Effect of Concentrations and Irradiation on the Etching of Soda-Lime-Silica Glass

[1]N.A. El-Alaily, H.H. Mahmoud, [2]T.D. Abd-elaziz and [1]F.M. Ezz-eldin

[1]National Center for Radiation Research and Technology, Nasr-City, Cairo, Egypt.
[2]MSA University (October University for Modern Sciences and Arts), 6th October City, Egypt.

Abstract: We present the results of experiments of etching on commercial soda-lime-silicate glasses (SLS) immersed in dilute hydrofluoric acid solutions. The effect of different parameters (such as concentration, immersion time, temperature and irradiation) on the etching of silica has been investigated and expressed by the loss in gm/cm^2. It has been found that the dissolution of glass increases with increasing both immersion time and HF concentration. The results show that the sodium concentration increases in the leachant solution as the concentration of HF increases. UV-VIS measurements of the leachate show strong UV absorption which is attributed to the presence of silica released from the corroded glass. Morphological and chemical composition changes were followed using scanning electron microscopy (SEM) combined with energy dispersive x-ray (EDX). The results indicate the formation of crust layers. The ionization of the glass during the passage of gamma-rays results in substantial changes to the chemical reactivity of the glass surface.The results showed an increase in the quantity of corrosion which indicates that irradiation might enhance the corrosion reaction mechanism and consequently the surface corrosion products. FTIR spectroscopy was performed for physico-chemical characterizations. In addition to the silanol band at ~ 3720 cm^{-1}, IR features are attributed to free hydrogen-bonded and structurally bound molecular water and to silanol which is hydrogen-bonded to neighboring groups. The existence of these species and their behavior during etching are related to a specific mechanism for the reaction between silica glass and molecular water.

Key words: SLS glass, HF Etching, SEM, EDX, FTIR, γ-irradiation.

INTRODUCTION

For many years, the scientific community felt quite comfortable with understanding and interpreting the interaction between glass and aqueous solution in terms of two distinct mechanisms, which are ion exchange or leaching and network dissolution. The durability of glass in an aqueous environment is a function of the kinetic approach to equilibrium and the final thermodynamic equilibrium with the aqueous environment (Paul, 1982). The kinetics of glass dissolution depends on the test parameters (surface area, time, temperature) while the thermodynamic contribution is a function of glass composition and structure (Jantzen 1992, Clark *et al.,*1979).

The chemical and electrochemical etching of silicon with aqueous fluoride solutions are a subject of major importance in the semiconductor industry. Accordingly, many studies were undertaken to elucidate the mechanism of silicon dissolution in these media. The anodic dissolution of silicon in fluoride media requires the presence of defect hole at interface (Lehman 1993).

Previous empirical studies show that the addition of K and Na can reduce the melting forming temperature of the glass, also it increase susceptibility to leaching. This can be attributed to the increase in the number of NBO's that decreases the connectivity of the structure combined with the relatively loose and high mobility of the alkali ions due to weaker bonding. The alkaline earth oxides (usually CaO & MgO) are usually added to improve alkali leaching resistance (Clark *et al.,*1979). Although each atom of Ca produces two NBO's in the glass structure, the alkaline earth ions are relatively less mobile than the alkali ions and therefore expected to retard or block alkali diffusion. Small amounts of Al_2O_3 are also known or accepted to increases bond or coupling strength, reducing specific volume, and resulting in a more durable structure (Clark *et al.,*1979, Sinton &LaCourse, 2001) because it forms further structural building AlO_4 groups with tightly bounded alkali to achieve neutrality and such alkali ions are not easily released by solutions.

It is accepted that silicon and fluorine combine to form one of the most stable bonds (if not the most stable at all) (Cerofolini, 1998). The Si-F bond is indeed stronger than the N=N, O=O and C=C double bonds. The Si-F bond energy is so high that it is sometimes ascribed to a double bond, which originates from a lone electron-pair donation from fluorine to empty d-orbitals of silicon (Cerofolini and Re 1998, Cerofolini, 1998).

Radiation effects are of important consideration because of the potential influence on glass corrosion and chemical stability. At an irradiated Si, the first step corresponds to the trapping of a hole at the surface and the formation of intermediates (silicon surface atoms in oxidized state). These intermediates develop toward the final dissolution of Si species, through consecutive chemical species in which electrons are injected into the conduction band (Strumper and Peter, 1991).

Corresponding Author: F.M.Ezz-Eldin, National Center for Radiation Research and Technology, Nasr-City, Cairo, Egypt. P.O.BOX; 29. Tel: 00202 26393962, Fax: 00202 22875926.
E-mail: fatthy1uk@yahoo.com

The overall goal of this study is to improve the understanding of etching of commercial soda-lime-silica (SLS) glass by dilute HF solutions as a function of concentration, temperature and irradiation. Towards this goal, the etching of this type of glass has been measured at room temperature and also at different elevated temperatures (45, 65, 80 and 100°C). Also the studied samples were exposed to γ rays with doses of 40 and 80 kGy. Infrared spectroscopy was chosen as the main analytical tool for this study because it is known to be highly sensitive to water-related species and can give information about hydrogen's binding state in the glass (Davis and Tomozawa 1996). It is hoped that the present study will be complementary to previously published results on etching of the same glass (Ezz-Eldin *et al.*, 2010).

Experimental Details:
Materials:
Multicomponent commercial soda-lime-silica glass (SLS) with the following composition (in mol.%): $SiO_2 \cong 70.768$, $Na_2O \cong 13.554$, $Al_2O_3 \cong 0.38$, $CaO \cong 9.07$, $MgO \cong 5.927$, $Al_2O_3 \cong 0.38$, $K_2O \cong 0.029$, $TiO_2 \cong 0.018$, $Fe_2O_3 \cong 0.03$, $SO_3 \cong 0.236$ was used as received. Glass samples have been cut to plates with dimensions 1×1 cm and with a thickness of 0.2 cm.

Etching Test:
A series of SLS glass plate (1x1x0.2 cm) was placed in polyethylene BD Falcon™ Conical Tube with Flip Top Cap, which allows the etchant solution (50ml) to completely cover the whole glass surfaces of the specimen, and then the tube is tightly closed. The inlet solutions (0.05, 0.1, 0.25 and 0.5N HF) used in this study were prepared from deionized water plus reagent grade of HF acid. The test duration experiment was carried out at room temperature (~25°C) and, at different temperatures (45, 65, 85 &100°C), for different interval times. After complete specified immersion regime in each acid solution, samples were cleaned in de-ionized water and left to dry completely in air and then accurately weighed three times to minimize the error (the balance error ~0.0001gm). As the etching is affected by surface area, so the relationship between the geometric area of the glass samples and the volume of the solutions was maintained as S/V= 0.042 cm^2/ml.

Ph and Optical Measurements and Determination of Released Sodium Ions:
Outlet fluid pH was measured immediately after sampling using an Orion Research (601A) pH meter at 25°C. Accuracy of measurements was ± 0.01 pH unit. Initial (before experiments) solutions were used as standards to minimize matrix effect. Outlet solutions were analyzed to determine the Na content. Reactive fluid sodium concentrations were determined using atomic absorption spectroscopy (Perkin Elmer, Zeeman 5000). In addition, ultraviolet-visible (UV-VIS) spectra of leachate recorded both before and after corrosion in 0.5N HF solution at 100°C for diffferent time intervals were obtained by means of a double beam spectrophotometer (type Jasco Corp., v-570, Rel-00, Japan) covering the range 200-1100 nm. For absorption measurements the spectral band width was kept at 1nm.

Fourier Transform Infrared (Ftir) Measurements:
FTIR Jasco FT/IR-430, Japan spectrophotometer at the 3000-4000 cm^{-1} range, was used in reflectance mode to monitor the surface changes caused by the etching treatment. Analysis was performed before and after all treatments for the specimens. The measurements were done using a spectrometer equipped with a liquid nitrogen cooled mercury-cadmium telluride detector and a variable angle specular reflectance accessory set to 84°C at room temperature with resolution 2 cm^{-1}. Each spectrum was taken as an average of 10 scans collected over the frequency range of 4000-3000 cm^{-1} with a resolution of 4 cm^{-1}.

Energy Dispersive X-Ray (EDX) and Scanning Electron Microscope (SEM) Measurements:
Scanning electron microscope JSM- 5400 was utilized to study the surface morphology of the specimen at high magnifications. A high -surface shape resolution image was screened on a T.V monitor that showed the detailed surface morphology of the specimens before and after each corrosion test. The glass samples were rinsed in deionized water followed by a final ethanol bath and drying. After etching, the analytical procedures were performed immediately to avoid uncontrolled alteration of the glass surface. Energy Dispersive X-ray analysis (EDXA) model Oxford attached to a SEM (Jeol-Jsm 5400) was used to analyze the characteristic X-ray radiation emitted from each component element when the specimen is bombarded with high energetic electrons, and is utilized to determine the kind of elements that exist in the specimen surface and their percentage. The electron beam was rapidly scanned over the flat surface of the specimen over an area of about 20x20 μm with a constant accelerating voltage of 20 keV and a constant probe current of 10^{10} A.

Irradiation Procedure:
A ^{60}Co gamma rays cell with a dose rate 2.56 Gy/sec was used for irradiation experiments. The required doses were achieved by calculating the required time for the desired overall doses (40 and 80 kGy).

RESULTS AND DISCUSSION

Etching:

The reactions between glass and different aqueous solutions with various pHs have been of interest for many years (Clark *et al.,* 1979). Chemical attack mechanism may be based upon two concepts; leaching characteristic of the acid attack and the specific characteristic etching effect of HF solution.

The relationship of data between time (days) and the quantity of etching (gm/cm^2) at room temperature for four different concentrations of HF (0.05, 0.1, 0.25 and 0.5N) are illustrated in Figure 1. It can be noticed that at low concentrations of HF, the amount of corrosion is small, but with the increasing of solution concentration to 0.25N, an obvious increase in the weight loss is observed. When the HF concentration becomes 0.5N, at such concentration the dissolution of glass is rapid and extensive.

The first explanation of this observation was in terms of polarization of Si-Si back-bonds to Si-F bonds. Assuming that the strength of the Si-F bond is derived from an electrostatic reinforcement due to electron transfer from silicon to fluorine, the ionicity of the Si-F bond polarizes the Si-Si.

Trukes *et al.,* 1990 have assumed that the attack of the HF aqueous solution to SiO$_2$ is completed with Si-F or SiHF termination. The following two possible attacks by an HF molecule can be advanced

(a) In diluted aqueous solution, HF is completely dissociated,

$$HF + H_2O \rightarrow F^- + H_3O^+; \tag{1}$$

The following chemical reactions represents the attack of HF acid on silica forming hexaflurosilicic acid or tetraflurosilicic acid at moderately high temperature (Koli *et al.,* 2009).

$$SiO_2 + 6HF \rightarrow SiF_6^{-2} + 2H_2O + 2H^+ \tag{2}$$

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O \tag{3}$$

(b) In concentrated aqueous solution, the H$_3$O$^+$ activity is increased because of the formation of the hydrogen-bonded adduct F$^-$….HF via the equilibrium (Cotton *et al.,* 1990)

$$F^- … H_3O^+ + HF \rightarrow F^-….HF + H_3O^+ \tag{4}$$

Though the concentrated aqueous solution contains undissociated HF, its binding energy to F$^-$ is so high that the adduct F$^-$….HF is considered as a well-defined ion (HF^{2-}). This can explain the increase of etching with the increase of HF concentration as shown in Figure1. Also, it can be noticed that the dissolution rate decreases at the last periods of immersion time (10-40 days). These results can be explained taking into consideration that a gel layer is formed in the glass surface, this layer become more dense and stable by proceeding ageing, also its thickness increases with reaction time, and by the concentrations of elements released from the glass onto the etching solution. These cations may intrude into the gel layer network and are sorbed onto ionizable functional groups of the gel forming a dense less porous surface layer (Lucksheiter & Kiezler 2001).

It can be noticed from Figure 2 that the weight losses of samples immersed in 0.5N HF solution increase with the increase of the leaching solution temperature, but when the temperature of the solution exceeded 85°C, the weight loss% begins to decrease. This decrease can be referred to deep diffusion of etching solution in the glass matrix at such high temperature, causing etching of some glass modifiers. Some oxides such as CaO, MgO or Al$_2$O$_3$ which are present in the glass composition are known to give insoluble products with HF solution such as CaF$_2$ which is Ca^{2+} + 2F$^-$, MgF$_2$ which is Mg^{2+} + 2F$^-$, and AlF$_3$ which is Al^{3+} + 3F$^-$. These insoluble products are deposited on the generated surfaces, (Smith & Pantano 2008, Hiescu *et al.,* 2005) and act as masking layers for the further progress of the etching mechanism.

Solution Analysis:

The results illustrated in table (1) represent sodium release in the solution and pH of the leachate at different times, the results indicate that increasing in either the concentration or immersion time causes an obvious increase in the amount of released sodium ions. It can also be noticed that the sodium content in the etchant solutions is small at the beginning of etching process, which is due to the attacking of HF solution which is concentrated at first to the main Si chain in the glass. As the etching process proceeds, the amount of sodium ions in the etchant solutions obviously increases. This can be interpreted to be due to the presence of these Na$^+$ ions in the interstices between the silicate networks. So, when the silicate network begins to break due to the attack of HF solution, Na ions become free to release in the solution. The observed drop of the released Na$^+$ ions after 30 days may be due to the additional Na$^+$ ions which are enriched in the solution besides Si ions, then

sodium silicate phase (Na$^+$Si$^-$) can be constructed and precipitate or sorbed (Lucksheiter & Nesovic 2004) to form precipitated layer in the glass surface. This means that the Na$^+$ ions which have been released in the solution are consumed, so the net result is the observed decrease in the sodium content. However, the observed sharp increase in the released Na$^+$ ions at both last periods and high HF concentration could be due to the detach in the protective layer from the glass surface which is not stable over longer immersion time to 40 days and, then the released sodium ions is markedly increased in the solution. The last results are confirmed by measuring the pH of the etchant solutions, which shows a decrease in the pH at the beginning due to the presence of Si ions followed by a remarkable increase in the pH of the etchant solution due to the increase in the release of both sodium and calcium ions.
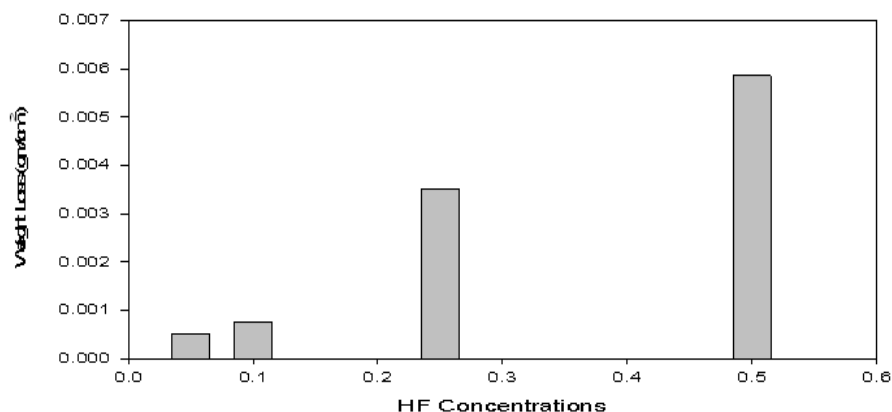
Fig. 1: Effect of different HF solution concentrations on the corrosion weight loss.
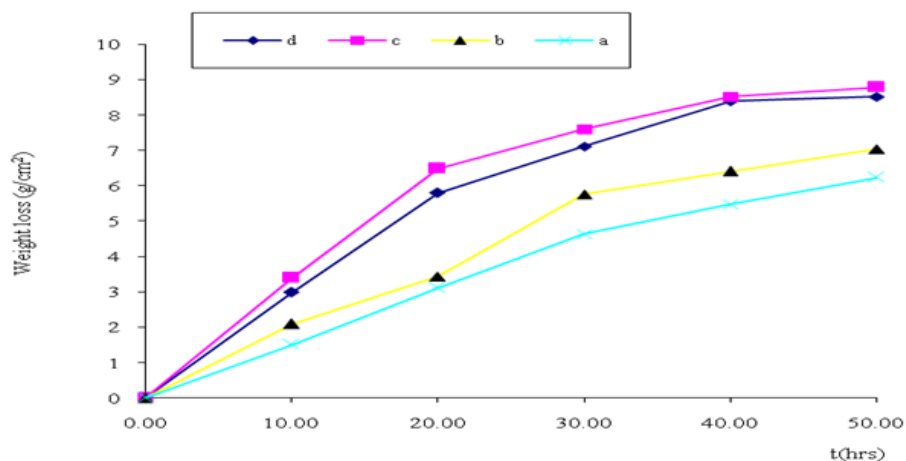
Fig. 2: Effect of temperature on the corrosion weight loss.

However, the effect of raising temperature of the etchant solutions (0.5 N HF) causes a dramatic decrease for either the amount of the released Na$^+$ ions or on the pH values of the etchant solutions as shown in table (1). These results are in agreement with the previous etching results where, the amounts of sodium released decrease at 85°C and then are sharply decreased at 100°C due to the formation of an insoluble layer precipitated at the glass surface protecting the glass against the penetration of the HF solution through the glass surface.

By tracking the UV band at 230 nm of the leachate after different immersing times in Figure (3). This band is corresponding to the characteristic optical feature of Si according to (DeRosa *et al.,* 2003). It can be noticed that after 20 days of immersion of glass in the solution the band has higher intensity and shifted to a higher wavelength, which give an indication of the increase of the amount of the released Si ions in the solution. This band showed a decrease in its intensity and slightly shifted to a lower wavelength after 30 days of immersion, which gives an indication of the decrease of the amount of Si in the solution. This result can be referred to a combination of Si and Na ions in the solution to form sodium silicate, which precipitates in the glass surface. This conclusion is proved by the EDX results in table (2), which shows an increase in the amount of both Si and Na ions in the glass surface. Another proof of the last conclusion is that the amount of Na released shown in table (1) is the resultant of the observed decrease of the Na ions found in the solution. The observed increase in the intensity accompanied with the observed shift to a higher wavelength of the solution, when the immersion time reached 40 days, reflecting the increase of Si ions in the solution. This result can be interpreted by

assuming the dissolution of the precipitated layer in the glass surface due to further prolonged immersion times. This assumption is also confirmed by the remarkable increase in Na released after 40 days as shown in table (1). On the other hand, it can be assumed that hydrolysis process begins to take place, where the amount of Si ions in the glass surface increases as shown in EDX results as they are prepared to be released in the solution.

Table 1: The pH values, the released Na$^+$ ions and weight loss of SLS glass immersed in 0.5N HF at different immersion time, temperatures and irradiation doses.

| Effect	Effect of Imm. time (days)				Effect of Temp. (°C)				Effect of Irrad. (kGy)		
t or T or dose	10	20	30	40	45	65	85	100	0.0	40	80
Na$^+$	167.3	246.7	167.3	448	696	640	504	109	448	240	136
pH	4.21	4.16	4.1	4.23	2.61	2.62	2.38	1.50	2.46	2.46	3.00
Wt. Loss	0.011	0.0116	0.12	0.0122	0.0419	0.0434	0.0459	0.1173	0.0122	0.1379	0.0393

Table 2: EDX of the glass surface before and after being immersed in 0.5N HF for different time intervals (5-40 days) at R.T.

Elements	before	10 days	20 days	30 days	40 days
Na	22.3	32.4	22.05	32.78	18.66
Mg	7.88	9.85	6.09	9.31	6.97
Al	- 2.63	- 1.44	-3.08	-1.74	-2.73
Si	67.76	56.68	68.92	57.11	70.32
Ca	4.66	2.5	6.03	2.54	6.78
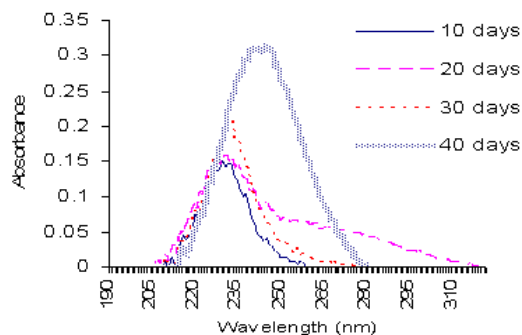
Fig. 3: Effect of immersion time on the absorbance spectra of the etchant solution of SLS glass immersed in 0.5N HF at R.T.

In addition leachates show quite optical absorption in the uv-vis wavelength region (190-320nm). Figures 4,5 show an increase in the intensity of the absorption band (~230nm) accompanied with a shift towards longer wave length as recorded when the heat or concentration were increased. This explains the relatively high dissolution, as the effect of temperature and exhibits more shift to the absorption band. The origin of this behavior has been associated with the presence of silicate and alkali ions. However, the presence of alkali and alkaline earth ions produced a significant shifting of the uv edge to longer wavelengths.
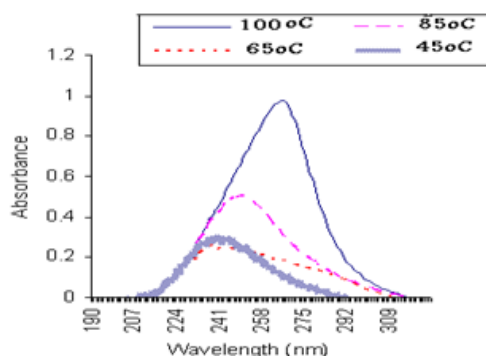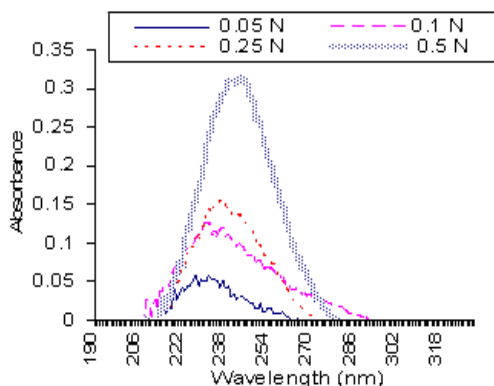

Fig. 4: The absorbance spectra of the etchant solution of SLS glass immersed in 0.5N HF at different temperatures (45°C, 65°C, 85°C, 100°C).

3.3 *Effect of Irradiation:*
The results illustrated in Figure 6 show that when glass samples are subjected to gamma-ray, with dose of 40 kGy, a remarkable increase is observed in the glass corrosion. However, increasing the irradiation dose from

40 to 80 kGy causes a decrease in the weight loss of the glass, although corrosion is still much higher than that in the unirradiated glass samples.

Fig. 5: The absorbance spectra of the etchant solution of SLS glass immersed in 0.5N HF at R.T different HF concentrations (0.05, 0.1, 0.25, 0.5N).

These results can be interpreted on the light of the fact that the most important effect of γ irradiation is the formation of induced point defects in alkali silicate glasses (Ezz-Eldin *et al.,* 2008), which are oxygen excess centers. There are two types of NBOs hole centers in silicate glasses; one is an analogue to a NBO hole center in silica glass and the second involves two NBOs on the same silicon. The NBO hole centers are formed by a radiation chemical reaction:

$$\equiv\text{Si-O-M} + \gamma \text{ irradiation} \rightarrow \equiv\text{Si-O}^{\bullet} + \text{M}^{+} \tag{5}$$

Where ● depicts an unpaired spin residing on silicon (or oxygen).

It is assumed that a free hole resulting from γ irradiation is first trapped at the ≡ Si-O-M site and then the alkali ions are free to diffuse away to the site of a trapped electron where it stabilizes the uncompensated charge (Weber *et al.,* 1997).

Mobilization of alkalis in irradiated glass has been confirmed by a large number of studies, being confirmed also by molecular dynamic simulations of alkali migration in silicate glasses (Cormak *et al.,* 2003, Delay & Ghaleb 2000). This demonstrates that the association with NBO confines the alkali to local motion, whereas the absence of a coordinating NBO allows the alkali to explore more easily its environment and to undergo long-range migration (Delay & Ghaleb 2000). According to the last reaction (eq.5), new irradiation-released alkali ions enable their free diffusion from the NBO sites. Moreover, the concentration of NBO hole centers created by γ-irradiation is proportional to the concentration of NBO sites and depends both on dose and dose rate of the radiation.
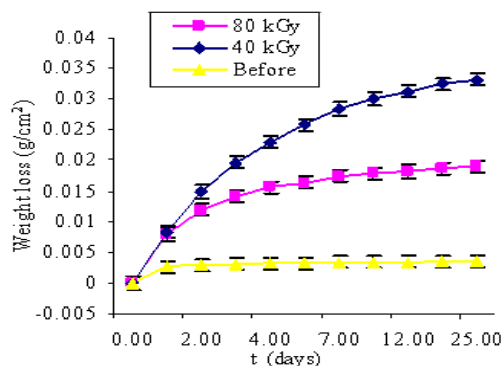
Fig. 6: The etching behavior of the SLS glass immersed in 0. 5 N HF for 40 days at R.T after being irradiated at different irradiation doses (40,80 kGy).

The results may be interpreted as follows. When glass samples are subjected to a dose of 40kGy, there is an ionization of the alkali and alkaline-earth-metal oxides (Na, K, Ca, Mg) and Al besides freedom of electrons from both surface and glass lattice. Moreover, there is recent evidence for the formation of sodium species,

resulting from electron trapping by sodium ions (Delay&Ghaleb 2000) ($Na^+ + e^- \rightarrow Na$). Then, there is a decrease in the amount of mobile sodium ions, which also may affect the behavior of sodium during ion exchange of irradiated glasses. According to the last approach, when the irradiated glass (40kGy) samples are immersed in the 0.5N HF aqueous solution, the HF begins to attack the silicon matrix due to the presence of defects in the silicon backbone in the irradiated samples. It thus becomes easier to the HF solution to attack the silicon matrices and causes a release of Si^+ ions to the solution, which in turn causes the observed remarkable increase in corrosion for the examined glass (Table 1). On the other hand, the remainder sodium ions which are freed from the interstices of the glass matrix, can easily migrate either inside the glass, or stayed in the glass surface. But the formation of strong bonded SiF or SiHF in the glass surface prevents the release and migration of Na^+ ions from the glass surface to the solution. This can explain the decrease of sodium content in the solution of the irradiated (40kGy) glass (Table 1). Exposing glass samples to a higher irradiation dose (80kGy) leads to an increase in the amounts of both alkali and alkaline-earth metal ions producing excess of electrons. These electrons neutralize a large part from Na^+ ions which have high electrophilicity (Boisot *et al.,* 2000) and some of the remainder Na^+ ions will be trapped in the holes in both matrix and surface of the glass. In addition, the amount of Si^{4+} ions at the glass surface also increased leading to a formation of thicker protective layer besides the insoluble layer formed from CaF_2, MgF_2 and AlF_3 causing the observed decrease for both corrosion (although it is still higher than the unirradiated samples) as shown in (Fig.6) and the released Na^+ ions (Table 1).

It is well known that, the pH of the leachate solutions generally increases when the amount of alkali leached is increased. Table 1 demonstrates that, the pH values increase while the released Na^+ ions in the solution decrease. We can only speculate that other factors can cause the anomalous change in pH, such as the dissolution of other ions from the glass. Due to the high irradiation dose (80kGy) there is a lot of K, Ca, Mg and Al ions which are assumed to be freed from either the matrix or glass surface. Due to the low strength of the HF solution, most of the F^- ions are consumed to react with Si^{4+} ions which are preferable for F^- ions while small part of the HF forms insoluble layer (CaF_2, MgF_2 & AlF_3) at the glass surface preventing the release of Na^+ ions. In the same time K^+ and some of Ca^{++}, Mg^{++}, & Al^{+++} ions were released onto solution forming KOH, $Ca(OH)_2$, $Mg(OH)_2$ and $Al(OH)_3$, in addition, some of released Na^+ ions are believed to precipitate as Na^+Si^-. All the previous mentioned factors lead to the observed increase in pH values.

Surface Microanalysis:

Visual observation of the treated glass samples gives the impression that the surfaces remained intact and without alteration. However, drastic changes of the glass-surface composition were found by EDX. Table (2) compares typical EDX results taken from glass before and after etching in HF. From the results it becomes evident of the last assumption that the etching process induces an increase in the Na ions at the glass surface at the first etching time, where the priority of HF solution is to attack Si ions. When the etching process is in proceeding, the freed Na ions migrate from the glass surface to the solution as mentioned before. The observed increase in the Na content in the glass surface can be an evidence of the precipitation of a formed layer with the increasing of the etching time. This is followed by a detaching of this layer represented by the sharp decrease in the Na content.

The surface morphology of the SLS glass, prior to the experiments, appears to be free of fine particles. The morphology of the glass surface after being etched with HF solution is illustrated by SEM images, (Figure 7). Numerous micro cracks are observed on the surface. Their number and density increase with increasing etching time. It also shows some rounding of originally sharp edges, possibly due to the result of dissolution. With progressive HF treatment, flakes are observed to be formed at the glass surface. So, the surface become rough, with a great deal of nonuniformities due to the presence of insoluble products deposited in the glass surface.

Infrared Reflectance Spectra:

Infrared reflection spectroscopy is accepted by several authors (Hench1975, Lee *et al.,*1997, Bianchini *et al.,* 2003) as a valuable tool to follow the aqueous corrosion of glass. Several studies tend to focus mainly on the structural silicate vibrations in the 500-1200 cm^{-1} range, but miss water, and OH bands in the 2500-3800 cm^{-1} range.

The FTIR spectra for as-received glass and the glass etched with different concentrations of HF solutions are shown in Figure 8. The most noticeable changes in this figure are the significant increase in the intensity of molecular water peak at ~3243 cm^{-1}. When the HF concentrations are increased, a significant reduction in the free silanols as indicated in the peak at ~3720 cm^{-1}, as well as vicinal groups and hydroxyle peaks at ~3500 and 3820 cm^{-1} are observed. In addition, a sharp peak of molecular water at ~3230 cm^{-1} is observed at low concentrations (0.05N) of HF acid solution. However, a significant increase in its reflectance % is observed at high concentrations (0.25 and 0.5N) HF acid solution. At the frequency of ~3560cm^{-1}, the low concentration treated samples retained the same shape of spectrum as the as-received SLS glass, indicating little change in the presence of the –OH bearing species. However, it is apparent that the amount of molecular water increases at the expense of the free silanol groups present as shown in the peak at ~3720 cm^{-1}. One can imagine the spectral

features in Figure 8 occurring for all three treatments just for different extents; (a) The initial glass surface contains species such as the free silanols groups and, (b) hydrogen bonded vicinal silanols, (c) further hydration leads to physisorbed water (Wakabayshi 1992).

The observed decrease of the silanol groups may be interpreted as a result of the attack of F$^-$ ions to the SiOH present at the glass surface, which cleaves the Si-OH bond leading to decrease in silanol group as observed at the peaks ~3720 and 3870 cm^{-1} and increase in molecular water visualized at ~3220 cm^{-1}.

FTIR spectra for etched SLS glass at different temperatures (65°, 85° & 100°C) are shown in Figure 9. The results show that the reflectance peak related to SiOH at ~ 3550 cm^{-1} decreased when the temperature reached 85^{0}C, which is related to OH group. The noticed decrease can be referred to the increase of the diffusion of HF solution through the glass matrix causing a disruption of SiOH bonds causing this observed decrease in the OH peaks. This result is also in agreement with the cited corrosion results, where this amount of corrosion increases with the increase of the immersion temperature until it reaches 85°C, where there is a decrease in the amount of corrosion. According to the mentioned interpretation, this decrease is due to the formation of a passivation layer, which prevents any further attack of HF solution, which can be indicated by a sharp increase at the OH peak at ~ 3550 and 3810 and 3872 cm^{-1} at 100°C. Consequently this formed layer is protecting SiOH and molecular water groups in the glass matrix.
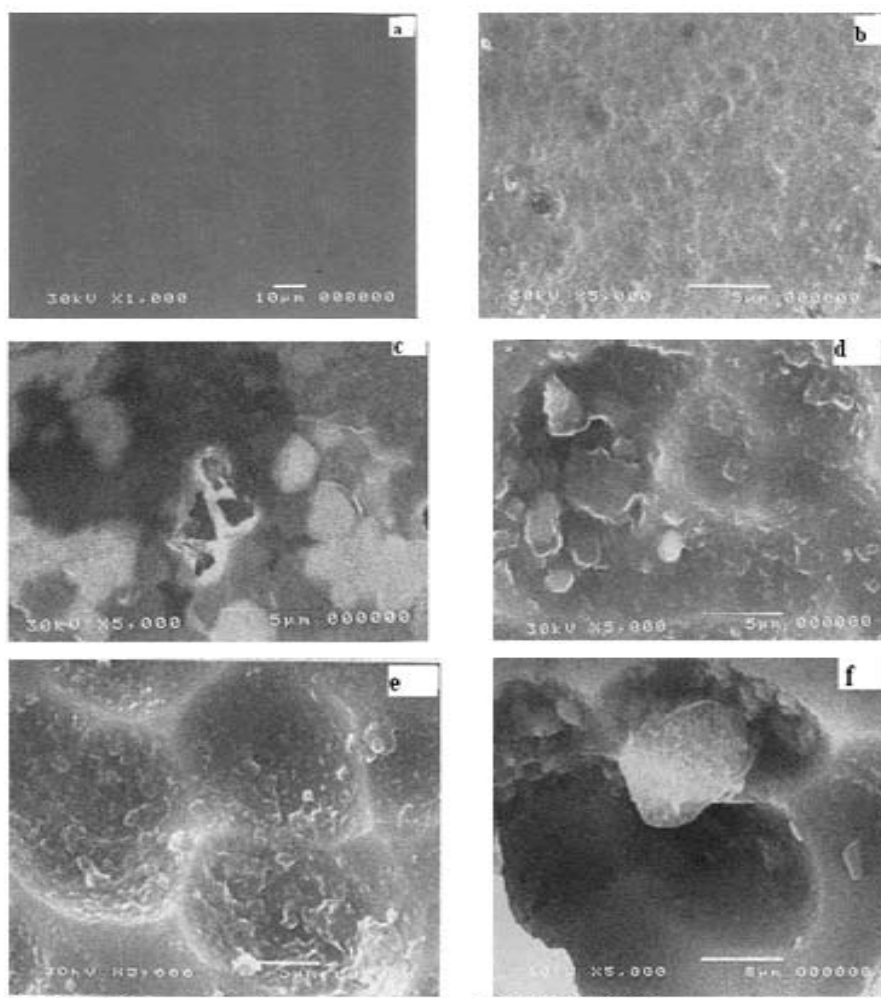

Fig. 7: SEM of SLS glass after being immersed in 0.5N HF at different interval periods; a- as-received, b- 5 days, c- 10 days, d- 20 days, e-30 days & f- 40 days at R.T.

As shown in Figure 10 the IR spectra of the irradiated samples (40kGy), which are immersed in different HF concentration for 40 days reveal an increase in all the silanol groups vibrations at ~3250 and 3800 cm^{-1} and molecular water peaks at ~3400 cm^{-1} in the observed spectra. This can be explained by adopting the following

hydration reaction (eq.6) taking into consideration the fact that, the ionization of the glass during the passage of gamma-rays results in substantial changes to the chemical reactivity of the glass surface. This is most apparent for the interface zone where the dissolution rate is generally increased. Also, irradiation leads to the formation of point defects in alkali silicate glasses as mentioned before (Weber *at al.,*1997).
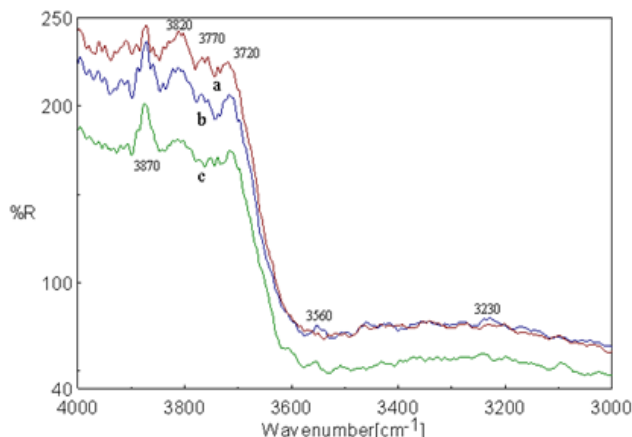
Fig. 8: IR spectra of etched SLS HF for 40 days in different HFconcentrations. a-0.05, b- 0.25, c- 0.5N.
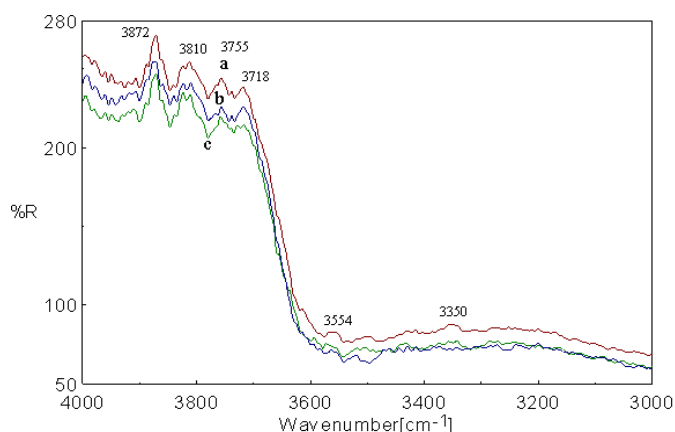
Fig. 9: IR spectra of etched SLS glass immersed in 0.5N HF for 40 hours at different temperatures. a- 65°C, b- 85°C, c- 100°C.

$$Si\text{-}O^- + H_3O^+ \quad \rightarrow \quad SiOH + H_2O \tag{6}$$

Generally, it can be concluded that, the increase of the formed SiOH and molecular water groups is expected to increase with the increase of HF concentration as shown in equation 1, at elevated temperature and irradiation. It was assumed that, the amount of molecular water increases in the expense of the hydroxy groups and, this is due to the increase of the amount of ionized F$^-$ ions which causes the continuous dissolution of ions in the corrosive attacking solution.

Conclusions:

The results of experiments are presented in which commercial soda-lime-silica glasses are subjected to a simple etching in dilute HF solution with various strengths. The results show that the amount of etching increases with the increase of either HF concentration or temperature. However, when the temperature of the etching solution reaches 100°C, the amount of etching begins to decrease. The last result is referred to the possible presence of insoluble products such as CaF$_2$, AlF$_3$ and MgF$_2$ in the glass surface (17, 18), which prevents the continuous transport of the etching solution to the glass surface. The results also show that both pH and Na$^+$ contents in the solution decrease at the beginning of the corrosion process, followed by a remarkable

increase. This is interpreted by assuming that the attack of HF begins directly and primarily on the Si backbone at the beginning of the corrosion process causing a release of Si ions in the solution and eventually Na$^+$ ions in the interstices, which become free to be released in the attacking solution. The results also show that the corrosion increases when glass samples are exposed to γ-irradiation. This is referred to the formation of NBO hole centers due to irradiation, which become easier sites to be attacked by HF solution. It can be also noticed that increasing irradiation dose from 40 to 80kGy causes a decrease in the corrosion. This is correlated with the increase of the NBO hole centers in the glass surface, which can rapidly reacted with HF solution forming a gel layer. The morphology of the glass surface was also examined using SEM.

The suggested glass-water reaction mechanism in this work is consistent with the bands assignments in the glass features, which appear in the IR spectrum for every stage of the reaction process. The reaction mechanism is also consistent with the order in which different bands may appear and disappear during etching or irradiation processes of the glass.
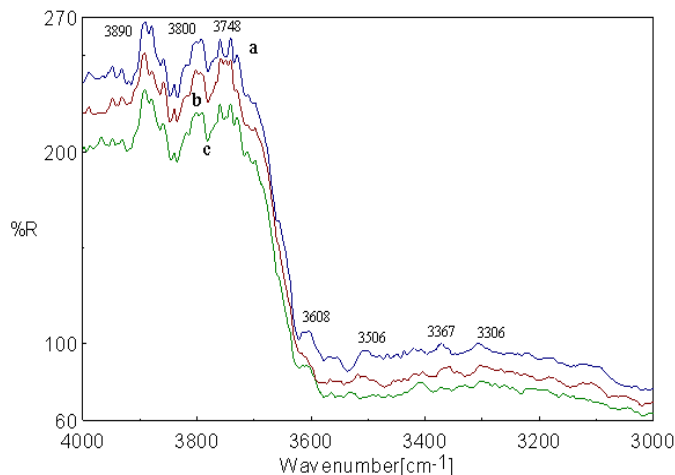
Fig. 10: IR spectra of irradiated SLS glass (40 kGy) immersed for 40 days at R.T in different HF concentrations. a- 0.05, b- 0.25, c- 0.5N.

REFERENCES

Boisot, B., G. Petite, D. Ghaleb, N. Pellerin, F. Fayon, B. Reynard and G. Calas, 2000. Nucl. Instr. & Meth. Phys. Res., B 166-167, 500.

Bianchini, F.G., M. Preo, M. Guglielni and C.G. Pantano, 2003. J. Non-Cryst.Solids, 321: 110 .

Cerofolini, G.F., 1998. J. Applied Surface Science., 133: 108.

Cerofolini, G.F., Re N., 1998. in: E. Garfunkel, E. Gusev and Y.A. Vul', Fundamental Aspects of Ultra thin Dielectric on Si-Based Devices, Kluwer, Dordrecht.

Clark, D.E., 1979. Pantano C.G. and Hench L.L., editors. Corrosion of Glass, Books for Industry, New, York.

Cormack, N.A., J. Du, and T.R. Zeitler, 2003. J. Non-Cryst. Solids, 323:147.

Cotton, F.A., G. Wilkinson, I. Kawanabe, M. Miyashita and T. Ohmi, 1990. IEEE Trans. Electron Devices., 37: 107.

Davis, K.M. and M. Tomozawa, 1996. J. Non-Cryst. Solids. 201: 177.

Delaye, J.M. and D. Ghaleb, 2000. Phys. Rev. B, 61: 14481.

DeRosa, R.L., P.A. Schader, J.E. Shelby, 2003. J. Non-Cryst. Solids, 331: 32.

Ezz-Eldin, F.M., T.D. Abd-Elaziz, N.A. El-Alaily, 2010. J. Mater. Sci., 45: 5937.

Ezz-Eldin, F.M., H.H. Mahmoud, T.D. Abd-Elaziz and N.A. Elalaily, 2008. J. Physica, B 403: 576 .

Hench, L.L., 1975. J. Non-Cryst. Solids, 19:27.

Iliescu, C., J. Jing, F.E.H. Tay, J. Miao and T. Sun, 2005. Surface & Coatings Technology 198: 314.

Jantzen, C., 1992. in: Clark D.E., Zoitos B.K., (Eds.). Corrosion of Glass, Glass Ceramics and Ceramics Superconductors, Noyes Park Ridge NJ.

Koli, M., M. Hamidouche, N. Bouaouadja and G. Fantozzi , 2009. J. Eur. Ceram. Soc., 29: 269.

Lee, Y., Y.L. Peng and M. Tomozawa, 1997. J. Non-Cryst. Solids, 222: 125.

Lehmann, V., 1993. J. Electrochem.Soc., 140: 2836.

Luckscheiter, B. and B. Kiezler, 2001. J. Nucl. Mater., 298: 155.

Luckscheiter, B. and M. Nesovic, 2004. J. Nucl. Mater., 327: 182.

Paul, A., 1982. The Chemistry of Glasses,1st Ed. Chapman & Hall. New, York.

Sinton, C.W. and W.C. LaCourse, 2001. Mater. Res. Bull., 36: 2471.

Smith , N.J. and C.G. Pantano, 2008. J. Amer. Cer. Soc., 91: 736.

Strumper, J.M. and L.M. Peter, 1991. J. Electroanal. Chem., 309: 325.

Truks, G.W., K. Raghavachari, G.S. Higashi and Y.J. Chabal, 1990. Phys. Rev. Lett., 65: 504 .

Wakabayashi, H., 1992. in: Proc., 3rd Int. Symp. on Structural Imperfections in SiO2- based Amorphous Materials, ed. Somiya S., Doyama M., Hasegawa M. and Agata Y., Trans. Mater. Res. Soc., Jpn., 8.

Weber, W.J., R.C. Ewing, C.A. Angel, G.W. Arnold, A.N. Cormack, J.M. Delaye, D.L. Griscom, L.W. Hobbs, A. Navrotsky, D.L. Price A.M. Stoneham and M.C. Weinberg, 1946. J. Mater. Res., 12: 1946.