INDUCTIVELY COUPLED PLASMA-OPTICAL EMISSION SPECTROSCOPY (ICP-OES) STUDY OF ION RELEASE FROM RAW AND ACID WASHED FLUOROALUMINOSILICATE (GLASS IONOMER) GLASSES

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ABSTRACT

Objectives: To measure the release of ions from fluoroaluminosilicate glasses, LG125, into deionised water and to compare the ion release from raw and acid washed glasses, taking account of the effect of acid wash on the ion release.

Design: Randomized Control Trials (RCT)

Place and Duration: Study was conducted at Department of Biomaterials in relation to Dentistry, Queen Mary University of London from Nov 2004 to Jun 2005.

Materials and Methods: Specimens of experimental glasses, LG125 raw and acid washed (aw), were stored in polyethylene (PE) tubes at 37 ºC in deionised water for a storage period of 1 to 28 days. Glass free solutions were collected after 1, 3, 7, 14, 21 and 28 days. The ions released were analyzed by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). ICP-OES is a very powerful tool for trace metal analysis that uses the phenomenon of atomic and ionic excitation to determine concentration of ions in aqueous solutions.

Results: (a) Ions releases from the glasses were observed at all time intervals. The amounts of ion release were decreased over time and minimal quantities were seen in week four. (b) After acid wash the amount of release of fluoride (F) and aluminum (Al) ions were increased from the glasses while the release of Strontium (Sr) and Calcium (Ca) were decreased. (c) It was also seen that the acid washing enhances the release of F ions more than Al ions. Although the amount of Al was increased after acid wash but the concentration was too lower as compared to F ions.

Conclusions: (a) Under both conditions substantial amounts of ions were released from the glasses but the release of ion were decreased after reaching a peak value. (b) F and Al were released more from aw glasses as compared to raw. (c) Release of Sr and Ca were greater from raw than aw.

Keywords: Ion release, glass-ionomer, dental cements.

INTRODUCTION

Fluoroaluminosilicate glasses (Glass Ionomer Cements) are used for cementing inlays, crowns, bridges, posts and orthodontic bands, as cavity liners or base materials and as restorative materials for class III and V cavities [1-3].

The two main features of Glass Ionomer Cements (GICs) which make them popular dental restorative cements, are their ability to bond chemically to the tooth structure by a strong bond [4] and to release/re-release fluoride ions for a longer period of time [5, 6].

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Fluoride ions replace the hydroxyl ions of the hydroxyapatite forming fluoroapatite, which is more resistant to the acid attack. The fluoride ion is smaller than the hydroxyl ion and sets more readily into the apatite crystal lattice [2, 7, 8].

$$\mathbf{Ca_{10}(PO_4)_6(OH) \longrightarrow Ca_2{+}{+}HPO_4}$$

$$\downarrow$$

$$\mathbf{Ca_{10}\,(PO_4)_6(OH.F)}$$

These cements are also capable of up taking fluorides 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 reservoir [9-12].

Studies on the ion release from GICs have been carried out over a long period of time and now there is a considerable body of information concerning the release of ions, specifically fluoride ion, is available. Most of the researchers have worked on the release of fluoride ions which is of clinical interest in GICs. Different investigators have also looked at release of ions other than fluoride and found that GICs release substantial varieties of ions other than fluoride ions [13]. Some of them are cations (Al, Sr, Ca, Na and K) and others are anions (F, Si and P). Different investigators have carried out research by different methods but no one has looked at ion release into deionised water from Fluoroaluminosilicate glasses. This area needs to be investigated for further information. This study is focused on the analysis of release of ions from Fluoroaluminosilicate glasses, raw and acid washed, into deionised water by ICP-OES. ICP-OES is an instrumental method of trace metal analysis that uses the phenomenon of atomic and ionic excitation to determine concentration of ions in aqueous solutions.

MATERIALS AND METHODS

Study was conducted at Department of Biomaterials in Relation to Dentistry, Barts and the London, Queen Mary University of London. Releases of ions were analyzed by ICP-OES at Biomaterials Group, School of Sciences, University of Greenwich, UK. Period of study was from Nov 2004 to Jun 2005.

Fluoroaluminosilicate glasses of LG125 raw and acid washed (aw) were taken. Six samples of each glass (raw and aw) were used in the experiment. LG125 contains fluoride, Aluminum calcium and strontium in its composition.

Raw glasses of LG125 were acid washed by 35% acetic acid which reduces the reactivity and makes the cement workable. Acid washing was done by mixing 20 grams of the glass with 67ml deionised water and 10ml of 35% acetic acid. This suspension was then placed on the electric magnetic stirrer for 24 hours before filtering through filter paper. The residual was placed in a ventilated fume cupboard for 24 hours to dry. All the dried glasses were then ground by pestle and mortar before being sieved by passing through a 50 micron sieve.

These glasses were prepared by mixing the acid washed glasses with acetic acid on a paper mixing pad using a plastic spatula. The powder to liquid ratio was 4:1 by weight. After mixing discs of 10 mm diameter and 1 mm thickness were made by using split ring moulds. The material was then allowed to set for one hour. After weighing these discs were ground by pestle and mortar for further experiment.

Six samples of each raw glass weighing 0.131 to 0.140 g were placed into a 15ml polyethylene (PE) test tube and then 10ml of deionized water was added. All the samples were shaken and stored at 37°C for the given period of time. After the predetermined times the samples were centrifuged at 4000 rpm for 40 minutes to separate the glass from liquid. Then 8ml of the glass free solution was transferred to another PE test tube and kept at room temperature. A fresh 10ml of deionozed water was added to the glasses and replaced in the oven. Samples were collected after 1, 3, 7, 14, 21 and 28 days of storage and 8ml solution was collected every time to measure the ions released from the glasses.

Six samples of each acid washed glass weighing from 0.132 to 0.138 g were also prepared. These samples were further processed using methods similar to that of raw glasses.

These solutions were tested by ICP-OES for the determination of F, Al, Ca and Sr. The instrument used was the Perkin Elmer Optima DV4300 ICP-OES.

Samples were introduced into the ICP at a controlled rate and were atomized in the intense heat of the ICP (7000-8000K). Photons of characteristic wavelengths were emitted from different types of atoms and were collected by a photomultiplier tube that acts as a detector. Electrical signals were generated and represented as spectra. These spectra were impractical to interpret, so using chemometric software, calculations were made to quantify the signals and the data was collected.

The results from ICP-OES were analyzed to give the concentration of the ions released in m.eq/g glass.

STATISTICAL ANALYSIS

The data was analyzed using SPSS (version 10). Mean and standard deviation (SD) were used to describe the data. Independent samples t-test was used to check the significance of difference of ions. P-value < 0.05 was considered as significant.

RESULTS

Particle size used for raw and aw before and after milling and sieving was 3.42 (µm) and 3.44 (µm) respectively.

Ions releases from both raw and aw glasses were observed at all time intervals. The ions releases were decreased over time and minimal quantities were seen in week four.

The cumulative ions releases for 1 to 28 days were calculated in m.eq/g glass to analyze the pattern of ions release in deionised water before and after acid wash.

Fig. 1 shows cumulative release of fluoride ions from LG125, before and after acid wash. It can be seen from table 2 that the release of fluoride ions from the acid washed glasses was almost four times of ions released from raw, which is statistically highly significant ($p < 0.001$).

Table-2 and (fig. 2) show that the release of aluminum ions into deionised water was significantly higher ($p < 0.001$) for aw than raw glasses. It can also be seen that after week three the release of aluminum ions was suddenly dropped from raw glasses while the release remained linear for the aw type (Table 1).

Table-2 and (fig. 3) show that unlike fluoride and aluminum, calcium ions releases were more from raw glasses than aw type which was highly significant ($p < 0.001$).

Like calcium ions the releases of strontium ions were also significantly more from raw glasses than from aw type ($p < 0.001$).

Table-1: Ions released at different times in m.eq/g

Lg125 Non Acid Washed						
ION	**1 day**	**3 days**	**7 days**	**14 days**	**21 days**	**28 days**
F	0.021	0.015	0.014	0.011	0.009	0.005
Al	0.004	0.016	0.013	0.013	0.013	0.004
Ca	0.006	0.006	0.005	0.005	0.004	0.002
Sr	0.016	0.013	0.012	0.012	0.01	0.009
Lg125 Acid Washed						
ION	**1 day**	**3 days**	**7 days**	**14 days**	**21 days**	**28 days**
F	0.038	0.058	0.058	0.056	0.048	0.049
Al	0.005	0.015	0.015	0.015	0.015	0.014
Ca	0.003	0.004	0.005	0.004	0.004	0.003
Sr	0.015	0.011	0.012	0.009	0.008	0.007

Table-2: Cumulative ions released for 1 to 28 day.

IONS	**ION RELEASE (m.eq/g glass)**		**P-value**
	Cul mean LG125 (raw) (n=6)	**Cul mean LG125 (acid washed) (n=6)**	
F	0.075 ± 0.001	0.307 ± 0.02	< 0.001
Al	0.063 ± 0.003	0.079 ± 0.005	< 0.001
Ca	0.028 ± 0.001	0.023 ± 0.002	< 0.001
Sr	0.072 ± 0.003	0.062 ± 0.004	< 0.001

Comparing the release of strontium with calcium ions, it can be seen from the table 2, that the release of strontium is higher than calcium (fig. 4).

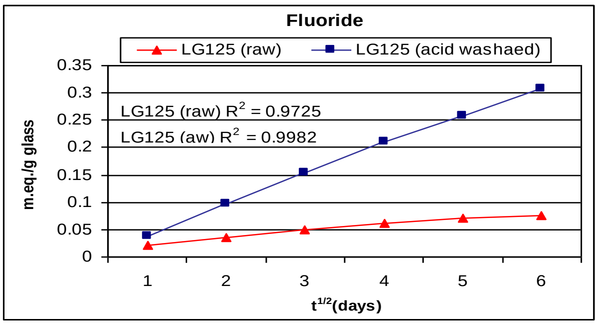

Fig.1: Cumulative release of fluoride ions showing correlation coefficients for linear least squares fit

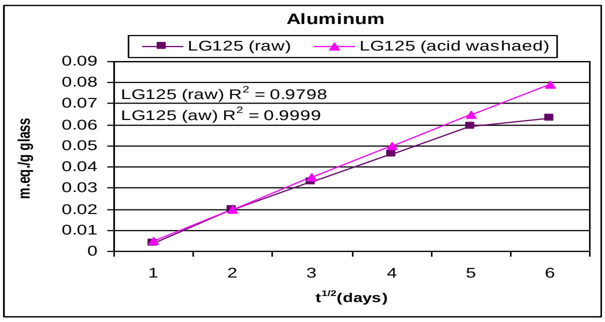

Fig. 2: Cumulative release of aluminum ions showing correlation coefficients for linear least squares fit

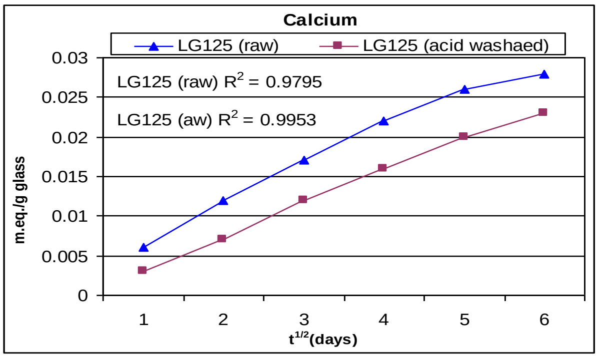

Fig. 3: Cumulative release of calcium ions showing correlation coefficients for linear least squares fit

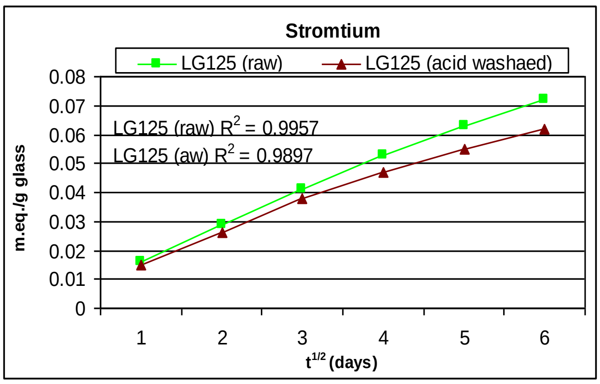

Fig. 4: Cumulative release of strontium ions showing correlation coefficients for linear least squares fit

DISCUSSION

Following each period of storage in deionized water LG125 was found to continuously leach out significant amount of ions into water over the whole duration of the experiment.

Ion release data showed a number of important features. Firstly, with the passage of the time the amount of release of ions decreased and this is similar to results reported by other studies [13, 14].

Secondly, the release of F and Al ions was found to be significantly higher from acid washed glasses as compared to raw glasses, a finding similar to that obtained previously for resin modified glass ionomers [15]. Comparing the release of fluoride ions with aluminum ions, it can be seen that in case of the non acid washed glasses the release of fluoride ions is slightly higher then aluminum ions, but in acid washed glasses this difference is almost three times higher for fluoride than aluminum. So, acid washing enhances release of fluoride ions more than aluminum ions. Thirdly, unlike fluoride and aluminum ions the release of strontium and calcium ions is significantly higher from raw as compared to acid washed glasses. This release is slightly higher for strontium as compared to calcium for both raw and acid washed glasses.

CONCLUSIONS

This study of evaluation of ion release by Fluoroaluminosilicate glasses leads to the following conclusions.

- Substantial amounts of ions were released from the glasses of LG125 before and after acid wash but the release of ions were decreased after reaching a peak value and by the end of the 4th week there was minimal ions released.
- Releases of fluoride and aluminum ions were found to be greater after acid washing.
- Strontium and calcium ions were released more from raw glasses than acid washed.

Future Work

The present study covers evaluation of release of ions into deionized water from raw and aw Fluoroaluminosilicate glasses.

- The release of these ions into deionised water should be compared to their release into artificial saliva.
- The same experiment should be done for longer duration and AH2, LG26 and LG 26Sr should also be included.

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