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The interaction of zinc oxide-based dental cements with aqueous solutions of potassium fluoride

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Abstract The ability of zinc oxide-based dental cements (zinc phosphate and zinc polycarboxylate) to take up fluoride from aqueous solution has been studied. Only zinc phosphate cement was found to take up any measurable fluoride after 5 h exposure to the solutions. The zinc oxide filler of the zinc phosphate also failed to take up fluoride from solution. The key interaction for this uptake was thus shown to involve the phosphate groups of the set cement. However, whether this took the form of phosphate/fluoride exchange, or the formation of oxyfluoro-phosphate groups was not clear. Fluoride uptake followed $\sqrt{}$time kinetics for about 2 h in some cases, but was generally better modelled by the Elovich equation, $dq_t/dt = \alpha \exp(-\beta q_t)$. Values for α varied from 3.80 to 2.48×10^4, and for β from 7.19×10^{-3} to 0.1946, though only β showed any sort of trend, becoming smaller with increasing fluoride concentration. Fluoride was released from the zinc phosphate cements in processes that were diffusion based up to M_t/M_∞ of about 0.4. No further release occurred when specimens were placed in fresh volumes of deionised water. Only a fraction of the fluoride taken up was re-released, demonstrating that most of the fluoride taken up becomes irreversibly bound within the cement.

1 Introduction

The development of fluoride-releasing dental restorative materials, such as the glass-ionomer dental cements, has triggered an interest in the dynamics of fluoride interactions that these materials may undergo [1]. Glass-ionomers, like their predecessors the dental silicate cements [2], are capable of both releasing and taking up fluoride [3–5]. They thus have the ability to act as fluoride reservoirs in situ when used in clinical dentistry [6].

The uptake of fluoride by glass-ionomers is associated with a decline in the quality of the cement surface, and with the appearance of the surface having been etched [7, 8]. This applies even with fluoride solutions of very low concentration. Indeed, there is evidence that the increase in fluoride release following such treatment is at least partly due to the release of fluoride as a result of the etching effect, rather than because of uptake then re-release [9].

To date, attention has been focussed on the glass-ionomer cements, and their closely related derivatives, the resin-modified glass-ionomers [10, 11] and the compomers [12, 13]. Each of these types of material has been shown to be altered by exposure to low concentration fluoride solutions, and to release increased amounts of fluoride on subsequent immersion in pure water [14, 15].

The present study has been undertaken to determine how zinc phosphate and zinc polycarboxylate cements behave in the presence of aqueous fluoride solutions. These cements are known to share many features of the glass-ionomer cements. They are acid-base cements that set by neutralization [16]; they are capable of buffering aqueous solutions of lactic acid [17]; and they release ions into solution at rates that vary with prevailing solution pH [18]. Hitherto, however, there have been no reports of studies of their interaction with fluoride solutions. The current article describes experimental work designed to determine whether these cements are able to take up fluoride from solution, and if so, by what mechanism. It goes on to report results of studies of fluoride release, and of the role of the zinc oxide filler/reactive base in this process.

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There have been previous studies of fluoride release from these cements where fluoride has been added as stannous fluoride mixed with the zinc oxide powder [19]. Exposure of set cements to water then leads to release of at least some of this fluoride. In the case of zinc phosphate, fluoride release has been studied in detail, and shown to follow diffusion-based kinetics up to M_t/M_∞ values of approximately 0.4, where M_t is the mass uptake at time t and M_∞ is the mass uptake at infinity [20].

2 Materials and methods

The materials used were a zinc phosphate dental cement (Kent Dental Zinc Phosphate, ex. Kent Express, UK) and a water-activated zinc polycarboxylate cement (PolyKent, ex. Kent express, UK). Each was prepared according to manufacturer's instructions, i.e. at powder:liquid ratios of 3.6:1 (zinc phosphate) or 5:1 (zinc polycarboxylate).

Freshly mixed pastes were placed in silicone rubber moulds to produce discs of dimensions 6 mm diameter × 2 mm depth. They were allowed to cure in an incubator at 37°C for 10 min, before being exposed in sets of five together to single 5 ml portions of aqueous solutions of potassium fluoride (General Purpose Reagent grade, ex. BDH, Poole, UK) at concentrations of 100, 250, 500, 750, 1,000 or 5,000 ppm with respect to fluoride ion. During exposure, fluoride concentration was measured at time intervals of 15 min, then 1, 2, 3, 4, 5 and 24 h, using a fluoride-ion selective electrode (type 309/1050/03 combination electrode, ex. BDH, Poole, UK). Uptake data were plotted in a variety of modes (pseudo-first order, pseudo-second order, Elovich equation and as a $\sqrt{\text{time}}$ plot) to determine the relationship between fluoride uptake and time.

After 24 h, specimens which showed fluoride uptake were transferred to deionised water (5 ml volume per specimen) in plastic sample vials. Fluoride release from them was determined at time intervals of 10 min, 20 min, 30 min, 1, 2, 3, 4, and 5 h, then at 24 and 48 h. Fluoride release typically reached equilibrium after 24 h. From the data thus obtained, release profiles were plotted and graphs of M_t/M_∞ against $\sqrt{t}$ were plotted, as required to determine whether release followed a diffusion mechanism.

Additional experiments were carried out in which specimens previously equilibrated in water were placed in fresh 5 ml volumes of deionised water, in order to determine whether further fluoride release could occur. Finally, samples of zinc oxide powder (0.2 g) were exposed to potassium fluoride solutions (100 and 1,000 ppm) for up to 5 h, to determine whether there was any fluoride take up by this cement component.

3 Results

Preliminary experiments were carried out by exposing sets of five specimen discs to KF solutions at 100 and 1,000 ppm at room temperature. Under these conditions, over 5 h, the zinc phosphate specimens were found to take up fluoride, whereas by contrast, there was no evidence of fluoride uptake by the zinc polycarboxylate specimens. After 5 h, the electrode reading was unchanged, and still showed the concentrations of the solutions to be 100 and 1,000 ppm respectively. Consequently, all further experiments were carried out using zinc phosphate cement specimens only.

Reductions in fluoride concentration with time for zinc phosphate cements are shown in Table 1 and the consequent fluoride uptake data shown in Table 2. Attempts to describe linear relationships involving uptake and time showed that the best fit occurred with plots of reduction in concentration against ln(time), as required by the Elovich equation [21]. Figure 1 shows such a plot for 250 ppm initial concentration, and Table 3 lists the equations, together with the correlation coefficients, for all initial concentrations. Only for 5,000 ppm did it prove impossible to find any kind of relationship, a feature which may arise because of the very high initial concentration and the consequently high rate of interaction between the fluoride

Table 1 Fluoride concentration in solution at varying time intervals (5 specimen discs together in a 5 ml portion of KF solution, room temperature)

Time	100 ppm	250 ppm	500 ppm	750 ppm	1000 ppm	5000 ppm
15 min	40	216	370	716	917	4979
60 min	34	169	327	620	810	4777
120 min	31	149	314	547	687	4777
180 min	19	137	289	515	659	4777
240 min	29	127	266	494	633	4584
300 min	29	112	245	464	633	4584
24 h	15	95	187	355	536	4221

Table 2 Reduction in fluoride concentration in solution at varying time intervals

Time	100 ppm	250 ppm	500 ppm	750 ppm	1000 ppm	5000 ppm
15 min	60	134	130	34	83	21
60 min	66	81	173	130	190	223
120 min	69	101	186	203	313	223
180 min	81	113	211	235	341	223
240 min	71	123	234	256	367	416
300 min	71	138	255	256	367	416
24 h	85	95	313	355	464	779

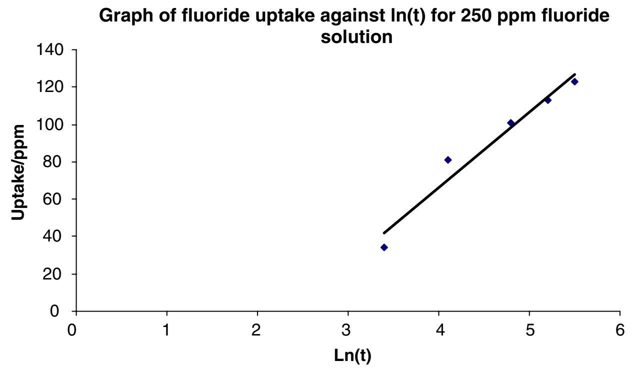

Fig. 1 Graph of fluoride uptake versus ln(t) for 250 ppm fluoride solution

Table 3 Equations for fluoride uptake (q_t) versus ln(time/min)

Initial concentration (ppm)	Equation	Correlation coefficient
100	$q_t = 5.14 \ln(t) + 43.6$	−0.969
250	$q_t = 40.5 \ln(t) - 95.8$	−0.979
500	$q_t = 45.5 \ln(t) + 22.4$	−0.981
750	$q_t = 106.0 \ln(t) - 314$	−0.993
1000	$q_t = 139.0 \ln(t) - 380$	−0.991
5000	–	–

ions in solution and the cement specimens.

Uptake at 500, 750 and 1,000 ppm showed some evidence for a diffusion process, over the first 2–3 h only. These gave reasonably linear plots of concentration against $\sqrt{}$(time). Unfortunately, the number of points was too few to be certain of this relationship.

After 24 h, specimens were transferred to individual 5 ml volumes of deionised water, and release of fluoride determined. Results for this are shown in Table 4. In all cases this release equilibrated, typically by 24 h. Plots of M_t/M_∞ versus $\sqrt{t}$ were found to be linear up to M_t/M_∞ of about 0.4, i.e. for the first 1–2 h of release. Diffusion coefficients were determined from these data (Table 5). The overall recovery of fluoride could be determined from the equilibrium values of concentration, and these values are listed in Table 6.

Finally, it was found that placing equilibrated specimens in fresh volumes of water led to little or no additional release of fluoride (measured values of fluoride in these solutions being 0.5 ppm or lower). Similarly, exposure of zinc oxide powder from the zinc phosphate cement to KF solutions showed no reduction in fluoride concentration

Table 5 Diffusion coefficients for fluoride release from conditioned zinc phosphate cement samples

Initial concentration (ppm)	Diffusion coefficient (10^{-3} m^{-2} s^{-1})
100	1.41
250	0.82
500	2.34
750	5.11
1000	4.24
5000	3.63

Table 6 Fluoride recovery from conditioned zinc phosphate cement samples

Initial concentration (ppm)	Fluoride recovery (%)
100	13.6
250	8.1
500	14.9
750	21.9
1000	22.6
5000	33.9

Table 4 Fluoride release data (5 specimen discs in individual 5 ml volumes of deionised water, room temperature)

Time	100 ppm	250 ppm	500 ppm	750 ppm	1000 ppm	5000 ppm
10 min	0.2 (0.0)	0.3 (0.0)	1.2 (0.2)	2.3 (0.5)	2.2 (0.5)	2.6 (0.3)
20 min	0.3 (0.0)	0.3 (0.0)	1.8 (0.4)	3.6 (0.6)	3.6 (0.7)	9.7 (0.5)
30 min	0.4 (0.0)	0.4 (0.0)	2.4 (0.7)	5.5 (0.5)	4.7 (0.7)	13.0 (0.5)
60 min	0.5 (0.0)	0.6 (0.1)	3.1 (0.5)	7.3 (0.7)	7.6 (1.2)	18.2 (1.0)
120 min	0.8 (0.1)	0.8 (0.1)	4.3 (0.7)	9.3 (0.9)	9.7 (1.9)	23.6 (1.7)
180 min	0.9 (0.1)	1.1 (0.1)	5.5 (1.4)	10.1 (1.3)	11.4 (2.5)	28.0 (1.9)
240 min	1.0 (0.1)	1.1 (0.1)	5.1 (1.9)	10.7 (1.2)	12.9 (3.0)	30.7 (2.0)
300 min	1.0 (0.1)	1.2 (0.1)	5.4 (1.8)	12.0 (1.1)	14.1 (3.1)	32.2 (1.8)
Equilibrium	2.3 (0.5)	2.9 (0.7)	9.3 (2.9)	18.0 (2.4)	21.0 (3.5)	52.8 (3.3)

over 5 h, indicating that the zinc oxide is not itself capable of taking up fluoride.

4 Discussion

Of the two cements studied, only the zinc phosphate was found to take up fluoride from aqueous solution. Neither the zinc polycarboxylate, nor the zinc oxide powder from the zinc phosphate cement, were shown to take up fluoride from solution. These findings demonstrate that the phosphate group is responsible for removing the fluoride from solution. The subsequent release was found to be low in all cases, showing that the fluoride uptake is only partially reversible.

There have been no previous studies of fluoride uptake by zinc phosphate, but there have been numerous studies of fluoride uptake by calcium phosphate, typically as the biomineral hydroxyapatite [22–24]. In all cases, the assumption has been that this uptake involves replacement of hydroxide groups by fluoride ions, an assumption that has been confirmed experimentally in several cases [23, 24]. However, when bone char was used as the sorbent, the data suggested that fluoride ions replace phosphate groups [25]. It is not clear whether this type of exchange occurs with zinc phosphate cements, or whether instead the uptake we have observed involves a process of the type:

$$\mathrm{H^+ + PO_4^{3-} + F^- \rightarrow PO_3F^{2-} + OH^-}$$

Either way, the uptake was not readily reversible for zinc phosphate. This finding is similar to that for fluoride uptake by calcium phosphate mineral [25].

Uptake of ions by solids from solutions has been modelled by various equations. These are pseudo-first order, pseudo-second order, and the Elovich equation. There is also the possibility of diffusion, which would give a straight line plot for uptake against $\sqrt{\text{time}}$. Pseudo-first order has been found to describe the uptake of thorium ions by alumina particles [26], pseudo-second order has been shown to apply to the uptake of, inter alia, $\mathrm{Sr^{2+}}$ and $\mathrm{Zn^{2+}}$ ions by synthetic tobermorite [27, 28]. The Elovich equation,

$$\mathrm{d}q_t/\mathrm{d}t = \alpha \exp(-\beta q_t)$$

which was originally developed to describe the process of adsorption of gas molecules onto solids [21], has been found to describe uptake of phosphate ions by soil [29]. All three of these were applied to the fluoride uptake data we have obtained, and most satisfactory results were obtained for the Elovich model (Table 3). This is an empirical equation and is not usually used to infer information about uptake mechanisms. From the resulting plot of q_t versus ln t is, the slope, $1/\beta$, and intercept, $(1/\beta)\ln(\alpha\beta)$, can be determined, and these enable values of α and β to be calculated. These are given in Table 7. As for the equation itself, these are arbitrary constants, so a trend in their values is not necessarily of use in understanding the underlying mechanism of uptake. However, there is a trend in the case of β, values of which diminish with increasing solution concentration.

Table 7 Elovich constants for fluoride uptake

Initial concentration (ppm)	Values of α (ppm)	Values of β (ppm)$^{-1}$
100	$2.48 \text{ x } 10^{4}$	0.1946
250	3.80	$2.468 \text{ x } 10^{-2}$
500	74.44	$2.198 \text{ x } 10^{-2}$
750	5.48	$9.43 \text{ x } 10^{-3}$
1000	9.04	$7.19 \text{ x } 10^{-3}$
5000	–	–

The subsequent release of fluoride followed diffusion kinetics, i.e. release varied linearly with $\sqrt{\text{time}}$. This suggests logically that at least part of the uptake must have involved some diffusion of fluoride ions into the cement, as suggested by the fact that $\sqrt{\text{time}}$ kinetics describes the uptake process, at least for a short time.

Diffusion-based release of fluoride has been found previously for zinc phosphate cements that contain intrinsic fluoride, i.e. fluoride that was added by mixing the ZnO powder with $\mathrm{SnF_2}$. Such preparation causes fluoride to be distributed throughout the cement, and not only in the surface layers. It also allows fluoride to be released in amounts that are clinically beneficial against caries [19]. A similar release was found in the present study. Amounts of fluoride were different in the two types of cement, hence making comparison of release levels meaningless. However, it was notable that the release process was found to deviate from simple $\sqrt{\text{time}}$ (diffusion) kinetics at M_t/M_∞ of about 0.4 [20], as in our study.

Overall, these results show that zinc phosphate cements are able to behave like glass-ionomer dental cements in that, by taking up and re-releasing fluoride, they are able to act as fluoride reservoirs. However, this is not true of zinc polycarboxylate cement. This indicates that phosphate groups are critical for these processes. This finding may be significant in understanding the precise mechanism of fluoride exchange by glass-ionomer cements.

5 Conclusions

Uptake of fluoride from aqueous solution was found to occur with zinc phosphate cement, but not with zinc polycarboxylate. Also, the zinc oxide filler of the zinc phosphate did not take up fluoride from solution. Hence we conclude that the key interaction for this uptake involves the phosphate groups. However, whether this involves phosphate/fluoride exchange, or the formation of oxyfluoro-phosphate groups is not clear.

Uptake showed some evidence of $\sqrt{}$time kinetics, though was actually better modelled by the Elovich equation, $dq_t/dt = \alpha \exp(-\beta q_t)$.

Fluoride was released from the zinc phosphate cements in processes that were diffusion based up to M_t/M_∞ of about 0.4. This is similar to previous findings for release of intrinsic fluoride, added by introducing stannous fluoride to the cement formulation. Cement specimens that had ceased to release fluoride into a particular solution showed little or no further release when placed in fresh volumes of deionised water, even though release amounted to only a fraction of the fluoride taken up. This demonstrated that the majority of the fluoride becomes irreversibly bound to the cement.

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References

1. R.W. Billington, J.A. Williams, G.J. Pearson, J. Dent. **34**, 544 (2006)
2. V. Lind, G. Wennerholm, S. Nystrom, Acta Odontol. Scand. **22**, 233 (1964)
3. L. Forsten, Scand. J. Dent. Res. **85**, 503 (1977)
4. R.J.G. De Moor, R.M.H. Verbeeck, E.A.P. De Maeyer, Dent. Mater. **12**, 88 (1996)
5. A.D. Wilson, D.M. Groffman, A.T. Kuhn, Biomaterials **6**, 431 (1985)
6. L. Forsten, Scand. J. Dent. Res. **91**, 241 (1991)
7. W.A.G. El-Badrawy, D. McComb, R.E. Wood, Dent. Mater. **29**, 63 (1993)
8. A.M.J. De Witte, E.A.P. De Maeyer, R.M.H. Verbeeck, Biomaterials **24**, 1995 (2003)
9. R.W. Billington, P.C. Hadley, M.R. Towler, G.J. Pearson, J.A. Williams, Biomaterials **21**, 377 (2000)
10. S.B. Mitra, J. Dent. Res. **70**, 75 (1991)
11. H. Forss, J. Dent. Res. **72**, 1257 (1993)
12. D. Sales, D. Sae-Lee, S. Matsuya, I.D. Ana, Biomaterials **24**, 1687 (2003)
13. J.W. Nicholson, B. Czarnecka, J. Oral Rehabil. **31**, 665 (2004)
14. M. Rothwell, H.M. Anstice, G.J. Pearson, J. Dent. **26**, 591 (1998)
15. X. Xu, J.O. Burgess, Biomaterials **24**, 2451 (2003)
16. A.D. Wilson, J.W. Nicholson, *Acid-Base Cements* (The University Press, Cambridge, 1993)
17. J.W. Nicholson, B. Czarnecka, H. Limanowska-Shaw, J. Mater. Sci. Mater. Med. **10**, 449 (1999)
18. B. Czarnecka, H. Limanowska-Shaw, J.W. Nicholson, J. Mater. Sci.. Mater. Med. **14**, 601 (2003)
19. Z. Ram, I. Gedalia, I. Reissten, J. Dent. Res. **52**, 1344 (1973)
20. R.W. Billington, P.C. Hadley, J.A. Williams, G.J. Pearson, Biomaterials **22**, 2507 (2001)
21. M.J.D. Low, Chem. Rev. **60**, 267 (1960)
22. N.H. De Leeuw, J. Phys. Chem. B **108**, 1809 (2004)
23. J.D.B. Featherstone, Community Dent. Oral Epidemiol. **27**, 31 (1999)
24. D.J. White, G.H. Nancollas, J. Dent. Res. **69**, 587 (1990)
25. I. Abe, S. Iwasaki, T. Tokimoto, N. Kawasaki, T. Nakamura, S. Tanada, J. Colloid Interface Sci. **275**, 35 (2004)
26. S.E.H. Niven, R.M. Moore, Geochim. Cosmochim. Acta. **57**, 2169 (1993)
27. N.J. Coleman, D.S. Brassington, A. Raza, A.P. Mendham, Waste Manag. **26**, 260 (2006)
28. N.J. Coleman, D.S. Brassington, A. Raza, A.P. Mendham, Environ. Technol. **27**, 1089 (2006)
29. S.H. Chien, W.R. Clayton, Soil Sci. Am. J. **44**, 265 (1980)