Glass ionomer materials as a rechargeable fluoride-release system

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Summary. It is well established that glass ionomers (GI) release fluoride (F). The degree of F released depends on the physical and chemical properties of the product. In the present study the fluoride release and the capacity of the GI to be recharged with fluoride was tested for five different brands: XR Ionomer (Kerr), Vitrebond (3M), GC Fuji Lining (G.C. Dental Industries Corp.), Baseline VLC (Dentsply) and Zinomer (Dent. Mat.). Fifteen test specimens were prepared for each brand. The specimens were immersed in deionized water. The F released was measured once a day for 11 days. Refluoridation of the test specimens was done with solutions of 0.02%, 0.04% and 0.2% NaF for 5 minutes on days 11, 16, 21 and 26. The F released from recharged specimens was measured daily until day 32. There was a positive correlation between the amount of F in the GI and the ability to release F. The five materials became ‘recharged’ with F following repeated F exposure in solution, the 0.2% solution being the most effective. XR Ionomer released significantly more fluoride than any other material and showed the greatest ability to be recharged. Zinomer released significantly less fluoride than any other material and showed the least ability to be recharged. The present results indicate that GI serves as a F reservoir and can act as a prolonged slow-release system for at least 32 days.

Introduction

The effect of fluoride on demineralization and remineralization of incipient caries lesions in enamel is recognized as the most important mechanism of fluoride action. It has been recognized that the initial carious lesion should be exposed to fluoride in the aqueous phase for a prolonged period of time to achieve the cariostatic effect [1]. This has increased interest in providing mechanisms of achieving an elevated concentration of fluoride in oral fluids. The concentration of fluoride in the oral fluids is elevated by fluoride exposure using: mouth rinse, fluoride toothpaste, varnish and sucking of fluoride tablets. Because of the relatively rapid clearance of fluoride from the oral fluids, the concentration of fluoride is back to its baseline value within a relatively short period of time [2–5]. Ekstrand [6], in a review on the oral pharmacokinetics of fluoride, confirmed that even a slightly elevated fluoride level for a prolonged period of time in the oral fluid surrounding the teeth is of importance for optimal fluoride therapy. The findings of other studies [7–12] have suggested that even a slight elevation of fluoride in frequent applications would be the best method to prevent demineralization and enhance remineralization of carious lesions.

It would be desirable to develop a method which could establish and maintain a low level of free fluoride in the oral fluid. One way of providing a low but effective quantity of fluoride over a
prolonged period would be to have a slow fluoride-release system from dental materials which could be rechargeable. Fluoride has been incorporated in many dental materials: silicates, glass ionomer cements (GIC), amalgam, liners, pit and fissure sealants and resins. All of these materials can release some fluoride (for review see references 13 and 14).

The aim of the present study was to investigate whether glass ionomer materials can be considered as potential caries preventive materials because of their fluoride release capability. The total fluoride content in five GI materials, the fluoride released from these materials, and their ability to adsorb and again release fluoride, was investigated.

**Materials and Methods**

The glass ionomer materials used in the present study were: XR Ionomer (Kerr), Vitrebond (3M), GC Fuji Lining (G. C. Dental Industries Corp.), Baseline VLC (Dentsply) and Zinomer (Dent. Mat.). All of these materials are most often used as lining materials. All materials are light cured, except for Zinomer which is chemically cured.

The total fluoride content originally incorporated in the glass ionomer material, expressed as a percentage of the total material, was determined by the method of Taves [15]. The procedure was carried out at Karolinska Institute, Stockholm, Sweden.

For the determination of the fluoride release and adsorption, 15 disc specimens (12 mm diameter, 2 mm thick, 301.6 mm² surface area, and 0.39-4.41 g mass) were prepared for each brand as follows. Each material was prepared according to the manufacturer’s instructions and placed into cylindrical Teflon moulds (interior dimensions: 12 mm diameter, 2 mm high) between two celluloid sheets. The specimens were light or chemically cured as required, and then gently taken from the moulds. Each prepared specimen was weighed and immersed in 20 ml deionized water in a polyethylene container, and incubated at a constant temperature of 36.5 ± 0.5°C during the whole experimental period.

The first measurement of fluoride concentration was done 24 hours after preparation of the specimens. From each container, 10 ml of liquid were taken, and 1 ml of TISAB (Total Ionic Strength Adjustment Buffer solution, Merch. No. 1538, Germany) was added to it. Fluoride concentration was measured by a fluoride-specific ion electrode (96-09-00). The electrode was maintained according to the manufacturer’s instructions and calibrated daily with standard solutions. The following concentrations of standard solutions: 0.1, 1, 10, 50 and 100 ppm were prepared from a 100 ppm F stock solution (Orion 94-09-07). After every 10 measurements the electrode was checked (recalibrated) with the standard solutions 1 and 10 ppm. All measurements were done in triplicate. The test specimens were then rinsed with 10 ml of deionized water and immersed in new containers with 20 ml of deionized water and again placed in the incubator. The same procedure was repeated once a day for 11 days.

Refluoridation of the test specimens was then carried out as follows. On day 11, after measurement of fluoride release, the specimens were cleaned by rinsing them three times with 5 ml of deionized water, dried for 2 minutes, and then immersed in three different fluoride solutions: (a) five specimens from each material were immersed in containers with a solution of 0.02% NaF for 5 minutes; (b) five specimens from each material were immersed in containers with a solution of 0.04% NaF for 5 minutes; (c) five specimens from each material were immersed in containers with a solution of 0.2% NaF for 5 minutes.

The specimens were then rinsed with 5 ml of deionized water. Following this, they were placed in new containers with 20 ml of deionized water and incubated as before. Fluoride concentration was measured (as described above), and the water replaced, every day until day 32. Every 5 days (days 16, 21 and 26) the refluoridation procedure was repeated as on day 11.

**Statistical analysis**

Repeated measures analysis of variance was carried out using the SPSS MANOVA package, to examine differences in fluoride released (expressed in ppm) for both the baseline period (the first 11 days) and the experimental phase. Tukey’s HSD (Honestly Significant Difference) test was used to perform multiple pairwise comparisons where this was indicated. For the baseline period, the independent variables in the analysis were the material (listed above), and day (days 1–11). For the experimental phase, the independent variables in the analysis were the material (listed above); concentration of refluoridation solution (0.2%, 0.04% and 0.02%); refluoridation period: period 1 (days 12–16), period...
2 (days 17–21), period 3 (days 22–26) and period 4 (days 27–31); and day (day 1 versus day 5). Day 1 refers to the first day after each refluoridation: days 12, 17, 22 and 27, and was of interest because the peak of fluoride release occurred on that day. Day 5 refers to the fifth day after each refluoridation: days 16, 21, 26 and 31 when the least fluoride was released.

Results

The total fluoride content of each material is shown in Table 1. XR Ionomer has more fluoride than all other materials, Vitrebond has the next most fluoride, Baseline has nearly the same amount of fluoride as Fuji, and Zinomer has the least fluoride incorporated in the respective materials.

Table 1. The total fluoride content of glass ionomer materials.

<table>
<thead>
<tr>
<th>Brand</th>
<th>No. of samples</th>
<th>Mass (g)</th>
<th>F-content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mean SD</td>
<td>Mean SD</td>
</tr>
<tr>
<td>XR Ionomer</td>
<td>15</td>
<td>0.41</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>Vitrebond</td>
<td>0.41</td>
<td>12.4</td>
</tr>
<tr>
<td></td>
<td>Baseline VLC</td>
<td>0.39</td>
<td>10.6</td>
</tr>
<tr>
<td></td>
<td>GC Fuji</td>
<td>0.39</td>
<td>10.3</td>
</tr>
<tr>
<td></td>
<td>Zionomer</td>
<td>0.41</td>
<td>7.8</td>
</tr>
</tbody>
</table>

During the first 11 days there were differences in the amount of fluoride released by each of the five materials, as shown in Table 2. Tukey’s HSD tests revealed that XR Ionomer released statistically significant more fluoride (mean 14.4 ppm) and Zinomer released significantly less fluoride (mean 0.33 ppm) than any of the other materials \( (P < 0.001) \). During this period there was a general decline over days in the amount of fluoride released. The amount of fluoride released decreased over each of days 1–6; the fluoride release remained relatively stable through days 7–11. Finally, there were significant differences in the pattern of initial fluoride release over days for the different materials. The decline in initial fluoride release over the first 6 days was significantly greater statistically \( (P < 0.001) \) for XR Ionomer than for any other material.

For the experimental phase, mean fluoride release after refluoridation with different concentrations of NaF (Table 3) shows that the effect of concentration was different across the different materials. Generally, more fluoride was released when the concentration of the refluoridation solution was 0.2% compared to 0.04% and 0.02% \( (P < 0.001) \) whereas solutions of concentrations 0.04% and 0.02% did not differ from each other.

The mean fluoride release by day over days 11–31 for the five materials is shown in Figs 1–5, respectively. The peak of fluoride release occurred on days 12, 17, 22 and 27, 1 day after each refluoridation. All five materials showed a decrease in the amount of fluoride released over the four refluoridation periods. Generally, fluoride release during each period was significantly less \( (P < 0.001) \) than that released during the baseline observation.

In particular, XR Ionomer (Fig. 1) showed a significant decline across all four periods. Vitrebond (Fig. 2) and Baseline (Fig. 3) showed a significant decline from period 1 to period 2, and remained relatively stable thereafter. For Fuji (Fig. 4) there was a small decline in the amount of fluoride released across the four periods, the amount of released fluoride in period 4 was significantly less than that released in period 1, but none of the other pairwise differences were significant. Finally, Zinomer (Fig. 5) showed significant decline in fluoride release.
Table 3. Mean and standard deviation (SD) of fluoride release by GI materials after refluoridation in solutions of different concentrations of NaF.

<table>
<thead>
<tr>
<th>Material</th>
<th>Period (days)</th>
<th>0.02% NAF</th>
<th>0.04% NAF</th>
<th>0.2% NAF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>SD</td>
<td>Mean</td>
<td>SD</td>
</tr>
<tr>
<td>XR Ionomer</td>
<td>1 (12-16)</td>
<td>6.7</td>
<td>2.0</td>
<td>7.6</td>
</tr>
<tr>
<td></td>
<td>2 (17-21)</td>
<td>6.6</td>
<td>3.2</td>
<td>7.2</td>
</tr>
<tr>
<td></td>
<td>3 (22-26)</td>
<td>5.2</td>
<td>2.1</td>
<td>6.9</td>
</tr>
<tr>
<td></td>
<td>4 (27-31)</td>
<td>5.0</td>
<td>1.8</td>
<td>6.4</td>
</tr>
<tr>
<td>Vitrebond</td>
<td>1 (12-16)</td>
<td>1.3</td>
<td>0.6</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>2 (17-21)</td>
<td>1.2</td>
<td>0.6</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>3 (22-26)</td>
<td>1.1</td>
<td>0.4</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>4 (27-31)</td>
<td>1.4</td>
<td>0.6</td>
<td>1.8</td>
</tr>
<tr>
<td>Fuji</td>
<td>1 (12-16)</td>
<td>0.8</td>
<td>0.3</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>2 (17-21)</td>
<td>0.7</td>
<td>0.1</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>3 (22-26)</td>
<td>0.9</td>
<td>0.2</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>4 (27-31)</td>
<td>0.6</td>
<td>0.1</td>
<td>0.6</td>
</tr>
<tr>
<td>Baseline</td>
<td>1 (12-16)</td>
<td>1.3</td>
<td>0.4</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>2 (17-21)</td>
<td>0.9</td>
<td>0.2</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>3 (22-26)</td>
<td>0.9</td>
<td>0.2</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>4 (27-31)</td>
<td>0.6</td>
<td>0.0</td>
<td>0.8</td>
</tr>
<tr>
<td>Zinomer</td>
<td>1 (12-16)</td>
<td>0.3</td>
<td>0.08</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>2 (17-21)</td>
<td>0.3</td>
<td>0.05</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>3 (22-26)</td>
<td>0.2</td>
<td>0.05</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>4 (27-31)</td>
<td>0.2</td>
<td>0.05</td>
<td>0.3</td>
</tr>
</tbody>
</table>

release when comparing period 1 to periods 3 and 4 respectively, marginal significant difference between period 1 and period 2, with no other pairwise differences being significant.

Fluoride release between day 1 and day 5 of all the refluoridation periods is also shown in Figs 1–5. Significantly more fluoride was released for all five materials, for all four refluoridation periods, and for all different concentrations on the first day after refluoridation compared to the fifth day after refluoridation (10.3 ppm for day 1, 1.4 ppm for day 5) ($P < 0.001$). Test of means revealed that each material had a significant decline in fluoride released when comparing day 1 to day 5. However, XR Ionomer (Fig. 1) had the greatest decline over day (day 1: $33.4 \pm 2.7$ ppm to day 5: $6.7 \pm 0.8$ ppm),
Vitrebond (Fig. 2) showed a smaller but substantial decline over day, and the effect for the other materials became smaller.

Discussion

The data from this study demonstrates that the five tested materials released fluoride in deionized water. It has been demonstrated [16] that GICs release less fluoride in artificial saliva than in deionized water. The use of artificial saliva should therefore be considered in studies that simulate clinical conditions such as in the following of remineralization of a caries lesion in close proximity to a GIC filling (our concurrent study).

During the last 10 years many authors [16–26] have shown that fluoride can be released from different fluoride-incorporating materials. The pattern of released fluoride is that of the greatest amount of fluoride being released during the first days, then decreasing to a nearly constant level. The findings of this study are similar.

Although the mechanism of fluoride release and 'recharging' is not yet completely clear, the research of Kuhn & Wilson [27] indicated that fluoride release occurs by means of three discrete mechan-
isms: surface wash-off, diffusion through pores and cracks, and diffusion through the bulk. The results of the present study seem to follow this explanation. The surface wash-off results in massive liberation of surface fluoride ions [27]. In this study this is shown by peaks of fluoride release 1 day after preparation of specimens and 1 day after every refluoridation. Release of fluoride by diffusion through pores and cracks is smaller but at a more constant level. This is presented by a long period of fluoride release at a nearly constant level, 7–11 days after preparation of the specimens and 2–5 days after each refluoridation. If the concentration of fluoride in the surrounding of the GIC is higher than in the pores and cracks, the process can be reversible [27]. The fluoride can flow into the pores and cracks and be harboured there until the concentration of fluoride in the surrounding of the GIC is negative and the fluoride can be released again. This seems to be the process that is occurring in the refluoridation process and the fluoride release which follows it.

Diffusion through the bulk occurs during the maturation of specimens, and presents a long-term continuing reaction [27,28]. The duration of this study was too short to make any inference regarding the occurrence of this process.

The findings of Zinomer releasing very little fluoride and XR ionomer releasing more fluoride than all other materials are in agreement with the findings reported by other authors [24–26].

There was a positive correlation between the quantity of originally incorporated fluoride and the ability to release–adsorb–release fluoride. This is in agreement with the findings of some studies [29–31] which reported that GICs would be expected to release more fluoride if the original fluoride content was higher. On the other hand, in other studies [17, 32], a lack of correlation between fluoride release and the fluoride content in GICs was found. This can be explained by the fact that they used metal-reinforced GICs (Miracle Mix and Ketac Silver), where formation of silver fluoride binds fluoride ions firmly. Fluoride associated with sodium is usually the most available for release [33]. The chemical composition of materials, difference in surface energy, and porosity all have significant influence on the amount and duration of fluoride release.

The experimental phase of the study demonstrated that XR ionomer and Vitrebond have the greatest ability to release–adsorb–release fluoride and to keep fluoride at an almost constant level for a prolonged period of time. The fluoride release–adsorption–release property of GIC in vitro may explain the long period of elevated fluoride found in saliva in vivo when the glass ionomer cement was used as a filling material [24] or as a bonding material for orthodontic appliances [34]. The results of this study showed that fluoride release from refluoridated specimens was lower than that from the freshly mixed material. This means that exposure of the specimens to the solutions of different concentrations of fluoride cannot completely restore the initial fluoride release rate. The release of fluoride was rapid, and after 5 days after refluoridation, it became lower than after 11 days of freshly mixed material. Even though the fluoride release was lower from refluoridated materials than from freshly mixed specimens, the amount of adsorbed and released fluoride was still significant. The most important finding is that GICs can be recharged for a long period of time and can keep a substantial and constant level of fluoride in their surrounding. This may be an important potential caries-preventive property. Investigation of the caries-preventive effect of GICs and other dental materials which have a release–adsorption–release ability should be carried out in future studies.

Conclusions

The following conclusions can be derived from this study: (1) All materials showed an ability to release–adsorb–release fluoride. (2) The quantity of released fluoride is positively correlated with the quantity of fluoride originally incorporated in the material. (3) Initial fluoride release cannot be completely restored by exposure of the materials to the fluoridated solution. (4) The potential caries-preventive effect of the release–adsorption–release of fluoride found in dental materials should be investigated in an extensive controlled clinical study as an ultimate test.

Acknowledgement

The financial support of the Swedish Institute in the form of a research scholarship was greatly appreciated.

Resumé. Il est bien établi que les verres ionomères (VI) libèrent des fluorures (F). La quantité de F libérée dépend des propriétés physiques et chimiques du produit. Dans cette étude, la libération de l’ionomer et la capacité du VI d’être rechargeé en fluoride on été étudiées pour cinq produits de différentes marques: XR Ionomère (Kerr), Vitrebond (3M), GC Fuji Lining (GC Dental Industries Corp.), Baseline VLC (Dentsply) et Zinomer (Dent. Mat). Quinze chantillons d'étude ont été préparé pour chaque marque. Les échantillons on été immergés dans de l’eau déionisée. Le F libéré a été mesuré une fois par jour pendant 11 jours. La refluoridation des échantillons étudiés a été réalisée avec des solutions à 0,02%, 0,04% et 0,2% de fluor de sodium pendant 5 minutes au jour 11, 16, 21 et 26. Le F libéré des échantillons rechargés a été mesuré chaque jour jusqu’au jour 32. Il y avait une corrélation positive entre la quantité de F dans les VI et leur capacité à libérer des F. Les cinq produits ont été ‘rechargés’ avec des F après des expéditions répétées aux F dans la solution, la solution 0,2% étant la plus efficace. Le ionomér XR libérait plus de fluorure de façon significative que les autres produits et avait une plus grande capacité à être rechargé. Le zinomer libérait moins de fluorure de façon significative que les autres produits et avait une capacité moindre à être rechargé. Ces résultats montrent que les VI se comportent comme des réservoirs et comme système de libération lente de F pendant au moins 32 jours.

Resumen. Está bien establecido que los ionómeros de vidrio (IV) liberan flúor (F). El grado de liberación de F depende de las propiedades físicas y químicas del producto. En el presente estudio se evaluó la liberación de F y la capacidad del IV de ser recargado con F. Los siguientes productos fueron evaluados: XR Ionomer (Kerr), Vitrebond (3M), GC Fuji Lining (GC Dental Industrial Corp.), Baseline VLC (Dentsply) y Zinomer (DenMat). Para cada producto se prepararon 15 muestras. Los especímenes fueron sumergidos en agua destilada. La liberación de F se midió diariamente por 11 días. La refluoruración de los especímenes se realizó con soluciones de 0-02%, 0-04% y 0-2% de NaF por 5 minutos los días 11, 16, 21 y 26. La liberación de F de los especímenes recargados fueron medidas diariamente hasta el día 32. Hubo una correlación positiva entre la cantidad de F en el IV y la habilidad para liberar el F. Los cinco materiales estuvieron ‘recargados’ con F después de repetidas exposiciones siendo la concentración al 0-2% la más efectiva. El XR Ionomer liberó significativamente más F que cualquiera de los otros materiales y mostró la mayor habilidad para ser recargado. Zinomer liberó significativamente menos F que los otros productos y mostró la menor habilidad para ser recargado. Los resultados indican que los IV sirven como reservorios de F y pueden actuar como un sistema de acción prolongada por los menos durante 32 días.

References