

THE INFLUENCE OF ALKALI METAL CHLORIDES ON THE LOSS OF WATER FROM GLASS-IONOMER DENTAL CEMENTS

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The water loss behaviour of a clinical glass-ionomer dental cement has been studied with and without the addition of alkali metal chlorides. Dehydrating conditions were provided by placing specimens in a desiccator over concentrated sulphuric acid. Cements were prepared using either pure water or an aqueous solution of metal chloride (LiCl, NaCl, KCl) at 1.0 mol/dm³. In addition, NaCl at 0.5 mol/dm³ was also used to fabricate cements. Disc-shaped specimens of size 6 mm diameter × 2 mm thickness were made, six per formulation, and cured at 37°C for 1 hour. They were then exposed to desiccating conditions, and the mass measured at regular intervals. All formulations were found to lose water in a diffusion process that equilibrated after approximately 3 weeks. Diffusion coefficients ranged from 2.27 (0.13) × 10⁹ with no additive to 1.85 (0.07) × 10⁹ m²/s with 1.0 mol/dm³ KCl. For the salts, diffusion coefficients decreased in the order LiCl > NaCl > KCl. There was no statistically significant difference between the diffusion coefficients for 1.0 and 0.5 mol/dm³ NaCl. For all salts at 1.0 mol/dm³ and also additive-free cements, equilibrium losses were, with statistical limits, the same, ranging from 6.23 to 6.34 %. On the other hand, 0.5 mol/dm³ NaCl lost significantly more water, 7.05 %.

INTRODUCTION

Glass-ionomer cements are widely used in dentistry in order to repair teeth following dental decay [1]. They may be used as liners and bases and as full restorations. They are tooth-coloured, and inherently adhesive to the tissues of the tooth; they also release clinically useful amounts of fluoride [1].

Glass-ionomers are made by reaction of an aqueous solution of polymeric acid (usually polyacrylic acid) with a special ion-leachable glass [1, 2]. Setting occurs by a neutralization reaction, and involves the poly-acid molecules becoming cross-linked with multi-valent ions (Ca²⁺, Sr²⁺, Al³⁺) which are leached from the glass. The glasses are complex, and often contain two-phases, either completely or partially separated [3]. Reaction is consequently complicated, and involves not only the formation of ionic crosslinks between the polymer molecules, but also hydration processes that reduce the mobility of the water within the cement, and formation of an ion-depleted silica gel [4]. There is also evidence of some sort of inorganic network formation, possibly involving either silicate or phosphate moieties displaced from the glass [5, 6].

Whatever the details of the setting reactions, they tend to take place fairly rapidly, typically in about 5 minutes [2]. Some subsequent reactions continue slowly after the initial hardening phase, and may be termed "maturation". These maturation processes are generally accompanied by gradual increases in translucency and

compressive strength and take place over several weeks following the initial setting [7]. The final product is a material that resembles porcelain in its appearance and mechanical properties [8].

Among the many studies that have been carried out on the chemistry of glass-ionomers has been the effect of adding alkali metal salts. These are known to shield the functional groups of acidic polyelectrolytes and to alter their conformation [9]. When added to glass-ionomer cements, these salts have been shown to affect the rate of the setting reactions, and reduce the compressive strength of the set cement [10].

Because of their high affinity for water, it is likely that these additives would alter the rate of water transport through glass-ionomer cements. However, there have been no reports of this to date in the literature. The present study was undertaken to address this point, and in particular to determine what effect the salts LiCl, NaCl and KCl had on the rate of water loss in a clinical glass-ionomer cement.

EXPERIMENTAL

All experiments were carried out using AquaCem, a water-activated glass-ionomer liner/base cement (ex Dentsply, Germany). That means all of the reactive components (basic glass and acidic polymer) were presented in a single pre-mixed powder, and reaction was brought about by the addition of an appropriate

amount of water. The cement was prepared according to manufacturer's instructions, *ie* at powder:liquid ratios of 3.6:1, with mixing of powder and liquid on a glass block with a metal spatula being undertaken for 1.5-2 minutes until mixing was complete. Cements were prepared with deionised water, or with aqueous solutions of LiCl, NaCl or KCl (concentration 1.0 mol/dm³, GPR ex BDH Poole, UK). For NaCl, an additional set of cements was prepared using a concentration of 0.5 mol/dm³.

Freshly mixed cements 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 60 minutes, before being weighed then exposed in sets of four to a desiccating atmosphere over concentrated sulfuric acid in a sealed vessel. During exposure to this desiccating atmosphere, they were weighed at time intervals of 1, 2, 3, 4 and 5 hours, then at 24 hours and weekly until their weight had equilibrated (which generally took 3 weeks). Mass loss data were plotted as a $\sqrt{\text{time}}$ graph, *ie* M_t/M_∞ vs. $\sqrt{\text{time}}$, as required for Fick's 2nd law [11], to determine whether release followed a diffusion mechanism.

Means and standard deviations for equilibrium mass loss were determined, and data were subjected to statistical analysis by the Student-Neumann-Keuls test where appropriate. Best fit slopes of all graphs were determined by least squares regression.

RESULTS

All cement specimens lost mass steadily over time and equilibrated at approximately 3 weeks. Typical mass loss data for a representative sample of cement (with 1.0 mol/dm³ NaCl as the mixing liquid) are shown in Figure 1, and plots of water loss as graphs of M_t/M_∞ vs. $\sqrt{\text{time}}$ for all cements are shown in Figures 2-5. The latter can be seen to give straight lines, indicating that the loss followed Fick's 2nd law, and thus can be seen to occur by diffusion.

All mass loss experiments showed similar behaviour, with the line passing more or less through the origin in all cases. This demonstrates that there was no significant induction period in the onset of water loss, unlike what has been observed in other acid-base cements, namely the zinc oxychlorides [12]. Table 1 shows equilibrium water losses for all of the samples, and also the diffusion

coefficients. These were determined from the so-called Stephan approximation, *ie* that diffusion can be represented as:

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

where t = time/s and $2l$ = thickness of sample (m).

When Fick's 2nd law is obeyed, the slope of M_t/M_∞ vs. $\sqrt{\text{time}}$ (s), can be used to calculate the diffusion coefficient, D , from the equation:

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

This was the basis of the calculation of the values shown in Table 1. In the presence of both NaCl and KCl, values of diffusion were significantly different (probability, $p < 0.01$) from those for the cement alone, whereas for LiCl, the difference was not statistically significant. Changing the concentration of NaCl had no effect on the diffusion coefficient, but raised the net water loss by an amount that was significant ($p < 0.001$).

DISCUSSION

Results show that including alkali metal chlorides as additives leads to differences in diffusion coefficients. Generally, however, equilibrium water losses were not significantly different from each other. Of the latter values, the only exception was for the use of 0.5 mol/dm³ NaCl, where the equilibrium water loss was significantly greater than from all the other cement ($p < 0.001$).

For the diffusion coefficients, the differences between 0.5 and 1.0 mol/dm³ NaCl were not significant. There was a trend of gradually decreasing diffusion

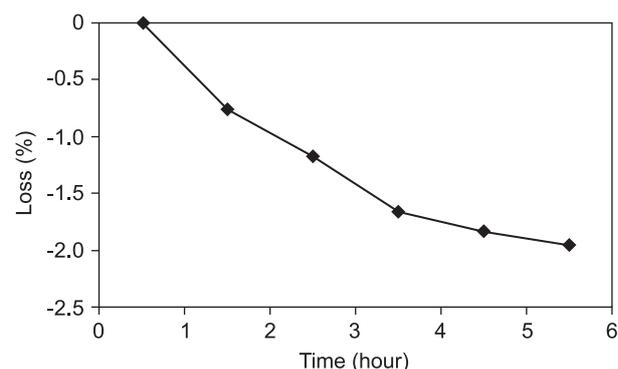


Figure 1. Graph of mass loss against time for cement prepared with 1.0 mol/dm³ NaCl.

Table 1. Equilibrium water loss and diffusion coefficients for glass-ionomer (AquaCem) with and without alkali metal chlorides (standard deviations in parentheses).

Additive	Concentration (mol/dm ³)	Equilibrium water loss (%)	Diffusion coefficient (m ² /s)
None	-	6.34 (0.24)	2.27 (0.13) × 10 ⁹
LiCl	1.0	6.28 (0.25)	2.15 (0.07) × 10 ⁹
NaCl	1.0	6.28 (0.18)	1.91 (0.12) × 10 ⁹
NaCl	0.5	7.05 (0.34)	1.94 (0.28) × 10 ⁹
KCl	1.0	6.23 (0.16)	1.85 (0.08) × 10 ⁹

coefficient from no additive, then down the alkali metal group from lithium to potassium. The difference between no additive and 1.0 mol/dm³ LiCl was not significant; neither was the difference between NaCl and KCl. Nonetheless, the trend going down the group remained.

There has been a previous study on the effects of salts, including NaCl and KCl, on the properties of the glass-ionomer cement AquaCem [10]. Both salts were found to extend the working time as determined by oscillating rheometry. For the additive-free cement, the working time at room temperature (approximately 22°C) was 12.4 minutes. This was lengthened to 15.6 and 17.8 minutes in the presence of NaCl and KCl respectively.

Both salts were found to cause reductions in compressive strength. Additive-free AquaCem had a reported compressive strength of 94.3 MPa, compared with 59.8 and 65.8 MPa for NaCl and KCl respectively. These values are significantly different from that of the additive-free cement ($p < 0.001$) and from each other ($p < 0.05$).

These earlier findings show that alkali metal halides have a distinct effect on the nature of the set cement. This is related to their effects on polyelectrolytes in solution. They are known to screen electrostatic interactions and this favours conformations with high charge density. This typically means a helical conformation with increased ionization [13]. Such behaviour has been shown for

both NaCl [14] and NaBr [15], though for the so-called *abundant salt* condition, ie where the salt is at least equal to the concentration of carboxylic acid groups on the polymer [9]. Similar behaviour has been attributed to other salts, including KCl [10].

One effect of this increased stabilisation of ionized conformations is that the *pH* of the polyelectrolyte solution is reduced [16]. For glass-ionomer cement, this has important effects. Their hardening has been attributed to a combination of both neutralization of the polyelectrolyte molecules and development of an inorganic network from the anions released by the glass [5, 6]. The balance between these is likely to be altered by the enhanced acidity of the salt-stabilised polyelectrolyte.

In the case of compressive strength, KCl appears to create a cement with a structure more similar to the pure material than does NaCl. Studies with other salts suggest that those containing the largest ions, eg KI, have the least effect [10]. However, results for diffusion have not been found to follow this pattern. Rather, the largest ion (K⁺) has been found to be associated with the lowest diffusion coefficient, one that is much smaller than that associated with the smallest ion (Li⁺). These ions are known to show differences in hydration behaviour.

When ions dissolve, individual water molecules become associated with them. Various techniques

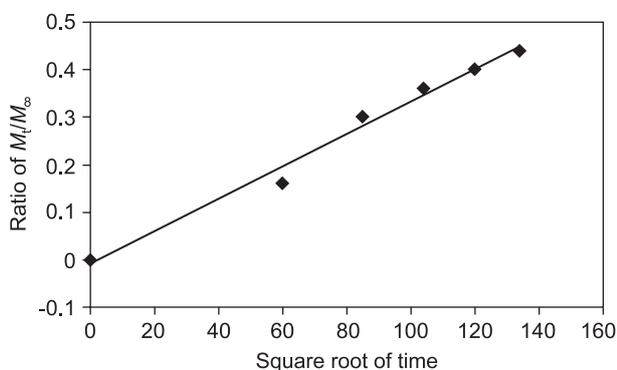


Figure 2. Graph of M_t/M_∞ vs. \sqrt{time} for cement with no additive.

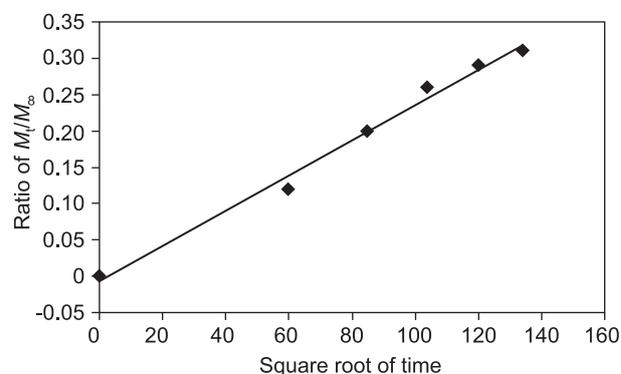


Figure 4. Graph of M_t/M_∞ vs \sqrt{time} for cement with 1.0 mol//dm³ NaCl.

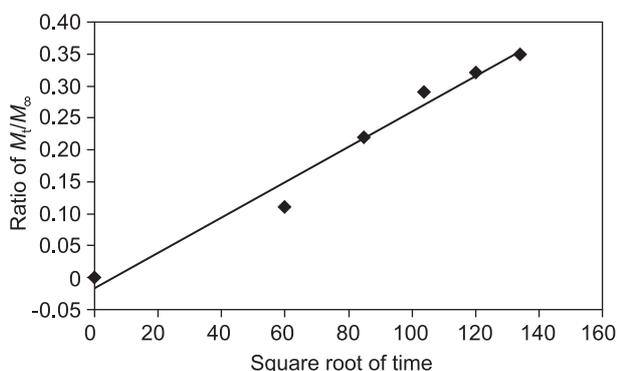


Figure 3. Graph of M_t/M_∞ vs. \sqrt{time} for cement with 1.0 mol//dm³ LiCl.

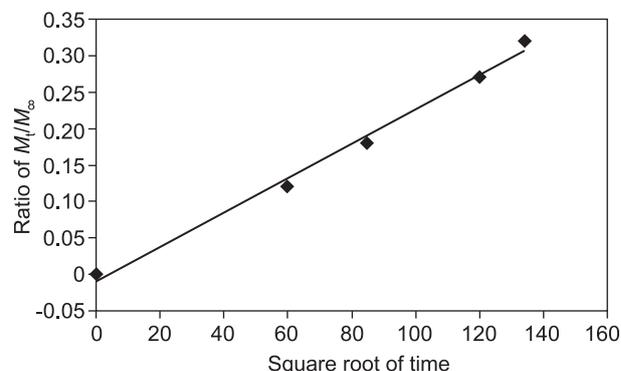


Figure 5. Graph of M_t/M_∞ vs \sqrt{time} for cement with 1.0 mol//dm³ KCl.

have been used to study this phenomenon, including transport number determination [17], compressibility [17], mass spectroscopy [18] and neutron scattering [19]. The hydration number assigned varies with the technique used, because the techniques involve different time scales, and water molecules tend to associate with specific ions over varying amounts of time. Nonetheless, all techniques agree on the general trend that ions of smaller size tend to bind more water molecules. For example, transport number determination has indicated the following hydration numbers: Li^+ 13-22, Na^+ 7-13, K^+ 4-6 [20].

On the basis of these results, the binding of water to the additive ions would be greatest for Li^+ and least to K^+ . However, it is potassium chloride rather than lithium chloride that shows the lowest diffusion coefficient. This suggests that the variations in diffusion behaviour are not controlled by binding of water by the additive cations, but to more complicated effects. These may be related to the initial *pH* of the cement, when polyacrylic acid is dissolved in water with or without different alkali metal chlorides. This in turn would influence resulting crosslink density and overall permeability of the set cement.

CONCLUSIONS

Inclusion of metal chlorides in a glass-ionomer dental cement has been shown to reduce diffusion coefficients. Adding the salts LiCl , NaCl and KCl at 1 mol/dm^3 concentration gave steadily decreasing diffusion coefficients, all of which were lower than for the additive-free cement. This trend is the opposite of that expected if binding of water molecules by cations was the most significant effect. Hence, it is concluded that such water binding makes little or no difference to diffusion behaviour. Instead, it is concluded that diffusion is more strongly influenced by differences in the set cement (crosslink density, permeability) that arise from the effect of the individual additives on the detailed setting processes of the cement.

Unlike diffusion coefficients, equilibrium water loss was unaffected by the presence of additives at 1 mol/dm^3 concentration. However, inclusion of NaCl at 0.5 mol/dm^3 led to a significantly greater loss of water

at equilibrium. Further work is required in order to understand this result and allow a full explanation for all aspects of the behaviour of ionic additives in these cements.

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