

Leaching of Ions from Materials used in Alternative Restorative Technique under Neutral and Acidic Conditions: A Comparative Evaluation

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This study was undertaken to gain an insight into the interaction of conventional glass ionomers (GC Fuji II, GC Fuji IX GP and Chem Flex™ restorative materials) commonly used in Alternative Restorative Technique (ART) with aqueous solutions in terms of water sorption, solution buffering and ion release. Both immature and mature specimens of all materials evaluated, showed a substantial increase in mass, pH and release of Na, Ca, Sr, Al, Si, P and F following immersion in deionized water, lactic acid (pH 2.7) and lactic acid (pH 5.2). However, the ion release profiles were found to be greater in acidic media (Lactic Acid pH 2.7 > Lactic Acid pH 5.2) than in deionized water.

Keywords: Ion release, buffering capacity, pH changes, mass gain, Glass ionomer cement.

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INTRODUCTION

Glass polyalkenoate cement is a material which has created a great impact on the world of restorative dentistry. Ever since its introduction in the early 1970s by Wilson and Kent its inherent characteristics have equally intrigued both scientists and clinicians.¹ It is a water-based restorative material consisting of leachable glass powder and a polyalkenoic acid which react together to form a cement mass.^{2,3} It exhibits true adhesion to tooth structure, and acts as a reservoir of fluoride ions, which are slowly released over prolonged periods of time.⁴

The antibacterial activity of these materials has been extensively studied, but data available in the literature is not conclusive in establishing whether this biological activity is solely due to its fluoride release or due to some other element. The release of fluoride from different glass ionomer cements has been studied, but very few reports are

available on the release of chemical elements other than fluoride.^{6,7,8,9,10,11}

Conventional glass ionomer cements represent the oldest category of glass ionomer cements (GICs) and have the disadvantage of inferior mechanical properties.³ To overcome this, newer, more-viscous, esthetic, reinforced glass ionomer cements were specifically developed for use in the Alternative Restorative Technique (ART). These materials have the ability to neutralize the salivary acids, by buffering the lactic acid via the release of chemical ions.¹³

The predominant factors controlling the stability of the enamel apatites will be the pH and the concentration of calcium, phosphate and fluoride in the surrounding solution. A pH drop of one unit within the pH range 4 to 7 gives rise to a 7 fold increase in the solubility of the hydroxyapatite.¹⁴ It stated that the release of fluoride and other elements from dental materials were affected by the changes in pH, especially that of the glass ionomer matrix forming elements like calcium, strontium and aluminium.¹⁵ Another aspect, which has not much been extensively studied, is the pH related difference in the ion release profiles of glass ionomers.

Considering the above aspects, the present study was undertaken to evaluate and compare changes in mass, buffering capacity and ion release profiles between the newer high viscous glass ionomer cements and conventional glass ionomer cement.

MATERIALS AND METHOD

Three restorative grade glass ionomers were employed in this study namely GC Fuji II, GC Fuji IX GP and Chem Flex™. 105 Cylindrical specimens of dimensions 12.8mm diameter x 1mm height were made using brass moulds with plastic strips on either side to avoid early moisture

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contamination or desiccation. The powder-to-liquid ratio employed for mixing the cement was according to the manufacturer's instructions. The setting material was held between two glass slabs one on either side of the mould under constant hand pressure. After setting, the pellets were removed from the mould and the excess was trimmed using a Swann-Morton no. 11 blade.

For phase I of the experiment a total of 63 specimens (21 from each restorative group) were used. Specimens were weighed, then stored in 10 ml volumes of the various aqueous solutions (deionized water, lactic acid pH 2.7 and pH 5.2) and agitated from time to time. At the end of 1 week, all the specimens were removed individually blot dried and reweighed using an electronic weighing machine.

For phase II of the experiment, 42 specimens (14 from each restorative group) were stored in water for 3 months at room temperature for maturation. At the end of this time, all the specimens were removed individually blot dried and weighed using an electronic weighing machine. They were transferred to 10 ml volumes of lactic acid pH 2.7 (L₁) and pH 5.2 (L₂), and stored for a further week.¹⁶

Following the various storage regimes, the pH values of the individual storage solutions were determined using a digital pH meter that had been calibrated with a standard buffer.¹ In addition, the pH values of water and lactic acid storage solutions without any specimens were determined.

Storage solutions of the respective restorative materials were then combined and the concentrations of ions released were determined as follows:

- Sr, Al, Si and P by Atomic Absorption Spectroscopy.
- Na, Ca by Flame Photometry

The Atomic Absorption Spectroscopy was calibrated for each element to be analyzed by a standard set of conditions as recommended by the manufacturers. Analysis was carried out after the instruments were calibrated with the standard conditions for a particular element.¹ Fluoride ion concentration of these solutions was also determined using a Fluoride Selective Electrode calibrated immediately before use. Fluoride in the sample solutions was determined with the addition of Total Ionic Strength Adjustment Buffer (TISAB) decomplexing agent.¹⁶

Statistical analysis

The data from phase I and phase II of the experimental procedure were tabulated and statistically analyzed using Student's t- test.

RESULTS

Changes in mass and solution pH are shown in Table 1 and Table 2 respectively. In water, the mean mass of GC Fuji II, GC Fuji IX GP and Chem Flex™ showed an increase in mass after immersion, which was statistically highly significant (P<0.001). In L₁ and L₂ also the mean mass increased which was statistically highly significant (P<0.001).

Comparison of mass changes among GC Fuji II and GC Fuji IX GP groups, GC Fuji IX GP and Chem Flex™ groups and GC Fuji II and Chem Flex™ groups respectively, in water, L₁ and L₂ showed statistically no significant differences.

Table 2 shows the variations in the mean pH for GC Fuji II, GC Fuji IX GP and Chem Flex™ groups following immersion in various media. The mean pH of water, L₁ and L₂ showed an increase which was statistically highly

Table 1. Shows the inter-comparison of mass changes (gm) among various groups between phases 1 and 2 of the experiment.

Groups	Particulars	Mass changes					
		L1 (2.7 pH)			L2 (5.2 pH)		
		Phase I	Phase II	p value*	Phase I	Phase II	p value*
GC Fuji II	Mean (SD)	0.29 (0.02)	0.294 (0.03)	0.75 NS	0.26 (0.02)	0.305 (0.03)	< 0.01 S
GC Fuji IX GP	Mean (SD)	0.27 (0.01)	0.264 (0.01)	0.07 NS	0.26 (0.01)	0.254 (0.02)	0.23 NS
Chem Flex™	Mean (SD)	0.24 (0.01)	0.243 (0.01)	0.07 NS	0.25 (0.01)	0.229 (0.02)	< 0.01 S

Table 2. Shows the inter-comparison of pH changes among various groups between phases I and II of the experiment.

Groups	Particulars	pH changes					
		L1 (2.7 pH)			L2 (5.2 pH)		
		Phase I	Phase II	p value*	Phase I	Phase II	p value*
GC Fuji II	Mean (SD)	3.38 (0.07)	3.42 (0.02)	0.14 NS	6.69 (0.35)	6.61 (0.30)	0.63 NS
GC Fuji IX GP	Mean (SD)	3.29 (0.02)	3.32 (0.10)	0.42 NS	6.37 (0.37)	5.94 (0.31)	< 0.05 S
Chem Flex™	Mean (SD)	3.57 (0.11)	3.72 (0.04)	< 0.01 S	5.68 (0.03)	5.64 (0.10)	0.33 NS

significant ($P < 0.001$) in all the three experimental groups after 1 week of immersion.

Comparing the pH changes between GC Fuji II with GC Fuji IX GP group, in water and L_2 the specimens showed statistically no significant results ($P > 0.005$) but in L_1 the specimens showed statistically significant results ($P < 0.01$). When GC Fuji IX GP was compared with Chem Flex™, the pH change in water was statistically not significant, but the pH change in L_1 and L_2 showed statistically highly significant results ($P < 0.001$). pH changes in GC Fuji II when compared to Chem Flex™ group, in water showed statistically no significant results ($P > 0.05$), and in L_1 was statistically significant ($P < 0.05, 0.01$), but in L_2 , the pH change was statistically highly significant ($P < 0.001$).

Ion release

Data for release of Na, Ca, Sr, Al, Si, P and F are shown in Table 3.

GC Fuji II group

In phase I of the experiment the specimens leached more ions in lactic acid compared to water. Following immersion in water and lactic acid the maximum ion released were sodium, followed by calcium and fluoride. Sr, Al, Si, and P were released in minimal amounts in various immersion media.

GC Fuji IX GP group

In phase I of the experiment the specimens leached most ions in lactic acid at pH 2.7 (L_1), followed by L_2 and then water. In the various immersion media, maximum ions released were sodium followed by calcium and fluoride. Sr, Al, Si, and P were released in minimal amounts in various immersion media.

Chem Flex™ group

In phase I of the experiment the specimens leached most ions in lactic acid at pH 2.7 (L_1), followed by L_2 and then water. In the various immersion media, maximum ions released were sodium followed by calcium and fluoride. Sr, Al, Si, and P were released in minimal amounts in various immersion media.

DISCUSSION

In this study, the two restorative materials evaluated i.e. GC Fuji IX GP and Chem Flex™ represent a group of improved, high viscosity glass ionomer cements used primarily in the Alternative Restorative Technique and for restoring primary molars.¹⁶ Evaluation of the buffering capacity and ion release profiles of these materials would definitely provide an insight into its inherent property of preventing secondary caries around the margins of the restorations¹⁷ and the third glass ionomer evaluated was a conventional GIC i.e. GC Fuji II.

Studies have shown that the release of ions from glass ionomers point towards two processes i.e. a fast elution period during the early periods and a long term diffusive process.¹⁸ Studies have also shown that the glass ionomer cement is more prone to water sorption and dissolution on exposure to liquid media during the early stages of setting.¹⁶ Keeping in mind the chemistry of setting and clinical long term performance of these materials it made sense to evaluate both mature and immature specimens for mass changes, pH changes and ion release profiles.

The remineralizing property of glass ionomer cements is tested primarily at times when the drop in plaque pH approaches or drops below the critical pH. The ion release profiles of glass ionomers is also greatly altered with pH changes.¹⁸

The glass polyalkeonate cements are the product of an acid base reaction between an ion leachable glass and polyalkeonic acid. As with any salt, they are susceptible to erosion under acidic conditions. This surface erosion could lead to mass changes as well as altered ion release profiles.¹⁹

The antibacterial activity of glass ionomers is a well documented fact. However, whether this antibacterial activity is solely due to its fluoride release or due to the release of other ions is a much debated entity. Furthermore there are other elements that are released simultaneously from the ionomeric materials which are leached over long periods of time.⁵ This was the strong objective behind evaluation of the ion release profiles from the various experimental groups.

When the prepared specimens were subject to the various immersion media i.e., water and lactic acid solutions, all the specimens of the experimental group showed complex inter-

Table 3. Shows the ion release profiles expressed in ppm from the GC Fuji II, GC Fuji IX GP and Chem Flex™ groups in phase I and Phase II of the experiment

Group	GC Fuji II					GC Fuji IX GP					Chem Flex™				
	Phase I			Phase II		Phase I			Phase II		Phase I			Phase II	
Ions	H ₂ O	L1	L2	L1	L2	H ₂ O	L1	L2	L1	L2	H ₂ O	L1	L2	L1	L2
Na	19.2	47.1	28.6	1062	365	18.6	111.7	45.6	1121	542.6	35.6	54.3	45	1119	465
Ca	20.6	233.1	164.6	272	134.5	22.1	235.6	164.7	275	168.1	28.1	165.2	158.4	217.2	140.5
Sr	0.051	0.069	0.061	0.129	0.078	0.139	0.149	0.14	0.152	0.145	0.141	0.152	0.148	0.152	0.148
Al	1.2	1.4	1.25	1.35	1.25	1.02	1.2	1.1	1.29	1.19	1.28	1.5	1.2	1.12	1.2
Si	0.148	0.3078	0.2765	0.589	0.362	0.2035	0.2577	0.2295	0.428	0.31	0.2044	0.2068	0.2016	0.394	0.214
P	0.056	0.31	0.282	0.482	0.302	0.054	0.445	0.149	0.684	0.219	0.055	0.22	0.193	0.369	0.2
F	1.53	40.5	7.45	62.16	15.03	1.98	43.03	7.48	61.14	20.76	4.63	57.42	15.03	81.61	28.21

actions with the aqueous solutions. The changes in solution pH were accompanied by changes in mass for the all materials studied.

In our study all the three groups of glass ionomers showed an increase in mass which was statistically significant compared to their pre-immersion masses. However there were no significant differences on comparing the mass gain after immersion in water and lactic acid (L₁ and L₂) solutions. These results of our study were in total agreement with a previous study,²⁰ which showed that the increase in mass of glass ionomers following immersion in liquid media was related to water absorption and that there were no significant differences in the mass gain following immersion in water and lactic acid!⁴⁰ Similar results were obtained in yet another study²¹ which observed significant increase in mass following immersion of GIC specimens in water and lactic acid.

Buffering is the term applied to the ability of these cements to raise the pH of deionized water and lactic acid solutions (L₁ and L₂) to which they were exposed, a phenomenon first reported several years ago.²² More recent studies have established that there is a predictable pattern of behavior, as follows. Initial exposure leads to an increase in pH that is greater than subsequent exposures, and is associated with a net gain in mass by the cement as it takes up the water it requires for maturation. Later exposures tend to lead to uniform but smaller changes in pH, and a steady erosion of the cement.²¹

Following one week's storage, either in water or in lactic acid (L₁ and L₂), all the cements caused a change in pH, moving the solution closer to neutral by amounts that were statistically significant.

However, there were no statistically significant differences in the buffering capacities of the immature specimens of the various experimental groups in deionized water and lactic acid (L₁ and L₂). These results were in total agreement with the results of previous studies that showed glass ionomers significantly raised the pH of the storage solution.²³

However, the mature specimens of the three experimental groups performed differently following immersion in lactic acid (L₁ and L₂). On exposure to lactic acid at pH 2.7 (L₁), the ChemFlex™ group showed significantly greater pH increase compared to the GC Fuji II and GC Fuji IX GP groups.

The acid neutralizing effect observed in this study was desirable since it may be a mechanism of protection against secondary caries. Active caries has been shown to have a pH of 4.9, with lactic acid being the principal substance responsible for the low pH. Such active caries can be arrested by a modest change of the pH to 5.7. The fact that in our experiment we were able to reach this latter pH, from a baseline value of 5.2 (Lactic Acid, L₂) demonstrates that these cements are capable of elevating the pH to the level of arresting caries and in principle able to confer localized protection to the teeth from acid attack.²³

In our study all the three groups of mature glass ionomer

specimens continued to show an increase in mass following immersion in L₁ and L₂ which was statistically significant compared to their pre-immersion masses. The measurements presented here showed that most of the mature specimens studied had gained weight compared to the immature specimens, first in water and then in lactic acid, in spite of the latter's acidic conditions. Moreover previous studies have reported that, most materials, including conventional glass ionomers, showed continuous weight gain for up to 122 days.¹³

Ion release profiles

The ions released were those to be expected from the reactive glass components. The attack at the matrix releases both polyacrylic acid and metal ions. Consequently, the storage solution becomes a mixture of lactic acid and metal lactates, the classic combination that creates a buffer solution. Measurements were made after 1 week, a time likely to be sufficient for the mixtures to have fully equilibrated.²³

The release of all ions was found to be greater in acid conditions than in neutral ones, a finding similar to that obtained previously for conventional and resin-modified glass ionomers which confirmed the results of previous studies.²⁴

Many authors have reported about the release of fluoride ions from GICs. There exists three mechanisms concerning fluoride release from glass ionomer cements- superficial rinse, diffusion through pores and micro fractures, mass diffusion. However, a more recent study concluded that for fluoride ions, diffusion seems to be the controlling process, at least for the first year.²⁵ Some authors suggest that fluoride is released from glass ionomers as F⁻, AlF₆ or as fluorophosphates compounds, principally derived from glass particles that had no reaction at mixture time.³

Some authors have also reported that the amount of fluoride released is influenced by the pH of the surrounding medium, with more ions being released in acidic media.¹⁷ Immediately upon mixing the glass powder with a polyalkenoic acid, the fluoride ions will be released by the initial attack of the acid on the surface of the glass particles. The fluoride ions will take no further part in the setting reaction but will remain within the matrix that is formed by the development of calcium and aluminum polyalkenoate chains.⁴

In our study though we did not find a predictable pattern of fluoride release from the glass ionomer specimens, it was evident that the acidic medium triggered a greater amount of fluoride release comparative to deionized water. It was also evident that a lower pH of 2.7 (L₁) eluted more fluoride ions compared to a slightly higher pH of 5.2 (L₂).

Other metallic ions like sodium and calcium also showed pH dependent ionic release, with the greatest amounts of ions being released in L₁ (most acidic) and the least amount in de-ionized water (neutral).

In water, little calcium was released, a finding which confirmed previous results for these materials.²¹ Calcium is known to be involved in the setting process of these cements

and that glass has been shown to be susceptible to attack at calcium-rich sites by polyacrylic acid during setting. The fact that only traces of calcium were leached into water in one week, and thereafter none was, suggests that the main reaction product is calcium polyacrylate, a substance known to be insoluble in water. Under acid conditions, calcium was released in substantial quantities, and this may arise from two possible sources. Either, there is acid attack primarily at the glass, as previously reported or there is displacement of polyacrylic acid, pKa 6.0, by the stronger lactic acid, pKa 3.86, resulting in the formation of highly soluble calcium lactate. There is also the possibility that the attack occurs by both of these mechanisms.²¹

The ion release profiles of calcium from mature specimens from all the three experimental groups in L₁ (lactic acid at pH 2.7) and L₂ (lactic acid at pH 5.2) were in total agreement to a previous study, which showed that in lactic acid the release of calcium ions continued to increase with time.²¹

Sodium plays little, if any, structural role and the amount present in the cement matrix can be taken as a measure of the extent of setting reaction. The amount of sodium eluted is dependent on the concentration of sodium in the cement matrix.¹⁰ Most GICs contain sodium and this is released in the highest proportion relative to its level in the glass. High amounts of sodium release observed in the acidic media in this study were in agreement with the findings of several other researchers.²⁵

Among the various substances released by glass ionomers, aluminium is important because of several reasons. It is the major constituent of these materials and it is leached over an extended period of time. In addition it may have synergistic anticariogenic properties, because the inhibition of *Streptococcus mutans* ATPase is highest when fluoride and aluminium are combined. Furthermore recent data have shown that dental materials that simultaneously release both fluoride and aluminium are more efficient in reducing *Streptococcus mutans* related acidogenicity than those that basically release fluoride alone.²⁶

The ion release profiles of aluminium from the various experimental groups also showed pH dependent ionic release, with the greatest amounts of ions being released in L₁ and the least amount in deionized water.

These results were similar to the results obtained by study²⁶ which concluded that greater amounts of aluminium were released in lactic acid compared to distilled water.

The amount of aluminium released by restorative materials has often evoked safety concerns. In fact levels of aluminium exceeding 1000 ppm have been detected in some drinking water supplies in America with no adverse effects being reported.¹⁶ However, aluminium released by the experimental groups in our study was far below this limit.

Strontium which is added to provide radiopacity to the cement which replaces calcium to some extent was also released in large quantities in both the acidic media and deionized water. This finding was in agreement with the study.¹ However, no convincing reason could be offered for

this phenomenon. It was hoped that the anticariogenic properties of strontium released by these glass ionomers would be beneficial.

Silicon and phosphorus also pose no health hazards. Both would be expected to be released in oxygenated forms, i.e., as silicate or phosphate. Silica is of very low toxicity, if any, and appears to have beneficial effects on the circulatory system by lowering cholesterol levels in blood. In the form of monomeric silicic acid, Si(OH)₄, it will react to form a hydroxyaluminosilicate species that gradually aggregates and condenses to form a polymeric structure. In this way, potentially aluminium species are removed from aqueous solution, thus eliminating the biological hazard of this latter element.¹⁶

Phosphorus in the form of phosphate is a key component of teeth and bones, and is thus biologically beneficial. It has high affinity for calcium and will form a variety of calcium phosphates, the most important being hydroxyapatite, the mineral phase of teeth and bones. There appear to be no health hazards associated with phosphate at any level and certainly not at the level we observed to be released by GICs.¹⁶

The specimens that had matured for 3 months in water and then transferred to lactic acid for 1 week, showed no major differences in metal ion release, or in buffering capacity, compared with the immature specimens. Maturation will not be complete for some months, but will have reached an advanced stage within the first week. Even after completion of maturation, the matrix remains porous to the extent that the smallest ions, such as the hydroxyl and the fluoride ions can move freely through it. This suggests that the moisture-induced acid-base reaction has been able to proceed to a much greater extent in these matured specimens, and thus made much greater amounts of ions available for release.⁴

In our present study it would have been desirable to determine the form along with the quantity of the ions released. Another major limitation of our study was lack of clinical correlation of our observations. Recent reports suggest that glass ionomers in *in vitro* and *in vivo* (presence of saliva) conditions may not be comparable, as the higher ionic concentration of saliva would influence the ion release. Also, it is unclear how long ion release, continues. Theory and experimental evidence do not seem to be entirely compatible.²⁵

CONCLUSIONS

All the glass ionomers evaluated showed substantial increase in mass and pH following immersion in the various storage media used.

The substantial increase in mass of all the glass ionomers evaluated may be a phenomenon associated with increased water sorption. However, following maturation, the newer high viscous glass ionomers showed greater water sorption compared to the more conventional glass ionomer.

ChemFlex™ showed substantial buffering capacity in highly acidic media, while Fuji II exhibited substantial buffering capacity in moderately acidic media. The

process of maturation had little or no effect on the buffering capacity of these cements.

All the materials evaluated showed substantial amounts of release of sodium, calcium, strontium, aluminium, silicon, phosphorus and fluoride. However, the ion release profiles were found to be pH dependent, being greater in lactic acid (pH 2.7 > pH 5.2) than in deionized water.

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