

# THE EFFECT OF IONIC SOLUTIONS ON THE UPTAKE AND WATER-BINDING BEHAVIOUR OF GLASS-IONOMER DENTAL CEMENTS

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*Water uptake in two glass-ionomer cements stored in various aqueous ionic solutions has been studied following a 6-week storage period, and the bound/unbound water ratio has been determined. Both types of cement took up water with net uptake varying with the storage solution. Uptake was greatest with KCl and lowest for 0.9 % NaCl. By comparison with an immature (1 hour old) specimen of each cement, specimens generally showed a distinct increase in bound/unbound water at 6 weeks, though for specimens stored in 0.9 % NaCl, there was an apparent reduction in this ratio, which is attributed to greater dissolution than uptake in this solution. Specimens stored in the artificial saliva solution Biotene contained significantly lower amounts of unbound water after 6 weeks than in all other solutions. Water was thus shown to become bound within these cements during a relatively slow process, and a mechanism for this water-binding is proposed.*

## INTRODUCTION

Glass-ionomer dental cements are widely used restoratives for the repair of teeth in clinical dentistry [1]. They have a variety of uses in the direct filling of teeth, including as liners/bases, full restorations, and adhesives in orthodontics [1].

Glass-ionomers are prepared from powdered glasses that are basic in character, and typically comprise calcium (or strontium) fluoro-aluminosilicate glasses that contain phosphate additions [2]. Glasses are complex, because of the need to react quickly to give clinically acceptable working and setting times, to develop strength rapidly and to form cements that become reasonably translucent and match the appearance of the tooth.

In addition to the glass powders, glass-ionomers contain a water-soluble polymeric acid. This is most commonly polyacrylic acid, but certain brands of commercial glass-ionomer contain acrylic/maleic acid copolymer instead. Cements may include (+) tartaric acid to modify the setting reaction, and they always include water in the final cement mixture. In some brands, the polymer is dissolved in water; in others it is included in the powder, and water (or an aqueous solution of (+) tartaric acid) is used to activate the setting process [1].

Water plays several roles in glass-ionomer cements [3]. It is the solvent for the polymeric acid, and typically represents some 55 % by mass of the liquid component [1]. It then becomes the medium in which the setting reaction occurs. During setting, all of the water is incorporated into the cement structure without any phase separation [3, 4]. There may be some early drying out, as water is lost from the cement by evaporation. This causes crazing of the surface, because microscopic cracks form and, in clinical service, cements are coated with a thin layer of petroleum jelly or varnish to prevent this drying effect and preserve the appearance of the cement [5].

Water is therefore a component of the fully set cement. A number of possible states have been identified as potential locations for this water when the cement has solidified [1, 3, [7]. These include co-ordination sites around  $\text{Ca}^{2+}$  (or  $\text{Sr}^{2+}$ ) and  $\text{Al}^{3+}$  ions [8] or hydration regions around the polymer chain [9, 10]. It is not clear how well such water molecules might be bound within the cement, but it has been reported that as glass-ionomer cements age, the proportion of loosely bound water decreases relative to the amount of tightly bound water [11]. These two states have been arbitrarily defined as, respectively, the amount of water that can be removed from the cement by storage over a strong desiccant,

such as concentrated sulphuric acid, and the amount that cannot be removed under such conditions. This latter water is retained strongly within the cement, even under severely desiccating conditions. These states have also been described as “unbound” and “bound”.

Loss of unbound water has been found to follow diffusion kinetics for relatively young cement specimens [12]. Three commercial brands were examined and water loss was found to obey Fick's law of diffusion for the first 4-5 hours of drying. Diffusion coefficients at 22°C were in the range  $5.87 \times 10^{-7}$  to  $3.08 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ . Diffusion plots did not quite pass through the origin for any of the cements tested, which indicated that for each materials there was a small amount (less than 1 % by mass in all cases) of water whose loss did not occur by diffusion. This water was assumed to be in the surface layers of the specimens and was termed “superficial water”. It represented a small fraction of the total unbound water.

Allowing the samples to desiccate completely (to constant mass) showed that all of these cements contained tightly bound water [12]. The ratio of bound to unbound water was determined in all cases and found to range from 1:5.26 to 1:1.25, depending on the brand.

In addition to studies of water loss and bound:unbound water ratios, there have been a few studies of the uptake of water by glass-ionomers from aqueous solutions [5, 13]. In the first of these studies, the change in mass of a glass-ionomer was compared with that of a zinc polycarboxylate. For the glass-ionomer, there were clear differences between uptake in pure water and that in 0.9 % NaCl, indicating that water uptake is influenced by ionic content of the storage solution. Uptake in 1 mol·dm<sup>-3</sup> sodium sulphate solution was small, but positive, whereas in this solution, the zinc polycarboxylate loss a reasonable mass [5]. This indicates that glass-ionomers have a stronger affinity for water than do zinc polycarboxylates. This finding can be attributed to the behaviour of the glass component, as zinc polycarboxylate cement has the same type of water soluble acidic polymer as glass-ionomers and metal ions (Zn<sup>2+</sup>, together with a small proportion of Mg<sup>2+</sup>) with similar co-ordination requirements [8]. The water sorption level in pure water for the glass-ionomer was 0.6 %, which was much lower than that found in a recent study of water sorption and desorption in a variety of tooth-coloured dental restorative materials [13]. Only one glass-ionomer was used in the latter study, Ketac Molar, and it was allowed to set for only 5 minutes before being transferred to distilled water. The specimen prepared in this way showed a net increase in mass of 10.70 % (standard deviation 1.70 %) after 15 days immersion, indicating that a substantial amount of water had been taken up by the specimens [13]. This may have been influenced by the cure conditions, since previous studies have used specimens cured at 37°C for 1 hour prior to exposure to water [5]

The present study has been undertaken to investigate further the nature of the water uptake and water binding

by conventional glass-ionomer cements. These processes are the part of maturation of these materials [3], but are not properly understood. We have determined the effect of differing ionic content and strength on both the overall water uptake and on the eventual ratio of bound/unbound water within the cements. Two contemporary brands of glass-ionomer cement have been used, and exposed to the various ionic solutions for periods of six weeks, with masses being determined initially and after 6 weeks. Finally, the bound:unbound water ratio has been determined for all specimens and compared with that for immature specimens. In this way, we have determined whether these materials undergo a change in the bound:unbound water ratios. Finally, conclusions have been drawn concerning the possible mechanism by which water becomes bound within the cements as they age/ mature.

## EXPERIMENTAL

Two commercial brands of glass-ionomer cement (Fuji Equia, ex GC Europe, Belgium and Ketac Molar Aplicap, ex 3M ESPE Germany) were used in this study. Both were capsulated versions, and prepared by mixing in a commercial vibratory mixer (Linear Tac s.r.l, ex Kent Dental, UK), after which they were extruded into rubber moulds of size 6 mm diameter × 2 mm height placed between glass microscope slides. Sets of six were prepared for each storage solution and allowed to cure for 1 hour at room temperature before being transferred to the storage solution.

The following aqueous media were used: deionised water, 1.0 mol·dm<sup>-3</sup> KCl, 1.0 mol·dm<sup>-3</sup> NaCl, 0.9 % NaCl, and Biotene (a commercial saliva substitute, ex GlaxoSmithKline, UK). The specimens were weighed before being placed in the storage medium, then at weekly intervals for 6 weeks. Prior to each weighing they were dried to remove obvious water using a tissue. Storage solutions were kept at room temperature (20 - 22°C) for the duration of the experiment, and the storage medium remained the same for the whole of the 6 week storage period.

After six weeks specimens were weighed then transferred to a desiccator and stored over concentrated sulphuric acid for 24 hours. They were then re-weighed.

In addition to experiments on stored cement specimens, another set 6 specimens of each cement was prepared, allowed to age for 1 hour at room temperature, then immediately desiccated over concentrated sulphuric acid for 24 hours. This provided data for bound/unbound water ratios in immature specimens. The water content of each poly-acid solution was determined by placing weighed amounts of the solution in the desiccator over concentrated sulphuric acid and weighing to constant mass. This gave information on the unbound (evaporable) water in the cement-forming liquids.

Data were analysed statistically using the Tukey HSD test.

RESULTS

The individual poly-acid solutions were found to lose 49.2 % and 42.1 % by mass for Fuji Equia and Ketac Molar Aplicap respectively. These results allowed an estimate to be made of the initial unbound water content of the cements, assuming a power:liquid ratio of 3.4:1 for both capsulated brands.

The results for the overall net gain in mass for both cements after 6 weeks are shown in Table 1 and in Figures 1 and 2. These were not significantly different from each other. Following storage in the various aqueous media, specimens were desiccated, and the overall net mass losses (i.e. loss on desiccation minus gain at 6 weeks) are shown in Table 2 and in Figures 3 and 4.

Table 1. Net gain in mass (%) after 6 weeks for cement specimens (standard deviations in parentheses).

Cement	Storage medium	Net mass gain (%)
Fuji Equia	Water	1.5 (0.4)
	0.9 % NaCl	0.7 (0.5)
	1 M KCl	1.7 (1.1)
	1 M NaCl	1.3 (0.6)
	Biotene	1.4 (0.9)
Ketac Molar Aplicap	Water	1.4 (0.5)
	0.9 % NaCl	0.5 (0.6)
	1 M KCl	1.8 (0.4)
	1 M NaCl	1.1 (0.4)
	Biotene	0.9 (0.6)

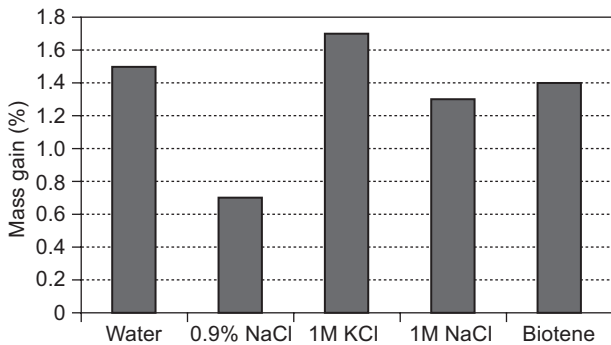


Figure 1. Mass gain (%) in 6 weeks by Fuji Equia.

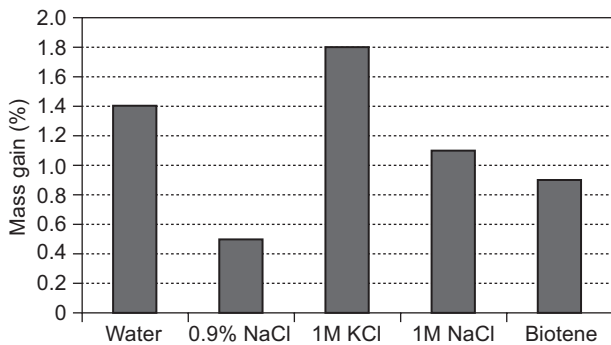


Figure 2. Mass gain (%) in 6 weeks by Ketac Molar Aplicap.

The proportion of unbound (evaporable) water in these specimens is shown in Table 3. These data allow values for bound:unbound water to be calculated, and the results for this calculation are shown in Table 4.

For Fuji Equia, the proportion of unbound water was lowest on storage in Biotene and highest on storage in 0.9 % NaCl (both significant to  $p < 0.05$ ). For Ketac Molar Aplicap, the proportion on unbound water was lowest on storage in Biotene (significant to  $p < 0.05$ ). It was highest on storage in 0.9 % NaCl, and this was significantly higher than for all other solutions except pure water (to at least  $p < 0.05$ ).

Table 2. Net mass loss (%) after drying at 6 weeks (standard deviations in parentheses).

Cement	Storage medium	Loss (%)
Fuji Equia	Water	5.1 (0.6)
	0.9 % NaCl	7.2 (0.9)
	1 M KCl	5.4 (0.7)
	1 M NaCl	4.8 (0.5)
	Biotene	4.0 (1.0)
Ketac Molar Aplicap	Water	4.9 (0.3)
	0.9 % NaCl	5.1 (0.3)
	1 M KCl	4.4 (0.3)
	1 M NaCl	4.5 (0.2)
	Biotene	2.4 (0.3)

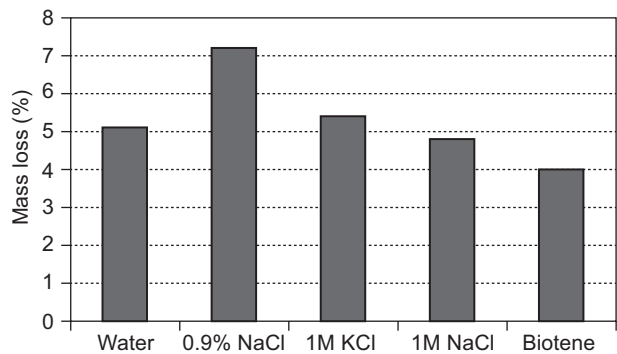


Figure 3. Mass loss after drying at 6 weeks for Fuji Equia.

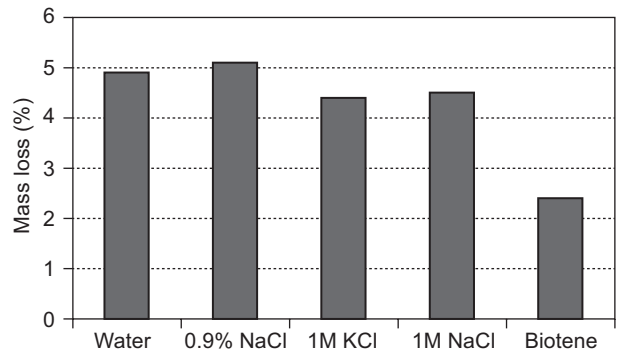


Figure 4. Mass loss after drying at 6 weeks for Ketac Molar Aplicap.

Table 3. Proportion of unbound water, % (standard deviations in parentheses).

Cement	Specimens	Unbound water (%)	Significance compared to immature
Fuji Equia	Immature	6.4 (0.7)	–
	Water (6 weeks)	6.6 (0.8)	NS
	0.9 % NaCl (6 weeks)	7.1 (0.8)	NS
	1 M KCl (6 weeks)	5.4 (0.8)	NS
	1 M NaCl (6 weeks)	4.8 (1.0)	NS
	Biotene (6 weeks)	4.0 (0.8)	Significant to $p > 0.01$
Ketac Molar Aplicap	Immature	5.1 (0.4)	–
	Water (6 weeks)	4.9 (0.4)	NS
	0.9 % NaCl (6 weeks)	5.1 (0.3)	NS
	1 M KCl (6 weeks)	4.5 (0.2)	Significant to $p > 0.02$
	1 M NaCl (6 weeks)	4.5 (0.4)	NS
	Biotene (6 weeks)	2.4 (0.6)	Significant to $p > 0.001$

Table 4. Estimated bound:unbound water ratios.

Cement	Specimens	Bound: Unbound water
Fuji Equia	Immature	0.77
	Water (6 weeks)	1.24
	0.9 % NaCl (6 weeks)	0.57
	1 M KCl (6 weeks)	1.12
	1 M NaCl (6 weeks)	1.36
	Biotene (6 weeks)	1.85
Ketac Molar Aplicap	Immature	0.89
	Water (6 weeks)	0.97
	0.9 % NaCl (6 weeks)	0.87
	1 M KCl (6 weeks)	1.16
	1 M NaCl (6 weeks)	1.13
	Biotene (6 weeks)	3.00

## DISCUSSION

Glass-ionomers are fabricated from solutions of poly-acid in water. Typical values for cements usually lie in the range 40 - 50 %, with values of 45 - 47.5 % being most commonly quoted [1, 3]. In the current experiments, the two proprietary solutions tested gave high values of solids, and correspondingly lower values of unbound water, than these ranges. This may be a reflection of the difficulty in fully desiccating the strongly hydrophilic polymers involved [14]. This, in turn, suggests that there is an amount of “bound” water even in the polymer, and this may be attributed to the formation of strong hydrogen bonds between a proportion of the water molecules and the carboxylic acid groups of the polymer molecules.

For the cements, when are placed in aqueous solutions, two possible processes may occur, namely dissolution and water uptake. Both are likely to occur simultaneously, with the resulting mass of the specimen dependent on which of them predominates. In the current study, there was a net gain in mass in both cements in all storage solutions, showing that liquid was taken up. There was probably also dissolution, especially in the

pure water and the 0.9 % NaCl solution. Studies have generally found that glass-ionomers dissolve to a modest extent, as shown either by mass changes [13, 15] or by the presence of ions such as  $\text{Na}^+$ ,  $\text{Al}^{3+}$ ,  $\text{SiO}_3^{2-}$  or  $\text{PO}_4^{3-}$  in solution as detected by ICP [16, 17].

Uptake has been studied very little. It appears to be associated with slight porosity in the set cements, but has been shown in previous studies to vary slightly with changes in the composition of the storage solution [6]. In the present study, uptake was found to vary slightly with the storage solution, and for both materials was highest with KCl than for any other medium and lowest with 0.9 % NaCl. However, the differences were not significant.

Results enabled the ratio of bound to unbound water to be determined, and these results could be compared to that in the immature specimens. For both cements, results were similar. In all solutions except 0.9 % NaCl, the ratio of bound:unbound water increased, and for both cements, the increase was greatest on storage in Biotene.

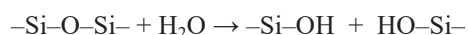
In the case of the 0.9 % NaCl solution, this may have occurred because of relatively high levels of dissolution, which may have had two effects. First, it may have meant that the true mass water uptake could not be determined, and second, it may have resulted in the washing out of ionic sites to which water would otherwise have become bound. The relatively dilute nature of this solution would certainly make it easier for any soluble matter to dissolve than would occur with the more concentrated solutions of 1 M NaCl, 1 M KCl or Biotene. Why a similar effect was not observed with water is not clear, and the latter results indicate the complexity of this balance of water uptake and dissolution in the presence of various solutes.

Biotene was found to have a profound influence on the proportion of bound water in the cements after 6 weeks. The reason for this is not clear. This solution is manufactured as an antiseptic mouth rinse and saliva substitute for use with xerostomic patients [18]. It contains the enzymes lysozyme, lactoferrin, glucose oxidase and lactoperoxidase, as well as thickeners (hydroxy-

ethylcellulose and propylene glycol), salts and flavouring. It is thus a complicated mixture, but its combination of viscosity; biological activity and salt concentration make it a useful saliva substitute. It has not been found to be effective as an antimicrobial rinse [19], but it remains a proprietary formulation that appears to relieve the discomfort associated with xerostomia in particular. Its composition means that it is likely to have a complicated influence on water uptake, and suggests that there may also be some ion uptake, possibly partitioning between the cement and the solution, and this may provide addition sites to which water molecules may become bound.

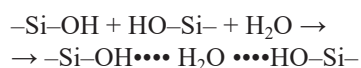
Our results indicate that the phenomenon of water binding in glass-ionomer cements is complicated, and influenced by both the external storage solution and the cement itself. In most solutions, there was a clear increase in the ratio of bound to unbound water, confirming previous observations that this ratio increases as part of the overall maturation process in these materials [11]. To date, there has been no explanation for this effect, apart from vague suggestions of co-ordination of metal ions by water molecules, and the formation of a hydration sheath around the ionised acid polymer molecules. This does not explain why the behaviour of zinc polycarboxylate is so different; it has never been shown to bind water in the way that glass-ionomers do, despite being made from identical polymers and containing metal ions with similar co-ordination requirements [8].

We now wish to propose a mechanism for the binding of water in these cements. Previous studies on the surface chemistry of both silica [20] and of silicate glasses [21] have suggested that the -Si-O-Si- units are susceptible to hydrolysis. The process can be written as:



This leads to the occurrence of silanol groups on the surface, which not only use up water molecules, but also occupy more space than the original -Si-O-Si- units. Studies have shown that specific surface area of silica particles increases linearly with concentration of OH groups per unit mass of silica [20], confirming that the surface area expands as a result of hydration of the surface.

The above step may be followed by the binding of a further water molecule through hydrogen bonding:



Such a step is likely to occur readily, and to result in a strongly adherent water molecule.

Glass-ionomer cements are made from glasses with high silica content [1, 2, 7], and these are clearly susceptible to attack by water. Indeed, reacting water alone with such glasses has been found to be capable of leaching

ions, leading to the formation of a solid if friable product [22]. There is thus evidence that the glass component of these cements is indeed susceptible to attack by water, in the same way as silica itself and also the silicate glasses studied previously [21].

Infrared spectroscopy has shown that the Si-O-Si group undergoes a stretching vibration at about 1050  $\text{cm}^{-1}$  [23], though this band can be quite broad, and range from about 1000 to 1130  $\text{cm}^{-1}$  [24]. A little below this range is a peak at 950  $\text{cm}^{-1}$ , which is attributed to Si-OH groups [25]. Si-OH groups also give rise to bands in the region 3200 - 3700  $\text{cm}^{-1}$  [24]. Discrete Si-OH groups occur at 3700  $\text{cm}^{-1}$  [26], but the band shifts to slightly lower frequencies when Si-OH groups are hydrogen bonded to significant amounts of water [23].

The majority of studies of the setting of glass-ionomers using infrared spectroscopy (or FTIR) have concentrated on the region due to carboxylate groups, i.e. 1550 - 1700  $\text{cm}^{-1}$  [26]. However, a few have explored other regions of the spectrum and made assignments. For example, Matsuya et al [26] showed that there was a broad band between 1350 and 800  $\text{cm}^{-1}$  in the spectrum of freshly made glass-ionomer cements, and that this shifted on ageing. By 1 day there was a distinct band with a maximum at 1060  $\text{cm}^{-1}$  (due to Si-O-Si) with a shoulder at 950  $\text{cm}^{-1}$  (Si-OH).

A peak at 950  $\text{cm}^{-1}$  in the FTIR spectrum of a glass-ionomer cement has been reported, and attributed to Si-OH [27]. Other reports of bands clearly attributable to Si-OH in set glass-ionomer cements were of the bands in the range 3435-3445  $\text{cm}^{-1}$  (hydrogen bonded silanol groups) [28] and one at 1358  $\text{cm}^{-1}$  reported recently and assigned to Si-OH [29].

If glass-ionomers do bind water at the glass surfaces as proposed, these surfaces would be expected to expand and become disrupted. Surface expansion within a setting cement would reduce the distance between the particles and consequently alter the translucency as the surfaces are pressed together and the refractive index differences are minimised. Hence our model is consistent with the known change in appearance of these cements on setting [1, 3]. Indeed, the translucency of glass-ionomers was noted in one of the earliest publications reporting them [30].

## CONCLUSIONS

Two modern brands of glass-ionomer cement have been shown to take up mass when stored in aqueous solutions of various salts, and also the commercial saliva substitute Biotene®. Results allowed changes in the ratio of bound to unbound water to be determined and compared with those immature versions of each cement.

In all cases except for specimens stored in 0.9 % NaCl solution, bound;unbound water ratios increased on ageing. Specimens stored in Biotene showed greatest

increases in bound-unbound water ratios after 6 weeks. Reasons for these differences are not clear, though are likely to be due to differences in levels of solubility and of water uptake that are each influenced in a complex way by the presence of solutes in the storage solution.

Water binding is proposed as arising from hydration of Si–O–Si units in the surface of the glass particles within the cement, with corresponding formation of Si–OH groups. This mechanism is consistent with previous observations using FTIR spectroscopy.

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