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# UPTAKE OF FLUORIDE BY GLASS-IONOMER DENTAL CEMENTS FROM A COMMERCIAL FLUORIDATED MOUTHWASH

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*The ability of glass-ionomer dental cements to take up fluoride from a fluoridated mouthwash has been determined, and shown to vary somewhat with the degree of maturation (ageing). Three commercial conventional glass-ionomer cements were used to produce sets of five discs (6 mm diameter by 2 mm thickness). Discs were aged for 24 h or 1 month at 37°C then placed in 5 cm$^3$ volumes of commercial fluoridated mouthwash (Plax, ex Colgate Palmolive, Guildford, UK) at a nominal concentration of 112 ppm. Free fluoride ion concentration was measured in samples stored at room temperature for 30 min, 1, 2, 3, 4 and 5 h, using an ion selective electrode. Under these conditions cements were found to take up similar amounts of fluoride at t = 30 minutes, regardless of their age. However, at 5 hours the cements samples matured for 24 hours took up significantly more fluoride than the samples matured for 1 month. In this way it was shown that degree of maturation influenced the ability to take up fluoride without affecting the initial uptake rate. These results suggest that fluoridated mouthwashes may be a valuable source of fluoride for recharging glass-ionomer cements.*

## INTRODUCTION

Glass-ionomer cements are ceramic-based materials that are used in clinical dentistry because of their twin advantages of inherent adhesion to mineralised tissue and fluoride release [1, 2, 3]. The latter property has been widely studied. For glass-ionomers, fluoride release is known to continue for several years [4], and to be influenced by pH, with greater acidity promoting increased fluoride release [5]. Fluoride release has been shown to be a two-stage process. Initially, there is a dissolution step, sometimes termed “early wash out”, which lasts up to 1 month [6, 7]. This is followed by a long-term diffusion process, which is characterised by its occurrence as a function of square root of time [8, 9].

Fluoride release is considered beneficial clinically [1], and its release is considered to be the main reason that glass-ionomers provide good clinical resistance to the development of proximal caries [10]. Fluoride is known to promote deposition of the mineral phase of the tooth, hydroxyapatite [11], and this leads to the formation of a mineral phase containing fluoride that is more resistant to acid attack that the fluoride-free mineral [12]. Such uptake only occurs only in the very surface layers, estimated not to exceed three atom layers in thickness [13], but this is sufficient to reduce the solubility of the mineral phase in the dilute acidic conditions produced by bacterial metabolism.

As well as releasing fluoride, glass-ionomers are capable of taking it up under appropriate circumstances [14]. This possibility was first suggested by Walls in 1986 [15], and has since been confirmed experimentally. A typical study was that of Creanor et al [16], who exposed samples to 1000 ppm fluoride for 2 minutes over a 20-day period, and showed that this treatment resulted in increased fluoride release. They were therefore able to conclude that fluoride had been taken up and subsequently released.

More recently, uptake of fluoride by glass-ionomer cements has been demonstrated directly by exposing specimens to potassium fluoride solutions, and determining the rate of reduction of fluoride concentration with time [17]. Specimens were exposed to fluoride solutions very early on in their lifetimes, *i.e.* after only 10 minutes maturation at 37°C. Under these circumstances, fluoride uptake followed pseudo-1st order kinetics, the integrated form of the rate equation being:

$$\ln(q_e - q_t) = \ln(q_e) + kt$$

Subsequently, the effect of maturation (ageing) on the kinetics of uptake of fluoride from aqueous sodium fluoride has been studied for various commercial brands of cement that had been matured for periods of time varying from 10 minutes to 1 month [18]. This study confirmed that uptake followed pseudo-1$^{st}$ order kinetics for specimens cured for only 10 minutes, and that this not only changed for specimens cured for 1 month at 37°C, but these latter specimens showed reduced uptake [18].

Glass-ionomers are known to change slowly after the initial hardening is complete. The processes that occur are known generally as "maturation", and they are not at all well understood. They have several characteristics, for example, compressive strength typically increases [19], as do biaxial flexure strength [20] and translucency [21]. The proportion of water that is tightly bound within the structure, and hence cannot be removed by desiccation in a dry atmosphere, also increases [22]. This latter feature has been attrubuted to the formation of extra silanol groups at the surface of the glass powder within the cement due to a slow hydration reaction [22]. These various properties all reach limiting values, typically within 4 - 6 weeks, by which time maturation is considered complete [2].

Despite the occurrence of changes due to maturation, release of fluoride continues from aged cements. This release may be affected by maturation processes, which may explain why "early wash out" (*i.e.* dissolution) ceases, and diffusion-based release predominates in older cement specimens [7].

Whilst it has been shown that the ability of glass-ionomer cements to take up fluoride from aqueous sodium fluoride varies with extent of maturation, it is not known whether this is true when fluoride is supplied in a fully formulated dental product, such as a mouthwash. The change in proportion of loosely bound water suggests that maturation involves reduction in mobility of lower molar mass species within the cement, and therefore that the reduced ability to take up fluoride ions on maturation may be a general effect. The present study was undertaken to examine this possibility, using a fluoridated mouthwash as the source of soluble fluoride, and commercial cements matured for two different time periods (24 hours and 1 month).

## EXPERIMENTAL

### Materials and Methods

Three commercial conventional glass-ionomer cements were used in this study, namely Fuji IX Fast (GC, Japan), AquaCem (Dentsply, Germany) and Ketac Molar Quick (3M-ESPE, Germany). All of these were prepared in accordance with manufacturers' instructions, either by vibrational mixing in a dental mixing device (Linea Tac Mixer, ex Kent Express, UK) for Fuji IX Fast and Ketac Molar Quick, or by spatulation of the glass/acid powder into deionised water on a ceramic tile for AquaCem. Freshly prepared pastes were placed in silicone rubber moulds to produce sets of five discs of dimensions 6 mm diameter by 2 mm thickness. They were cured at time intervals of 24 h or 1 month at 37°C in an incubator. They were then removed from their moulds and placed in 5 $cm^3$ volumes of commercial fluoridated mouthwash (Plax, ex Colgate Palmolive, Guildford, UK) at a nominal concentration of 112 ppm with respect to fluoride ion in the form of NaF.

Fluoride ion concentration was measured at time intervals of 30 min, 1, 2, 3, 4 and 5 h, using a calibrated fluoride ion selective electrode (type 309/1050/03 combination electrode, ex BDH Poole, UK).

Means and standard deviations of fluoride concentration were determined and data converted to equivalent uptake values by subtracting readings from the mean value obtained for $t = 0$. Graphs of equivalent uptake against time were plotted and data examined for conformity to 1st order uptake kinetics. Changes in equivalent uptake were examined for significance using Student's t-test, values with significance less than $p < 0.05$ being considered not significant.

## RESULTS

The mean value of fluoride content, resulting from measuring the value at $t = 0$ for every experiment, was 104.9 ppm (Standard deviation 2.7 ppm), which was slightly below the level of 112 ppm claimed on the packaging of the mouthwash.

Concentrations of fluoride at various time intervals are shown in Tables 1 and 2. These data show reductions in the first 30 minutes in all cases (significant to $p < 0.001$ for each material). For both AquaCem and Ketac Molar, the uptake did not differ significantly between the 1 week and 1 month cured specimens, whereas for Fuji IX, the

Table 1. Fluoride concentration in the mouthrinse at various time intervals for cements cured for 24 hours (Standard deviations in parentheses).

| Time (min) | Aquacem | Fuji IX | Ketac Molar |
|---|---|---|---|
| 30 | 82.9 (4.4) | 84.8 (2.5) | 83.9 (8.4) |
| 60 | 75.4 (6.8) | 79.5 (5.2) | 75.2 (7.2) |
| 120 | 68.5 (5.0) | 75.5 (3.6) | 67.8 (2.8) |
| 180 | 55.5 (1.7) | 67.2 (1.4) | 63.5 (2.2) |
| 240 | 51.7 (0.8) | 64.3 (0.8) | 62.2 (2.1) |
| 300 | 51.4 (1.0) | 66.5 (0.6) | 64.5 (1.6) |

Table 2. Fluoride concentration in the mouthrinse at various time intervals for cements cured for 1 month (Standard deviations in parentheses).

| Time (min) | Aquacem | Fuji IX | Ketac Molar |
|---|---|---|---|
| 30 | 80.7 (1.6) | 78.4 (1.2) | 77.9 (0.7) |
| 60 | 79.9 (1.7) | 76.9 (0.7) | 75.1 (1.7) |
| 120 | 77.7 (2.1) | 74.3 (1.0) | 73.1 (1.2) |
| 180 | 74.9 (1.1) | 73.3 (0.9) | 72.3 (1.0) |
| 240 | 74.3 (1.5) | 73.5 (0.8) | 72.3 (1.0) |
| 300 | 76.0 (2.3) | 74.1 (1.3) | 73.0 (1.9) |

1 month cured specimens took up less than the 24 hour cured specimens, and this difference was significant (to $p < 0.05$). For specimens cured at each time period, there continued to be uptake of fluoride up to 5 hours, but the changes between $t = 30$ min and $t = 300$ min were smaller for the 1 month specimens than the 24 hour specimens in all cases. These changes were generally highly significant for 24 hour cured specimens ($p < 0.005$ for both AquaCem and Fuji IX, but only to $p < 0.05$ for Ketac Molar. Changes for the 1 month cured specimens were either not significant (AquaCem) or just significant (*i.e.* to $p < 0.05$ for Fuji IX and Ketac Molar).

The concentration data have been recalculated as equivalent fluoride uptake values by subtracting the fluoride concentration at any given time interval from the value at $t = 0$. The resulting data have been plotted as Figures 1 and 2 for the 24 hour cured and the 1 month cured specimens respectively.

## DISCUSSION

Mouthwash samples in which cements were stored showed reduced amounts of free (*i.e.* uncomplexed) fluoride by $t = 30$ minutes. Measurements were made with the fluoride ion selective electrode without the addition of decomplexing agent, such as TISAB, which means that only free $F^-$ ions were able to be determined, not total fluoride. It is possible that the measured reduction in free fluoride was due to complexation, for example with aluminium released from the cement. However, since it is known that exposing glass-ionomer cement to fluoridated mouthwash results in subsequent increased fluoride release [23], it seems likely that most if not all of the reduction in fluoride concentration is due to uptake by the cement specimens.

Assuming this to be fluoride uptake, results showed that it differed from previous findings for fluoride uptake from aqueous sodium fluoride solutions [19]. For the latter, specimens cured for 1 month showed little or no uptake, whereas specimens cured for either 10 minutes or 24 hours showed distinct uptake. The specimens cured for 24 hours showed fluctuating uptake and release in aqueous NaF, suggesting that there are complex interactions with this solution over time.

In the present study, experiments were run for 5 hours only, and not extended to a longer time, such as 24 hours or 1 week, to represent equilibrium uptake. This is because cements cured for 24 hours are still undergoing maturation, which means that any notional equilibrium value at extended time intervals would not represent the situation for 24 hours maturation only. Instead, rather than exposing samples to fluoride solutions for extended periods of time, the leveling out of fluoride concentration within 5 hours was taken as an indication of the fluoride uptake capacities of the cements.

Maturity of the glass-ionomers was found to affect the uptake pattern of fluoride from the mouthwash. In general, specimens cured for 24 hours showed a greater overall uptake of fluoride in the time up to 5 hours than specimens cured for 1 month. There was also a different pattern of uptake, at least in the case of AquaCem and Fuji IX, where there appeared to be a step change in uptake between 120 and 180 minutes.

However, differences in uptake behaviour did not manifest themselves in the first 30 minutes of exposure to fluoridated mouthwash. For all three brands, there was significant uptake in specimens cured for either 24 hours or 1 month, and in the case of AquaCem and Ketac Molar, these did not differ significantly. For Fuji IX, the difference between specimens cured for 24 hours and specimens cured for 1 month was small but statistically significant ($p < 0.05$). Despite this minor difference, the overall pattern for all cements was of similar or identical initial uptake rates, regardless of state of maturity.

These results confirm the previous finding that the age of the cement influences the overall uptake capacity. They also support previous findings that glass-ionomer orthodontic adhesives exposed to a fluoridated mouthwash can release increased amounts of fluoride when exposed to pure water [23].

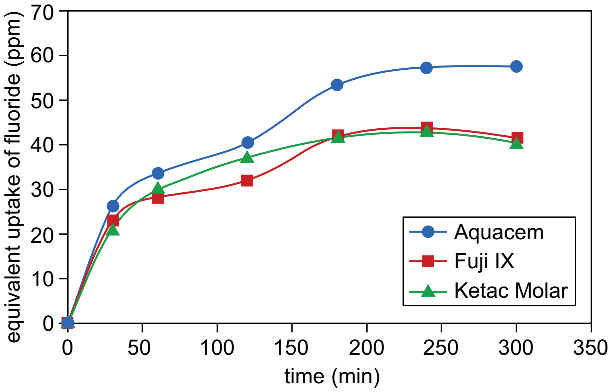


Figure 1. Plot of equivalent uptake of fluoride (ppm) against time (min) for specimens matured for 24 hours.

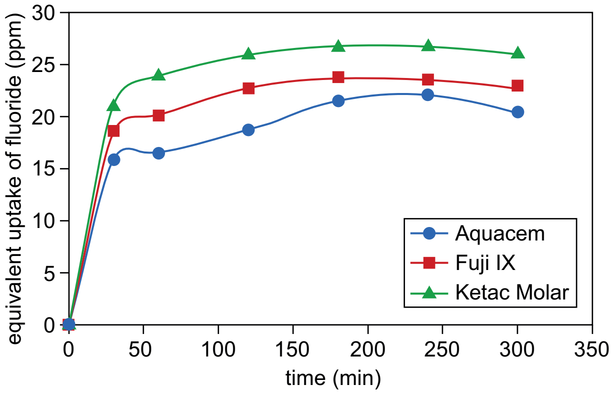


Figure 2. Plot of equivalent uptake of fluoride (ppm) against time (min) for specimens matured for 1 month.

Mouthwashes, including Plax, as used in the current study, are known to have an effect on dental restorative materials. Such formulations are widely used, despite their limited clinical effect [24], and they have been shown to reduce the hardness of materials by statistically significant amounts [25]. No conventional glass-ionomer cements have been studied, but one resin-modified glass-ionomer was used in the reported study, namely the brand Vitremer, and its surface hardness fell considerably as a result of the action of mouthwash on its surface [25]. It seems probable the conventional glass-ionomer cements would be similarly affected. The reason for this effect is not clear as the pH of Plax is pH $7.00 \pm 0.04$ [26], so any effect is not due to etching by an acidic composition. There seem to be a component in mouthwash formulations, possibly ethanol, that enhances the initial uptake of fluoride ion from solution, and this may also be responsible for reducing the hardness of the cement surface.

## CONCLUSIONS

Three brands of clinical grade glass-ionomer cement have been shown to vary in their uptake of fluoride from a commercial mouthwash, depending on state of maturity. Over the shortest duration uptake (30 minutes), there were generally no significant differences between amounts of fluoride taken up by cements of varying maturity, indicating that initial rates were not affected by maturation. Cements aged for longer time periods (up to 5 hours) had reduced capacity for taking up fluoride compared with relatively immature cements. These results confirm the previous finding that ageing influences the fluoride uptake process. However, the effect of interaction of cements with fluoridated mouthwash is different from that with aqueous sodium fluoride, in that there is a measurable fluoride uptake even in mature specimens, and this uptake takes place at the same initial rate in all cements. This suggests that using mouthwash as the source of fluoride may ensure an adequate recharge of fluoride by cement restorations, despite the fact that more mature cements have lower uptake capacities.

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