

## Chemical durability of soda-lime glass in aqueous acid solutions

Ionela CARAZEANU POPOVICI<sup>a</sup> and Naliana LUPASCU<sup>b</sup>

<sup>a</sup>Department of Chemistry and Chemical Engineering, Ovidius University of Constanta, 124 Mamaia Blvd, 900527 Constanta, Romania

<sup>b</sup>Pedological and Agrochemical Studies Office, 17-19 Revolutiei Street, 900735 Constanta, Romania

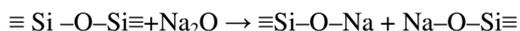
**Abstract** Acid dissolution of soda-lime glass was rigorously investigated. Aqueous solutions containing 1N HNO<sub>3</sub>, HCl, H<sub>2</sub>SO<sub>4</sub> and CH<sub>3</sub>COOH were used to measure the durability of the soda-lime glass samples. Flame emission spectrometry (FES) and UV-visible absorption spectroscopy were used to determine the concentration of Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Si<sup>4+</sup> ions in solutions after dissolution. Weight loss analyses and microstructural characterization were used to evaluate the compositional changes of the glass samples.

**Keywords:** glass, chemical durability, silicates.

### 1. Introduction

Oxide glasses are known and used for thousands of years and tuning of properties like color, durability, viscosity of the molten state were mostly known and dominated by glass makers. Despite this millenary knowledge, the range of glass forming system of interest is still expanding and many non-elucidated points remain in the understanding of the glass and melts structure and properties.

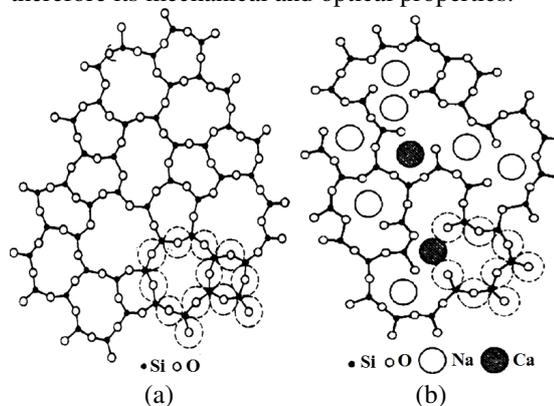
Glass is made of polymeric silica and other minor components, which are necessary for turning the silica into a material more easily mouldable and resistant to temperature changes. In order to lower the melting temperature (~2000°C) of the pure silica glass, sodium oxide is added to the glass melt. The reaction between silica and sodium oxide turns silica into silicate and reduces the melting temperature to a value below 1600°C since the polymeric silica chains are interrupted according to the reaction (1) [1-8].



Silicate glasses are more prone to react with water than pure silica glass. A two-dimensional representation of both structures is shown in **Fig. 1**, where is possible to see the rupture in the silica network due to the presence of sodium (and calcium) atoms bound to terminal oxygen atoms.

These are points in the network that weaken the hydrolytic resistance of glass.

One of the most important properties of glass is its durability and any dissolution on its surface may lead to a rough surface of the glass altering therefore its mechanical and optical properties.



**Fig.1.** Schematic representation of a two-dimensional structure for (a) pure silica glass and (b) silicate glass (adapted from Bohrer, 2008, [1]).

Glass containers for packaging material are classified according to their resistance to a chemical attack, a test carried out in the presence of water, acids and heat. Glass containers should be chemically stable. This stability is reached by adding certain constituents to common glass, which reduce its interaction with water. Although highly resistant, it should not be assumed that glasses in general are

not soluble in aqueous solutions. Even those glasses that exhibit excellent chemical durability in water may be readily dissolved if exposed to substances such as hydrofluoric acid which are able to attack the glass network [9-14].

The corrosion is a chemical phenomenon which can affect the quality of a glass surface, since the glass can fail as a result of its continuous exposure to a corrosive environment. If a glass surface is put into contact with water or with any aqueous solution, it may chemically react with this medium and this chemical exchange may spread all over the surface of the glass, hence causing some undesirable effects, particularly a change in mechanical strength as well as the transmittance [5].

The present study focuses on the effect of acid solution on the chemical durability of soda-lime glass used as packaging material.

## 2. Experimental

To assess the chemical durability of glass were used samples of window glass obtained from the Scăieni factory (Romania). Most glass used for windows and drinking-vessels is soda-lime glass — made from 75% silica, 15% soda and 10% lime (although 1 wt% aluminum oxide is often added as well).

Soda-lime glass (SLG) cast samples were cut into 20x20x3 mm rectangular blocks with a diamond hacksaw. One side of each sample was polished with rough SiC paper to 3000 grit. Before dissolution, the sample was degreased by rinsing in a 2-propanol cleaning solution for 5 min. The samples were then washed with deionized water and dried at 60°C for 4 h. They were weighed by a NAPCO ESJ 200-4 electronic balance having ±0.0001 g accuracy.

HNO<sub>3</sub>, HCl, H<sub>2</sub>SO<sub>4</sub> and CH<sub>3</sub>COOH were used for SLG dissolution. Dissolution tests were carried out with 1 N acid concentration for 4h to 48 h.

The *weight specific loss* was determined by weighing the glass samples before and after chemical attack and taking into account the corroded surface. Specific weight loss was calculated with the formula:

$$\Delta w = \frac{(w_0 - w_t)}{S} \quad (\text{mg/cm}^2) \quad (1)$$

where:

$w_0$  = weight of the sample before contacting the solution (mg);

$w_t$  = weight of the sample after contacting the solution (mg);

$S$  = surface area of the sample (cm<sup>2</sup>).

Each value results for specific weight loss was the average of three determinations.

After dissolution, concentration of sodium, potassium and calcium was determinate using Flame emission spectrometry (FES) (410 Sherwood flamfotometer) and the silicon concentration was investigated by UV-visible absorption spectroscopy (Cecil 1000 spectrometer).

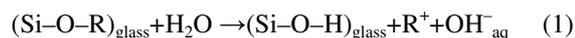
Characterization of the glasses surface after dissolution experiments was carried out by using a Trinocular Upright Metallurgical Metallo-graphic microscope. The surfaces of corroded SLG glass were observed after careful rinsing in distilled water.

The SLG durability in water is also confirmed by the pH and conductivity measurements (720 Inolab Multiparameter).

## 3. Results and Discussions

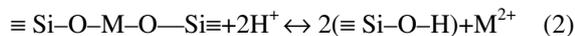
The dissolution kinetics depends on many experimental parameters such as surface area, time, and temperature of the surrounding medium, while the thermodynamic contribution is a function of the composition of glass and its structure.

Dissolution mechanisms involve generally two steps [1, 2]. The first step is an exchange on the glass surface between alkali atoms with a hydrogen atom from water through the following reaction (1):



The glass surface is then dealcanized, and a layer of silica can be formed. This process depends on whether this aqueous system is an open or a closed one, and secondly on whether or not the surface of glass is in contact with the solution.

When a glass probe contacts an acidic aqueous solution, the H<sup>+</sup> ions of the medium replaces the modifier cations in the glass network:



The results of investigations on the weight loss versus time, for each acid are presented in **Fig.2**.

The specific weight loss is even more important as the contact time is longer. The lowest weight loss has sample immersed in double distilled water and the highest weight loss was obtained when the sample placed in 1N HCl. In conclusion, specific weight loss increases as:



Figures 3 – 6 show the FES and UV-vis results of the dissolution of SLG in acid solution for 4, 8, 24 and 48 hours soaks.

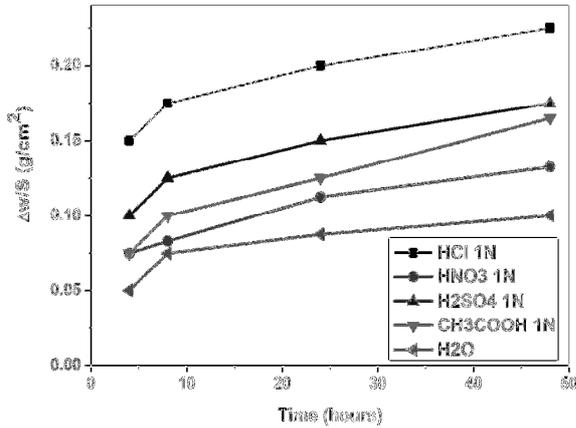


Fig.2. The weight loss of soda-lime glass samples held for 48 h in 1N acids solution.

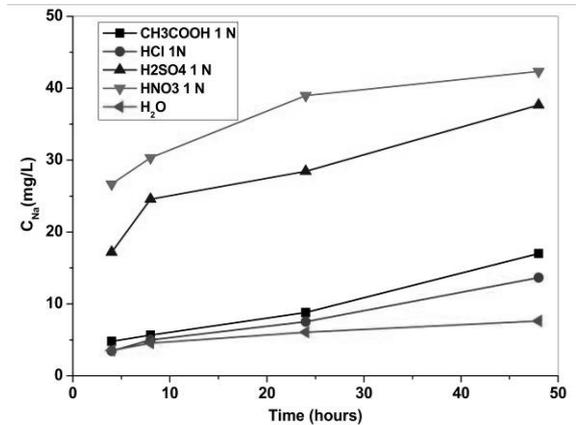


Fig.3. Evolution of sodium concentration after SLG dissolution in acid solution for specific time intervals.

The release of sodium, potassium and calcium always increased with time. The evolution of silicon concentration after SLG dissolution also increases in time, except the samples soaked in HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> where after 8 hours the evolution seems to be constant. This increase in leaching of mobile ions out from a glass can be attributed to a uniform superficial dissolution of the glass network and to a difficult precipitation of insoluble compounds. So we can conclude that the glass from packaging material may be a source of ions to the organism.

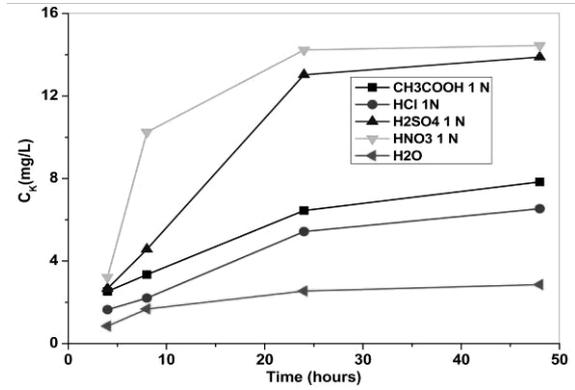


Fig.4. Evolution of potassium concentration after SLG dissolution in acid solution for specific time intervals.

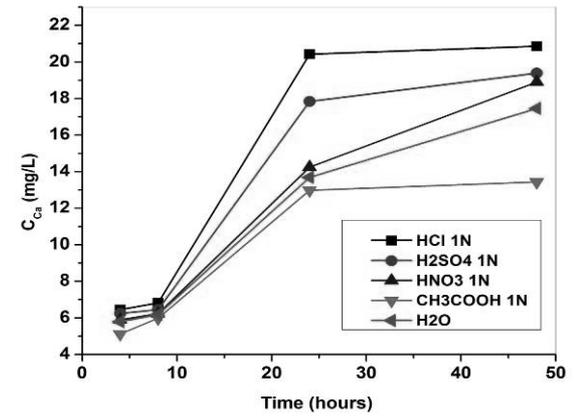


Fig.5. Evolution of calcium concentration after SLG dissolution in acid solution for specific time intervals.

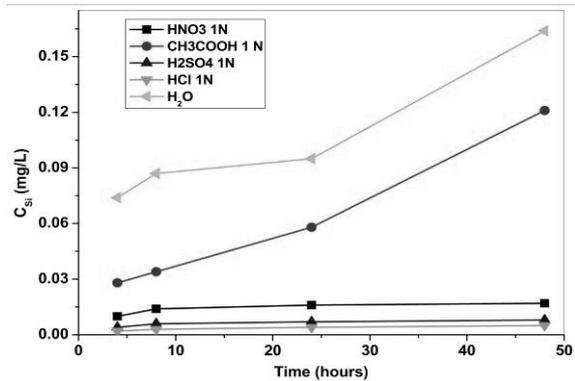
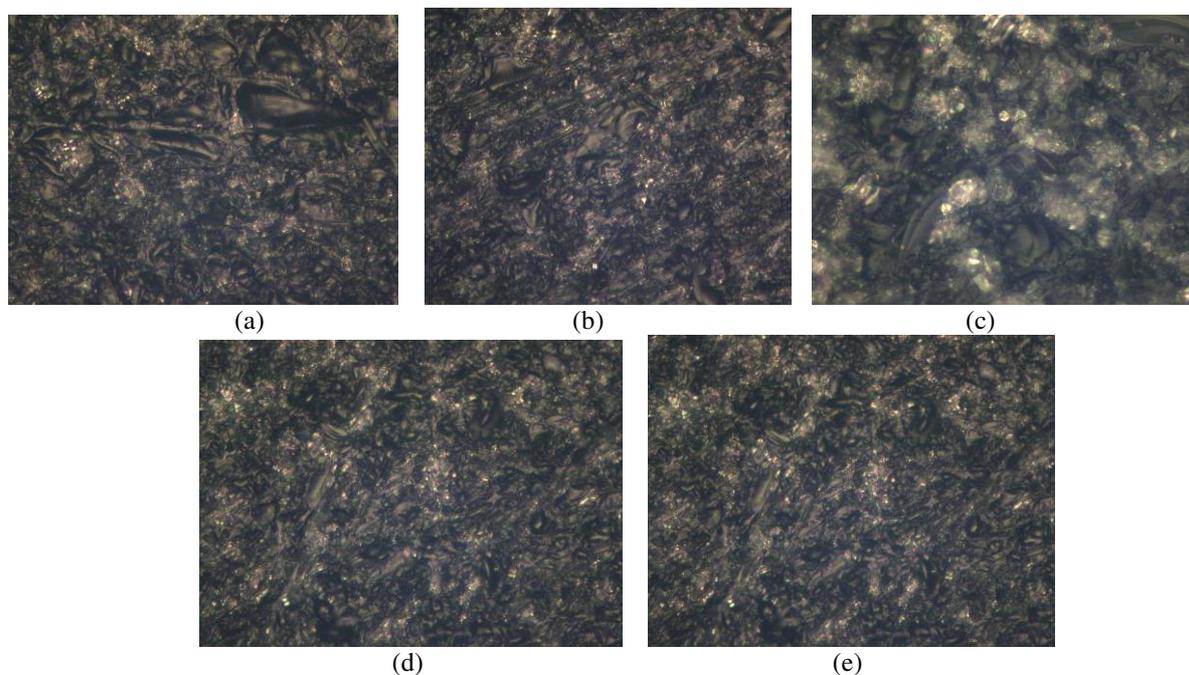


Fig.6. Evolution of the silicon concentration after SLG dissolution in acid solution for specific time intervals.

Figures 7 a-e show the microphotographs of corroded samples after immersion in acid solutions. At early stages of glass corrosion, isolated pits

appear; those further grow and connect with each other forming craters, which increasingly become deeper and more abundant.



**Fig. 7.** Microphotographs of corroded samples after immersion in: a)  $H_2O$ ; b)  $HCl$ ; c)  $HNO_3$ ; d)  $H_2SO_4$ ; e)  $CH_3COOH$

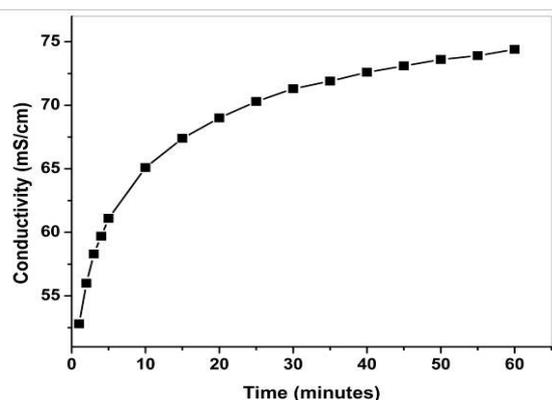
In turns, the craters grow and become interconnected in such a way that they form a continuous altered, opaque corrosion crust. In early research works, the attention was focused on the phases formed at the surface of weathered glasses, the so-called “hydrated silica” layer and calcium/potassium sulphates and carbonates may be formed [5,12,14]. A description of the corrosion process was proposed but without trying to consider the modification of the glass network itself in relation with the leaching of  $K^+$ ,  $Na^+$  and to some extent  $Ca^{2+}$  ions.

Hydrolytic stability of SLG was evaluated by conductivity and pH measurements (Fig. 8 and 9).

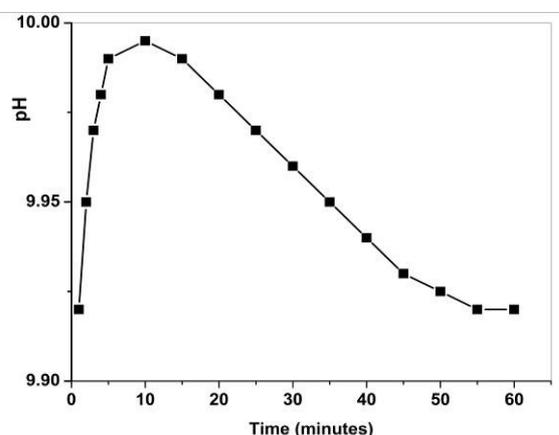
The conductivity increases continuously as a result of ionic exchange that takes place at water-glass interface. The glass –water interaction involves two processes:

- ion exchange reaction of alkali ions with  $H_3O^+$  from water;

- reaction of water with silicate network, leading to its dissolution.

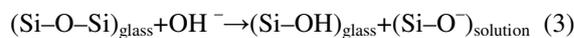


**Fig.8.** The conductivity evolution after SLG dissolution in acid solution for specific time intervals.



**Fig. 9.** The pH evolution after SLG dissolution in acid solution for specific time intervals.

Figure 9 presents the evolution of pH after SLG dissolution in acid solution for 1h. The pH increases in the first 10 minutes, reaching a maximum and then it decreases. In the first minutes the pH evolution is due to the increasing of the OH<sup>-</sup> ions concentration. After that, these ions attack chemical bonds Si-O from the glass network and then a hydrolysis process occurs, leading to decreasing of pH, according to reaction (3):



#### 4. Conclusions

The chemical interaction of water and acids with glass surfaces is negligibly small; only very small amounts, primarily monovalent ions, are dissolved from the glass. These ions form a very thin, almost non-porous layer of silica gel on the glass surface, inhibiting further attack.

#### 5. References

\*E-mail address: icarazeanu@univ-ovidius.ro

- [1]. D. Bohrer, F. Bortoluzzi, P. C. Nascimento, L.M. Carvalho and A.G. Ramirez, International Journal of Pharmaceutics **355**, 174 (2008)

- [2]. E. Axinte, Materials and Design **32**(4), 1717 (2011)
- [3]. A. Tournié, P. Ricciardi and Ph. Colombar, Solid State Ionics **179**, 2142 (2008)
- [4]. R.A. Rahimi, S.K. Sadrezaad and G. Raisali, Journal of Non-Crystalline Solids **355**, 169 (2009)
- [5]. S. Benbahouche, F. Roumili, A. Seghir and R. Zegadi, Journal of the European Ceramic Society **26**, 1673 (2006)
- [6]. C. Fredericci, H.N. Yoshimura, A.L. Molisani and H. Fellegara, Journal of Non-Crystalline Solids **354**, 4777 (2008)
- [7]. N. Carmona M. Oujja, E. Rebollar, H. Romich and M. Castillejo, Spectrochimica Acta Part B **60**, 1155 (2005)
- [8]. J. Paillier, C. Mickel, P. F. Gostin, and A. Gebert Materials characterization **61**, 1000 (2010)
- [9]. M. Arbab, V.K. Marghussian, H. Sarpoolaky and M. Kord, Ceramics International **33**, 943 (2007)
- [10]. L. Barbieri, A. Karamanov, A. Corradi, I. Lancellotti, M. Pelino and J. Ma. Rincon, Journal of Non-Crystalline Solids **354**, 521 (2008)
- [11]. Bin Wei, Hailin Cao and Shenhua Song, Materials Science and Engineering A **527**, 4708 (2010).
- [12]. V. Cannillo, F. Pierli, I. Ronchetti, C. Siligardi and D. Zaffe, Ceramics International **35**, 2853 (2009)
- [13]. D. Radu and O. Dumitrescu, Revista Romana de Materiale/Romanian Journal of Materials **40**, 50 (2010).
- [14]. G. Bolelli, V. Cannillo, L. Lusvarghi, T. Manfredini, C.Siligardi, C. Bartuli, A.Loreto and T.Valente, Journal of the European Ceramic Society **25**, 1853 (2005)

Submitted: April 17<sup>th</sup> 2012

Accepted in revised form: May 2<sup>nd</sup> 2012