FLUORIDE RELEASE FROM GLASS IONOMER CEMENTS

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INTRODUCTION

Dental researchers are constantly searching for the "ideal" restorative material. A tooth-coloured dental material, glass ionomer cement (GIC)* was developed in 1969 by Wilson and Kent in response to the need for a biocompatible, adhesive filling material. (53, 54) It was found to have some useful properties, such as, an ability to adhere to tooth structure** and to release small amounts of fluoride over a period of time.*** Its discovery was significant in that it provided a potentially viable alternative to silicate cement and composite resin for the aesthetic restoration of Class III and Class V cavities.

* The abbreviation GIC when used throughout this thesis denotes glass ionomer cement.

** References 4, 7, 12, 21, 45, 47, 49, 56, 57, 59, 62, 71, 80, 82, 85, 89, 93, 97, 112, 133, 138.

*** References 8, 14, 17, 21, 34, 48, 104, 110, 117, 118.
GIC is based on the hardening reaction between a powder of an ion-leachable aluminosilicate glass and an aqueous solution of poly (acrylic) acid and other poly (alkenyl) acids.\(^{(27,53,55,128,129)}\) The reaction is an acid-base ionic reaction; the cations reacting with anions to form a neutral salt.

The GIC powder is a fluorine-containing aluminosilicate glass, and it is from this source that complex fluorides such as AlF\(_2^+\), AlF\(_2^+\) and CaF\(^+\) are formed during the setting process.\(^{(1)}\)

It has been found that GIC has little or no deleterious effect on the pulp and the gingival tissues.* Other clinically acceptable properties have led to its wide use in cervical erosion lesions,** as luting agents,\(^{(5,11,41,63,91,126,130,138)}\) for fissure sealing,\(^{(52,67,69,76,77,99,119,120)}\) for the restoration of deciduous,\(^{(69,76,88,94,111,120)}\) and permanent teeth\(^{(10,11,30,66,67,69,79,94)}\) and as a root filling material.\(^{(87)}\)


Many of the early clinical trials reported in the literature use an earlier brand of GIC (Aspa).* However, although this material is no longer marketed, other brands are available.

Despite the importance of fluoride release from GIC, as far as can be ascertained from the literature, this parameter has not been examined fully for all the brands of GIC now marketed in Australia.

This investigation was undertaken to determine the comparative fluoride release profiles of each of the 4 currently available products, Fuji, Ketac, ChemFil and Hy-Bond. Embodied in this thesis is a description of the structure of GIC, and a review of the literature relating to studies carried out to determine fluoride release from GIC. In addition, a description of the materials and methods used in the study, the results obtained, and a discussion of the results, are given.

* Aspa: Glass Ionomer Cement, AD International Limited, Amalgamated Dental Company, LONDON, W.1., U.K.
REVIEW OF LITERATURE

STRUCTURE OF GLASS IONOMER CEMENTS

Glass ionomer cements (GIC's) are formed by reacting special calcium aluminosilicate glasses with aqueous solutions of poly (acrylic) acid and other poly (alkenyl) acids. The basic constituents of the cement are a liquid and a powder component.

Liquid Component

The liquid in GIC is a concentrated solution of a polycarboxylic acid, or, a linear polymer, containing several carboxyl groups (-COOH) such as polyacrylic acid. It is believed that some current formulations of commercially available GIC liquid contain a 47.5% aqueous solution of a 2:1 copolymer of an acrylic acid and itaconic acid. This combination gives stability and low viscosity to the aqueous solution. Usually, 5% tartaric acid is incorporated into the polyacrylic
acid solution to act as an accelerator of the chemical reaction. It does this by facilitating the extraction of ions from the glass powder, thereby giving higher concentrations of cations capable of reacting with the polyanions. (17, 18, 27, 90, 113, 125)

Crisp et al. (18, 20, 21) in the mid 1970's studied the effect of the polyacid concentration of the liquid on the physical properties of the final GIC. They concluded that high acid strength is desirable as it results in a decrease in the powder/liquid ratio and solubility, and an increase in working time and both compressive and tensile strengths.

The mean molecular weight of the polyacrylic acid is 23,000 (54, 124) and its chain is only 0.1 μm long when fully extended. (25) The liquids are essentially Newtonian in that their viscosity remains constant whatever the shear rate. (63, 115)

A recent form of GIC introduced in 1978 by Wilson and Prosser (132) is the "water-setting" version, where the polyacid is incorporated into the powder in a dry form, and the cement paste is formed by mixing in the appropriate amount of distilled water.
Powder Component

The GIC powder is a finely ground fluorine-containing calcium aluminosilicate glass with a mean particle size of 45 \( \mu \text{m} \). It is formed by fusing the basic constituents, silica, aluminium oxide, calcium fluoride, cryolite, aluminium fluoride and aluminium phosphate to the appropriate temperature and then shock cooling the melt. The resulting glass mass is then finely ground. The three component system, silica-aluminium oxide - calcium fluoride, is the basis of the powder from which all other more complex GIC's are derived.

The calcium fluoride gives the glass opacity and the high alumina content makes it ion-leachable in acids. The most important factor is the silica/aluminium oxide ratio as it controls the setting rate of the cements.

The basic constituents of both the powder and liquid components of GIC may vary considerably. Different amounts of each ingredient together with additives such as tartaric acid may result in GIC's which vary in their properties.

Setting Reaction

All the reactants and products of the setting reaction, apart from water, are polymeric. As
far as can be determined from the literature, there are no toxic monomers, initiators or activators involved in the setting reaction. (121)

The setting reaction for GIC's shown in Figure 1 is that proposed by McLean and Wilson. (68) In this reaction hydrated protons from the liquid penetrate the surface of the powder particles. Ions of aluminium, calcium, sodium, fluoride and dihydrogen phosphate are displaced from the glass and it is degraded to a hydrated siliceous gel. The cations, either simple or as cationic complexes, migrate into the liquid phase where they form metallic salt bridges between the long chains of charged polycarboxylate ions, cross-linking them and causing the aqueous phase to gel and the cement to set. As the pH of the system increases, the ions (except sodium) precipitate, together with the polyanions, as hydrated salts. This is illustrated in Figure 2.

Spectroscopic analysis (24) has shown that calcium ions are bound within 3 hours to the polyacrylate chains and are chiefly responsible for the initial set of the material. The aluminium salt forms later and is responsible for final hardening, the reaction continuing for 48 hours. The calcium ion, is less charged, and has a greater mobility than the more heavily solvated
Fig. 1. Chemical reactions occurring during the setting reactions of glass ionomer cement. (27, 54)
Fig. 2. Variation of soluble ion content during the setting and hardening of glass ionomer cement (Aspa) for the first 48 hours. (121)
aluminium ions. (25) The trivalent aluminium ion ensures a much stronger cross-linking than is possible with divalent ions alone. In the fully set cement, the calcium and aluminium salts are present in approximately equal amounts.

There is a need to protect the freshly placed material from moisture contamination or dehydration in the oral cavity for the first 60 minutes. (74, 75, 78, 95) If contamination does occur, the material is more susceptible to staining and abrasion. Clinically, a varnish or surface protector is necessary to successfully control the environment of a newly placed restoration.

Wilson and Prosser (132) state that once the final set of the GIC is reached, it is no longer vulnerable to contamination by moisture because of a significant proportion of $\text{Al}^{3+}$ salt links present. They report that only sodium fluoride is leached from the hardened cements. They claim that much of the fluoride released is absorbed by neighbouring enamel.

There is evidence that even after the precipitation reaction is complete and the cements are stable, some reactions continue. (131)
Theoretically, the setting reaction could continue indefinitely as long as free carboxyl groups are present. (24)

Recently, Crisp et al. (22) have investigated the effects on setting behaviour of the addition of simple metal salts such as tin fluoride and calcium chloride. Depending on their concentration, these salts can act either as accelerators or inhibitors, but do not necessarily improve hydrolytic stability.

The role of fluoride is important in the setting reaction of the GIC. (23, 24) It has to be in its crystalline form, as fluorite (CaF$_2$) in the glass, if it is to be efficiently extracted by the polyacid. The formation of complex fluorides during the setting process, such as AlF$_2^+$, AlF$_4^{2+}$, and CaF$^+$, plays a role in the transfer of ionic species and their subsequent interactions with polyacrylic acids. (1) If the fluoride was not extracted, the free acid level in the system would rise too quickly leading to possible deleterious pulpal effects and an unworkable cement. There is less fluoride released from GIC than silicate cement because polyacrylic acid binds cations more tightly than phosphoric acid, and these are not then available for fluoride transport. (128)
A recent brand of GIC introduced in Japan, incorporates a tannin-fluoride preparation to assist in reduction of secondary caries around restorations. According to the literature, this additive consists of zinc fluoride (50% by weight), strontium fluoride (25% by weight), tannic acid (20% by weight) and a pH adjuster (5% by weight). (96, 106, 109, 136, 137)

GLASS IONOMER CEMENTS - TOOTH STRUCTURE INTERACTIONS

GIC bonds to enamel and dentine by means of a physico-chemical adhesion. (7, 12, 68, 80, 132, 133) This is an important attribute for a restorative material as it decreases the possibility of any problems initiated through micro-leakage and marginal breakdown.

GIC's can only bond to surfaces with which they can react chemically. They do not adhere to porcelain, pure platinum or gold. (120) The adhesion between Aspa and various substrates has been investigated by Hotz et al. (49) and is summarised in Table 1.
<table>
<thead>
<tr>
<th>SUBSTRATE</th>
<th>BOND STRENGTH (N/mm²)</th>
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<tbody>
<tr>
<td>Enamel</td>
<td>4.0</td>
</tr>
<tr>
<td>Dentine</td>
<td>2.9</td>
</tr>
<tr>
<td>Stainless Steel</td>
<td>6.8</td>
</tr>
<tr>
<td>Tin oxide/platinum</td>
<td>3.8</td>
</tr>
<tr>
<td>Tin oxide/gold</td>
<td>4.3</td>
</tr>
<tr>
<td>Platinum</td>
<td>0.0</td>
</tr>
<tr>
<td>Gold</td>
<td>0.0</td>
</tr>
<tr>
<td>Porcelain</td>
<td>0.0</td>
</tr>
</tbody>
</table>

**Table 1.** Adhesion of a glass ionomer cement *(Aspa IV)* to various substrates. *(49, 120)*
One proposed mechanism of adhesion of GIC to enamel and dentine was given in 1977 by McLean and Wilson (68) and is shown in Figure 3. They suggest that adhesion is a result of electrostatic attractions with cations placed between negatively charged oxide surfaces and carboxyl groups in the cement.

A different mechanism to that put forward by McLean and Wilson was proposed by Wilson et al. (133) in 1983 and is illustrated in Figure 4. Using infrared spectroscopy, they showed how polyacrylate ions become irreversibly attached to the surface of hydroxyapatite by displacing existing phosphate ions.

The pretreatment of the enamel and dentine surfaces with "wetting" agents to enhance ionic and dipole interactions with GIC has been reported by various researchers. (42, 49, 80, 90, 97, 112) Some of these agents include phosphoric acid, citric acid, EDTA, iron (III) chloride and sodium hypochlorite.

Moisture is the principal barrier to effective adhesion of GIC to tooth structure as it competes with a potential adhesive for the surface of a substrate and can also hydrolyse adhesive bonds. (80)
Fig. 3. A possible mechanism for the adhesion of glass ionomer cement to enamel apatite and dentine collagen as given by McLean and Wilson. (68)
Fig. 4  A schematic representation of a mechanism for adhesion of a polyelectrolyte cement to enamel apatite as proposed by Wilson et al. (133)
Enamel possesses a much greater calcium content than dentine and thus, GIC tends to bond more strongly to it. (62)

**FLUORIDE RELEASE FROM GLASS IONOMER CEMENTS**

1. **Early Research**

The precursor of GIC's, the silicate cements, have long been known for their ability to release fluoride. Phillips and Swartz (86) in 1957, and many other researchers including Wilson and Batchelor, (122) Forsten, (33) together with Paunio, (36, 37) Rytömaa et al. (38) and Legrand et al. (60) have demonstrated the occurrence of this phenomenon. As GIC was a natural development from the silicate cement, it, too, was expected to release fluoride. The literature of the early 1970's mentions the possibility of fluoride release from the fluoro-alumino-silicate glass component but, at that time, no detailed work appears to have been published on this aspect.

Crisp and Wilson (24, 25) in 1973, examined the ionic species eluted in water from a glass ionomer cement material, prepared in the Laboratory of the Government Chemist, England. The
amount of fluoride released during the initial and precipitation phase of the setting reaction was surprisingly small when the total fluoride content of the glass was considered. Crisp and Wilson suggested that this may be due to the fluoride being transported as metal cationic complexes, such as $\text{AlF}_2^+$, $\text{AlF}^2+$ and $\text{CaF}^+$ which react with the polyacrylic acid in an acid-base reaction. The cation-polyacrylic acid bond of GIC is a stronger one than that of the cation-phosphoric acid bond in silicate cements. Thus, more fluoride remains in the setting cement, and less is liberated into solution than from the silicate cement.

2. **Research on Commercial Brands of Glass Ionomer Cements and Comparisons to other Restorative Materials**

Most of the initial research work on fluoride release from GIC was carried out on the first commercially available brand - Aspa.

Crisp et al.\textsuperscript{(17)} in 1976, undertook a 3-month study of the chemistry of the water erosion of two forms of Aspa cement. Samples of
the material were made, and suspended in demineralised water at 23°C. The storage medium was changed regularly over a 13-week period. Rates of elution of various chemical species were then determined. Fluoride release was detected using a specific fluoride ion electrode. They then compared the erosion behaviour to that of the silicate, silicophosphate, and zinc polycarboxylate dental cements, from earlier studies.\textsuperscript{(122)} It was found that no species was eluted to any great extent. After 23 hours only 0.4% of the total fluoride content of the specimens had been released. They showed that even though the rate of elution of fluoride ions decreased over the 13-week period, there was no indication that they ceased to be eluted altogether.

The fluoride loss from GIC was found to be similar to that from dental silicates and silicophosphates, but this was not indicative of similar disintegration patterns. Crisp \textit{et al.} \textsuperscript{(17)} showed that \textit{Aspa}, unlike the silicates, does not continuously lose significant amounts of the metal ions involved in cement matrix binding. The three main species eluted, silica, Na\textsuperscript{+} and F\textsuperscript{−} are
not important in the final structure of the set material. They stated, however, that fluoride elution is of importance clinically as it has a cariostatic effect.

In 1977 in an in vitro study, Forsten (34) compared the release of fluoride from Aspa to that from silicate cement under the same conditions. The specimens were shaken in 10 ml 0.01M phosphate buffer solution together with 100 mg of synthetic hydroxyapatite. The solution was changed weekly over a 7-week period and the apatite was analyzed for fluoride. The release of fluoride from Aspa (132 µg/mg) was greater than that from the silicates (73.6 µg/mg). Forsten showed that the rate of release of the fluoride ion was greater in the first 2 weeks than in the subsequent 5 weeks, and that, as Crisp et al. (17) had shown, it did not decrease altogether with time.

It is interesting to compare Forsten's GIC results with his earlier research. He had previously examined the fluoride release pattern from fluoride containing amalgam and composite, and two luting cements, using a similar method to that used in his Aspa research. (33, 35, 36, 38)
The fluoride concentrations in the alloy powder, the silicophosphate cement and the polycarboxylate cement were 2.0 μg/mg, 70 μg/mg and 20 μg/mg respectively. He stressed that the total fluoride content was not of such importance as the rate of release. The release of fluoride from amalgam was only significant initially but the cements mimicked the silicates and Aspa in their marked initial release and significant continued release of this ion. The initial fluoride release from composite resin was 4-10 times less than from silicates and became comparable to them with time.

In 1978, Maldonado et al. (71) in the U.S.A. investigated the tooth bonding properties of Aspa and its fluoride release. The specimens were suspended in distilled water and transferred to a fresh storage medium at 24-hourly intervals, for a period of 21 days. Each day each solution was analysed for fluoride using a fluoride-ion electrode. Like Forsten, (34) they compared their results to silicate cement, and found, with both materials, that there was a marked release of fluoride in the first few days which gradually decreased to a constant level at
day 11. During the 21 days, almost 2.5 times the amount of fluoride was released from GIC (1,800 μg) as from the silicate cement (710 μg).

In 1981, Causton, (8) reported on a long-term study in which he examined the rate of fluoride release from Aspa. He showed how exposing the setting cement to an aqueous environment too soon will interfere with the setting process. Specimens of Aspa were prepared and allowed to set for periods of 1 to 48 hours in an incubator before they were placed in 10 ml of distilled water at 37°C. These solutions were changed regularly over a period of 365 days. Fluoride detection was carried out with the fluoride ion electrode. It was demonstrated that the fluoride ion release from GIC is classically Fickian and originates from one finite source, probably the gel/polymer matrix of the cement. It never exceeded 1% of the total fluoride content of the cement, and was considerably greater in the first few hours after setting. He also showed that nearly all the fluoride that is to be released occurs in the first 6 months - after that time it is negligible.

Around the same time that Causton performed his study, Crisp et al. (21) re-examined
Aspa for fluoride release and compared it to a commercially available silicate cement and a zinc polycarboxylate cement. The samples were made as in their earlier experiments(17) and suspended first in 50 ml of demineralised water and then in lactic acid, each for a period of 7 days. Using the fluoride ion electrode, they showed once more that the rate of release of fluoride ion was greatest on the first day, and that it was released in both neutral and acidic conditions. They concluded that GIC and the silicates were similar in their fluoride releasing ability. However, the chemical constituents of the zinc polycarboxylate cement dissolution products were markedly different.

Cranfield et al. (14) in 1982 undertook a similar study to that by Crisp et al. in 1976. Cranfield et al. examined the fluoride release from three brands of GIC - ChemBond*, Aspa and Fuji** and, like most


** Fuji Ionomer. G-C Dental Industrial Corp., Japan
other researchers, compared their results with those obtained with silicate cements. The cements were made into discs, and, after allowing them to set for 1 hour at 37°C, they were suspended in 50 ml of de-ionized water. The solutions were changed daily initially and then each 7 days over a 13 week period. The fluoride content was assessed at weekly intervals using a fluoride ion electrode. TISAB solution was added to the solutions being tested to dissociate complexed fluoride ions. Throughout the study the fluoride release from the GIC's was consistently greater than from the silicate cement. Fuji showed the greatest release which was still at measurable levels at the end of the experiment. Approximately 0.7 per cent of the total fluoride content of GIC was released. Their data suggested that fluoride is derived from the entire volume of the specimen and that the relationship between this volume and the concentration of fluoride release is near-linear.

Tveit and Gjerde (110) in 1981, used a very complicated method to detect fluoride release from Aspa and other restorative materials. Specimens were made and stored in artificial
saliva for 7 weeks with no changes in the solution during this time. The fluoride content in the saliva was then measured using a spectrophotometric method. Specimens of a fluoride-containing amalgam, a GIC (A3Pz) and a silicate cement were tested. They found that the fluoride release from silicate cement was 5 times greater than that from GIC, which was itself 4 times greater than that from the fluoride-containing amalgam.

There appears to be great contradiction between the results of Tveit and Gjerdet (110) and other studies. (8, 17, 21, 34, 48, 71, 104) This may be due to the fact that Tveit and Gjerdet (110) differed from others in the method used for fluoride detection, the medium in which the tests were conducted, and the frequency with which it was changed.

3. Glass Ionomer Cement - Research on Enamel and Dentine Reactions

It can be postulated that any source of fluoride placed in contact with a tooth, will render it more resistant to decay. The
incorporation of fluoride into dental restorative materials alone, opens up a multitude of caries-preventive possibilities.

There are several reports in the literature, on the anticariogenic properties of GIC. Wesenberg and Hals, (117, 118) Swartz et al., (104) Smith et al., (101) and Hotz (48) have all demonstrated and examined the fluoride releasing capacity of GIC. Decalcified areas adjacent to cavity margins have shown evidence of increased radio-opacity following the placement of GIC restorations. Similarly, electron probe micro-analysis has detected higher fluoride content in areas adjacent to GIC restorations. Swartz et al. (104) mentioned the possibility of fluoride altering the metabolic activity of plaque formed at the margins of restorations and thus preventing secondary caries.
MATERIALS AND METHODS

Glass Ionomer Cement

Four different brands of GIC were used in this study:

(See Figs. 5 – 8)

<table>
<thead>
<tr>
<th>Brand Name</th>
<th>Manufacturer</th>
<th>Batch No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuji Ionomer - Type II</td>
<td>G-C Dental Industrial Corp. (Japan)</td>
<td>280721</td>
</tr>
<tr>
<td>Ketac</td>
<td>Espe Pharmaceutical Company (W. Germany)</td>
<td>G23990</td>
</tr>
<tr>
<td>ChemFil</td>
<td>DeTrey (U.K.)</td>
<td>Lot A154 81/12</td>
</tr>
<tr>
<td>Hy-Bond glastonomer-F</td>
<td>Shofu Dental Mfg. Co. (Japan)</td>
<td>Pdr:-108103 Lqd:-028216</td>
</tr>
</tbody>
</table>

Chemicals

Fluoride standards were prepared from a commercially available stock solution. (Orion 100 ppm sodium fluoride standard solution, Orion Research Inc., Cambridge, Mass., U.S.A.). An ionic strength adjustment buffer (Tisab II Ionalyzer, Orion Research Inc., Cambridge, Mass., U.S.A.) was used to dissociate metal fluoride complexes. A dilute (0.1 M HCl) hydrochloric acid solution (Ajax Chemicals, Sydney, Australia) was used in the initial cleaning of glassware and plasticware. Double distilled, deionised water was used throughout (Fig. 9).
Ketac brand of glass ionomer cement.
Fuji brand of glass ionomer cement.
ChemFil brand of glass ionomer cement.
Figure 8

_Hy-Bond_ brand of glass ionomer cement.
Figure 9

Vaquapura water déminéraliser.
Apparatus

'E-MIL' Bora volumetric glassware (Corning Ltd., Laboratory Division, Stone, Staffordshire, England) was used to prepare standard fluoride solutions. One litre plastic containers and 50 ml plastic sterilized containers with screw lids were used for storage of solutions. Rinsing of apparatus and transfer of solutions were with plastic rinse bottles and plastic pipettes. Test solutions were placed on plastic coated surfaces (Microsample dishes, Orion Research Inc., Cambridge, Mass., U.S.A.). A fluoride specific ion electrode (Orion Model 94-09, Orion Research Inc., Cambridge, Mass., U.S.A.) connected to a pH/mV meter (Pye Unicam Model 290 Mark 2, Pye Unicam Ltd., Cambridge, England) was used to determine fluoride concentration. (2, 3, 31, 39, 61) The apparatus is shown in Figure 10. Samples were stored in an incubator (QUALTEX-Solidstat, Watson Victor Ltd., Australia) between readings. A Mettler balance (Type H16, E. Mettler, Zurich) was used to weigh samples.

Method

The method used in this study was based on that used in 1967 by Wilson and Batchelor (122, 123), in their investigation of fluoride release from silicate cements. More recently, Cranfield et al. (14)
A fluoride specific ion electrode connected to a pH/mV meter.
and Kuhn et al. (58) in the U.K. tested fluoride release from GIC and silicate cements using similar methods.

Each sample was prepared according to the manufacturer's instructions using a paper pad and a plastic spatula, excepting Ketac which was in a capsulated form (Table 2). The material was placed into a PTFE* mould of diameter 7 mm and height 3 mm to standardize sample size. (Figure 11). Each sample was allowed to set for 1 hour at room temperature under the constant pressure of a glass slab (371.6 g), which completely covered the sample surfaces and thus prevented dehydration. The samples were then tied with pre-measured lengths of cotton and were weighed before being immersed and fixed in containers with 40 ml of double distilled, de-ionised, demineralised water (Figure 12). Each container had been rinsed once with 0.1M HCl and 10 times with double distilled, de-ionised water. These were then placed in an incubator at 37°C.

At exactly 7-day intervals, the containers were removed from the incubator and allowed to cool to room temperature. Each sample was raised from the solution and rinsed with 1 ml of double distilled, de-ionised, demineralised water. The rinse solution

* polytetrafluoroethylene
<table>
<thead>
<tr>
<th>BRAND</th>
<th>POWDER/LIQUID RATIO</th>
<th>MIXING TIME</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuji ionomer</td>
<td>2.4 : 1</td>
<td>40 seconds</td>
</tr>
<tr>
<td>Type 2</td>
<td>- powder mixed</td>
<td>- powder mixed into liquid in 2 increments.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ketac</td>
<td>3.4 : 1</td>
<td>10 seconds.</td>
</tr>
<tr>
<td></td>
<td>- capsule mixed</td>
<td>- capsule mixed in high energy amalgamator.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ChemFil</td>
<td>6.8 : 1</td>
<td>30 seconds</td>
</tr>
<tr>
<td></td>
<td>- powder mixed</td>
<td>- powder mixed into liquid in 3 increments.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hy-Bond</td>
<td>2.5 : 1</td>
<td>45 seconds</td>
</tr>
<tr>
<td></td>
<td>- half the powder</td>
<td>- half the powder is mixed into the liquid in</td>
</tr>
<tr>
<td></td>
<td>is mixed into the</td>
<td>first 10 seconds, then the rest of the material</td>
</tr>
<tr>
<td></td>
<td>liquid in first 10</td>
<td>is added over 25 seconds.</td>
</tr>
<tr>
<td></td>
<td>seconds, then the</td>
<td></td>
</tr>
<tr>
<td></td>
<td>rest of the material</td>
<td></td>
</tr>
<tr>
<td></td>
<td>is added over 25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>seconds.</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Powder/liquid ratios and mixing times for the 4 brands of glass ionomer cements used in this study.
Figure 11

PTFE mould used to standardise sample size.
Sample of glass ionomer cement immersed in closed containers filled with double distilled, de-ionised, demineralised water.
was added to the solution remaining in the container then allowed to air dry freely suspended for 5 minutes at room temperature \((23 \pm 1^\circ C)\) and then weighed. An aliquot of solution \((0.05 \text{ ml})\) was removed from each container for fluoride assay with a plastic pipette.

The aliquot was mixed with equal volume of total ionic strength adjustment buffer (TISAB). The fluoride concentration was read directly in parts per million on a calibration curve drawn for a pH/mV meter.\(^{(44)}\) The fluoride ion detector was rinsed with double distilled, de-ionised, demineralised water and dried thoroughly between sample solution testing. The fluoride ion electrode was calibrated at room temperature \((23 \pm 1^\circ C)\).

Each sample was again weighed before being re-immersed in 40 ml of fresh solution, and replaced in the incubator for another 7 days.

Fluoride ion release in \(\text{mgF/g}\) of sample was determined taking into account the weight of each sample and using the following procedure:

- \(\text{mV}\) reading obtained from voltmeter
- \([\text{F}^-]\) read off logarithmic standards graph
- ppm determined from \([\text{F}^-]\)

\[
\text{F ion content} = \frac{\text{ppm} \times \text{volume of solution}}{\text{weight of sample}} \quad (\text{mg/g})
\]
The accuracy of the method was checked by testing fluoride recovery from 5 known concentration replicate solutions. The mean percentage recovery was 92.66 ± 1.29.

Statistical analysis of the results was carried out using Duncan's new multiple-range test. Individual comparisons between means were made at the 0.05 level of significance.
RESULTS.

Each of the 4 brands of GIC released fluoride throughout the 12-week experimental period. Data on the fluoride release from each individual sample are presented in Tables 3-6.

Figure 13 shows the weekly mean fluoride release from Fujé, Ketac, ChemFül and Hy-Bond. Each brand showed a large release of fluoride after 7 days immersion. The highest release was for Hy-Bond and the least for Ketac. The fluoride released dropped dramatically in the second week to approximately one-quarter the initial values, and then continued to decrease steadily for the following 3 weeks. From week 5 till week 12 the results indicate a relatively steady elution of fluoride from the samples. Throughout the experimental period, Hy-Bond had a higher release rate than each of the other brands.
at any given time. *Ketac* showed the lowest fluoride release with the exception of week 10 when it rose slightly above *ChemFil*.

Figure 14 shows the accumulative fluoride release over the 12-week experimental period for *Fuji, Ketac, ChemFil* and *Hy-Bond*. *Hy-Bond* released the most fluoride, and at the greatest rate, followed by *ChemFil, Fuji* and *Ketac*. *Ketac* released overall one-third the amount of fluoride released by *Hy-Bond*.

Statistical analysis of differences in fluoride release between brands is shown in Table 7.

Weekly weight changes for each sample of *Fuji, Ketac, ChemFil* and *Hy-Bond* after 7-day immersion in aqueous solutions are included in the Appendices. There was a slight fluctuation in the weight of each sample over the 12-week experimental period.
**TABLE 3.** FLUORIDE RELEASE FROM *FUJI* (μgF/g sample)

<table>
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<tr>
<th>Week</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>Mean F loss (S.D.)</th>
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<tr>
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<td>2595.0</td>
<td>2745.0</td>
<td>2091.0</td>
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<td>616.0</td>
<td>529.0</td>
<td>841.0</td>
<td>593.0</td>
<td>662.0</td>
<td>630.5 (114.1)</td>
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<td>375.0</td>
<td>483.0</td>
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<tr>
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<td>467.5</td>
<td>290.9</td>
<td>369.3</td>
<td>388.5 (73.2)</td>
</tr>
<tr>
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<td>155.8</td>
<td>180.7</td>
<td>252.2</td>
<td>255.1</td>
<td>182.2</td>
<td>235.6</td>
<td>210.3 (42.5)</td>
</tr>
<tr>
<td>6</td>
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<td>228.6</td>
<td>326.7</td>
<td>326.7</td>
<td>215.6</td>
<td>278.5</td>
<td>254.4 (69.2)</td>
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<td>179.3</td>
<td>206.4 (51.9)</td>
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<td>170.5</td>
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**Total accumulative loss** 4500  5505  5903  6679  4796  5785  5528.0 (790.5)
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<th>Sample 4</th>
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Total accumulative loss: 4577 3764 4512 3562 2965 3159 3756.5 (673.1)
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<th>Sample 3</th>
<th>Sample 4</th>
<th>Sample 5</th>
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<th>Mean F loss (S.D.)</th>
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<td>83.6</td>
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Total accumulative loss 5015  6451  6596  6564  5947  6194  6127.8 (598.2)
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<th>Sample 3</th>
<th>Sample 4</th>
<th>Sample 5</th>
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<th>Mean F loss (S.D.)</th>
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<td>259.0</td>
<td>222.6</td>
<td>246.9</td>
<td>227.5 (21.7)</td>
</tr>
</tbody>
</table>

Total accumulative loss: 9106, 7751, 7710, 8258, 8368, 8751, 8324.0 (548.7)
The weekly release of fluoride from glass ionomer cement.
Figure 14.

ACCUMULATIVE RELEASE OF FLUORIDE FROM GIC.

Accumulative release of fluoride from glass ionomer cement over a 12-week period.
**TABLE 7.** ANALYSIS OF DIFFERENCES IN FLUORIDE RELEASE BETWEEN BRANDS AT EACH TIME INTERVAL

(Duncan's New Multiple Range Test (102))

<table>
<thead>
<tr>
<th>Week</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
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<tr>
<td>10</td>
</tr>
<tr>
<td>11</td>
</tr>
<tr>
<td>12</td>
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</table>

*FUJI*  
*KETAC*  
*CHEMFIL*  
*HY-BOND*

Fluoride release not significantly different at 0.05 level between brands connected by bars.
DISCUSSION

Any restorative material which has the ability to adhere to tooth structure and to release fluoride ions should be of great value in dentistry. GIC is a relatively new restorative dental material shown to have these properties, and as a result comparatively little data has been published.

The fluoride ion is present in the initial fusion mixture of the glass powder component of the cement in the form of calcium fluoride, cryolite and aluminium fluoride. The setting reaction, as described in detail earlier (p. 6), releases fluoride ions which then migrate, probably as complexed ions such as $\text{AlF}_2^+$, $\text{AlF}^{2+}$ and $\text{CaF}^+$. These cause a cross-linking of polyanionic chains, resulting in the gelation and setting of the cement. Fluorine must be incorporated into the basic ingredients in carefully calculated quantities as it may erode crucibles and furnace linings during the fusion process. The fluoride acts as a flux.
in the preparation of the glass powder component of the cement. According to Wilson et al. (127), it appears to have a strengthening effect on the final cement and in excessive amounts, tends to withhold cations from the polyanions, thus retarding the set.

It is believed that fluoride exerts its anticaries effect through one or more of the following mechanisms: (73, 134)

- increasing enamel resistance
- increasing the rate of enamel maturation
- remineralising incipient lesions
- interfering with microbial metabolism

Fluoride is thought to increase enamel resistance by being incorporated into the developing tooth structure as fluorapatite, which is less soluble than hydroxyapatite. Thus, the greater the amount of fluorapatite, the greater the resistance to dissolution of the surface enamel. (13, 28, 105)

An increased rate of maturation due to the presence of fluoride, occurs in the following manner. The enamel of newly erupted teeth may have areas where mineral deposition is not entirely complete. It is postulated, that if fluoride, even in very small quantities, is present during the maturation of hypomineralised areas, it should
result in enamel more resistant to acid attack.

Fluoride is also an important means of remineralising incipient lesions. Incipient lesions in enamel may have a sound surface but with substantial mineral loss, 30 to 50 μm below the surface. Their remineralisation may occur by a deposition of mineral from saliva.

Mellberg et al. (73) have also postulated that fluoride interferes with the metabolism of microorganisms involved in caries formation. Thus, topically applied fluoride can affect the activity of microorganisms contained in saliva and plaque. It can act as an inhibitor of the bacterial enzymes responsible for the production of acids.

It is not known which of the above mentioned mechanisms is responsible for the potentially cariogenic effect of GIC materials.

The effect of fluoride from GIC restorations on the surrounding tooth structure, has been examined by several researchers. Early work has mainly been carried out on laboratory prepared materials such as
the G-200 glasses and on Aspa, the first commercially available brand. (81)

Wesenberg and Hals (117, 118) simulated carious lesions in extracted human teeth and then showed by microradiography, polarised light microscopy and by electron probe microanalysis, that after restoration with GIC (Aspa), a zone of increased radiopacity was present adjacent to the restoration. This zone, probably a hypermineralised zone, was seen in both dentine and enamel. They hypothesized that fluoride ions from the filling material may cause a re-precipitation of the dissolved calcium and phosphorus mineral salts.

Swartz et al. (104) in 1980 examined the fluoride releasing properties of Aspa and silicates. They examined the fluoride content on the surface enamel and at a distance of 3 mm from the margins of cavities restored with either GIC or silicate cement. Biopsies were obtained by abrading layers of surface enamel. These layers were then dissolved in perchloric acid, and after centrifuging, aliquots of supernatant were analysed with the fluoride ion electrode. Their study, carried out over a 12 month period, related fluoride content of enamel samples to
the depth of each sample from the tooth surface. It was observed that the fluoride content of enamel decreased from the surface of the tooth towards the dentino-enamel junction. As with silicate cements, GIC showed a greater fluoride release in tooth structure adjacent to it, than at a 3 mm distance. The lateral spread of fluoride was not specified by the authors. The overall fluoride release pattern mimicked that of silicate cement by increasing steadily to a peak at 6 months and then decreasing slowly.

Smith et al. (101) in 1982 confirmed the results of Swartz et al. (104). They tested Aspa, Fuji and a new brand of GIC, Ketac and found, using the same method, that over a 28 day period, GIC is an effective fluoride source. Successive enamel layers were measured for both fluoride and calcium, which were shown to increase as the experiment progressed. The extent of the lateral spread of fluoride into dentine and enamel was not given.

Hotz (48) in 1979, carried out an in vitro study to examine artificial carious lesions in enamel and dentine adjacent to amalgam, composite and GIC (Aspa and Fuji) restorations. In 60% of cases the
tooth structure adjacent to the GIC showed significant zones of inhibition of demineralisation after the 10-day test period. Though the degree of fluoride spread into the enamel and dentine was not specified, Hotz, as did the previous researchers, confirmed the protecting properties of GIC.

More recently, Retief et al. (92) examined the fluoride uptake from GIC into enamel and cementum. The Fuji brand of GIC was placed in Class V lesions at the cemento-enamel junction of extracted teeth. They were then individually suspended in synthetic saliva at 37°C, which was changed regularly for periods up to 6 months. The fluoride content of each tooth had previously been estimated. After suspension, enamel and cementum samples were again taken by means of perchloric acid etching. The fluoride content of these solutions was determined by gas chromatography. The authors showed that fluoride uptake by enamel after 1 month was retained at 3 and 6 months and was in the order of 2,500 ppmF. The fluoride acquired by the cementum after 1 month (15,000 ppmF) decreased considerably after 3 months (6,000 ppmF) and then stayed the same for the remainder of the experimental period. The enamel fluoride content tended to decrease with increasing distance from the GIC restoration. The authors state
that the cementum fluoride uptake at the biopsy sites for a specific time interval was not significantly different from baseline values. They deduce that fluoride is more firmly bound to the apatite structure of enamel than to the cementum.

It can thus be seen from the previous in vitro studies that enamel, dentine and cementum can take up substantial amounts of fluoride from a GIC restoration.

All four brands of GIC examined in this study, (Fuji1, Ketac, ChemFil and Hy-Bond), released detectable amounts of fluoride during the 12-week experimental period. It is difficult to compare the results of this study with those of previous researchers as not all relevant information has been presented in the published scientific literature.

The results of this study may be juxtaposed with those of Crisp et al. They examined two types of Aspa over a 13-week period. The fluoride range obtained at this time interval was in the order of some two-fold less than that obtained in this study even though very similar working conditions were used. Perhaps, discrepancies in results may be explained by different materials being used. At the time of this study, Aspa was not
available commercially in Australia and was therefore not used in this investigation. It is thus difficult to make quantitative comparisons between studies when materials differ.

A later study by Crisp et al. (21) examined 4 types of Aspa over 7 days. The fluoride release they showed over the period was 1.4–2.1 mgF/g cement as compared to this study's higher values of 1.8–3.1 mgF/g cement. Again, value discrepancies may be explained by brand differences.

Causton (8) presents the only long-term results of fluoride release from GIC in the literature. He found, that over a period of 52 weeks, the fluoride release from Aspa never exceeded 1 mgF/g sample, and that it all occurred in the first 6 months. The results of this study are considerably higher than those of Causton.

Several researchers, such as Maldonado et al. (71) and Hotz (48) did not present sample weights in their data and thus exact comparisons cannot be made in this study. They did present, however, total fluoride release values. The values of Maldonado et al. were more than double those of Causton (8) and Hotz's results were less. Cranfield et al.'s (14) recent study in 1982, though using
almost the identical method to this study, obtained higher fluoride values, expressed in ppm (parts per million) from Fuji and Aspa. The sample size used differs from this study and sample weights are not presented.

It is interesting to note in this study, the final week's weight of each sample as compared to week 1 value. Each sample of Fuji decreased in weight at week 12; 5 out of 6 samples of Ketac increased in weight; 4 out of 6 samples of ChemFil decreased in weight, as did 5 out of 6 samples of Hy-Bond. Possibly it can be hypothesized that the weight increase for the samples of Ketac indicates a high water sorption capability of the material.

Another point worth noting in this study is that the Japanese brand of GIC, Hy-Bond, released almost twice the amount of fluoride than did the 3 other brands. Its superior fluoride releasing ability could be due to the tannin-fluoride additive incorporated by the manufacturer in an attempt to minimise the possibility of secondary caries. (106)

Though discrepancies are present in the studies available in the literature, the trend of fluoride release in this study is basically similar
to that observed by other researchers; that is, a higher release of fluoride initially which decreased with time. In terms of absolute values there are discrepancies. The values of this study are intermediate between those obtained by Cranfield et al. (14), which were higher than those of Crisp et al. (21), and Maldonado et al. (71).

Reasons for discrepancies may be varied. The solubility of GIC and its subsequent fluoride release may be influenced by many factors. Intrinsic factors relate to the preparation of the cement and include power/liquid ratios, curing time and temperatures, mixing times and sample sizes. Extrinsic factors relate to the environment to which the samples are exposed and include medium solution types, volumes of solutions used and frequency of changing them. Other reasons for disagreement in the literature may be due to research being carried out on laboratory prepared specimens of GIC as opposed to commercially available brands which may differ somewhat in basic composition of the powder and liquid components.

Several researchers (17, 19, 24, 27) have observed constituents other than fluoride to be released from GIC. Silica, phosphorus pentoxide as well as Na⁺, Ca²⁺, Al³⁺ and PO₄³⁻ have also been detected and shown to be of benefit to tooth
structure.

What the researchers all have in common is the agreement that GIC is a fluoride releasing material and that the rate of elution of fluoride ion decreases with time.
SUMMARY AND CONCLUSIONS

This study was developed to examine the fluoride releasing properties of glass ionomer cement. Four commercially available brands of GIC, Fuji, Ketac, ChemFil and Hy-Bond, were tested for their fluoride releasing ability.

Six samples of each material were made according to the manufacturers' instructions, and allowed to set for 1 hour at room temperature, protected from dehydration. Each sample was weighed, then tied and suspended in containers filled with 40 ml of double-distilled, de-ionised, demineralised water, and placed in an incubator at 37°C for 12 weeks. At weekly intervals, the sample solutions were changed and tested for their fluoride ion content and each sample was weighed. Fluoride levels in the solutions were determined using a specific fluoride ion electrode.

All 4 brands of GIC tested were sources of fluoride. Rates of release varied considerably and
were up to 4 times greater in the first week than at any other time during the experimental period. *Hy-Bond* released the most fluoride overall, followed by *ChemFil, Fuji* and *Ketac*. Accumulatively, *Hy-Bond* released 3 times as much fluoride as *Ketac*. No sample of GIC failed to release fluoride at any time during the 12 week period.

The superior fluoride releasing property of *Hy-Bond* can perhaps be explained by its tannin-fluoride additive.

GIC is capable of releasing fluoride ions, and this property, together with its ability to adhere to tooth structure, make it very beneficial as a dental restorative material.
## APPENDIX 1. WEIGHT OF EACH SAMPLE. - *FUJI* (mg)

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