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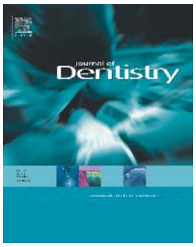

Kinetics of fluoride release from glass components of glass ionomers

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ABSTRACT

Objectives: To compare the F release from glass ionomer glasses (GICs) into water changed periodically with release into an unchanged "sink" [Williams JA, Billington RW, Pearson GJ. The glass ionomer cement: the sources of soluble fluoride. *Biomaterials* 2002;**23**:2191–200]. To evaluate the effect of replacing Ca wholly or partially by Sr. To compare two different methods of decomplexing F containing species.

Methods: All four glasses contained Al, Si, P, O and F. Glass AH2 (Advanced Healthcare Ltd.) had Na and Ca, LG26 (Advanced Healthcare Ltd.) had Ca, LG26Sr (ULTRASET project) had Ca and Sr, and LG125 (ULTRASET project) had Sr. Glasses were tested: after ball-milling, after washing in dilute acid, and W mixed with 35% acetic acid to form a "pseudo-cement". F^- release was from 130 mg samples into 10 ml of deionised water changed at 1, 3, 7, 14, 21, 28, 35, and 42 days. Analysis was carried out: (a) using ISE without decomplexing, (b) using TISAB buffer, and (c) acid hydrolysis + TISAB (after Hattab).

Result: The cumulative release rates from all glasses and treatments are linear with respect to $t^{1/2}$ with $r = 0.97$ or greater ($p = <0.001$). F release into a "sink" showed no such correlation. The higher release rate from AH2 is more than accounted for by its higher F content. Most F release is not complexed except of AH2. AH2 has 20% of complex fluoride from raw glass, 44% from acid-washed glass and 51% from pseudo-cement. More fluoride is released after acid treatment from all 4 glasses, these are on average 4.4 times higher from acid-washed glass and 5.3 times higher from pseudo-cement. For TISAB fluoride release, LG26Sr is 26% more than LG26. Hattab fluoride > TISAB fluoride only for raw glasses.

Conclusions: Changing water produces diffusion controlled kinetics. Acid treated will increase the complex fluoride from AH2. Replacing Ca by Sr enhances F release rate slightly.

1. Introduction

Glass ionomer cements (GICs) are formed by the reaction between a polymer with pendant acidic groups and an aluminosilicate glass in the presence of water. The pendant acidic groups are most often carboxylic acid ones and the glasses are generally calcium (or strontium) fluoro-aluminosilicates. The release of fluoride ion from GICs has been widely reported since the first commercial dental GIC was introduced in 1975. Tay and Braden showed the release kinetics to be linearly related to $t^{1/2}$.[1] This indicates a diffusion controlled process. Release is reported for periods up to five years.[2] Analysis of this data shows that the rate at five years has not dropped below that predicted by a $t^{1/2}$ relationship.[3] Only one material containing a very high loading over silver shows a release rate that deviates from a $t^{1/2}$ relationship after 155 days.[3,4]

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Although attempts have been made to understand the nature of the release process by adding different metal fluorides to GICs not containing fluorine,[5,6] it is not clear what component or components of the cement release the F ion. In a previous study it was shown that F ion release occurred from ground glass particles into water.[7] If the particles had previously been acid-washed the release was much greater. This study is designed to examine the area more fully.

The aim of this study was to analyse F ion release from ground glass particles and from the same particles after acid-washing. The release is into de-ionised water to be changed at regular intervals. In addition, release from "pseudo-cement" (i.e., one where the polymeric acid used in GICs is replaced by acetic acid) is to be determined. In modern GICs radiopacity is required and Ca is often replaced by Sr. Three of the four glasses used had similar formulations except that the Ca in one was partially replaced by Sr in another and wholly in the third. The fourth was a conventional radiolucent glass widely used in commercial dental GICs and previously used for many years in dental silicate cement.

Many studies of GI cements, F analysis was carried out using TISAB buffer which broke up F complexes and without TISAB which determined free, or uncomplexed, F ion. Recently it has been reported[8] that a technique described by Hattab[9] using acid hydrolysis in addition to TISAB indicated significantly more F than analysis by TISAB alone in the release from GICs. It was proposed to use this technique also in the analysis of F ion release in this study.

In the previous study the release was into an unchanged sink from which small aliquots were removed after various times for analysis. This is in contrast to most studies on F ion release from cements. In these, the cement sample is removed from the water after a time interval and placed fresh F-free water for the next release period. It is an additional aim of this study to use the above method and to compare the results with those from the "unchanged sink" study.[7]

2. Materials and methods

2.1. The glasses

Four different formulations of glass were examined, AH2, LG26, LG26Sr and LG125. The composition of these glasses is shown in Table 1.

Table 1 – Composition of the four glasses used.

Element	F	Na	Ca	Sr	Si	Al	O	P
AH2*	12.9	5.5	7.1	0	18.7	15.8	38.4	1.6
LG26◆	6.8	0	18.0	0	11.4	14.5	40.9	8.4
LG125◆	6.1	0	6.4	20.9	10.1	12.9	36.2	7.4
LG26Sr◆	5.6	0	0	32.5	9.4	12.0	33.6	6.9

*Composition from analysis if fired glass.
◆Composition from unfired glass charge.

2.2. Preparation of the glasses

The glasses were received as milled frit from participants in the ULTRASET project [Project NoGRD1-2000-25152]. On receipt, the particle size distribution was measured using a Malvern Mastersizer. From the evaluation of these, sieving and additional milling were decided on, these produced similar particle size distribution for all four glasses.

2.2.1. Raw glasses

The glasses were utilised without any additional treatment.

2.2.2. Acid-washed glasses

20 g of each raw glass was mix with 67 ml deionised water and 10 ml 5% acetic acid. This was stirred for 24 h. After filtering and washing with deionised water, the solid was washed with acetone and this was then dried in a ventilated fume cupboard at room temperature to avoid modifying the surface produced by heating to remove water. This was then re-sieved to break up agglomerates and was then used in release measurements.

2.2.3. Pseudo-cement

Acid-washed glasses mixed with acetic acid as P/L ratio of 4:1 (except LG26 which was not mixable at this P/L and was mixed at 2.7:1). The mixed cement was packed into a split ring diameter 1 cm and 1 mm thickness and allowed to set for 1 h at 37 °C. It was expected that the pseudo-cement would disintegrate when exposed to water. However, as this did not happen, the cement was ground to a fine powder by a pestle and mortar. The whole procedure is shown diagrammatically in Fig. 1.

2.3. Fluoride release measurement

0.12–0.14 g of each glass was mixed with 10 ml of deionised water in a centrifuge test tube and then stored in a 37 °C oven representing the temperature of the oral cavity. The number of samples (*n*) in each cell of the experiment was 5. After 24 h, each sample was removed and centrifuged at 4000 rpm for 60 min. 8 ml of the clear solution above the suspension were decanted off and replaced with fresh deionised water and the test tube and contents replaced in the oven at 37 °C. At predetermined times up to 42 days, this process was repeated.

Three aliquots were taken from the decanted liquid. Each was measured (a) without decomplexing to determine free F,[7] (b) with decomplexing of the complex ions with TISAB IV, (c) and decomposing monofluorophosphate by Hattab method.

2.3.1. Free method

The free fluoride in the storage solution from either the glasses or the pseudo-cement was measured directly with the electrode as: 1 ml of deionised water was mixed with 1 ml of standard solution and stirred. A calibrated fluoride electrode was inserted and the electrode potential used to determine fluoride ion concentration. A back ground reading was measured on the sample of the deionised water used and subtracted as a blank.

2.3.2. TISAB method

TISAB IV solution was freshly prepared from 500 ml deionised 86 ml concentrated HCl (36–38%), 242 g Tris (hydroxymethyl)