The kinetics of water loss from zinc phosphate and zinc polycarboxylate dental cements

John W. Nicholson · Beata Czarnecka

Abstract The water desorption behaviour of three different zinc oxide dental cements (two polycarboxylates, one phosphate) has been studied in detail. Disc-shaped specimens of each material were prepared and allowed to lose water by being subjected to a low humidity desiccating atmosphere over concentrated sulfuric acid. In all three cements, water loss was found to follow Fick's second law for at least 6 h (until M_t/M_∞ values were around 0.5), with diffusion coefficients ranging from 6.03×10^{-8} cm^2 s^{-1} (for the zinc phosphate) to 2.056×10^{-7} cm^2 s^{-1} (for one of the zinc polycarboxylates, Poly F Plus). Equilibration times for desorption were of the order of 8 weeks, and equilibrium water losses ranged from 7.1% for zinc phosphate to 16.9% and 17.4% for the two zinc polycarboxylates.

1 Introduction

Zinc polycarboxylate and zinc phosphate cements both belong to the class of materials known as acid–base cements [1]. Both are used extensively in dentistry as luting or lining cements. Both are prepared from deactivated zinc oxide powder, though the degree of deactivation varies with the cement, since the acids used, polyacrylic and phosphoric respectively, vary widely in their acid strength

J. W. Nicholson (✉)
Department of Chemical and Pharmaceutical Sciences,
University of Greenwich, Medway Campus, Chatham,
Kent ME4 4TB, UK
e-mail: J.W.Nicholson@gre.ac.uk

B. Czarnecka
Department of Biomaterials and Experimental Dentistry,
University of Medical Sciences, 60-812 Poznan, Poland

[1]. Deactivation is achieved by mixing high purity zinc oxide with up to 10% by mass of magnesium oxide, followed by heating. The heating process drives off small amounts of oxygen, resulting in the formation of a slightly non-stoichiometric oxide that can formulated as $ZnO_{(1-x)}$, where x < 70 ppm [2].

As originally formulated, zinc polycarboxylates were prepared from aqueous poly(acrylic acid) at about 45% by mass [1]. Modern cements consist of both deactivated zinc oxide and dried poly(acrylic acid) as a powder, and are activated by reaction with the appropriate amount of water. When water is added to the cement mixture in this way, it remains entirely within the cement during setting, and there is no phase separation [3]. Having set, these cements can lose large amounts of water without adverse effect on strength, and this shows that the water is labile and has no structural role [4].

Zinc phosphate cements are prepared from aqueous solutions of phosphoric acid, typically at concentrations in the range 45–65%. These solutions are slightly deactivated by the addition of aluminium (1.0–3.1%) and possibly zinc (up to 10%) [5]. The presence of the metals moderates the rate of the setting reaction and also reduce the temperature rise that occurs during setting.

Zinc phosphate cements set to yield a variety of phases in the solid state, most of which are amorphous [1]. For a long time it was assumed that the main reaction product is zinc orthophosphate, $Zn_3(PO_4)_2$ [6], a substance that is completely insoluble in water. However, more recently zinc has been shown to be leached from these cements up to at least 4 weeks after setting [7], suggesting that it is the slightly soluble hydrated form, $Zn_3(PO_4)_2 \cdot 4H_2O$ that is present instead. This is also consistent with the finding that hopeite, $Zn(H_2PO_4)_2 \cdot 4H_2O$, gradually crystallises as specimens of zinc phosphate cement age [8].

Although the state of water in these cements has been the subject of several published studies, to date there has been no information on the kinetics of water transport. Both cements are known to lose a proportion of water on storage under drying conditions, for example over sulfuric acid at room temperature, or at ambient humidity at 105 °C [9]. However, the kinetics of these processes have not been considered and the present study has been carried out to address this oversight.

Conventionally, water transport through solids can be described by Fick's second law of diffusion [10]. For disc-shaped specimens, edges represent a minor part of the sample and so edge effects can be neglected. Water uptake or loss then follows the form of the so-called Stefan approximation as originally developed for infinite plane sheets, i.e.:

$$M_t/M_\infty = 2(Dt/\pi l^2)^{1/2}$$

where M_t is the mass uptake/loss at time t (s), M_∞ is the equilibrium uptake/loss, 2l is the thickness of the specimen and D is the diffusion coefficient [10]. The later stages up to equilibrium are given by:

$$M_t/M_\infty = 1 - (8/\pi^2)\sum 1(2n+1) \times \exp[-\pi^2 D/4l^2(2n+1)t]$$

The diffusion coefficient, D, can be determined by measuring water uptake at convenient time intervals, then plotting M_t/M_∞ against $t^{1/2}$. Where Fick's law is obeyed, this gives a straight line of slope s, where:

$$s = 2(D/\pi l^2)^{1/2}$$

from which

$$D = s^2\ \pi l^2/4$$

.

In the present study, specimens of zinc phosphate and zinc polycarboxylate cement were allowed to lose water under desiccating conditions, with mass being recorded every hour for the first six hours. Specimens were then allowed to equilibrate, after which values of M_t/M_∞ were determined and plotted as Fick's second law of diffusion. By comparison, we have recently shown that this describes precisely the kinetics of water loss from both glass-ionomer dental cements [11] and zinc oxy-chloride cements [12].

2 Materials and methods

Three commercial dental cements were used in this study and mixed according to manufacturer's instructions (see Table 1). Cements were mixed by spatulating them on a glass block to incorporate all of the powder into the liquid. Having mixed the pastes to a homogeneous consistency, they were transferred to silicone rubber moulds held between microscope slides and allowed to harden. The moulds gave circular specimens of diameter 6 mm and depth of 2 mm. Four specimens were prepared per cement and results for mass loss were averaged.

Specimens were allowed to mature for 10 min in the moulds in an incubator at 37 °C, then weighed and transferred to a controlled low humidity environment in a glass desiccator. This atmosphere was that which occurred at equilibrium when concentrated sulfuric acid (Spectrosol®, ex BDH, Poole, approximately 98% H_2SO_4) was present in the base of the desiccator as drying agent. Specimens placed under these conditions were weighed at hourly intervals for the first 6 h, then at weekly intervals until equilibrium was achieved. Plots were then made of M_t/M_∞ against $t^{1/2}$ and using the slope of this graph, s, diffusion coefficients were determined from the equation $D = s^2\ \pi l^2/4$.

Differences in values were examined for statistical significance using the Student's t-test as appropriate.

3 Results

Results for water loss against time are shown in Table 2 for each cement. In each case, these were plotted as M_t/M_∞ against $t^{1/2}$, plots which gave straight lines with the equations shown in Table 3. A representative graph for the zinc polycarboxylate Poly F Plus is shown in Fig. 1. Other data for water loss from the cements are given in Table 4.

4 Discussion

All three cements were found to lose water by a diffusion process, and are thus similar to the related glass-ionomer dental cements. However, glass-ionomers, despite their known high affinity for water [1], showed much higher diffusion coefficients, i.e. between 5×10^{-6} and 13×10^{-6} $cm^2\ s^{-1}$. These values are at least one order of magnitude greater than the diffusion coefficients found for the zinc polycarboxylate and the zinc phosphate cements. Zinc polycarboxylate cements have previously been shown to have a much lower affinity for water than glass-ionomers [4]. They contain comparable amounts of water to glass-ionomers, so it might have been anticipated that they would lose water more easily, i.e. show higher diffusion coefficients. As our data show, this is not the case. Water loss is a slower process than in glass-ionomers, and took approximately 8 weeks to complete.

The equations for the straight lines obtained from the Fick's law plots did not pass through the origin in any case.

Table 1 Details of cements used in this study

Brand	Manufacturer	Type	Mixing ratio
Poly F Plus	Dentsply, Konstanz, Germany	Water-activated zinc polycarboxylate	3.3 g to 1 cm^3 water
Poly Kent	Kent Express, Maidstone, UK	Water-activated zinc polycarboxylate	3.3 g to 1 cm^3 water
Zinc Phosphate	Kent Express, Maidstone, UK	Zinc phosphate	3.6 g to 1 cm^3 acid solution

Table 2 Mass loss (%) from cements with time (standard deviations in parentheses)

Time/hour	Poly F Plus	Poly Kent	Zinc Phosphate
1	4.7 (0.4)	3.1 (0.2)	1.3 (0.1)
2	7.0 (0.4)	4.5 (0.2)	1.7 (0.2)
3	8.8 (0.5)	5.7 (0.1)	2.2 (0.1)
4	10.3 (0.4)	6.5 (0.3)	2.6 (0.1)
5	11.4 (0.4)	7.2 (0.2)	2.7 (0.1)
6	12.4 (0.4)	8.0 (0.3)	3.0 (0.1)
∞	17.4 (0.1)	16.9 (0.1)	7.1 (0.1)

Table 3 Equations for the straight line portion of the graphs of M_t/M_∞ (x) against $t^{1/2}$ (y)

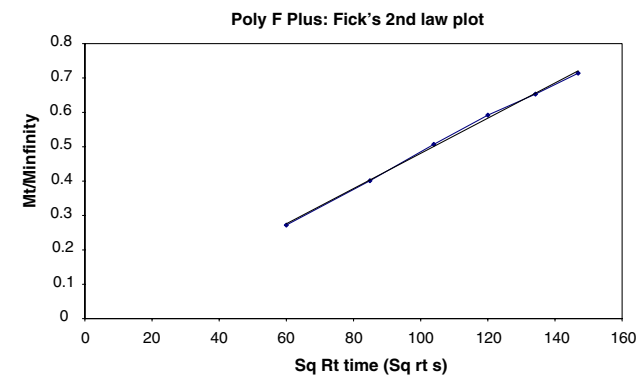| Material	Equation	r value
Poly F Plus	y = 0.00511x − 0.0031	0.999
Poly Kent	y = 0.00319x − 0.0097	0.999
Zinc Phosphate	y = 0.00277x + 0.0166	0.995

Fig. 1 Graph of M_t/M_∞ against $t^{1/2}$ for the zinc polycarboxylate cement Poly F Plus

However, they missed doing so by only negligible amounts. For example, for the zinc polycarboxylate Poly Kent, the line passed through the M_t/M_∞ axis at $t^{1/2} = 0$ at 0.0097 which corresponds to only 0.16% by mass. This is in contrast with the behaviour of glass-ionomers, where the M_t/M_∞ against $t^{1/2}$ plot missed passing through the origin by considerable margins, in one case corresponding to 3.5% by mass of the specimen [11]. These values were sufficient to suggest that glass-ionomers contained a reasonable though minor fraction of what was termed *superficial water*. This represented around 1% of the specimen mass for restorative grade materials, and up to 3.5% for lining grades. This water was assumed to occur in the surface layers, and to be so readily lost that no diffusion process was necessary prior to its escape. It may be that zinc polycaboxylates also contain *superficial water* thus defined, but in lower amounts.

The equation for the zinc phosphate cement deviated in the opposite direction to those for the zinc polycarboxylates. In this case, it may be that there is a slight time lag before diffusion per se is able to commence. This lag may arise from the fact that water is slowly changing its state within the cement, for example by hydrating the various possible zinc phosphate reaction products. Diffusion appears to have become reasonably well established by 1 h, and it continued thereafter for the remaining few hours of the experiment.

5 Conclusions

In desiccating conditions, all three cements lost water, and the process followed Fick's second law for a considerable time, generally well above M_t/M_∞ values of 0.5. Diffusion coefficients varied from 2.056×10^{-7} (Poly F plus) to 6.03×10^{-8} (Zinc Phosphate), values which are significantly lower than those observed previously for glass-

Table 4 Equilibrium mass loss, equilibration times and diffusion coefficients for cements in desiccating conditions

Composition	Equilibrium mass loss (%) [Standard deviations]	Equilibration time/weeks	Diffusion coefficient/cm^2 s^{-1}
Poly F Plus	17.4 [0.1]	8	2.056×10^{-7}
Poly Kent	16.9 [0.1]	8	7.98×10^{-8}
Zinc Phosphate	7.1 [0.1]	8	6.03×10^{-8}

ionomer dental cements [11] but similar to those observed for zinc oxy-chloride cements [12]. Neither of the zinc polycarboxylates showed much evidence of "superficial water", i.e. water in very thin surface layers that can be lost without appreciable diffusion, though such a water fraction has recently been observed in glass-ionomer cements [11].

Equilibration under desiccating conditions took 8 weeks for each of the cements. Equilibrium water losses were respectively 17.4% (Poly F Plus), 16.9% (Poly Kent) and 7.1% (Zinc Phosphate) and all differences were statistically significant.

References

1. A. D. WILSON and J. W. NICHOLSON, "Acid-base cements" (The University Press, Cambridge, 1993)
2. N. N. GREENWOOD and A. EARNSHAW, "The chemistry of the elements" (Pergamon Press, Oxford, 1984)
3. J. W. NICHOLSON and A. D. WILSON, *J. Mater. Sci. Mater. Med.* **11** (2000) 357
4. J. W. NICHOLSON, E. A. WASSON and S. HAWKINS, *J. Mater. Sci. Mater. Med.* **4** (1993) 32
5. A. D. WILSON, B. E. KENT and B. G. LEWIS, *J. Dent. Res.* **49** (1970) 1049
6. A. D. WILSON, G. ABEL and B. G. LEWIS, *Br. Dent. J.* **137** (1974) 313
7. B. CZARNECKA, H. LIMANOWSKA-SHAW and J. W. NICHOLSON, *J. Mater. Sci. Mater. Med.* **14** (2003) 601
8. J. MARGARET, B. CLUZEL, J. M. LEHOUP, J. NURIT, B. PAUVERT and A. TEROL, *J. Mater. Sci. Mater. Med.* **7** (1996) 623
9. S. CRISP, B. G. LEWIS and A. D. WILSON, *J. Dent.* **8** (1980) 68
10. J. A. BARRIE, in "Water in polymers", edited by J. CRANK and G. S. PARK, (Academic Press, New York, 1969) p. 259
11. J. W. NICHOLSON and B. CZARNECKA, *J. Mater. Sci. Mater. Med.* (in press)
12. J. W. NICHOLSON, *Ceram. Silikaty.* **51** (2007) 69