# Analysis of Release of Ions into Deionized Water From Raw and Acid Washed (AW) Fluoroaluminosilicate Glasses by Using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)

**Shahab Ud Din[2]\*, Muhammad Hassan[3], Mohtada Hassan[4], Bilal Ahmed Sheiks[5] and Richard Billington[1]**

[1]Department of Dental Physical Sciences, Barts and the London School of Medicine and Dentistry, Queen Mary University of London, UK

[2]Dental Department, Shaheed Zulfiqar Ali Bhutto Medical University (SZABMU), Pakistan Institute of Medical Sciences (PIMS), Islamabad, Pakistan

[3]University College of Dentistry, UoL, Raiwind Road, Lahore, Pakistan

[4]College of Dentistry, HITEC IMS, Taxila Cantt, Pakistan

[5]Abbottabad International Medical College, Abbottabad, Pakistan

## Research Article

## ABSTRACT

**Aims and objectives:** To evaluate the release of ions into deionized water from fluoroalumino silicate glasses (LG26Sr) before and after acid wash and to determine the effect of acid wash on the glasses.

**Materials and methods:** Specimens of fluoroalumino silicate glasses (experimental glasses; LG26Sr raw and acid washed) were stored in polyethylene (PE) tubes at 37°C in deionized water for a time period of 28 days. Glass free solutions were collected after 1, 3, 7, 14, 21 and 28 days. The cumulative ions release from the glasses from 24 hours to 28 days was calculated to compare the pattern of ions release in deionised water. The ions released were analysed by using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). ICP-OES has the ability to perform multi-element analysis simultaneously to determine the concentration of ions in aqueous solutions.

**Results and discussion:** (a) The ions released from the fluoroalumino silicate glasses (experimental glasses; LG26Sr raw and acid washed) were observed at all-time points. It was seen that the release of ions decreased over time and there was minimal amounts of ion released in week four. (b) Acid washed glasses increased the amount of release of fluoride (F) and aluminium (Al) ions while the releases of strontium (Sr) ions were decreased. (c) The acid washing of the glasses demonstrated the higher amounts of release of F ions compared to Al ions. Although the amount of Al is increased after acid wash but it was too low as compared to F ions. (d) Immediately after week 3 the release of Al ions from raw glasses were decreased.

**Conclusion:** (a) Considerable amounts of ions were released from both the glasses (raw and acid washed) into deionized water throughout the experimental period. (b) The release of ions was decreased after reaching a peak value and minimal quantities were released in week four. (b) F and Al ions were released more from AW glasses as compared to raw glasses. (c) Release of Al ions were suddenly dropped in week 4. (d) Release of Sr ions were greater from raw than AW.

## INTRODUCTION

Fluoroalumino silicate glasses (Glass Ionomer Cements) were derived from silicate and polycarboxylate cements to overcome the deficiencies and flaws in these materials. Glass Ionomer Cements (GICs) were initially used as dental restorative materials [1]

and luting agents for crowns and bridges [2,3]. Later on these materials were widely used as restorations of primary teeth, class III and V restorations and as temporary filling materials for longer duration because of their highly developed properties [4-6].

The ability of GICs to bond to dental tissues, especially to dentine [7] and long-term fluoride release [8,9] make them advantageous for their use in restorative dentistry. By their strong bond with the tooth structure, the cavity is sealed, leakage at the margins is prevented and the risk of secondary caries is eliminated. This also allows cavity forms to be more conservative [10]. Bonding is achieved by chemical means through ionic exchange at the interface of the tooth structure and restoration [11,12]. Moreover the coefficient of thermal expansion of GICs is close to that of dental hard tissues and is a strong basis for good marginal adaptation [12].

The anticariogenic effect of GICs is well known and considered a result of fluoride release. These cements are also capable of recharging fluoride ions from topical applications if exposed to the solutions containing fluoride ions and subsequently re-release them depending on the concentration of fluoride and therefore act as a reservoir [9,13-16].

GICs have been investigated for ion release since long. There is already much evidence of release of ions from this material specially fluoride ions. Many researchers have worked on the release of fluoride ions but some have also worked on the release of other ions depicting that fluoride is not the only ion released [17]. Some of the ions found are cations like Al, Sr, Ca, Na, and K and others are anions like F, Si and P. The investigations have been carried out by different methods but ion release into deionized water from fluoroalumino silicate glasses was not investigated. Therefore, it was realized that this area needs to be investigated for further information. The current study is focused on the analysis of release of fluoride, aluminium and strontium ions from fluoroalumino silicate glasses; raw and acid washed into deionised water by ICP-OES.

### Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)

ICP-OES can be used to determine the concentration of ions in aqueous solutions. It uses the phenomenon of atomic and ionic excitation for trace metal analysis in aqueous media. It is rapidly becoming popular among investigators for its accuracy and multi-element analysis simultaneously.

Samples are introduced into the ICP at a controlled rate where they are atomized in the intense heat of the ICP (7000-8000°K). Different types of atoms emit photons of characteristic wavelengths and these are collected by a photomultiplier tube that acts as a detector. The electrical signals thus generated can be represented as spectra. These spectra are very difficult and impractical to interpret. Soa chemometric software is used to make calculations and to quantify the signals and provide useful data. With the help of ICP-OES, elemental concentrations to parts per billion (ppb) levels can be easily determined.

## MATERIALS AND METHODS

Fluoroalumino silicate glasses of LG26Sr raw and acid washed (aw) was used. LG26Sr contains Al, P, Sr, Si and F. There is no calcium in LG26Sr, calcium is replaced by strontium.

The glasses (LG26Sr) were acid washed by mixing 20 grams of the glass with 67 ml deionised water and 10 ml of 35% acetic acid. This suspension was then placed on the electric magnetic stirrer for 24 hours and then filtered through filter paper. The residual was first washed in water to eliminate the surface ions and then in acetone to aid drying. Finally the residual was placed in a ventilated fume cupboard for 24 hours to dry. The dried glasses were then ground down by pestle and mortar before sieved by passing through a 50 micron sieve.

The particle size of the glasses was measured using a Malvern Particle Size Analyser. The reservoir was filled with deionized water to the required level. A suitable amount of the sample for particle size was added in increments till the required amount revealed by the computer. Computer directions for further processing were followed and once the measurement had settled down the data was printed.

Six sample of each glass (raw 0.131 to 0.140 g and, aw 0.131 to 0.139 g) were prepared. Each glass was placed into a 15 ml polyethylene (PE) test tube and then 10 ml of deionized water was added. All the samples were shaken and stored at 37°C for the given period of time. Six samples, each containing 10 ml of deionised water but no glass was also placed in the oven as control. After the predetermined time points the specimen were centrifuged at 4000 rpm for 40 minutes to separate the glass from liquid. Then 8 ml of the glass free solution was transferred to another PE test tube and kept at room temperature. A fresh 10 ml of deionized water was added to the glasses and replaced in the oven again. Samples of 8 ml solution were collected after 1, 3, 7, 14, 21 and 28 days of storage to measure the ions released from the glasses. These solutions from along with the blanks were tested by ICP-OES for the determination of Al, Sr, P, Si and F.

Glass free solution collected in PE tube glasses (raw and AW) were analysed by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) for the determination of the levels of ions released, at the Biomaterials Group, School of Science, University of Greenwich, Medway Campus, Pembroke, Kent ME4 4AW, UK. The instrument used was the Perkin Elmer Optima DV4300 ICP-OES. ICP-OES can determine elemental concentrations to parts per billion (ppb) levels with relative ease. The results from ICP-OES were analysed to give the concentration of the ions released in m.equiv./g glass.

## Statistical Analysis

The data was analysed by using SPSS PASW statistical 21 software. Mean and standard deviation (SD) were used to describe the data. Sample t-test was used to check the significance of difference of ions released from LG26Sr raw and AW. P-values <0.05 were considered as significant.

# RESULTS

Cumulative ion release from LG26Sr (raw and AW) into deionised water during the time period of 1, 3, 7, 14, 21 and 28 days are shown in **Table 1**. The results were calculated as m.equiv/g of glass. Particle size used for raw and AW before and after milling and sieving was 3.40 (μm) and 3.43 (μm) respectively.

**Table 1.** Cumulative mean ion release from LG26Sr during the period of 1 to 28 day.

| Ions | Ion release (m.eq./g glass) | | P-value |
|---|---|---|---|
| | LG26Sr (raw) | LG26Sr (AW) | |
| F | 0.087 ± 0.0022 | 0.318 ± 0.0034 | <0.001 |
| Al | 0.068 ± 0.001 | 0.080 ± 0.002 | <0.001 |
| Sr | 0.119 ± 0.002 | 0.099 ± 0.001 | <0.001 |

**Figure 1** plotted against the square root of time for 1 to 28 days, show cumulative release of fluoride ions from LG26Sr, before and after acid wash. Y axis is the concentration of the ions released in m.eq./g of glass and the X axis is the square root of the time in days. The plot shows a highly significant (p=0.001) result where the release of fluoride ions from the acid washed glasses is almost four times compared to the ion release from raw glasses.
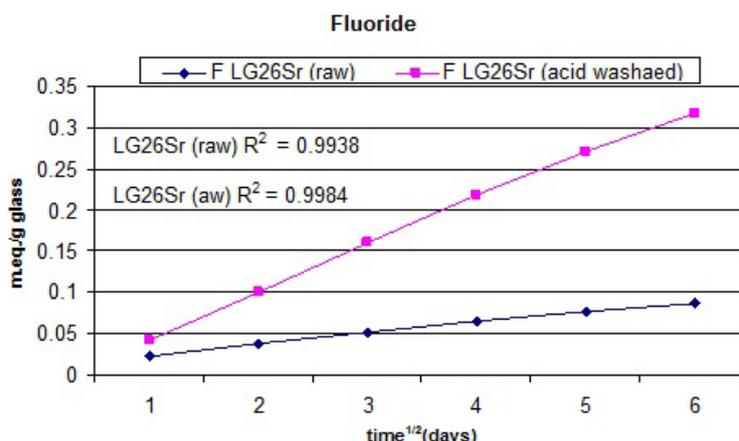


**Figure 1.** Cumulative release of fluoride ions into deionised water showing correlation coefficients for linear least squares fit.

The graph in **Figure 2** plotted against the square root of time for 1 to 28 days, shows cumulative release of aluminium ions from LG26Sr (raw and AW). The graph shows a specific pattern of the release of the ions and there is a linear relationship for both raw and AW glasses. But after week three the plot for LG26Sr raw glasses drops between 21 to 28 days while the release remains linear for AW type. **Table 1** shows that the release is highly significant (p=0.001). The $R^2$ values were also better for both types with lowest R2 value 0.9779 which is reasonably good.
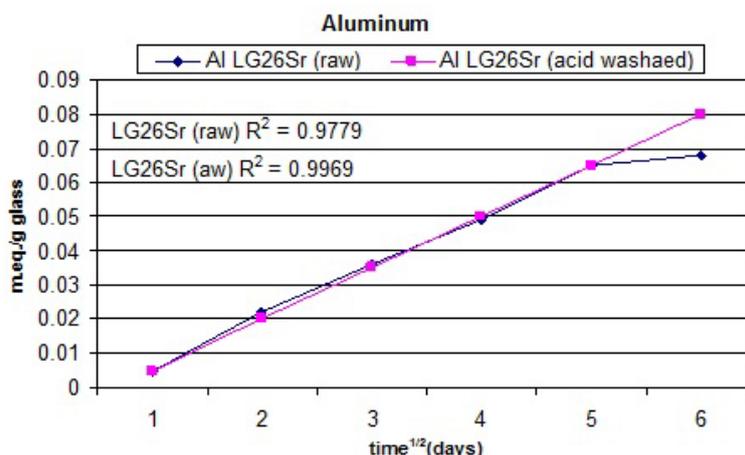


**Figure 2.** Cumulative release of aluminium ions showing correlation coefficients for linear least squares fit.

The graph in **Figure 3** shows the release pattern of ions from raw and aw glasses and there is a linear relationship for both the glasses. Unlike fluoride and aluminium, strontium ions released more from raw glasses than acid-wash type with highly significant values (p=0.001). The R2 values were also better for both types with lowest R2 value 0.9908.
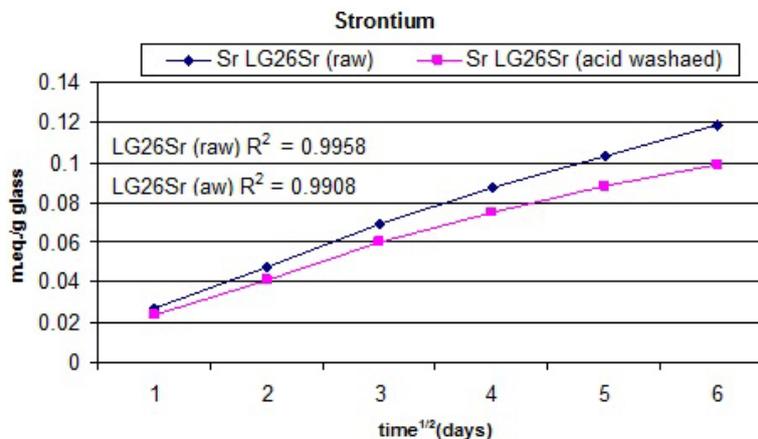


**Figure 3.** Cumulative release of strontium ions showing correlation coefficients for linear least squares fit.

## DISCUSSION

In this study it was found that LG26Sr continuously released significant amount of ions into deionized water for each period of storage over the whole duration of the experiment.

The data thus obtained from the ion release featured some important aspects to consider. Firstly, the amount of ions released with the passage of time decreased which is similar to the results reported by other researchers [9,17,18]. Secondly, the amount of F and Al ions released was significantly greater from acid washed glasses than raw glasses. This was in accordance with a previous study for resin modified glass ionomers [19]. There was a sudden drop of Al ions from raw glasses by the end of the 4th week and this release was very low as compared to its acid wash type. When the release of fluoride ions was compared with aluminium ions, it was seen that the raw glasses released slightly higher fluoride ions than aluminium ions. Whereas in acid washed glasses the difference was almost three times higher for fluoride than aluminium. Therefore, it can be said that acid washing increases the release of fluoride ions significantly more than the aluminium ions. Thirdly, the release of strontium ions was significantly higher from non-acid washed glasses as compared to acid washed glasses which are in contrast to the pattern of release of fluoride and aluminium ions in this study.

## CONCLUSION

The evaluation of ion release from Fluoroalumino silicate glasses carried out in this study leads to the following conclusions.

Both the raw and acid washed LG26Sr glasses and its subtype released substantial amounts of ions until they reached a peak after which the release decreased and by the end of the fourth week there was minimal release of ions.

Acid washing increased the release of fluoride and aluminium ions. It was also found that acid washing enhanced the release of fluoride ions more than the aluminium ions.

By the end of the fourth week the release of aluminium ions suddenly dropped and it was also very low as compared to its acid washed type. Raw glasses released more strontium ions as compared to the acid washed type.

## REFERENCES

1. Milne KA, et al. Glass-ionomer dental restorative (Part I: a structural study). J Mater Sci. 1997;8:349-356.

2. Pameijer CH and Nilner K. Long term clinical evaluation of three luting materials. Swed Dent J. 1994;18:59-67.

3. Mount GJ. Clinical performance of glass-ionomers. Biomaterials. 1998;19:573-579.

4. McCabe JF and Walls AWG. Applied dental materials. 8th edn. The University Press, Cambridge, England; 1998.

5. VanNoort R. Introduction to dental materials. 2nd edn. Elsevier Science Limited, London; 2002.

6. Ana ID, et al. Effects of added bioactive glass on the setting and mechanical properties of resin-modified glass ionomer cement. Biomaterials. 2003;24:3061-3067.

7. Nicholson JW. Adhesive dental materials and their durability. Intern J Adhes Adhes. 2000;20:11-16.

8. Patrícia W, et al. Fluoride release and uptake from glass ionomer cements and composite resins. Braz Dent J. 2000;11:89-96.

9.    Watts DC, et al. Dimensional changes of resin/ionomer restoratives in aqueous and neutral media. Dent Mater. 2000;16:89-96.

10.   Erickson RL and Glasspoole EA. Bonding to tooth structure: a comparison of glass-ionomer and composite-resin systems. J Esthet Dent. 1994;6:227-244.

11.   Wilson AD, et al. Mechanism of adhesion of polyelectrolyte cements to hydroxyapatite. J Dent Res. 1983;62:590-592.

12.   Wilson AD and McLean JW. Glass ionomer cement. Quintessence, Chicago; 1988.

13.   Jones FH, et al. Fluoride uptake by glass ionomer cements: A surface analysis approach. Biomaterials. 2003;24:107-119.

14.   Williams JA, et al. Comparison of ion release from glass ionomer cement as a function of the method of incorporation of added ions. Biomaterials. 1999;20:589-594.

15.   Hadley PC, et al. Effect of monovalent ions in glass ionomer on their uptake and re-release. Biomaterials. 1999;20:891-897.

16.   Billington RW, et al. Glass ionomer cement: evidence pointing to fluorine release in the form of monofluorophosphate in addition to fluoride ion. Biomaterials. 2004;25:3399-3402.

17.   Czarnecka B, et al. Buffering and ion-release by a glass-ionomer cement under near-neutral and acidic conditions. Biomaterials. 2002;23:2783-2788.

18.   Gao W and Smales RJ. Fluoride release/uptake of conventional and resin-modified glass ionomers, and compomers. J Dent. 2001;29:301-306.

19.   Hill RG, et al. The influence of poly (acrylic acid) molecular weight on the fracture toughness of glass ionomer cements. J Mater Sci. 1989;24:363-371.