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# Kinetic studies of water uptake and loss in glass-ionomer cements

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**Abstract** The water sorption and desorption behaviour of three commercial glass-ionomer cements used in clinical dentistry have been studied in detail. Cured specimens of each material were found to show slight but variable water uptake in high humidity conditions, but steady loss in desiccating ones. This water loss was found to follow Fick's law for the first 4–5 h. Diffusion coefficients at 22 °C were: Chemflex $1.34 \times 10^{-6}$ cm$^2$ s$^{-1}$, Fuji IX $5.87 \times 10^{-7}$ cm$^2$ s$^{-1}$, Aquacem $3.08 \times 10^{-6}$ cm$^2$ s$^{-1}$. At 7 °C they were: Chemflex $8.90 \times 10^{-7}$ cm$^2$ s$^{-1}$, Fuji IX $5.04 \times 10^{-7}$ cm$^2$ s$^{-1}$, Aquacem $2.88 \times 10^{-6}$ cm$^2$ s$^{-1}$. Activation energies for water loss were determined from the Arrhenius equation and were found to be Chemflex 161.8 J mol$^{-1}$, Fuji IX 101.3 J mol$^{-1}$, Aquacem 47.1 J mol$^{-1}$. Such low values show that water transport requires less energy in these cements than in resin-modified glass-ionomers. Fick's law plots were found not to pass through the origin. This implies that, in each case, there is a small water loss that does not involve diffusion. This was concluded to be water at the surface of the specimens, and was termed "superficial water". As such, it represents a fraction of the previously identified unbound (loose) water. Superficial water levels were: Chemflex 0.56%, Fuji IX 0.23%, Aquacem 0.87%. Equilibrium mass loss values were shown to be unaffected by temperature, and allowed ratios of bound:unbound water to be determined for all three cements. These showed wide variation, ranging from 1:5.26 for Chemflex to 1:1.25 for Fuji IX.

## 1 Introduction

Glass-ionomer cements are widely used in clinical dentistry as repair materials [1]. They are water-based materials that consist of a special ion-leachable glass and a water-soluble polymeric acid, such as poly(acrylic acid) or acrylic acid/maleic acid copolymer [1–3].

Water occurs in glass-ionomer cements in at least two different states, classified as "loosely bound" and "tightly bound" respectively [1, 4]. This distinction is based on whether or not the water can be removed from the cement by vacuum desiccation over silica gel, or by heating at 105 °C [4]. These treatments typically remove some 18–28% of the total cement mass [5], which is considered to be the loosely bound water, and to leave behind an amount of water corresponding to about 5% by mass, the tightly bound water. The amount of tightly bound water indicates that there are 5–6 molecules of water for each neutralized acid group in the cement [2]. As cements age, the ratio of tightly bound to loosely bound water increases [6], a phenomenon that is generally accompanied by increases in strength and modulus of the cement.

To date, studies of water content have been essentially carried out under equilibrium conditions. Specimens have been allowed to equilibrate, either under vacuum or at 105 °C, and the water loss determined. No kinetic studies have been reported. The current study has been undertaken in order to rectify this situation and to gain information about the movement of water in these materials. Two

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circumstances have been considered, namely (a) water uptake in high humidity conditions, and (b) water loss in desiccating conditions over concentrated sulphuric acid.

Water sorption and desorption have been widely studied in polymeric materials used [7], including those used in dentistry. Composite resins [8, 9], soft lining [10] and poly(methyl methacrylate) denture bases [11] have all been shown to absorb and desorb water. At the early stages, this water transport follows Fick's law of diffusion. For disc-shaped specimens, edge effects can be neglected, and sorption/desorption follows the form of the so-called Stefan approximation, i.e.: $M_t/M_\infty = 2(Dt/\pi l^2)^{1/2}$ where $M_t$ is the mass uptake at time t (s), $M_\infty$ is the equilibrium uptake, 2l is the thickness of the specimen and D is the diffusion coefficient [7]. The later stages up to equilibrium are given by:

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

The diffusion coefficient, D, can be determined by measuring water uptake or loss at convenient time intervals, then plotting $M_t/M_\infty$ against t½. If Fick's law is obeyed, this gives a straight line of slope *s*, where:

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

from which $D = s^2 \pi l^2/4$.

Typically, sorption studies have been carried out with specimens immersed in pure water, but in the present study, specimens were stored in controlled humidity environments in order to prevent the loss of cement-forming ions. This approach has previously been used by Hornsby [12], in the work in which he demonstrated that glass-ionomers are dimensionally stable at relative humidities of 80% and above. For desorption, kinetics were studied at both room temperature (22 °C) and at the temperature of the refrigerator (7 °C), in order to allow the activation energy for water loss to be determined.

## 2 Materials and methods

The following materials were used:

Aquacem luting/lining cement (ex. Dentsply, Konstanz, Germany, a water activated material used at a powder:liquid ratio of 3.3:1 with deionised water);
Fuji IX Fast (ex. GC, Japan, a restorative grade material used at a powder:liquid ratio of 3.6:1 of polyacrylic acid supplied by the manufacturer);
Chemflex (ex. Dentsply, Konstanz, Germany, a restorative grade material used at a powder:liquid ratio of 3.8:1 using polyacid solution supplied by the manufacturer).

For each material disc-shaped specimens of dimensions 6 mm diameter × 2 mm depth were prepared by placing freshly mixed glass-ionomer pastes in silicone rubber moulds of the appropriate dimensions, then compressing them between glass microscope slides. They were allowed to cure for 10 min in an incubator set at 37 °C, then removed from the moulds, weighed and exposed to the storage environment. Four specimens were prepared for each material, and all were used in the determinations of weight loss. Each point thus represents the mean of four readings.

Specimens were stored in a sealed chamber over either saturated sodium sulphate solution, a medium that gives 93% relative humidity at 22 °C [13] or concentrated sulphuric acid (Spectrosol®, ex BDH, Poole, approximately 98% $H_2SO_4$), a medium that gives a desiccating atmosphere. They were weighed at hourly intervals for the first 6 h, daily for up to 5 days, then weekly thereafter until equilibrium was achieved. For sulphuric acid, a second set of experiments were also conducted with the specimens stored in the desiccator at 7 °C in the refrigerator.

Data were plotted as $M_t/M_\infty$ against $t^{1/2}$, as required for Fick's law. Slopes of the straight line portions of the graphs were determined by least squares regression, and the results used to calculate diffusion coefficients. Mean equilibrium mass changes were determined, and the statistical significance of differences between results estimated using Student's *t*-test. In addition, activation energy values for water loss were determined from the diffusion constants at 22 and 7 °C by substituting into the Arrhenius equation:

$$\ln(D_1/D_2) = R\,E_{act}(1/T_1 - 1/T_2),$$

where R is the gas constant (8.314 J $K^{-1}$ $mol^{-1}$) and $E_{act}$ is the activation energy.

## 3 Results

Mass gains were highly variable in all three materials, and were typically no more than 0.0002 g/h for the first 5 h or so. Certain individual specimens showed losses of similar amounts in successive hourly measurements, suggesting that the measurement of such small mass changes was unreliable. It was therefore decided to concentrate on determining mass loss under desiccating conditions.

Figures 1–3 shows mass loss data with time for all three cements. This is replotted in Figs. 4–6 in terms of $M_t/M_\infty$ against $t^{1/2}$, as required for Fick's law. These plots show the linear region of the plots, as occur for $M_t/M_\infty$ values below 0.5.

The equations for $M_t/M_\infty$ against $t^{1/2}$ for each material at room temperature (22 °C) derived from the data plotted in Figs. 4–6 are shown in Table 1. The equations in Table 1

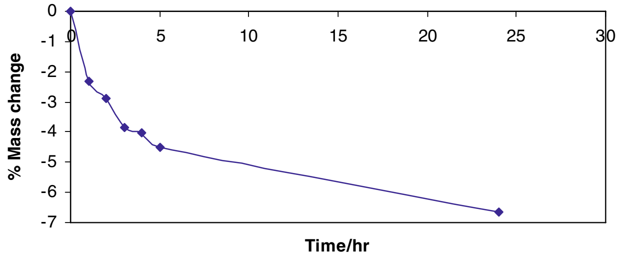

**Fig. 1** % Mass loss versus time for Chemflex

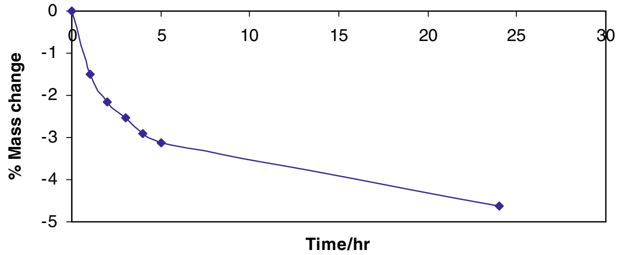

**Fig. 2** % Mass loss versus time for Fuji IX

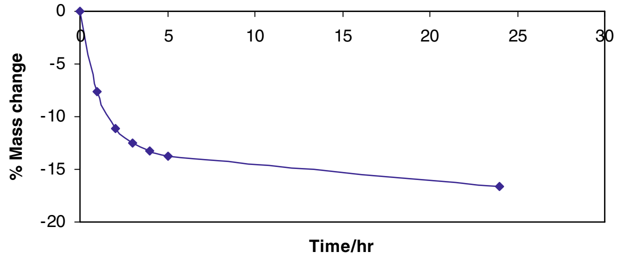

**Fig. 3** % Mass loss versus time for Aquacem

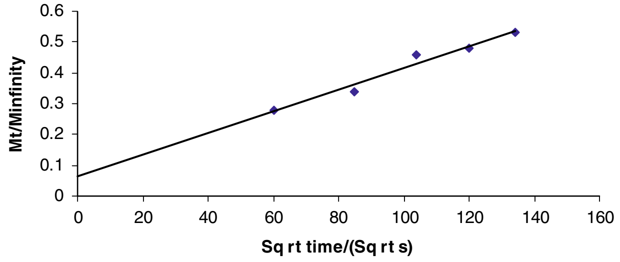

**Fig. 4** $M_t/M_\infty$ versus square root of time at 22 °C for Chemflex

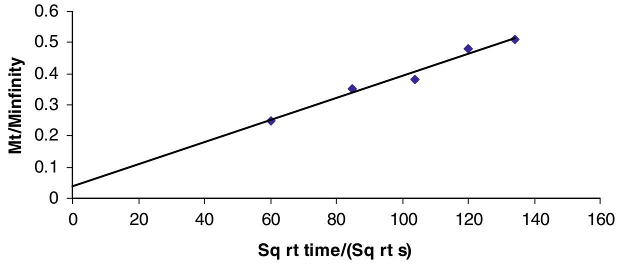

**Fig. 5** $M_t/M_\infty$ versus square root of time at 22 °C for Fuhi IX

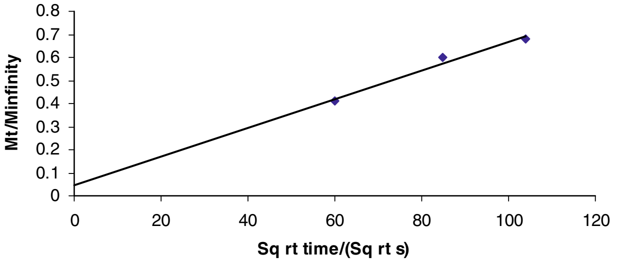

**Fig. 6** $M_t/M_\infty$ versus square root of time at 22 °C for Aquacem

**Table 1** Equations of lines for $M_t/M_\infty$ versus square root of time at room temperature, 22 °C

| Cement | Equation | Computed fraction of "superficial water" (%) |
|---|---|---|
| Chemflex | $y = 3.5 \times 10^{-3}x + 0.066$ | 0.56 |
| Fuji IX | $y = 3.5 \times 10^{-3}x + 0.038$ | 0.23 |
| Aquacem | $y = 6.2 \times 10^{-3}x + 0.047$ | 0.87 |

**Table 2** Equilibrium mass losses (%) (Standard deviations in parentheses)

| | 22 °C | 7 °C |
|---|---|---|
| Chemflex | 8.30 (0.28) | 8.32 (0.14) |
| Fuji IX | 6.03 (0.39) | 5.43 (0.17) |
| Aquacem | 18.25 (0.21) | 19.29 (0.61) |

**Table 3** Bound:unbound water values in cements (%)

| Cement | Unbound water | Estimated total | Bound water | Ratio of bound: unbound water |
|---|---|---|---|---|
| Chemflex | 8.31 | 9.89 | 1.58 | 1:5.26 |
| Fuji IX | 5.73 | 10.33 | 4.60 | 1:1.25 |
| Aquacem | 18.77 | 23.25 | 4.48 | 1:4.19 |

refer to the linear portion of the graph only. In all three cases, this line does not pass through the origin. Values for equilibrium mass loss are shown in Table 2 for all three materials at room temperature (22 °C) and refrigerator temperature (7 °C). In all three cases, the differences at the two temperatures were not statistically significant.

Table 3 shows calculated ratios of bound:unbound water. For both Chemflex and Fuji IX, these were calculated with the assumption that the concentration of polymeric acid in the solution was 47.5%, a value that is known to be typical for proprietary glass-ionomers [1]. Knowing the powder:liquid ratio enabled the initial water content to be calculated. The difference between this value and the equilibrium water loss was taken to be the "bound water" value. By definition, the measured water loss was taken as the "unbound water".

**Table 4** Data for water loss from cements

| | Diffusion coefficients (cm $s^{-1}$) at: | | Activation energies |
|---|---|---|---|
| | 22 °C | 7 °C(J $mol^{-1}$) | |
| Chemflex | $1.34 \times 10^{-6}$ | $8.90 \times 10^{-7}$ | 161.8 |
| Fuji IX | $5.87 \times 10^{-7}$ | $5.04 \times 10^{-7}$ | 101.3 |
| Aquacem | $3.08 \times 10^{-6}$ | $2.88 \times 10^{-6}$ | 47.1 |

Diffusion coefficients were determined from the linear portion of the graphs shown in Figs. 4–6 taking the slope and substituting into the equation $D = s^2 \cdot \pi l^2/4$. These are listed in Table 4. Similar plots, though of lower slopes, were found for specimens stored at 7 °C, though these are not shown. The linear relationship between $M_t/M_\infty$ against $t^{½}$ was found to last for the first 5 h at 22 °C and the first 4 h at 7 °C for all three cements.

Finally, the activation energy for water loss in each material is shown in Table 4. As described above, these values were determined using the Arrhenius equation, and taking the diffusion coefficients as measures of the kinetics of water loss.

## 4 Discussion

Glass-ionomers are known to be water-sensitive and especially to be susceptible to loss of water before they are fully matured [1]. For this reason, the recommended clinical procedure is to protect them with varnish to prevent loss of water and the associated chalky appearance that develops on drying [1]. Despite this well known feature of these materials, there have been no previous reports of the kinetics of the water loss process.

The present study has shown that in the three representative materials, water loss occurs by a diffusion-based mechanism, at least in the early stages (i.e. the first 4–5 h). Diffusion coefficients were found to be of the same order of magnitude as for water uptake in resin-modified glass-ionomers [14] (see Table 4), even though the processes and driving forces are different. Previous studies have distinguished at least two types of water in glass-ionomers, so called “bound” and “unbound”. In all three materials studied in the present work, graphs of $M_t/M_\infty$ against square root of time were found to be linear in their early stages but not to pass through the origin. In other words, there was a small fraction of water found whose loss requires no diffusion. It can be assumed that this occurs in the outermost surface layers of the cement, and may be termed “superficial”. The amount can be calculated from the intercept (i.e. $M_t/M_\infty$ at $t = 0$) and the value of the equilibrium water loss (i.e. $M_\infty$). The amount of this superficial water was found to vary from 0.56% in Chemflex to 0.87% inAquacem.

The amounts of bound and unbound water were estimated from the data obtained, and had similarities with values reported previously [5] in that bound water was found to be much less than unbound. However, levels of bound water were lower than the 5% or so that have previously been reported, albeit not much lower in the cases of Fuji IX and Aquacem.

Water loss was shown to be a facile process, partly by the ease with which the superficial fraction of the unbound water was lost, and partly from the very low activation energies for water loss determined for each cement. Previous studies have shown that the activation energy for water uptake in resin-modified glass-ionomers is in the range 4–30 kJ $mol^{-1}$ depending on the material and the aqueous medium from which the water was taken up. Water uptake might be expected to require a greater driving force than water loss, but even so, the extremely low values determined for water loss from glass-ionomer cements are striking. It suggests that any barriers to water loss are negligible in these cements, a result which reflects the fact that water is abundant in them, and has no hydrophobic domains to move through. This contrasts with the situation in other dental materials for which diffusion coefficients have been determined, which typically are substantially hydrophobic, and which typically show much higher activation energies.

The process of water loss took approximately 1 week to occur in full (i.e. this was the time at which the specimen masses equilibrated). During this time, maturation processes would also be occurring, one feature of which is an increase in the proportion of bound water [6]. Given this, it was notable that equilibrium values of water loss were found not to vary significantly at 22 and 7 °C. Thus, although the rate of water loss at the lower temperature was found to be lower than at room temperature, this did not permit any additional binding of water in the maturation reaction(s). At both temperatures, therefore, it can be concluded that there was sufficient water to allow maturation to occur to its own equilibrium state.

This work has demonstrated the ease of water loss by glass-ionomers, and confirmed the clinical observation that these materials require protection against drying out during their setting and hardening phases in vivo.

## 5 Conclusions

Loss of water from glass-ionomer cements has been shown to be a diffusion process and to follow Fick’s law for the first 4–5 h. Diffusion coefficients were of the same order of magnitude as those previously determined for resin-modified glass-ionomers, but showed only slight variation with temperature. This allowed activation energies for water loss to be determined, using the Arrhenius equation, and values were found to be of the order of 50–150 J $mol^{-1}$. These values were significantly lower than for water uptake by resin-modified glass-ionomers, the only other relevant system for which data are available.

Not all loss was diffusion based however, but in all three cements, there was a small loss that appeared to be non-diffusive. It was assumed to arise from loss from the surface water from the specimens and was termed “superficial water”.

Equilibrium loss values were not affected by temperature, suggesting that there was sufficient water in all cases to allow the maturation reactions to proceed in full.

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