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Dissolution behavior and fluoride release from new glass composition used in glass ionomer cements

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Abstract

The degradability in an acidic environment and the release of different ions, such as Na^+, Ca^{2+}, Al^{3+} and F^- from a calcium fluoro-aluminosilicate glass (used in glass ionomer cements) during different exposure times at 37 °C has been the object of this study. The formation of a leached layer on the surface of the glass has proved to be an important factor in the ionic release from the glass.

The structural change in the silicate network of the glass during the dissolution and formation of the leached layer on the surface of the glass has been analyzed by Fourier transform infrared (FTIR) spectrometer.

The present study has investigated topographic profiles as a function of time through atomic force microscope (AFM). Also, the formation of the leached layer on the surface of the glass has been described with AFM by measuring the corrosion depth for different times of acidic treatment.

Keywords: D. Glass; Glass ionomer; Dissolution behavior; AFM; Fluoride release; FTIR

1. Introduction

Nowadays glass ionomer cements are widely used in dentistry as a restorative material, luting, and lining cements [1–3]. Worldwide interest in these materials has increased due to their biocompatibility, esthetics, adhesion to dentin and enamel [4], and cariostatic action because of the fluoride release [5–9]. It has been said that the leachable fluoride is produced by acid attack upon the glass during the cement forming process [10].

Glass ionomer cements are set through an acid–base reaction. The acid is an Alkenoic acid polymer such as polyacrylic or its copolymer with iticonic [$CH_2{=}C(CO_2H)CH_2$-$H)CH_2CO_2H$] or maleic [$HO_2CCH{=}CHCO_2H$] or tricarballylic acids [$HO_2CCH{=}C(CO_2H)CH_2CO_2H$]. The base part is typically an acid-soluble glass such as calcium fluoro-aluminosilicate glass that may often contain sodium and phosphorus. In such cases they include zinc, strontium, and lanthanum for conferring radio-opacity.

Hydrolysis of Al–O–Si bonds of glass networks by H^+ acid is the first step in the setting reaction of these cements. That is how the metallic ions such as Ca^{2+}, Al^{3+}, and Na^+ leached out from the glass and subsequently the gel structure formed by the cross-linking of metallic ions with polyacrylate chains [11–13].

With respect to the cariostatic action of the glass ionomer cement and the cement forming ability of the glass, the acid degradability and consequently ion leaching from the glass is very essential. However, there are few studies on the leaching of the same specific constituents out of the glass used in glass ionomer cements. In this study the acid degradability and profile of calcium, sodium, aluminum and fluoride release from a calcium fluoro aluminosilicate glass into a dilute acetic acid solution [ISO 6872] in different times have been investigated.

2. Experimental procedure

2.1. Preparing glass

The glass was prepared from mixtures of finely powdered silica >99.9% pure (Iran, Hamedan), alumina (Martinzwerk, Zs402, Germany), calcium fluoride (Merck, 2840, Germany),

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Table 1
Chemical composition of the studied glass

Materials	wt.%
SiO_2	40
Al_2O_3	25
CaF_2	13
Na_3AlF_6	11
$AlPO_4$	5
TiO_2	4
La_2O_3	2
Al^{3+}	15.74
Si^{4+}	18.66
Na^+	3.62
Ca^{2+}	6.66
P^{5+}	1.27
Ti^{4+}	2.4
La^{3+}	1.7
F^-	12.27
O^{2-}	37.6

cryolite (Merck, 106457, Germany), aluminum phosphate (Merck, 1098, Germany), lanthanum oxide (Merck, 1220, Germany) and titanium oxide (Merck, 100808, Germany). Table 1 shows the batch composition of the glass.

The pre-fired batch was placed in an alumina crucible (due to the compatibility with the glass composition) and heated at 1350 °C in an electric furnace for 2 h. The glass melt was then poured into a preheated stainless steel mould with the inner dimensions of 50 mm × 50 mm × 10 mm to produce a glass specimen. The glass plate was rapidly transferred to a heat treatment furnace to remove stress, which was generated during the cooling process. The new glass was analyzed using X-ray fluorescence spectroscopy (XRF; model ARL-8410) to determine the concentrations of elements present in the material sample.

2.2. Glass surface preparation

The glass plate was cut with a diamond saw blade (0.25 in. thickness) to 10 mm × 10 mm × 2 mm. Samples were then ground with 220, 400, 600, 1000 and 1200 grit silicon carbide papers. Between each grits change, the samples were thoroughly rinsed with Deionized water and wiped gently. After the final polish samples were cleaned ultrasonically in deionized water for 15 min before being dried at 150 ± 5 °C for 4 h.

2.3. Solubility test

The prepared glasses were then place in polyethylene bottles containing 75 ml of 4% acetic acid solution in accordance with BS EN ISO 6872-1999 [14]. The containers were tightly capped and placed in incubator at 37 °C for 16, 24, 48, and 96 h, respectively. The solubility tests were carried out for five specimens for each exposure time in acidic media and the storage volume for each case was 75 ml.

With required times over, the samples were removed from the solutions, rinsed in deionized water and dried at 150 ± 5 °C for 4 h. The remaining solutions were then used for measuring the concentration of Na^+, Ca^{2+}, Al^{3+}, and F^- ions.

The amount of Na^+, Ca^{2+}, and Al^{3+} ions is determined by inductive coupled plasma (ICP; model ARL-3410). Fluoride measurements have been carried out using ion selective electrode potentiometer (Mettler Toledo-MA 235 Ion analyzer, 152153000 Mettler Toledo fluoride selective electrodes, and 373-90-WTE-ISE-57 Mettler Toledo reference electrode). The equipment was calibrated by means of a standard method immediately prior to use. equal volume of total ionic strength adjustment buffer (TISAB) was added to the collected solutions as a decomplexing agent.

The quantities of ions release per unit surface area ($\mu g/cm^2$) for each samples were calculated by multiplying the ion concentration ($\mu g/ml$) by the volume of the solution (75 ml) divided by the total surface area of the specimens ($2.8\ cm^2$). The results are expressed as mean and standard deviation (S.D.).

FTIR spectra were recorded with a FTIR spectrometer (BOMEM, Canada) in the 400–4000 cm^{-1} range at room temperature. Pellets were prepared for FTIR measurements by mixing and grinding a small quantity of glass powder with dried spectroscopic grade KBr powder and then compressing the mixtures to form pellets for measurements. All measurements were at a 4 cm^{-1} resolution.

The features of the glass specimens before and after leaching at different times were studied using atomic force microscopy (AFM). The contact AFM analysis was carried out using a Park CP instrument (Park Scientific Instruments), which used the constant force mode and silicon nitride tips from Park.

3. Results and discussion

3.1. X-ray fluorescent spectroscopy

XRF analysis of the bulk composition of the glass after synthesis is shown in Table 2. The data indicated no significant deviation from the batch composition after glass production.

3.2. Leaching test

The quantities of ions release per unit surface area ($\mu g/cm^2$) for each sample into acetic acid with Standard deviations are shown in Table 3. Fig. 1 also illustrates the mean concentration

Table 2
Chemical composition of the prepared glass samples after synthesis

Elements	wt.%
Al^{3+}	15.29
Si^{4+}	16.73
Na^+	4.28
Ca^{2+}	7.51
P^{5+}	1.58
Ti^{4+}	3.12
La^{3+}	1.91
F^-	11.3
O^{2-}	37.78

Table 3
Mean ions release from the glass as μg/cm^2 (Standard deviation)

Ions	Time (h)			
	16	24	48	96
Ca^{2+}	6.064 (0.94)	20.174 (0.88)	28.266 (1.01)	8.11 (1.29)
Al^{3+}	12.986 (1.24)	33.628 (1.56)	19.202 (0.912)	7.742 (1.4)
Na^+	8.744 (1.01)	15.064 (1.14)	7.244 (1.63)	37.822 (1.17)
F^-	0.884 (0.31)	1.68 (0.28)	2.238 (0.25)	2.394 (0.43)

of sodium, calcium, aluminum, and fluoride ions in different soaking times.

The leaching process started by the reaction of an aqueous acid with a surface of calcium fluoro-aluminosilicate glass. Therefore, the hydrogen-bearing ions attacked the glass, causing it to release ions such as Na^+, Ca^{2+}, Al^{3+}, F^-, AlF_2^+, AlF^{2+}, etc. In this study, ions release data revealed a number of significant aspects:

First, there was high initial concentration of Ca^{2+} in the solution but as time passed, their amount declined. This is due to the formation of insoluble calcium compounds in the solutions. Moreover, by extracting mobile ions from the glass; and subsequently the disruption of Si–O–Si or Si–O–Al bonds in the glass network and the repolymerizing of the resulting silanol group, a silica gel layer will form. This layer acts as a diffusion obstacle and restricts the rate of ion extraction. This is also consistent with previous reports that the dissolution rate of the glass is controlled by diffusion of ions from the formed leached layer [12,15].

Second, aluminum release data was similar to those found for calcium ions which were a high concentration and a declining amount over time due to the formation of insoluble aluminum complexes in the solutions and the leached surface layer on the corresponding glass.

Third, the amount of Na^+ ions leaching in different periods is variable. An augmentation has been registered. A decrease followed by an increase comes next. An initial release of sodium similar to the other ions is due to acid attacks. Increasing the concentration of Na^+ ions in the solution over a period of time (Fig. 1) is due to the formation of soluble sodium salts. In accordance with the assumption of Douglas and Israd [15] the quantity of sodium ions in the leaching solution depends on the diffusion of mobile Na^+ ions into the glass, electrical neutrality of the glass, inter-diffusion of other ions, and consequently the formation of an electric double layer on the surface of the glass. However, in the present study the reduction in the amount of Na^+ ions after passage of time is related to the formation of an electric double layer on the surface of the glass that prevents further removal of sodium ions. Furthermore, a look at the sodium ions release data in Fig. 1 indicated that the amount of Na^+ ions in later time periods increased. This suggests that with longer time-spans, the condition for exchange of ions in the structure was created. So the electric double-layer disappeared and resulted in further rise in the number of Na^+ ions.

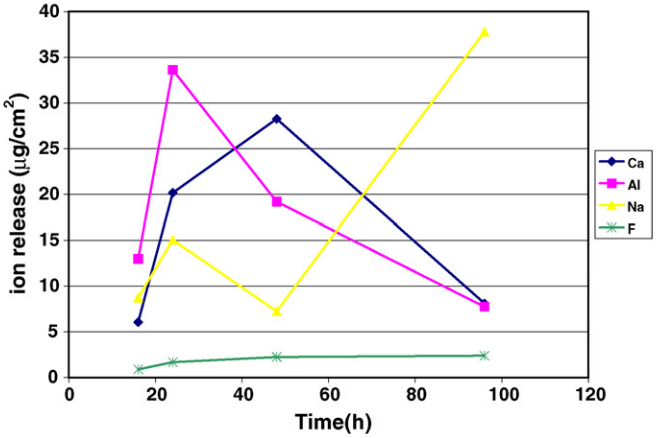

Fig. 1. Mean concentration of eluted ions such as Na^+, Ca^{2+}, Al^{3+} and F^- vs. time (data coming from Table 3).

Fourth, the action of the fluoride released from the glass is based on two mechanisms; dissolution and diffusion and it shows the similarities of fluoride concentration data with those found previously [16]. Experimental results of fluoride measurements in the present study indicated that there is a high elution rate after a short time followed by a slower rate. The high concentration of fluoride in the first hours of the analysis (Fig. 1) is related to the protons or hydronium ions attacking the surface of the glass and consequently a release of cations and negative fluoride ions. It has to be mentioned that some of these positive ions leached from the aluminosilicate glass are complex in structure and contain fluoride, e.g. AlF^{2+} and AlF_2^+ [17]. So, the fluoride of these complex ions was replaced by acetate groups of the acetic acid solution, causing an additional release of fluoride from the studied glass. In addition, a part of fluoride ions in the glass structure was changed with hydroxyl groups of the surrounding aqueous medium and this caused an increase in the amount of fluoride. Also, it was found that the diffusion of fluoride from the sub-layers entails a slight decrease in the rate of fluoride liberation in later time periods.

3.3. Infrared spectroscopy

Fig. 2 illustrates the infrared reflectance spectra of the studied glass before and after corrosion by dilute acetic acid solution. The spectrum of the pristine glass is composed of the following reflectance bands:

(a) A very sharp reflectance band at 460 cm^{-1}.
(b) A broad and very sharp reflectance band at 1050 cm^{-1}with a shoulder at 1175 cm^{-1}.
(c) A small sharp reflectance band at ~1635 cm^{-1}.
(d) A broad and sharp reflectance band with a maximum of ~3430 cm^{-1}.

Fig. 2 demonstrates that the infrared reflectance spectrum of the studied glass after corrosion is different from the corresponding spectrum before corrosion. The spectrum of the glass upon corrosion by acidic solution confirms the suggested mechanism to proceed by the ion-exchange process in acidic media. The mid-reflectance bands in the region of

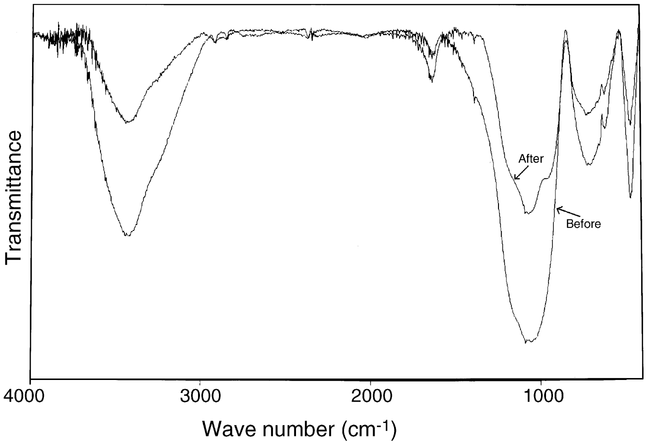

Fig. 2. The change in IR spectra of the experimental glass after a 48 h leaching in solution.

950–1200 $\mathrm{cm^{-1}}$ reveal the transformation of the nonbridging oxygen sites to a structure resembling that of hydrated silica gel (according to the Eq. (1)); which had a strong band around 1050 $\mathrm{cm^{-1}}$ due to the –Si–O–Si– stretching vibration and a medium band at 950 $\mathrm{cm^{-1}}$ due to the Si–OH deformation vibration [18–21]. This result is in accordance with the results obtained by AFM images (Fig. 4)

$$-\mathrm{M}-\mathrm{O}-\mathrm{Si}-+\mathrm{H_3O^+}\rightarrow\mathrm{M^+}+\mathrm{HO}-\mathrm{Si}\equiv+\mathrm{H_2O} \qquad (1)$$

Furthermore, the reduction in the amount of bands at frequencies of ~1050 $\mathrm{cm^{-1}}$ (related to the stretching vibration modes of –Si–O–Si– band) and ~460 $\mathrm{cm^{-1}}$ (attributed to the bending vibration modes of –Al–O–Si– bands) [18–21] reflects a weakening of these bands, which is an indication of the lower network connectivity and dissolution of the corresponding glass.

The characteristic reflectance bands at ~1635 and ~3430 $\mathrm{cm^{-1}}$ increases in their intensities after 48 h corrosion. This supports the assumption of Smets and Lommen and the recent deduction by Pantano and Hamilton [20] which indicate that the ion-exchange process of corrosion (cited in Eq. (1)) requires that the modifier ions have to be replaced by hydrogen ions accompanied by one or more water molecules ($n\mathrm{H_2O}$).

3.4. AFM measurements

Fig. 3 depicts the topographic profile of the glass surface before and after a 24 and a 48 h exposure to the corrosive media. The AFM images of polished, unreacted glass plates shows a surface with numerous polishing grooves. Soaking in the acidic medium resulted in a significant change of surface morphology characterized by peak-to-valley structures. Furthermore, the surface feature changes to rounded and smooth characteristic as the exposure time increases.

In addition, AFM scans reveal changes in the depth of corrosion as a function of time (Fig. 3). After immersing the glass in the dilute acetic acid solution for 24 h, the maximum depth of valley changed from 805 °A in the initial glass to 2700 °A. This change is due to the corrosive attack of acid on the surface of the glass as discussed before. While surface morphology of the glass shows significant changes after a 48 h soaking, the depth of corrosion compared to the early stages of dissolution (24 h) decreased from 2700 to 843 °A. In fact, the

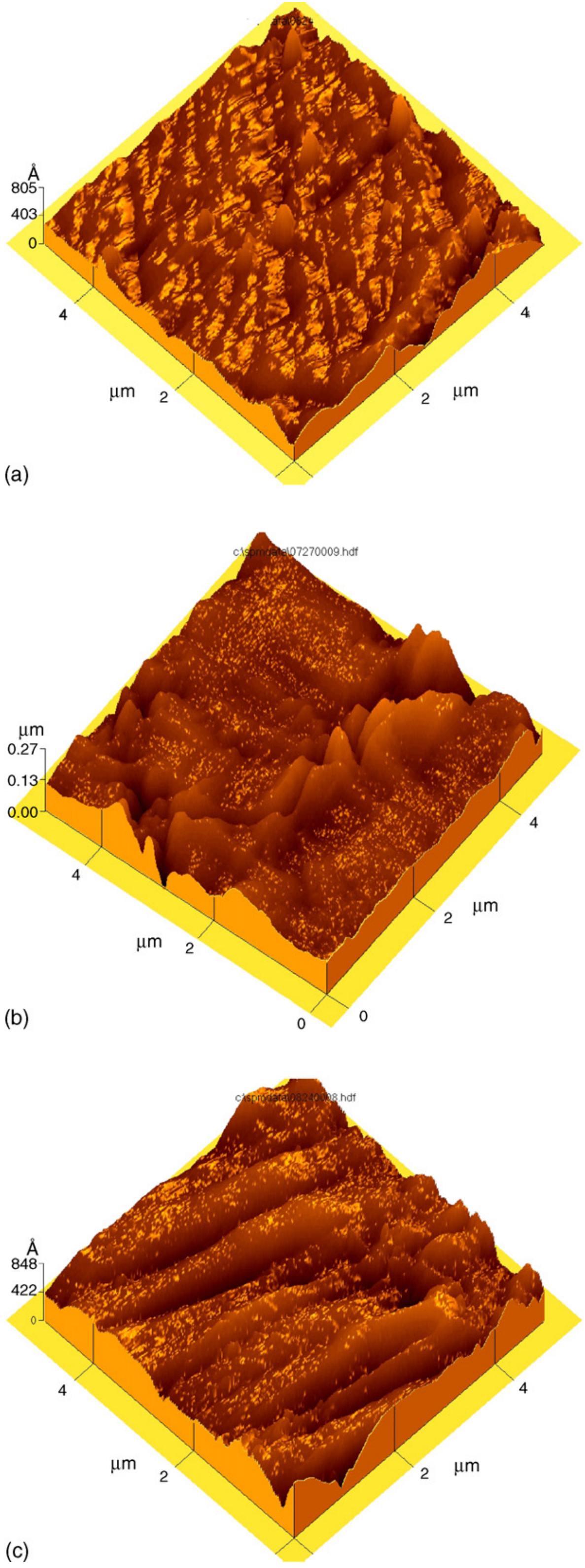

Fig. 3. Time related surface of calcium fluoroaluminosilicate glass at: (a) 0 h (b) 24 h and (c) 48 h after leaching.

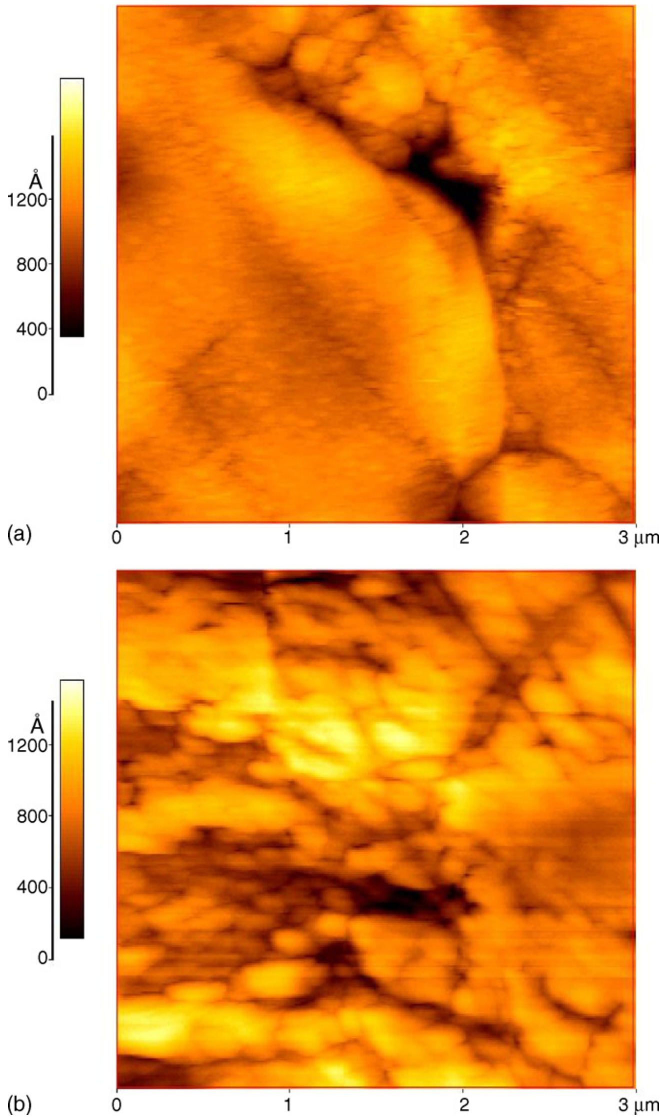

Fig. 4. The feature of the original surface of the base glass: (a) before (b) after 96 h leaching.

reduction in the depth of corrosion at this time is related to the formation of the leached surface layer on glass. The FTIR spectra and ICP results also confirm the presence of this layer on the surface of the glass after leaching.

Furthermore, an increase in the percentage of light colors in the AFM scans as shown in Fig. 4; confirms the time related morphological change of pristine glass during a 96 h dissolution.

4. Conclusion

FTIR spectroscopy showed the structural change in the silicate network of the glass during the dissolution and formation of the hydrated silica gel layer on the surface of the glass. The results of the present work suggest that different ions released from calcium fluoro-aluminosilicate glass accelerated through the corrosive attack of hydrogen-bearing ions to the surface of the glass at the early stages of dissolution and diminished their concentration by increasing the exposure time due to the ion-exchange process in acidic media and formation of the leached layer on the surface of the glass that controlled the ion release process. Furthermore, formation of some insoluble calcium and aluminum complex in the solution sparked reduction in the amount of these ions.

Morphological changes of the glass surface resulting from corrosion in the solution were observed. By increasing the immersion time, the glass surface features are more rounded and smooth and tend to create the peak-to-valley features. After a 48 h soaking, a decrease in the depth of corrosion due to the formation of the leached surface layer on the studied glass was observed.

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