium extracted from a unit area of the glass surface vs. the dealkalization temperature.

pendence on temperature. The amount of lead determined was always substantially lower than that of potassium. For example, the maximum lead content in the rinse following dealkalization at 450°C corresponded to an extraction of approx. 0.4 µg Pb from 1 cm² of the internal surface, whereas with potassium, the same dealkalization conditions yielded an average value of 5.1 µg from 1 cm². The lead crystal in question contained 24 wt.% PbO and 11.7 wt.% K₂O.

The amounts of components extracted from the glass surface allow the thickness of the layer, from which the components have been completely eliminated by extraction, to be approximately calculated on the simplifying condition that a jump-type change is involved [13]. For our case of dealkalization at 450°C, the thickness of the extracted layer amounts to approx. 200 nm for potassium and to merely approx. 20 nm for lead. The experiments also indicated that the amount of lead in the deposit was significantly influenced by the way the dealkaling agent had been introduced. Placing of the agent inside the containers yielded higher lead contents in the deposit than its placing freely into the furnace area, apart from the glasses. At the same time, the way of introducing the agent had no significant effect on the extraction of potassium and the final improvement of chemical durability, including the leaching of lead [14]. Lead is obviously extracted from the glass surface much less readily and to a lesser degree than the alkalis, and extraction of the former seems to be more affected by the conditions of treatment, such as the presence of

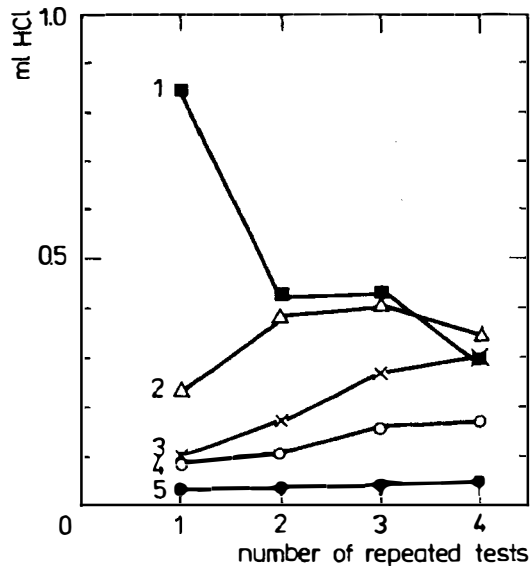


Fig. 2. Consumption of HCl (0.01 mol/l) in the titration of 25 ml of extract after the autoclave test in terms of the number of repeated autoclave cycles. 1 - untreated surface, 2 - 5 dealkalized surfaces (2 - 250°C, 3 - 350°C, 4 - 450°C, 5 - 500°C)

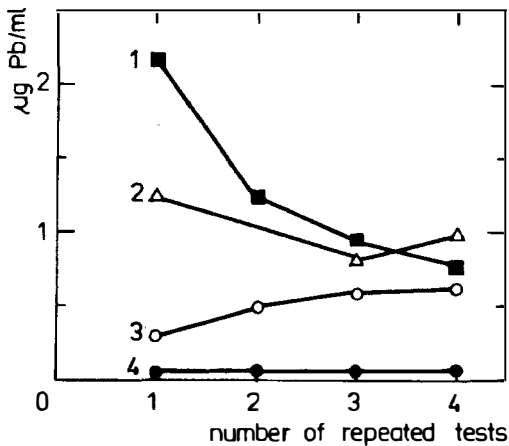


Fig. 3. Concentration of lead in extracts after the autoclave test in terms of the number of repeated autoclave cycles. 1 - untreated surface, 2 - 4 dealkalized surfaces (2 - 250°C, 3 - 450°C, 4 - 500°C)

adequate amounts of reactive gases at the glass surface.

The results of assessing the effect of dealkalinization on the surface chemical durability are plotted in Figs. 2 through 5 and listed in Table I. Figs. 2 through 4 demonstrate the results of leaching the inner surfaces in distilled water at 121°C in an autoclave as the individual quantities measured (total leachate alkalinity, lead concentration, SiO₂ concentration) vs. the number of repeated autoclave cycles.

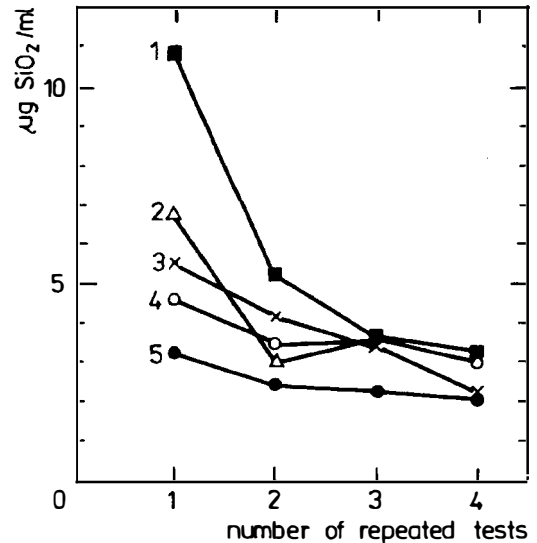


Fig. 4. Concentration of SiO₂ in extracts after the autoclave test in terms of the number of repeated autoclave cycles. 1 - untreated surface, 2 - 5 dealkalized surfaces (2 - 250°C, 3 - 350°C, 4 - 450°C, 5 - 500°C)

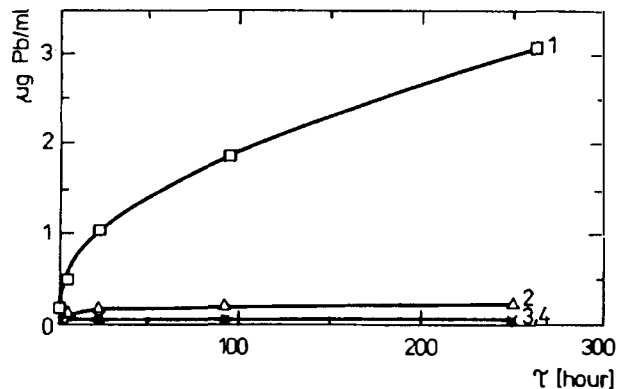


Fig. 5. Time dependence of the concentration of lead in extracts into acetic acid (4% v/v) at 60°C. 1 - untreated surface, 2 - 4 dealkalized surfaces (2 - 250°C, 3 - 350°C, 4 - 450°C)

Fig. 2 which shows the dependence of total leachate alkalinity expressed as HCl consumed ($c = 0.01$ mol/l) in leachate titration, vs. the number of autoclave cycles, indicates a distinct alkalinity reduction of dealkalinized surfaces compared to a non-treated surface after the first autoclaved cycle. With the other repeated autoclave cycles, the alkalinity of leachates from the original untreated surface decreases as a result of gradual leaching of alkalis from the surface, while it increases somewhat in the case of treated surfaces in consequence of gradual dissolution of the dealkalinized surface layer, so that the alkalinity values of extracts from untreated and treated samples approach one the other. At the same time, the results

Table I

The effect of dealcalization on the leaching of lead into dilute acetic acid (4% v/v) at room temperature. Sample: glass of 300 ml capacity, inner surface area 203 cm²

Surface treatment	Time of leaching	Pb ($\mu\text{g/ml}$)		
		24 h	72 h	645 h
Untreated surface		0.24	0.32	0.64
Dealcalized surface (NH ₄ Cl, 250°C)		0.020	–	0.029
Dealcalized surface (NH ₄ Cl, 350°C)		0.014	0.015	0.019
Lead concentration in the initial dilute acetic acid		0.013		

show that the chemical durability increases with increasing dealcalization temperature. The best chemical durability was exhibited by a glass surface treated at 500°C.

A course similar to that of total alkalinity is shown by the dependence of lead concentration in the extracts on the number of autoclave cycles (cf. Fig. 3). Surface dealcalization thus markedly suppresses leaching of alkalies, as well as that of lead. Even in this case, the efficiency of the treatment increases with increasing temperature of dealcalization.

The dependence of the amount of SiO₂ in the leachates on the number of autoclave cycles (Fig. 4) shows that the dealcalization not only suppresses the leaching of alkalies and lead from the surface of glass, but also reduces the rate of dissolution of the surface glass layer. The reduction of the rate of dissolution of the dealcalized layer, occurring even under relatively drastic conditions such as those provided by the autoclave test, indicate a structural toughening of the surface layers of glass resulting from the dealcalization [3]. It is this structural toughening which is probably responsible, jointly with lead extraction, for suppression of the leaching of lead from the surface layer of dealcalized lead crystal. It is significant that the surface durability of the surface is substantially improved even by dealcalization at relatively low temperatures (250°C), which are well below the transformation point of the glass ($T_g = 450^\circ\text{C}$). In the literature, temperatures close to, or rather higher than, the T_g of glass are generally recommended for efficient dealcalization of soda-lime-silicate glasses.

The resistance of dealcalized surfaces to extraction of lead was further tested by leaching with standard dilute acetic acid (4% v/v). An earlier study [15] showed that at room temperature, dealcalized surfaces exhibited low lead extraction even on long-term exposure. Table I compares lead concentrations in acetic acid room-temperature extracts from one untreated sample and two dealcalized ones for three times of measurement. The lead concentration was determined by AAS using the graphite furnace method. The results show that the amount of lead leached from dealcalized surfaces were very low even with very long time of leaching (645 hours). Even here, the efficiency of dealcalization was higher at higher temperatures. It was again found that even surfaces dealcalized at relatively low temperatures (250°C) showed a very satisfactory resistance to long-term leaching of lead. Fig. 5 shows the relationship between leaching of surfaces into dilute acetic acid at 60°C. Even at elevated temperatures, the dealcalized surfaces retain a satisfactory long-term durability and yield significantly lower extraction of lead than untreated surfaces. In this case, the effect of the temperature of dealcalization on its efficiency was also marked.

It is known that the chemical durability of glasses can likewise be improved by preliminary leaching of the surfaces in suitable solutions, such as those of acetic acid in the case of lead glasses. The results listed in Table I make it possible to calculate that e.g. after the first 24 hours of leaching in a solution of this acid at room temperature, 0.34 μg Pb are leached from 1 cm² of the untreated glass surface. In this case, the amount of lead leached from the unit surface during the first 24 hours is comparable to the amount established in the case of products dealcalized at 450°C (0.4 $\mu\text{g/cm}^2$). If one assumes that in our case the amount leached by dealcalization at this temperature is approximately identical with the amount leached by acetic acid during the first 24 hours, it follows from the results in Table I that the leaching rate of lead from dealcalized surfaces is several times lower than that from the surface treated by preliminary leaching with acetic acid. This fact is in agreement with the assumption that apart from the extraction of a not very significant amount of lead from the surface layer, formation of a high-silica surface layer with a toughened structure is obviously the decisive factor leading to reduced leaching of lead from dealcalized lead crystal. The layer acts as a barrier to diffusion of alkalies and lead from the interior layers to the surface.

CONCLUSION

The results of the present study showed that dealcalization of the surface of lead crystal by reactive

gases formed by decomposition of solid substances result not only in reduced leaching of alkalies from the glass surface, but also to a significant suppression of the leaching of lead.

Also lead was established in the dealcalization products on the glass surface, but its amount was relatively low. Over the temperature range of 200 to 500°C studied, the efficiency of dealcalization, assessed according to the amount of potassium extracted and the chemical durability of surfaces achieved, was increasing with increasing temperature of dealcalization. Surprisingly favourable results were already obtained at the lowest treatment temperatures employed (250°C).

The dealcalized surfaces retain low lead extractability even under conditions of long-term leaching in acetic acid at room or elevated temperature.

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SNÍŽENÍ VÝLUHŮ OLOVA Z OLOVNATÉHO KŘIŠTÁLU

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U výrobků z olovnatého křišťálu přicházejících do kontaktu s potravinami je požadován nízký výluh olova z povrchu.

V práci byla studována dezalkalizace povrchu olovnatého křišťálu o obsahu 24% hmot. PbO produkty rozkladu chloridu amonného a její vliv na snížení množství olova ve výluzích. Dezalkalizace probíhala při teplotách 200–500°C dávku 0.1 g chloridu amonného. Upravené i původní povrchy byly hodnoceny následujícími zkouškami:

- 1) stanovením obsahu alkálií a olova v depozitu vytvořeném při reakci na povrch skla;
- 2) hodnocením chemické odolnosti povrchů proti vodě autoklávovou zkouškou při 121°C s opakováním autoklávových cyklů. Ve výluzích byly stanoveny alkálie, olovo a SiO₂;
- 3) loužením vnitřních povrchů výrobků v roztoku kyseliny octové (4 obj.%) při laboratorní a zvýšené teplotě (60°C) a stanovením obsahu olova ve výluzích.

V depozitu na povrchu skla byly nalezeny alkálie, především draslík, jehož množství výrazně rostlo s teplotou (obr. 1). Vedle alkálií bylo v depozitu nalezeno i olovo, jehož množství však bylo v porovnání s draslíkem nízké.

Hodnocení chemické odolnosti povrchů proti vodě autoklávovou zkouškou s opakováním autoklávových cyklů ukázalo, že dezalkalizací se sníží nejen výluh alkálií z povrchu (obr. 2), ale i výluh olova (obr. 3). Dezalkalizací se potlačí i rozpouštění povrchové vrstvy skla, jak je patrné ze stanovení obsahu SiO₂ ve výluzích (obr. 4). výrazně se sníží vyluhování olova do roztoku kyseliny octové za laboratorní (tab. I) i zvýšené teploty (obr. 5) a to i z dlouhodobého hlediska.

Účinnost dezalkalizace posuzovaná na základě výsledků všech použitých zkoušek roste s teplotou. Významně je zjištěno, že k výraznému snížení vyluhování olova i alkálií dochází již při dezalkalizaci za poměrně nízkých teplot (250°C) hluboko pod transformační teplotu skla.

Obr. 1. Závislost množství draslíku vyextrahovaného z jednotlivky povrchu skla na teplotě dezalkalizace.

Obr. 2. Spotřeba HCl (0,01 mol/l) při titraci 25 ml výluhu po autoklávové zkoušce v závislosti na počtu opakovaných autoklávových cyklů.

- 1 ... neupravený povrch,
- 2 až 5 ... dezalkalizované povrchy
(2 - 250°C, 3 - 350°C, 4 - 450°C, 5 - 500°C)

Obr. 3. Koncentrace olova ve výluzích po autoklávové zkoušce v závislosti na počtu opakovaných autoklávových cyklů.

- 1 ... neupravený povrch,
- 2 až 4 ... dezalkalizované povrchy
(2 - 250°C, 3 - 350°C, 4 - 500°C)

Obr. 4. Koncentrace SiO₂ ve výluzích po autoklávové zkoušce v závislosti na počtu opakovaných autoklávových cyklů.

- 1 ... neupravený povrch,
- 2 až 5 ... dezalkalizované povrchy
(2 - 250°C, 3 - 350°C, 4 - 450°C, 5 - 500°C)

Obr. 5. Časové závislosti koncentrace olova ve výluzích do kyseliny octové (4 obj.%) při teplotě 60°C.

- 1 ... neupravený povrch,
- 2 až 4 ... dezalkalizované povrchy
(2 - 250°C, 3 - 350°C, 4 - 500°C)