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Ion-release, dissolution and buffering by zinc phosphate dental cements

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The interaction of zinc phosphate dental cement with aqueous solutions has been studied in order to elucidate the relationship between pH change and ion release (dissolution). For each storage medium (deionized water, lactic acid at pH 2.7 and lactate buffer at pH 2.2) five cylindrical specimens of zinc phosphate cement (6 mm diameter × 12 mm height) were prepared and weighed. They were stored individually in 8 cm^3 of solution for a week, then the pH was determined and the specimens reweighed. The solutions were replaced and the specimens stored for a further week, then the pH and the weight were again measured. This was repeated for four weeks. For each storage solution at each time interval, the concentration of ions leached (Na, Mg, Al, Zn and P) were determined using ICP-OES.

The lactate buffer was particularly erosive and reduced specimens to 4.1% (± 0.9%) of their original mass after 4 weeks. The lactic acid was also erosive, but in water, specimens showed no significant mass change after 4 weeks. In all media, Na, Al, Mg, Zn and P ions were released, with mole ratios varying at each time interval. In all cases, the pH shifted towards neutral, but the relationship between ion release and solution pH was not straightforward. From the mole ratios of ions, estimates could be made of the relative proportions of attack at matrix to attack at filler, and this showed attack at filler predominated in most solutions at most time intervals.

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Introduction

Zinc phosphate cement has been used in dentistry for many years and has been widely studied. It consists of a liquid component which is phosphoric acid, typically in the concentration range 45–65% and which contains aluminum (1.0–3.1%) and possibly zinc (up to 10%) [1]. These metal additives have the effect of moderating the rate of reaction between the acid and the base, and they also reduce the heat of reaction. The properties of the set cement, both mechanical and chemical, depend critically on the concentration of H_3PO_4 in the liquid [2]. For this reason the liquid component must be stored carefully and not allowed to gain or lose moisture to the atmosphere.

The other component of the zinc phosphate cement is finely divided zinc oxide powder. This is a special form of zinc oxide which has been deactivated by mixing with magnesium oxide (∼ 10%) followed by being sintered at temperatures between 1000 and 1400 °C. This sintering produces a cake which is reground to a fine powder to use in the cement. The process of heating causes the zinc oxide to become slightly yellow in color and less reactive. This is due to loss of oxygen during firing and the formation of the slightly non-stoichiometric oxide corresponding to $Zn_{(1+x)}O$, where x is up to 70 ppm [3].

For zinc phosphate, there have been numerous previous studies of the setting process and of changes in solubility as setting proceeds. It is known that the initial product formed is a soluble acidic zinc phosphate but that this rapidly undergoes further reaction, resulting in steadily decreasing solubility. This has been attributed to the formation of zinc orthophosphate, $Zn_3(PO_4)_2$ [4], a substance that is insoluble in water. The phases present in the set cement are essentially amorphous and remain amorphous, rather than crytallizing, due to the presence of aluminum in the cement-forming liquid [5]. However, over long periods of time, some material does crystallize, forming the hydrated phase $Zn(H_2PO_4)_2 \cdot 4H_2O$ known as hopeite [6]. Growth of hopeite, which occurs at the surface, is favored by elevated temperatures and high

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humidity, but even in cements retrieved after more than 40 years in the mouth, it has been shown to represent only a small fraction of the total cement mass [6].

The solubility of zinc phosphate cement depends not only on the stage of maturation it has reached, but also on the pH of the external medium. Solubility has been shown to drop rapidly as pH rises from 4.5 to 5.0 then to rise again more slowly as neutral conditions are approached [7].

Zinc phosphate cements have been shown to be capable of influencing the pH of acidic storage solutions [8]. Storing cylindrical specimens in lactic acid at pH 2.7, with weekly replacement, was shown to result in consistent changes in pH to 4.6, and to an erosion of 14.2% after six months [9]. More recently, these cements were shown to be capable of increasing the pH of a sodium lactate/lactic acid buffer solution [10]. This solution also proved to be highly erosive to these cements, more so than lactic acid alone.

The current study was carried out with a view to elucidating aspects of the mechanism of these reported pH changes. The main focus of the study has been to determine the concentration of ions eluted after weekly intervals of storage in aqueous media (deionized water, lactic acid solution at pH 2.7, and sodium lactate/lactic acid buffer at pH 2.2). These determinations enabled conclusions to be drawn about the location of the attack, and were related to the rate of erosion and the change in pH of the storage solution.

Materials and methods

Zinc phosphate cement (''normal set'') (ex. Kent Dental Ltd) was used in this study, and mixed, using a metal spatula and a ceramic mixing tile, at a powder : liquid ratio of 2.1 : 1. Following mixing, fresh pastes were packed into cylindrical molds (6 mm diameter × 12 mm height) and stored at 37 °C for 1 h, before being removed from the mold, weighed and stored at room temperature, either in deionized water (pH 5.9, SD 0.1), 20 mmol dm^{-3} lactic acid solution (pH 2.7, SD 0.2) or lactic acid/sodium lactate buffer (pH 2.2, SD 0.5). Storage volume was 8 cm^3 in each case; and, for each storage medium, five specimens were prepared. After 1 week, the specimens were blotted dry and weighed, then transferred to a fresh 8 cm^3 volume of solution. The pH of the previous solution was determined using a glass electrode (Type CW711, ex. Whatman, UK). This was repeated at weekly intervals up to 4 weeks, and the solutions from each week were bulked, and used for determination of Zn, Na, Al, Mg and P by ICP-OES at a commercial analytical laboratory (Morgan Materials Technology Ltd, Stourport-on-Severn, Worcestershire, UK). In addition, the phosphoric acid solution from which the cements were prepared was diluted by making a 0.5 cm^3 aliquot up to 10.0 cm^3. The concentration of ions in this solution was also determined using ICP-OES.

TABLE I Initial composition of phosphoric acid solution

Element	Concentration in acid/ppm
Na	142
Al	36 000
P	292 600
Zn	182 200
Mg	2

Changes in mass and pH were subjected to statistical analysis by one-way ANOVA followed by Neumann–Keuls test ($p < 0.05$) as tests for significance.

Results

The initial concentrations of ions in the phosphoric acid solution are shown in Table I. This acid solution was the one used to prepare all of the specimens in the study. Mean specimen masses after each week of storage are shown in Table II and in water there was a significant gain in mass during Week 1, but thereafter none of the changes was significant. In lactic acid, the change after each weekly interval was significant ($p < 0.05$), as it was in lactate buffer. Also, in lactate buffer, specimens became covered with a fluffy white deposit on storage, which was presumably the product of degradation of the cement. This was easily removed by wiping with a tissue prior to weighing the specimens.

Table III shows the results for pH determination in each of the storage solutions. In all cases except lactate buffer in Week 4, the changes in pH compared to the initial pH were significant and in all three media, the greatest change in pH occurred in Week 1.

Tables IV–VI show the concentration of ions released in the three storage media at each time interval. In all media, the amount of zinc exceeded that of phosphorus, with the excess of zinc over phosphorus being greatest in Week 1, but declining with increasing storage time.

TABLE II Changes in mass of zinc phosphate cement specimens ($n = 5$; original mass = 100.0%; SD in parentheses (%))

	Week 1	Week 2	Week 3	Week 4
Water (%)	101.0 (0.2)	100.8 (0.2)	100.9 (0.2)	100.9 (0.2)
Lactic acid (%)	100.2 (0.1)	99.5 (0.2)	99.0 (0.2)	98.3 (0.2)
Lactate buffer (%)	76.6 (0.6)	51.8 (0.7)	25.2 (1.4)	4.1 (1.0)

TABLE III Variations in pH with time (SD in parentheses)

Storage medium	Initial pH	Week 1	Week 2	Week 3	Week 4
Water	5.9 (0.3)	7.1 (0.1)	6.6 (0.3)	6.6 (0.1)	6.2 (0.2)
Lactic acid	2.7 (0.2)	5.2 (0.1)	4.6 (0.1)	4.2 (0.1)	3.8 (0.1)
Lactate buffer	2.2 (0.5)	3.7 (0.1)	3.3 (0.1)	3.3 (0.1)	2.1 (0.1)

TABLE IV Ion release (ppm) from zinc phosphate into water (pH 5.9)

Ion	Week 1	Week 2	Week 4	Week 4
Na	2.1	3.6	—	—
Al	0.13	—	—	—
Mg	0.05	8.48	2.85	2.31
Zn	0.76	16.0	2.27	1.53
P	—	0.31	1.39	0.80

TABLE V Ion release (ppm) from zinc phosphate into lactic acid (pH 2.7)

Ion	Week 1	Week 2	Week 4	Week 4
Na	5.0	2.6	1.58	1.28
Al	0.45	—	—	—
Mg	34.8	32.2	30.5	23.1
Zn	403	425	431	439
P	5.27	12.2	15.9	28.2

TABLE VI Ion release (ppm) from zinc phosphate into lactate buffer (pH 2.2)

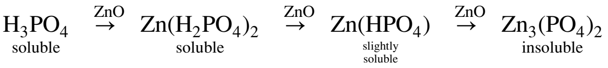
Ion	Week 1	Week 2	Week 4	Week 4
Na	190	10	120	70
Al	587	208	216	181
Mg	857	807	842	729
Zn	14 808	14 980	13 570	11 968
P	1484	1594	1634	1476

Discussion

Results in Table II show that there is measurable dissolution of zinc phosphate cement in all three storage media. The mass changes (Table II) suggest that this is only minimal in deionized water, and more than compensated for by the uptake of water. By contrast, in lactic acid and in lactate buffer, there is considerable loss of mass, so that by Week 4 in lactate buffer the specimens had almost completely eroded away. This shows that lactate buffer is the most aggressive of these three media, and confirms the findings of Nomota and McCabe [10]. That this medium is the most erosive can be attributed, in part, to its character as a buffer solution. Initially, interaction with zinc phosphate cement would not alter pH, so that the rate and extent of attack would continue for some time unaltered. It is only after this has continued to the extent that the pH has begun to rise that the rate of attack moderates. By contrast, for lactic acid solution, the immediate attack of the acid on the cement would lead to an increase in pH, and a corresponding reduction in the rate and extent of attack on the cement.

Ion release showed a similar pattern to the mass loss data, i.e., lactate buffer > lactic acid > water. However, the results for change in pH cannot be correlated with final composition of the storage solutions. For example, in water at Weeks 2 and 3, final values of pH were the same, and the value in Week 4 was similar, yet the ions present in solution differed greatly. At Week 2, there was detectable sodium, and significant concentrations of magnesium (8.48 ppm) and zinc (16.0 ppm), with some phosphorus (0.31 ppm). At Week 3, there was no detectable sodium, concentrations of magnesium and zinc were both well down (2.85 and 2.27 ppm, respectively) and the concentration of phosphorus was higher (1.39 ppm). Despite these variations the pH of both solutions was 6.6.

The results show a much greater release of all ions in water in Week 2 than in Week 1, implying a greater solubility for the cement stored for a week in water. However, the suggested sequence of the setting reaction implies a growing insolubility with time. These reactions have been represented as follows:



$$\underset{\text{soluble}}{H_3PO_4} \xrightarrow{ZnO} \underset{\text{soluble}}{Zn(H_2PO_4)_2} \xrightarrow{ZnO} \underset{\text{slightly soluble}}{Zn(HPO_4)} \xrightarrow{ZnO} \underset{\text{insoluble}}{Zn_3(PO_4)_2}$$

This suggests that relatively young cements still contain at least some of the slightly soluble $Zn(HPO_4)$ salt, but in our experiments this species could not have been present during Week 1, because no soluble phosphorus species was found at this time period. A possible explanation is that exposure of the cement to the slightly acidic water, containing as it does dissolved CO_2, forms zinc and magnesium carbonates by reaction with the filler. These are insoluble in water under neutral conditions, but are reported to be sparingly soluble under acid conditions [11]. In Week 2, exposure to a fresh volume of mildly acidic water (pH 5.9) might cause some of these newly formed carbonates to dissolve slightly, and release the Zn^{2+} and Mg^{2+} ions that were determined experimentally.

Previous studies [1] have shown that the ratio of $Na + Mg + Zn$ to P is approximately 1 : 1 in water, suggesting that the main species dissolving are $Zn(HPO_4)$, with some $Mg(HPO_4)$ and $Na_2(HPO_4)$. However, in our experiments, results suggest that there was more than simple dissolution taking place. The combined amount of sodium, magnesium and zinc eluted in all media, including water, was found to exceed by some way that of phosphorus. The data from Table I show that phosphorus exceed zinc by a factor of approximately 3.3 in the cement-forming liquid. At the very least, therefore, the rest of the zinc must have come from the filler. Consequently it was possible to calculate the proportion of the zinc in solution that had originally been associated with the phosphorus in the liquid, and to subtract this from the total amount of zinc determined experimentally. This calculation gave the amount of zinc originating in the filler, and the ratio of this to the amount of phosphorus could be taken as an estimate of the relative attack at filler to attack at matrix. This is the basis of the data shown in Table VII.

These calculations show that, under all the conditions used in our experiments, there was significant attack at the filler, and that such attack predominated. This is to be expected because (i) there is a high concentration of filler per unit mass of set cement, (ii) it is much more basic than the matrix, and (iii) all storage media used were

TABLE VII Estimate of ratio of attack at filler to attack at matrix

Medium	Week 1	Week 2	Week 4	Week 4
Water	100% filler	25.2 : 1	0.8 : 1	0.6 : 1
Lactic acid	37.3 : 1	17.1 : 1	13.0 : 1	7.4 : 1
Lactate buffer	4.6 : 1	4.3 : 1	3.8 : 1	3.7 : 1

acidic. Even the water employed in our experiments was slightly acidic, a finding which may explain the differences between our results and those of Wilson *et al.* [1], whose water may have been at, or closer to, pH 7.0. However, their results are consistent with simple dissolution of matrix-forming zinc phosphate salts under neutral conditions, so this is a likely explanation for the differences between the two sets of results.

On the other hand, Wilson *et al.* [1] suggest that the final matrix consists mainly of the insoluble compound $Zn_3(PO_4)_2$. Our results for water after 4 weeks cast doubt on this, because there was still a measurable amount of Zn and Mg dissolved after this time. This suggests either that the setting reaction does not proceed quite as far as $Zn_3(PO_4)_2$ or that the final species is the hydrated version, $Zn_3(PO_4)_2 \cdot 4H_2O$, which is known to be slightly soluble under acidic conditions [11]. This latter explanation seems more likely, given that zinc phosphate cement contains a large proportion of water, and this is not lost on setting [12]. The fact that another zinc salt, $Zn(HPO_4)_2$, is known to occur in its hydrated form [6] in these cements supports this interpretation. Our results thus suggest that the final structure of zinc phosphate cements is more complex than previously suggested [1].

In all three media, attack at filler was found to greatest in Week 1, but to decline gradually with time. In water, in Weeks 3 and 4, attack at matrix was slightly greater than attack at filler, but in all other circumstances, attack at filler predominated. The decline in relative importance of attack at filler probably arises as the more accessible filler surfaces are eroded, thus reducing their effective concentration relative to that of matrix. Of the three media, the most aggressive (lactate buffer) showed the least preference for filler, the ratio of attack at filler to attack at matrix being only 4.6 : 1 at Week 1, compared with 100% attack at filler by the mildly acidic water.

There have been no previous studies of the location of attack on zinc phosphate cements, but there have been related studies for both glass-ionomer and zinc polycarboxylate cements [13, 14]. In both cases, it has been shown that attack occurs predominantly at the filler rather than at the matrix. Our results are thus consistent with those for related acid-base dental cements.

Conclusions

The current study enables the following conclusions to be drawn:

1. Interaction of zinc phosphate cements with aqueous solutions involves attack mainly at the filler, but the relative importance of filler and matrix depends on length of exposure to the aqueous medium and on that medium's pH.
2. The change in pH of the storage medium is associated with dissolution, but the relationship between composition of the final solution and pH is complicated, and no simple correlation can be identified.
3. The presence of zinc, magnesium and phosphorus in water at pH 5.9 at all time intervals up to 4 weeks suggests that the set cement does not contain the completely insoluble compound $Zn_3(PO_4)_2$ as has previously been proposed [1], but the hydrated form, which is slightly soluble in mild acids.
4. Of the three storage media employed, lactate buffer proved by the far the most erosive, a result that confirms previous findings of Nomota and McCabe [10].

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