

Attack on soda–lime–silica glass bottles by acetic, citric and oxalic acids

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The corrosion resistance of soda–lime–silica glass bottles toward the action of aqueous solutions of citric, acetic and oxalic acids was studied and compared with that toward HCl and water. The corrosion resistance was tested by subjecting the internal surface of the bottles to the action of solutions of different concentrations of the organic acids at 95°C for periods in the range of 15 min to 6 h. The quantities of Na₂O and SiO₂ extracted from the bottles under the conditions of attack were taken as a measure of the resistance to corrosion.

The results obtained indicated that the extraction of Na₂O by solutions of low concentrations of the different acids and water can be arranged in the following order: H₂O > citric acid > acetic acid > HCl > oxalic acid. Such behaviour was found to follow the order of the solubility of the corresponding sodium salts formed with the aqueous solutions rather than the proton availability in these solutions.

The relative magnitude of dissolution of SiO₂ was found to follow another order: H₂O > HCl > oxalic acid > citric acid > acetic acid. The decreasing solubility of SiO₂ by the organic acids, in comparison with that by HCl or water, was attributed to the formation of oxalate, citrate and acetate complexes with silica which cover the glass surface and retard further dissolution of silica.

Differences between the various organic acids in the dissolution of Na₂O or SiO₂ were not observed by increasing their concentrations. This behaviour was attributed to the increase in the concentration of the organosilicon compound formed which is adsorbed on the glass surface acting as an effective barrier to further dissolution of glass.

Angriff von Kalk–Natronsilicatglasflaschen durch Essig-, Zitronen- und Oxalsäure

Die Korrosionsbeständigkeit von Kalk–Natronsilicatglasflaschen gegenüber der Einwirkung wäßriger Lösungen von Zitronen-Essig- und Oxalsäuren wurde untersucht und mit der gegenüber HCl und Wasser verglichen. Die Korrosionsfestigkeit wurde geprüft indem man die inneren Oberflächen der Flaschen der Einwirkung von Lösungen mit unterschiedlichen Konzentrationen der organischen Säuren bei 95°C für Zeiten zwischen 15 min und 6 h aussetzte. Die unter Angriffsbedingungen aus den Flaschen herausgelösten Mengen an Na₂O und SiO₂ wurden als Maß für die Korrosionsbeständigkeit angesehen.

Die Ergebnisse ließen erkennen, daß für die Extraktion von Na₂O durch niedrigkonzentrierte Lösungen der verschiedenen Säure und Wasser folgende Reihenfolge aufgestellt werden kann: H₂O > Zitronensäure > Essigsäure > HCl > Oxalsäure. Es wurde festgestellt, daß ein solches Verhalten eher der Löslichkeitsordnung der entsprechenden Natriumsalze folgt, die sich in den wäßrigen Lösungen bilden, als der Verfügbarkeit von Protonen in den Lösungen.

Für die Auflösung von SiO₂ wurde eine andere Reihenfolge gefunden: H₂O > HCl > Oxalsäure > Zitronensäure > Essigsäure. Die abnehmende SiO₂-Löslichkeit durch die organischen Säuren wurde im Vergleich zu der durch HCl oder Wasser der Bildung von Oxalat-, Citrat- und Acetatkomplexen mit Siliciumdioxid zugeschrieben, die die Glasoberfläche bedecken und dadurch die weitere Lösung von SiO₂ verzögern.

Auch bei Erhöhung der Konzentrationen wurden keine Unterschiede zwischen den verschiedenen Säuren bezüglich ihrer Lösungsintensität für Na₂O und SiO₂ beobachtet. Dieses Verhalten wird dem Anstieg der Konzentration der siliciumorganischen Verbindung zugeschrieben, die von der Glasoberfläche adsorbiert wird und dort als effektives Hindernis für die weitere Auflösung von Glas wirkt.

1. Introduction

Corrosion of glass containers used for packaging of food, beverages, medicaments and high-purity chemicals is of particular interest to glass manufacturers. The purpose for which a container can be used is determined by the extent of this corrosion which is a function of several parameters. Among the principal parameters is the type of attacking solution. One of the consequences of chang-

ing the type of the attacking solution is the change in the pH value of the solution which may also determine the primary mechanism of glass corrosion [1].

The attack on glass bottles by different aqueous solutions was studied by many workers [1 to 3]. However, comparatively few investigations were conducted into the action of acid solutions on the corrosion of glass containers [1 to 4]. HCl and H₂SO₄ are probably the acids which attracted the attention of most authors [4 to 7]. Also, several of these studies are carried out

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powdered or crushed glass samples [5 to 7]. Organic acids, on the other hand, did not attract much attention. The studies available were concerned mainly with the attack on glass by citrate and other anions in neutral solutions [8]. The data showed that neutral solutions of sodium citrate attack silicate glasses with a severity similar to that of substantially alkaline solutions. The effect becomes perceptible at a pH value of about 5.

Static leaching of glasses of different chemical composition by aqueous solutions of formic, acetic and phosphoric acids was recently studied by Salem et al. [9] to examine the influence of time, glass composition and acid concentrations on the leaching kinetics and mechanisms. For this purpose, they determined the amounts of sodium, potassium, calcium and magnesium released into leaching solutions as well as the quantities of hydrogen ion consumed by the glass as a function of leaching time. They found that formic acid was somewhat more corrosive than acetic and phosphoric acids which was attributed to the higher degree of ionization of formic acid than that of acetic acid. The smaller corrosive effect of H_3PO_4 as compared to formic and acetic acids was attributed to the possible formation of a passive layer of the insoluble $Ca_3(PO_4)_2$ on the surface of the glass specimen. In [9] it was concluded that the acid type has only a small effect on the leaching process compared to the acid concentration (i.e. the pH value).

Also, recently the results of a study of the extraction of potassium, sodium, lead and silicon from a commercially available lead crystal glass (24% PbO) as well as of the loss in weight by the action of acetic, citric and oxalic acids at 95 °C for times in the range 30 min to 6 h were published by Ahmed et al. [10]. They found that the dissolution of modifier cations (K^+ , Na^+ and Pb^{2+}) is dependent on the pH value of the organic acid solutions as well as the solubility of the corresponding salts of these acids with the former parameter playing the dominant role. This study revealed the importance of the solubility of the salts formed during reactions between glass and aqueous solutions in addition to the pH value of the attacking solution.

Of the various organic acids acetic acid is probably the one that has been extensively studied. It is used as a standard test fluid to assess the stability of lead-containing glasses under specified conditions of attack [11 to 14]. The release of lead and other cations from lead-containing silicate glasses was shown by Lehman et al. [5] to proceed through replacement by hydroxyl groups in a parabolic manner [16] for short times of attack (<2 h). The extraction of lead by acetate and other anions was found by El-Shamy and Taki-Eldin [17] to follow the order of the solubility of the corresponding lead salts. Paul [18] studied the effect of buffering complex agents, e.g. ammonium citrate, acetate and tartarate on the extraction of metal cations from glass. He found that the corrosion resistance of a lead glass depends on the nature and concentration of these buffering ions as well as the pH values of the agents.

This brief survey makes clear that a detailed study of the extraction of metal cations from glass by organic acids is not available. Also, the relation between extraction of metal cations, the pH value of the attacking solution and solubility of the salts formed is not clear. The purpose of this work was to study the attack on soda–lime–silica glass bottles by aqueous solutions of acetic, citric and oxalic acids. The extent of attack was evaluated by the determination of Na_2O and SiO_2 extracted by the different acids under the conditions applied. A comparison between the attack of these acids and that of HCl and water under the same conditions was also made.

2. Experimental procedure

2.1 Glass bottles

The bottles used in this work, 125 amber, were taken during the normal production programme at ElNasr Glass & Crystal Co. (Mostorod Factory, Cairo (Egypt)). The bottles are produced from a continuous melting furnace by automatic machines. The overflow capacity is (140 ± 2) ml and the internal surface area is (152 ± 2) cm², whereas that of the part of the bottle filled with 100 ml solution is (102.94 ± 1.5) cm². The ratio SA/V (surface area/volume of the attacking solution) is 1.03 cm⁻¹. The chemical composition of the bottles belongs to the normal soda–lime–silica glass system. According to chemical analysis it is as follows (in wt%): 71.43 SiO_2 , 9.27 CaO , 2.37 MgO , 1.56 Al_2O_3 , 0.19 Fe_2O_3 , and total alkalis ($Na_2O + K_2O$) are equal to 15.18 determined by difference. The other main characteristics of the bottles are given elsewhere [19].

2.2 Procedure for the determination of chemical durability

The chemical durability of the internal surface of the glass bottles (the bulk form) was determined as follows:

- The bottles were rinsed three times with about 15 ml distilled water.
- The bottles were filled with 100 ml of the attacking solution, covered with plastic caps and immersed directly in a water bath maintained at the required temperature. The temperature used in this work was (95 ± 1) °C. Two minutes were allowed for the attacking solution to attain the temperature of the water bath. The time of attack applied in this work varied between 15 min and 6 h after which the bottles were taken out of the water bath and the solutions in the bottles were immediately transferred into plastic bottles. The glass bottles were washed three times with 50 ml of distilled water which were then added to the attacking solution in the plastic bottles.
- The extent of attack on the internal bottle surface by the action of the various aqueous solutions was evaluated by the determination of the amounts of Na_2O (by flame photometry) and SiO_2 (by spectrophotometry) [20] extracted under the specified conditions of attack.

2.3 Attacking solutions

a) Aqueous solutions of the following acids:

- = 0.033 M and 0.33 M citric acid;
- = 0.1 M and 1 M acetic acid;
- = 0.05 M and 0.5 M oxalic acid;
- = 0.1 M and 1 M hydrochloric acid.

These concentrations are equivalent to 0.1 and 1.0 N solutions of the various acids. The two concentrations for each acid are referred to in the text as the lower and higher concentrations.

b) Distilled water.

3. Results

The main features of the results obtained are summarized in the following.

3.1 Effect of time of attack

In general, increasing the time of attack by any of the acids used or by water increased the amounts of both Na_2O and SiO_2 extracted from glass (figures 1a, b, 2a, b, 3a, b and 4). The rate of increase was faster at the initial stage of attack and slowed down at later stages. The relations take, in general, a parabolic form (figures 1 to 4).

3.2 Effect of type of the attacking agent

a) Dissolution of Na_2O : The amount of Na_2O extracted from glass was dependent on the type of attacking agent (figures 1a, b, 3a, b and 4). The various acids in their lower concentrations (equivalent to 0.1 N) as well as water can be arranged according to their ability to extract Na_2O in the following order:

$\text{H}_2\text{O} > \text{citric acid} > \text{acetic acid} > \text{HCl} > \text{oxalic acid}$.

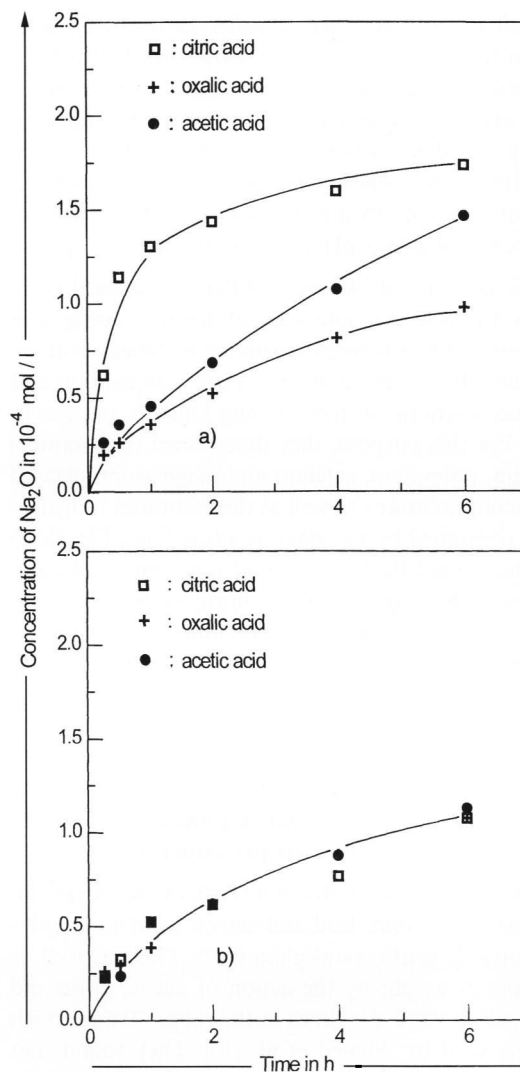
b) Dissolution of SiO_2 : For SiO_2 (figures 2a, b, 3a, b and 4) the same agents can be arranged in the following order:

$\text{H}_2\text{O} > \text{HCl} > \text{oxalic acid} > \text{citric acid} > \text{acetic acid}$.

3.3 Effect of concentration of acids

a) Dissolution of Na_2O : The amount of Na_2O extracted from glass decreased with increasing the concentration of acetic, citric or hydrochloric acids. When the attack was conducted with oxalic acid, the amount of Na_2O extracted was not significantly affected by increasing its concentration (figures 1a, b and 3a, b).

b) Dissolution of SiO_2 : Regarding SiO_2 , the extracted amounts decreased with increasing the concentration of oxalic acid (figures 2a, b and 3a, b). On the other hand, the increase in the concentration of citric, acetic or



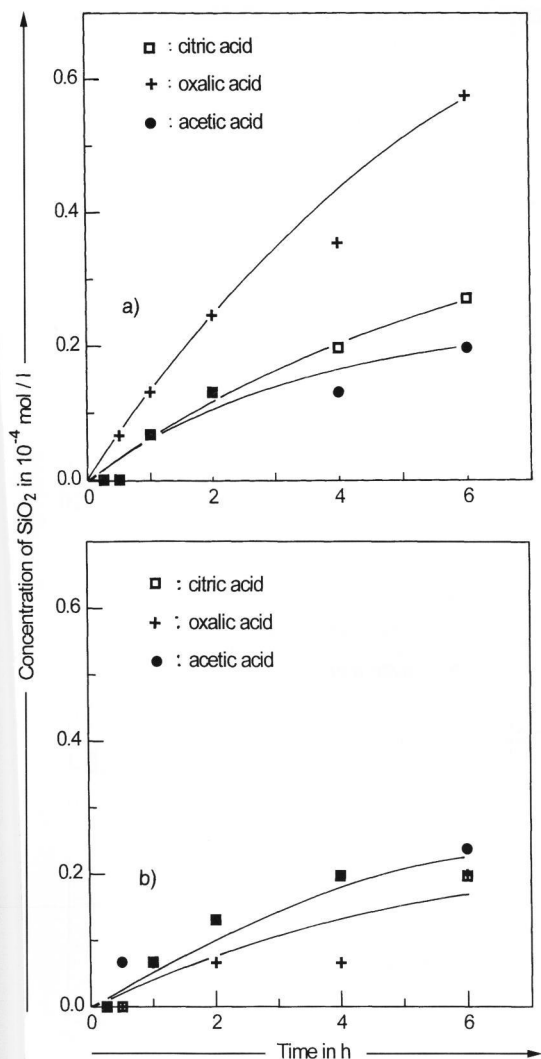
Figures 1a and b. Time dependence of Na_2O dissolution in aqueous solutions of the lower (figure a) and the higher concentration (figure b) of citric, acetic and oxalic acids at 95°C .

hydrochloric acid did not practically affect the amount of SiO_2 extracted.

In summary, when the concentration of the different acids was increased to the higher concentration (equivalent to 1.0 N), the different acids extracted almost identical amounts of either Na_2O or SiO_2 (figures 1a, b, 2a, b, 3a, b). Also, the amounts of Na_2O or SiO_2 extracted by water remained higher than those extracted by any of the acids.

3.4 Relative proportions of Na_2O and SiO_2 extracted from glass

In all cases, the amounts of Na_2O extracted from glass by the various acids and water exceeded that of SiO_2 (figures 1a, b, 2a, b, 3a, b and 4).

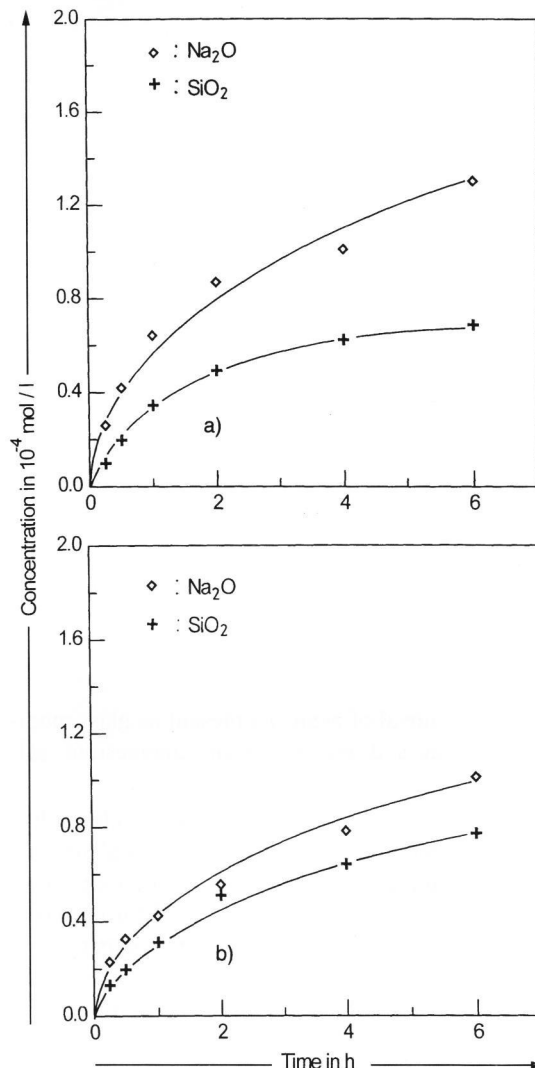


Figures 2a and b. Time dependence of SiO₂ dissolution in aqueous solutions of the lower (figure a) and the higher concentration (figure b) of citric, acetic and oxalic acids at 95°C.

Discussion

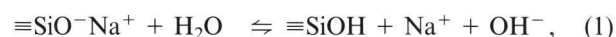
1 General considerations

Soda-lime glasses are generally characterized by being markedly resistant to attack by liquids. Usually, they act slowly with aqueous solutions in the pH range from 1 to 9 and more rapidly in strongly basic solutions. The reactions of solutions with glass can broadly be classified into two categories. The first category, leaching, includes preferential extraction of alkali ions from glass into solutions. This leaching entails the substitution of hydrogen-bearing ions for sodium ions in the glass surface leaving behind a silica-rich layer containing hydrated micropores. This silica-rich layer may be partially or completely depleted of alkali and/or alkaline earth ions. In relatively durable glasses, such as soda-lime-silica glasses, this substitution in which the main constituents are not altered, occurs without changing the network structure of the surface hydrated



Figures 3a and b. Time dependence of Na₂O and SiO₂ dissolution in solutions of the lower (figure a) and the higher concentration (figure b) of HCl at 95°C.

layers of the glass [21 and 22]. Smets and Lommen [23 and 24] proposed another model in which the rate of leaching of less durable glasses is controlled by the rate of diffusion of water molecules into the hydrated layer. A mechanism that incorporates features of both the ion exchange and molecular water was proposed by Ernsberger [25]. Accordingly, three species, sodium ions, molecular water and hydronium ions (H₃O⁺), are involved in the exchange which can be represented by the following equations:



The rate of leaching is found in many cases to be proportional to the square root of time, i.e., the leached layer continues to thicken so that in a practical sense it may become a protective film [26]. In general, there will

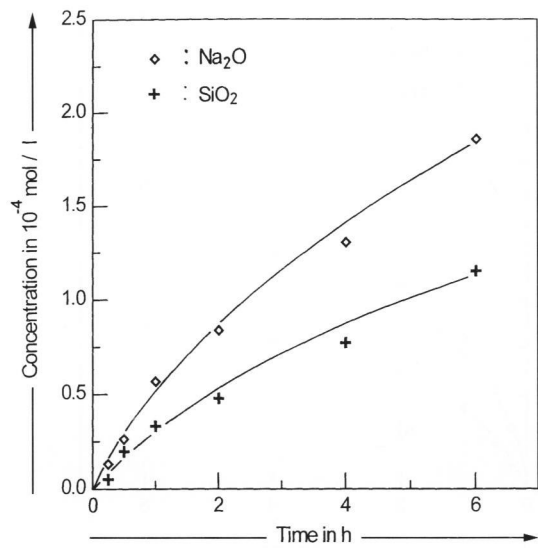
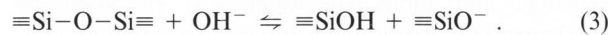


Figure 4. Time dependence of Na₂O and SiO₂ dissolution in water at 95°C.

be a selective removal of elements present as glass modifiers, e.g. lithium, sodium, potassium, magnesium, calcium, lead.

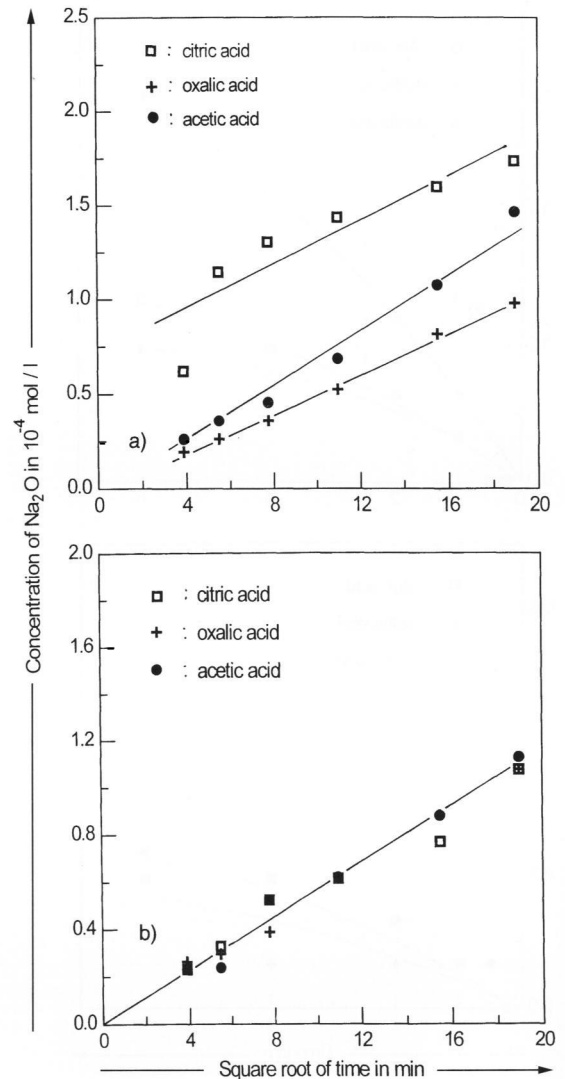
The rate-determining step in glass leaching has usually been considered to be the diffusion of alkali ions from bulk glass under the influence of the concentration gradients (bulk/solution). The values of diffusion coefficient of alkali measured from leaching experiments were found by El-Shamy [27] to be 10⁴ times higher than that of the bulk glass. This led to the assumption that the leaching process is an ion exchange process in which the diffusion of hydrogen (or possibly H₃O⁺) is the rate-determining step. This conclusion was confirmed by Doremus [28], Bunker et al. [29] and recently by Salem et al. [9].

The second category of reactions of solutions with glass, etching, involves the breakdown of silica network through a reaction with OH⁻ ions from reaction (1) leading to total glass dissolution. By total dissolution, a destruction and dissolution of the leached surface layers on bulk glasses is usually implied. Equation (3) is usually assumed to express this kind of reaction:



This reaction may take place either without or after leaching.

The initial process of attack on glass by water is chiefly the ion exchange between the alkali ions in glass and H⁺ or H₃O⁺ ions in water. This reaction begins immediately after contact between glass and water, even at room temperature [30]. As the exchange process continues, H⁺ ions are thus consumed by the glass. Therefore, more water molecules continue to dissociate furnishing more H⁺ ions available for reaction, which creates an increasing concentration of OH⁻ ions. The im-



Figures 5a and b. Square root of time dependence of Na₂O dissolution in aqueous solutions of the lower (figure a) and the higher concentration (figure b) of citric, acetic and oxalic acid at 95°C.

mediate impact of increased OH⁻ ion concentration is an increase in the pH value of the solution which becomes alkaline and attacks the glass network leading to its dissolution. Accordingly, corrosion of multicomponent silicate glasses by water represents combined mechanisms of leaching and etching of the silica network.

In acid media, the attack on silicate glass remains essentially of the leaching type at least at the early stage. It follows that the alkali liberated from glass is not neutralized.

4.2 Effect of time of attack

It was found that the extraction of Na₂O (figures 1a, 3a, b and 4) follows a parabolic behaviour. It follows that its dissolution from glass is controlled by diffusion through the sodium-depleted layer and accordingly the relationship between the quantities of sodium extracted and the square root of time would be represented by a straight line. Figures 5a and b show the relation for the

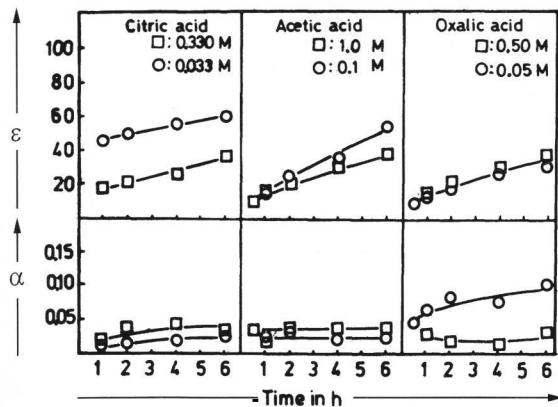


Figure 6. Variation of the values of α and ϵ with corrosion time by aqueous solutions of citric, acetic and oxalic acids at 95°C.

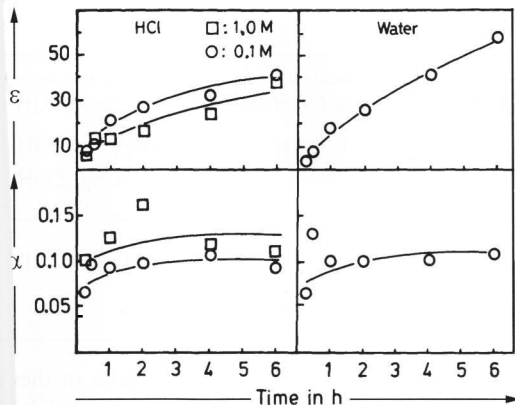


Figure 7. Variation of the values of α and ϵ with corrosion time by HCl and water at 95°C.

dissolution of sodium by the different concentrations of organic acid solutions studied. The straight line relationship obtained in every case confirms this postulation and further indicates that the diffusion-controlled mechanism of leaching holds for the whole period of attack, e., 6 h, as no deviation from the straight line relationship is observed.

The relative extent of selective leaching of alkali ions from glass can approximately be evaluated by using the data of concentration of Na_2O and SiO_2 extracted from glass by the attacking solution under specified experimental conditions for the quantitative calculation of the dissolution parameter, α , using the following equation [31 and 32]:

$$\alpha = \left(\frac{c_{\text{SiO}_2}}{c_{\text{R}^+}} \right) \left(\frac{m_{\text{R}^+}}{m_{\text{SiO}_2}} \right) \left(\frac{n_{\text{R}_2\text{O}}}{1 - n_{\text{R}_2\text{O}}} \right) \quad (4)$$

where n = mole fraction of R_2O in glass, m = molecular weight, c = concentration in parts per million of R^+ or SiO_2 in solution. When the value of α tends towards zero, it indicates that the glass is reacting with the environment in a mode of selective alkali leaching, the first

stage of corrosion, which results in the formation of a silica-rich film on the glass surface. On the other hand, when α tends towards unity, total dissolution is indicated [31 and 32]; the glass network is being attacked and an equivalent amount of SiO_2 is released along with the alkali. Such a case corresponds to the second stage of corrosion. Intermediate values of α indicate that selective and total dissolution occur concurrently.

The tendency of the leached surface silica layer to form or to dissolve can also be deduced by calculating the parameter ϵ from equation (5) proposed by Sanders and Hench [32]:

$$\epsilon = \beta - c_{\text{SiO}_2} \quad (5)$$

The value of β can be calculated from the following equation:

$$\beta = \frac{c_{\text{SiO}_2}}{\alpha} \quad (6)$$

Increase of the value of ϵ indicates the increase of the tendency of formation of the SiO_2 film and vice versa.

The change in the values of both α and ϵ as a function of time of attack and type of attacking medium is shown in figures 6 and 7. It is clear that α has a value of zero at the initial stage of attack, which indicates that the dissolution of glass starts with selective leaching of sodium ions from glass. The resultant increase of the pH value of the attacking solution would lead to the initiation of dissolution of SiO_2 which increases with time. Accordingly, with increasing time of attack, the value of α would be expected to show a corresponding increase associated with the simultaneous dissolution of both Na_2O and SiO_2 (figure 7).

It is also noticed that the value of ϵ , which is a measure of the amount of SiO_2 available for film formation, increases with increasing time of attack by the various organic acids, HCl and water (figures 6 and 7). Accordingly, the dependence of α and ϵ on time of attack reveals that both rates of selective dissolution of Na_2O and formation of sodium-depleted silica layer increase with increasing time of attack (figures 6 and 7). Both α and ϵ increase at a faster rate during the initial stage of attack, which subsequently decreases as the diffusion distance of Na^+ ions increases with time. The same conclusion can also be reached by considering the change of the ratio of $\text{Na}_2\text{O}/\text{SiO}_2$ (mass ratio of cations extracted from glass) as a function of time of attack. This ratio yields information about the relative rates at which leaching and etching proceed under the specified conditions of attack. The results of such calculation are given in table 1, which shows that the $\text{Na}_2\text{O}/\text{SiO}_2$ ratio in the bulk glass is 0.21. The data given in the table show also that in all cases the ratio for glasses corroded with any of the acids or water is substantially higher than that in the bulk. The ratio is also considerably higher for organic acids than for HCl, and water as well. It

Table 1. Ratios of Na₂O to SiO₂ in the extract of bottles attacked with different aqueous solutions at 95°C for 6 h

attacking solution	molarity ¹⁾	Na ₂ O/SiO ₂ ratio ²⁾ after time of attack (in h)					
		1/4	1/2	1	2	4	6
acetic acid	0.1 M	-	-	7.1	5.3	8.3	7.6
	1.0 M	-	5.1	8.1	4.8	4.5	4.8
citric acid	0.033 M	-	-	20.2	11.1	8.3	6.5
	0.33 M	-	-	8.1	4.8	4.0	5.6
oxalic acid	0.05 M	-	4.05	2.8	2.16	2.4	1.7
	0.5 M	-	-	6.1	9.6	13.7	5.6
HCl	0.1 M	2.7	1.8	1.9	1.8	1.7	1.9
	1.0 M	1.8	1.7	1.4	1.1	1.2	1.3
water		2.7	1.4	1.8	1.8	1.7	1.6

¹⁾ The concentrations studied are equivalent to 0.1 N and 1.0 N acid solutions, respectively.

²⁾ The Na₂O/SiO₂ ratio for the parent glass is 0.21.

generally decreases at different rates with increasing time of attack by different organic acid solutions, but not for HCl, where the ratio remains almost constant for times longer than 15 min. For the organic acids studied and water, the ratio decreases with time, i.e., the leaching and etching processes are not in dynamic equilibrium and the total dissolution gradually increases at a rate faster than that of the leaching process. However, as the ratio remains significantly higher than that in the bulk glass, it follows that the rate of increase in the thickness of the leached layer gradually decreases with time of attack in agreement with data of α and ε .

4.3 Effect of type and concentration of attacking solution

The relative effects of the different acids used in this work can be explained by considering their effects on the dissolution of Na₂O and SiO₂.

a) Effect on Na₂O extraction: The results obtained (figures 1a, 3a, b and 4) indicated that the amounts of Na₂O extracted by the lower concentrations of acid solutions are not much different from those extracted by HCl and are slightly lower than those extracted by water. The various acids and water can, according to their ability to extract Na₂O, be arranged in the following order:

H₂O > citric acid > acetic acid > HCl > oxalic acid.

The extraction of Na₂O from glass depends on the pH value of the aqueous solution, i.e., the concentration of H⁺ or H₃O⁺ in the attacking medium, as well as on the solubility of the corresponding sodium salts of the attacking medium.

The effects of the different acids can be compared by correlating their degrees of dissociation. Strong acids have high dissociation constants, i.e., they are capable of furnishing active protons and accordingly should extract more sodium ions from glass than do weak acids (acetic,

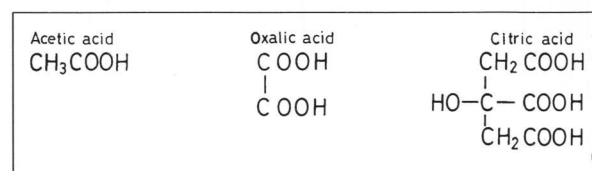


Figure 8. Chemical formulas of acetic, oxalic and citric acids.

citric and oxalic acids). The structural formulas of these acids, shown in figure 8, indicate that citric acid has three replaceable hydrogen atoms, oxalic acid two, whereas acetic acid has only one replaceable hydrogen atom. Table 2 shows the dissociation constants of the different acids. According to the data of dissociation constants, the order of acids in respect of the amount of sodium extracted from glass should be as follows:

HCl > oxalic acid > citric acid > acetic acid.

Table 2 also shows values of the solubility of the sodium salts (in g/100 ml H₂O) by the action of the different acids. It is apparent that the solubility increases in a different order:

sodium citrate with 5H₂O > sodium acetate > sodium citrate with 2H₂O > sodium chloride > sodium oxalate

Comparison of the order of acids according to the experimentally determined amounts of Na₂O they could extract from glass with the order of the dissociation constants and that of the solubility data indicates the predominance of the role played by the solubility of the reaction products over the magnitude of the dissociation constants of the attacking medium. The dependence of the amount of Na₂O extracted from glass on the solubility of the corresponding sodium salt of the various acids can also

Table 2. Dissociation constants of some acids and the solubility of their sodium salts [22]

acid	dissociation constant	temperature in °C	pH value (0.1 N acid)
acetic acid	$1.753 \cdot 10^{-5}$	25	2.9
citric acid			
first hydrogen	$8.4 \cdot 10^{-4}$	25	} 2.2
second hydrogen	$1.8 \cdot 10^{-5}$	25	
third hydrogen	$4.0 \cdot 10^{-6}$	25	
oxalic acid			
first hydrogen	$6.5 \cdot 10^{-2}$	25	} 1.6
second hydrogen	$6.1 \cdot 10^{-4}$	25	
salt	solubility in g/100 ml H ₂ O		temperature in °C
sodium acetate	119.00	0.0	}
	170.15	100.0	
sodium citrate with 2H ₂ O	72.00	25.0	}
	167.00	100.0	
sodium citrate with 5H ₂ O	92.60	25.0	}
	250.00	100.0	
sodium oxalate	3.70	20.0	}
	6.33	100.0	
sodium chloride	35.0	70.0	}
	39.12	100.0	
sodium hydroxide	42.0	0.0	}
	347.0	100.0	

is manifested by figure 9. The figure shows the relation between the concentrations of Na₂O extracted from glass as well as the solubilities of the corresponding sodium salts of the different attacking solutions as a function of the pH values of the low concentration acid solutions and water. Also shown in the figure are data, taken from [10], for Na₂O extraction from a lead silicate glass containing 24 wt% PbO by the same solutions. It is evident that the trend of extraction follows closely, irrespective of the base glass composition, the solubility of the sodium salts and not the proton availability which readily increases with decreasing pH value of solution. The best fit solubility data, shown in figure 9, suggest that the sodium citrate with 5H₂O is formed during reaction between glass and citric acid rather than sodium citrate with 2H₂O.

However, such distinct difference in behaviour between the various organic acids vanishes with increasing acid concentration. The extent of corrosion by citric and acetic acids decreases to levels similar to that of oxalic acid (figures 1a, b and 3a, b) which is almost similar to that obtained by the lower concentration of the acid solutions. Examination of table 2 reveals that the dissociation constants of the second hydrogen of oxalic and citric acids are not much different from each other or from that of acetic acid (see also figure 5b). Also, the

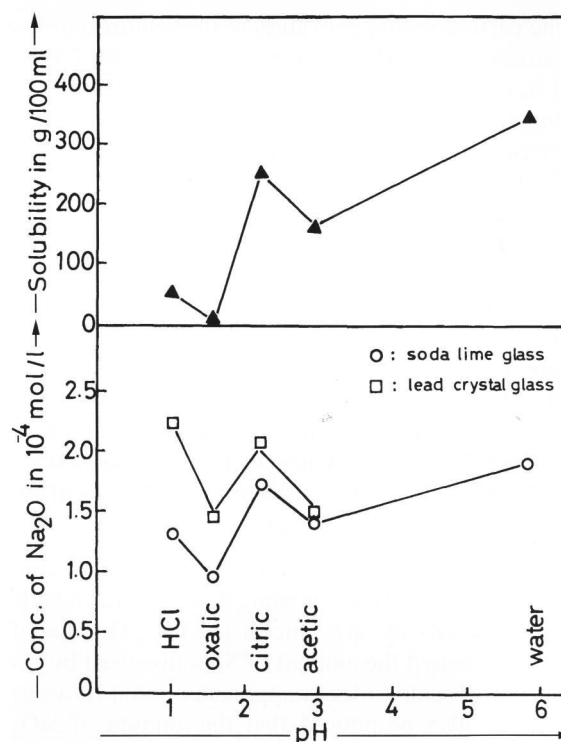


Figure 9. Relation between the Na₂O concentration extracted from the soda-lime-silica glass studied in this work and a lead crystal glass (24 wt% PbO) as well as the solubilities of the corresponding sodium salts of the different attacking solutions, taken from [33] as a function of the pH values of the low-concentration acid solutions and water. Data for the lead crystal glass are taken from [10] and were multiplied by 10 for clarity.

decrease in the pH values of the different organic acids with increasing their concentration may decrease the importance of differences in the dissociation constants of the various organic acids and the solubility of the corresponding organosodium salts.

b) Effect on dissolution of SiO₂: Figures 2a, b and 3a, b show that SiO₂ is extracted in concentrations that are slightly dependent on the type of acid when the low concentration solutions are used. Such dependence vanished by increasing the acid concentration. The figures also show that the dissolution of SiO₂ decreased by increasing concentration of acids.

The effect of citrate, oxalate and tartarate anions on the chemical resistance of soda-lime-silica glass bottles was studied by Ragon and Bacon [8] who found that neutral solutions of these anions promote the attack. The severity of attack observed was similar to that of substantially alkaline solutions. The effect becomes perceptible at a pH value of about 5 and increases rapidly with pH increase up to 7.6. This effect was attributed to the ability of these anions to form soluble complexes with silicon in neutral solutions, i.e., the anions have a digestive action on silica and the Si-O-Si structure of the soda-lime-silica glass. The promotional effect of such anions can, however, be avoided by reducing the pH value to <5.

The corresponding pH values of the solutions of low concentrations of acetic, citric or oxalic acids are 2.9, 2.2 and 1.6, respectively [33]. The pH values of solutions of the higher acid concentration are lower than these values. Accordingly, the anions lose their ability to attack the Si–O–Si bond and have no promotional effect on the dissolution of silica. It may also be observed that the concentrations of SiO₂ extracted by HCl are practically not much different from those extracted by the various organic acids studied. The decreasing solubility of silica by oxalic, citric or acetic acids can be attributed to the formation of oxalate, citrate or acetate complexes covering the silica surface with a strongly sorbed film which acts as a protective layer retarding the dissolution of SiO₂ [8 and 34]. This is in agreement with what was reported by Jagitsch [35] who showed that solutions of citric acid extract only Na⁺ cations.

Figures 2a and b reveal that solutions of the low concentration of the different organic acids extract slightly different amounts of SiO₂. Increasing the pH value of the acids decreased the amount of SiO₂ dissolved by citric and oxalic acids to levels approaching that of acetic acid. It can also be noticed that the amount of SiO₂ dissolved by acetic acid is independent of the concentration of the acid within the concentration range used in this work (figures 2a and b). This behaviour may be attributed to the increase in the concentration of the organosilicon complexes formed, which results in the formation of a sorbed film of greater thickness acting as an effective barrier protecting the glass surface from further dissolution of SiO₂. The decrease in the pH values of the different organic acids with increasing their concentration may have a slight effect on decreasing the dissolution of SiO₂.

The amount of SiO₂ extracted by H₂O was higher than that extracted by any of the acids used. The pH value of the distilled water used in this work was 6, which subsequently increases as leaching of Na₂O increases. The substantially higher pH values of water compared to those of any of the acids used will give rise to the higher extraction rate of SiO₂.

The relative concentrations of Na₂O and SiO₂ extracted from glass by the different attacking media are in agreement with the order predicted from the pH dissolution diagrams in the pH ranges encountered in this work [36 and 37].

5. Summary and conclusions

Static corrosion testing of soda–lime–silica glass bottles by aqueous solutions of citric, acetic, oxalic and hydrochloric acids and water was conducted to examine the effect of time of corrosion as well as type and concentration of the acids on the corrosion resistance of such bottles. The extent of corrosion was evaluated by the determination of the quantities of Na₂O and SiO₂

released into the leaching solutions from the internal surface of the bottles under specified conditions of attack.

The extraction of Na₂O from glass by all the acids used and water follows a straight-line relationship with the square root of time of attack. In all cases the quantities of Na₂O were higher than those of SiO₂.

The quantities of both oxides were dependent on the type of attacking acid only when low concentrations of such acids were used. Such dependence vanished by increasing the concentration of the acid solutions. Variations in the concentrations of Na₂O released by the various attacking solutions were found to be best related to the solubilities of the corresponding sodium salts, which play the dominant role, rather than the value of pH. The quantities of SiO₂ released from glass by solutions of lower concentration of the various acids were only slightly dependent on the type of acid.

6. References

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