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SOME ASPECTS OF SOLUBILITY OF SILICATE
AND GLASS IONOMER CEMENTS
A LABORATORY STUDY

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2. ABSTRACT

Three aspects of the in-vitro solubility of silicate and glass-ionomer dental cements were studied.

a)   The solubility of silicate cements was studied using the "weight of evapourated eluate" method. It was shown that the dissolution of these cements depends on the volume of solution in which they are immersed and also the frequency in which this was changed. It was seen that these cements were capable of taking up fluoride ions from concentrated solutions while releasing the same ions in more dilute solutions. Studies with samples of varying surface area:volume ratios confirm that dissolution is not only dependent on the surface area but that matter is also lost from the bulk of the specimen.

b)   The release of organic materials from glass ionomer cements immersed in water or phosphate solution was studied using a total organic content (T.O.C) analyser. It was seen that upto 0.10mg of organics could be detected in such solutions. The concentration of detected organic species rises with increasing time, then falls off again. This is explained in terms of re-adsorption of the organic species by the cement.

c)   Thermogravimetric analysis studies of glass ionomer cement samples with various histories were made. Weight loss (presumably of water) was shown to be related to the history of the samples as well as to the thermogravimetric conditions. The thermogravimetric conditions used in this study were air and Nitrogen atmospheres. The results are used to assess the merits of the

"sample—weight loss" method for investigating solubility.
This method, in view of the simultaneous water loss or uptake
by the sample, is not recommended.

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5. INTRODUCTION

5.   INTRODUCTION

Dental cements have a wide variety of clinical applications in Conservative Dentistry. In general cements are employed for two primary purposes.

   a) to serve as a restorative material

   b) to serve as a luting agent for the retention of

       restorations such as inlays, crowns, and bridges.

This comprehensive range of applications makes various and exacting demands of aesthetic, mechanical, chemical and biological properties of dental cements. There is no single cement that satisfies all the ideal requirements and is therefore universally suitable for all usages Wilson (1975).

Materials used in restorations should ideally possess the following properties.

   a) Should be insoluble in oral fluids.

   b) Should have a low thermal conductivity.

   c) Thermal coefficient of expansion similar to that
       of tooth.

   d) Should be biologically compatible with dental tissues
       especially the pulp.

   e) Should have adequate compressive, tensile and abrasive
       strengths.

   f) Should have ability to adhere to tooth structure such
       as enamel or dentine.

   g) Should have a colour and texture similar to that of tooth.

   h) Should be easy to manipulate and apply under oral conditions.

   i) Should be aesthetically acceptable.

The first dental cements to be used as restorative material were based on zinc oxide powder reacting with organic or inorganic acids to yield rapid setting cements. The first of these was Sorel's cement (1855) which utilised aqueous solution of zinc chloride reacting with zinc oxide powder. Subsequent development of zinc oxide cements led to the production of zinc phosphate and zinc oxide-eugenol cements resulting from the use of aqueous solution of concentrated phosphoric acid and eugenol respectively. The most important drawback of these cements was their very high solubility in oral fluids.

Silicate cements based on the reaction of an ion-leachable glass, calcium aluminosilicate, and a concentrated aqueous solution of phosphoric acid were introduced by Fletcher (1878). Fluoride containing cements were introduced by Schoenbeck (1908) by the use of a fluoride flux and since then these cements have persisted. Several other experimental cements have been reported, but as far as is known no fundamental changes have been made in their formulations, Smith (1975).

Silicate cements became popular as restorative material because of its favourable properties such as translucency, high compressive strength, and more importantly their cariostatic properties results from continuous slow release of fluoride ions, Skinner and Phillips, (1967 Phillips, (1969); Norman et al (1961); Hallsworth (1969). Silicate cements still retained disadvantageous properties such as a relatively high solubility and susceptibility to oral fluids.

In 1969 Wilson and Kent introduced the glass ionomer cements based on a reaction between a powder containing ion-leachable glass alumino-silicate and aqueous solution of polyacrylic acid, a linear polymer containing several pendant carboxyl groups as a liquid. Glass ionomer cement is subject to water solubility and acid erosion though to a lesser extent than the silicates.

Probably the one property of cement that is of greatest clinical significance is   solubility and disintegration in oral fluids. Studies on marginal leakage indicate the necessity for reduction in the solubility of these cements in oral conditions. Most of the published data for solubility of various cements is measured 'in vitro' by immersion of cement in distilled water. When attempting to measure the exact amount of solubility to a select clinically suitable material it is found that the rates of dissolution can be influenced by many factors related to the conditions of the test. Some of these factors are not included in the present Dental Specification tests.

Hence no single laboratory test can wholly duplicate oral conditions.

6.   STATEMENT OF THE PROBLEM

Numerous studies have shown that the test environment i.e. nature
of the media, have great influence on the solubility of dental silicate
cements, however, some studies suggest that factors other than the test
environment i.e. surface area:volume ratio have some influence on
the reported solubilities. There are likewise strong indications that
a build up of relatively small concentrations of species such as
phosphate in the test solution themselves impede further dissolution
of the cements.

There is no published data at all on the solubility of glass
ionomer cements except for a single recent abstract MacBae (1982).
The solubility of glass ionomer cements known from clinical observation
is smaller than that of silicate cements, however, such knowledge
is only qualitative. Some of the dissolution products from glass ionomer
cements are organics hence it is difficult to obtain accurate results
by high temperature drying methods as used for silicate cements.

It is therefore the aim of this study to examine:

A.   a) the effect of intrinsic factors such as surface area: volume
         ratio   on the solubility of silicates.

     b)   the effect of extrinsic factors such as the volume and
          composition of test solution on the solubility of silicate
          cements.

B.   The release of organic material from glass ionomer cements - making
     use of facilities made available by the Water Research Centre.

7. REVIEW OF THE LITERATURE

7.1 GLASSES, SILICATES, GLASS IONOMER CEMENTS

Glass is a single-phase solid which may be considered as a super cooled liquid. It consists essentially of silica or mixtures of silica with metal oxides such as Na_2O, PbO and other oxides. Silicates exists as long chains hence they can be considered as polymers.

Silicates and glass ionomer cements have two phases, a matrix amorphous gel which is a hydrated salt, and unreacted glass. It is therefore important to realize that silicates and glass ionomer cements are not strictly glasses. However the mechanism of dissolution of glasses is important in the understanding of the dissolution of these cements.

When a single phase glass is in contact with an aqueous solution, the alkali metal ions in the glass are leached out and replaced by protons. Hence the formation of a hydrated silica gel on the outer surface of glass takes place. In a two phased glass and glass ionomer cements there exists a hydrated glass, hence dissolution involves the increase of the degree of hydration when in contact with aqueous solution.

7.2   DENTAL CEMENTS

7.2.1   DEVELOPMENT OF SILICATE CEMENTS

The early history of silicate cement is obscure. However it may have been introduced as early as 1878 when Fletcher invented a cement based on the reaction of an ion leachable glass, calcium aluminosilicate, and a concentrated aqueous solution of phosphoric acid. Stoenbeck (1903) used beryllium silicate as a flux but the introduction of fluoride flux, Shoenbeck (1908) apparently yielded a better cement which led to successful application in dentistry. Early examples of these cements have been described by Voelker (1916) whilst Paffenbarger et al (1938) comprehensively reviewed these materials. There has been no major fundamental change in the formulation of silicate cements since then Peyton and Craig (1971), Skinner (1976).

7.2.2   DEVELOPMENT OF GLASS IONOMER CEMENTS

Glass ionomer cements consist of a powder containing special ion leachable glasses and a liquid, an aqueous solution of polycarboxylic acid such as polyacrylic acid.

A carboxylic acid is an organic acid which contains one or more carboxyl groups. Polyacrylic acid is a linear polymer containing several pendant groups, Wilson (1972).

The necessity to improve upon the performance of silicate cement which for long has been the chief material for anterior restorations led to the introduction of original Alumino Silicate Polyacrylic Acid (ASPA) by Wilson and Kent (1969, 1971, 1972).

ASPA cements have some of the favourable properties of silicate cements particularly those of compressive strength, translucency

and   anti-cariogenic properties resulting from the slow release of fluoride. They also have a higher acid resistance.

The original form of cement known as ASPA I was formed from 50% m/m aqueous polyacrylic acid and aluminiosilicate glass. This cement had two main disadvantages:

(i)   Slow setting and surface hardening rate.

(ii)   Polyacrylic acid solution slowly gelled on storage.

These properties made the dental applications, Wilson (1978) of ASPA I impracticable. The working and hardening characteristics were improved by addition of chelating acid co-polymers i.e. tartaric acid, to the liquid.   In this form it was known as ASPA II, Wilson (1975).

The shelf life of the liquid still remained limited varying from 10 to 30 weeks before gelation occurred. The reason for this behaviour was unknown. However it was reversible by heat treatment or mechanical agitation, suggesting that the reason for this behaviour could be a slow rearrangement of polymer coils giving rise to entanglements due to hydrogen bonding Crisp et al (1975).

Addition of methanol stabilized the liquid against gelation by methylating some of the carboxyl acid groups thus reducing the incidence of hydrogen bonding. In this form the cement was designated ASPA III. ASPA III was found to be weaker than other forms of cement because of the reduction of the number of carboxyl groups. As the liquid aged, though remaining mobile, the properties of the remaining cement deteriorated markedly.

The use of polyalkenoic acid co-polymer (acrylic and itaconic acid) which has an indefinite shelf life with less stereo-irregularity than polyacrylic acid reduced aggregation caused by hydrogen bonding. This liquid with the addition of tartaric acid resulted in the production

of ASPA IV. During the whole of the above development of glass ionomer cement, there was no change in the glass component. Crisp (1975).

Following the introduction of ASPA IV for a period of years the entire ASPA range is now understood to have been discontinued. Chemfil replaces it. In this product the glass is premixed with the de-hydrated organic acid and a cement is formed on addition of water. No further details of this product are known at present.

7.3 SILICATE CEMENT

7.3.1 CHEMISTRY OF SILICATE CEMENT

POWDER:

The powder used in silicate cement is based on aluminosilicate glass which is ion-leachable in acid solutions. The fusion mixtures consists primarily of silica, alumina, lime, sodium fluoride, calcium fluoride, cryolite or any combinations of these Skinner (1967). These are fused in a fluoride flux at a temperature of $1450^{o}C$, cooled, and then ground to give opal glasses containing phase separated droplets of fluorite.

Aluminosilicate glass has a negatively charged network which is susceptible to acid attack decomposing to liberate metal ions into the liquid to participate in the cement forming reaction, Wilson and Kent (1972).

LIQUID:

The liquid is an aqueous solution of concentrated phosphoric acid containing metal salts. It is not significantly different from that used in phosphate cements though it contains more water. The metal ions aluminium and zinc exist as simple salts or complexes and play an important role in cement forming reaction Wilson and Kent (1972); Wilson (1978).

7.3.2 SETTING REACTION OF SILICATE CEMENT

The cement forming reaction occurring in overlapping stages is essentially an acid-base reaction between the glass powder and the acidic liquid. Studies of the setting reaction with infra-red spectroscopy Wilson (1968) showed that this is an initially rapid

reaction where phosphoric acid ionises into $H_2PO_4^-$ and the hydrogen
ions released attack the surface of glass powder particles liberating
ions Al^{+3}, Ca^{+2}, Na^+ and F^- leaving behind an ion depleted silica
gel at the surface of the glass powder particles. The liberated ions
Al^{+3}, Ca^{+2}, Na^+ and F^- migrate into aqueous phase of the cement
and as the pH increases the ionic species precipitate as salts
Wilson (1972); Kent and Fletcher (1970). The principal reaction is
the formation of insoluble aluminium phosphate salt. The gel matrix
associated side reactions are precipitation of calicum fluoride and
formation of soluble sodium dihyrogen phosphate. The cement sets
hard when about 50% of the total phosphate has precipitated.

C_T UC

TABLE 1

CHEMICAL COMPOSITION OF SILICATE CEMENT

Powder	% w/w
SiO_2	41.6
Al_2O_3	28.2
CaO	8.8
Na_2O	7.7
F^-	13.3
P_2O_5	5.3
ZnO	0.3
H_2O	2.2
Less O for F^-	-5.6
Liquid	
Total phosphate H_3PO_4	48.8
Al^{+++}	1.6
Zn^{++}	6.1
Water upto	100.0

(Wilson and Kent (1972))

FIGURE 1

SCHEMATIC REPRESENTATION OF CEMENT FORMING REACTION

OF DENTAL SILICATE CEMENT

A.D. Wilson (1978)

LIQUID

(PHOSPHORIC)
(ACID)

H^+

MATRIX

$AlPO_4$

CaF_2

NaH_2PO_4

GLASS CORE

SILICA JEL

Al^{+3}

Ca^{+2}

Na^+

F^-
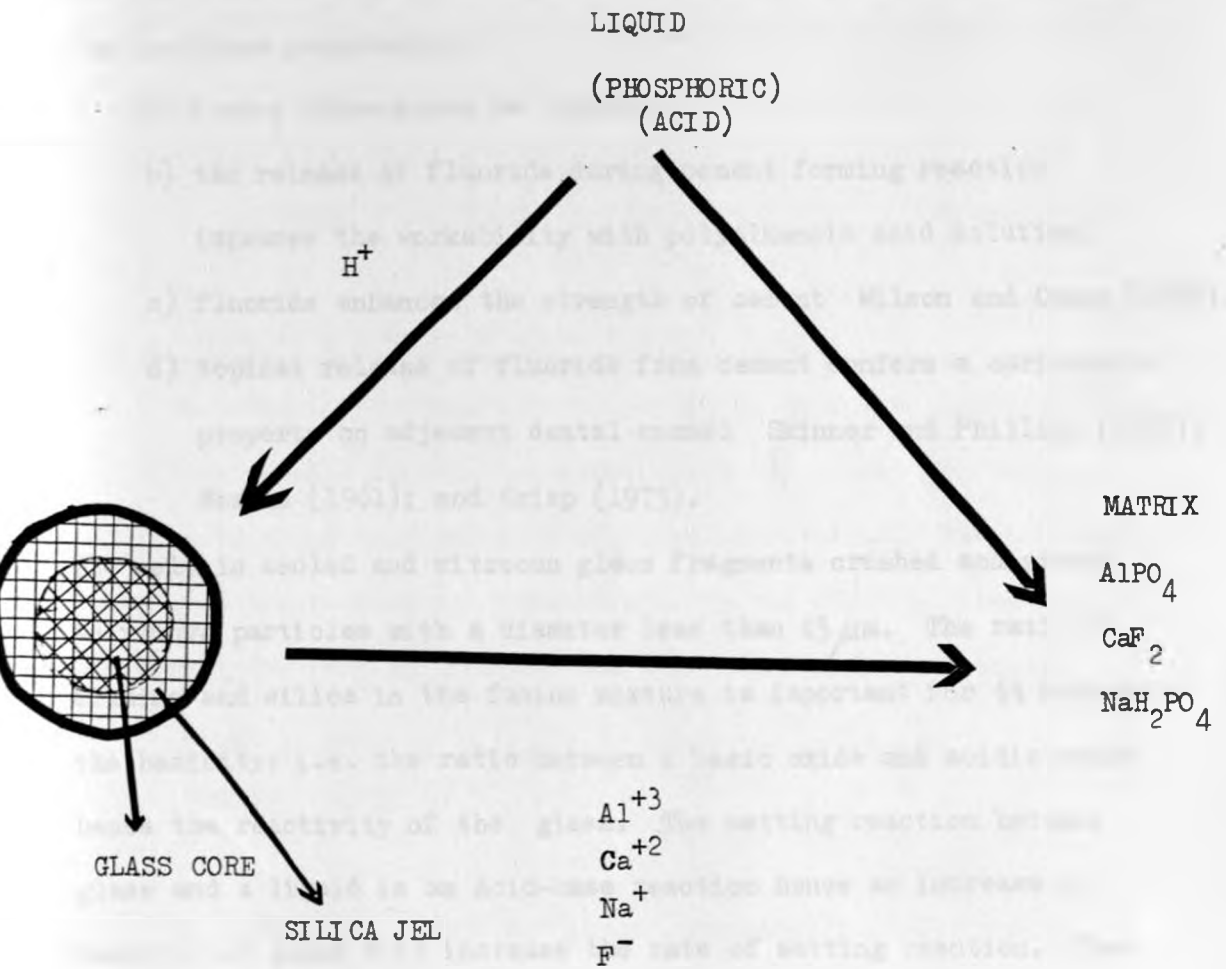
7.4   GLASS IONOMER CEMENTS

7.4.1   CHEMISTRY OF GLASS IONOMER CEMENTS

POWDER:

The powder used in this cement system is a special ion leachable glasses similar to those used for silicate cements except that they have a high alumina silica ratio. They are prepared by fusing mixtures of alumina silica, fluorides of Na^+, Ca^{+2}, Al^{+3} and phosphate at temperatures of between 1100^oC and 1300^oC in an electric furnace. There are a number of advantages which acrue from the use of fluoride flux in glass preparation.

a) fusion temperature is lowered.

b) the release of fluoride during cement forming reaction improves the workability with polyalkenoic acid solution.

c) fluoride enhances the strength of cement Wilson and Crisp (1974).

d) topical release of fluoride from cement confers a cariostatic property on adjacent dental enamel Skinner and Phillips (1967); Norman (1961); and Crisp (1975).

The melt is cooled and vitreous glass fragments crushed and sieved to remove particles with a diameter less than $45 \mu m$. The ratio of alumina and silica in the fusion mixture is important for it determines the basicity: i.e. the ratio between a basic oxide and acidic oxide hence the reactivity of the glass. The setting reaction between glass and a liquid is an acid-base reaction hence an increase in basicity of glass will increase the rate of setting reaction. Thus cements with different setting times and strengths can be formulated Wilson and Kent (1972).

LIQUID

All commercially available glass ionomer cements are based on
ASPA IV/IVA with liquids consisting of polyalkenoic acid which is a
co-polymer of acrylic and itaconic acids.

MOLECULAR STRUCTURE OF POLYACRYLIC ACID

$$- CH_2 - CH - CH_2 - CH - CH_2$$
$$\qquad\quad | \qquad\qquad |$$
$$\qquad\; COOH \qquad COOH$$
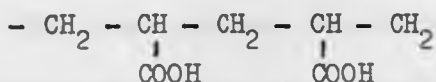
MOLECULAR STRUCTURE OF COPOLYMER OF ACRYLIC ACID AND ITACONIC ACID

$$\qquad\qquad\qquad\qquad\quad CH_2COOH$$
$$\qquad\qquad\qquad\qquad\quad |$$
$$- CH_2 - CH - CH_2 - C - CH_2 - CH$$
$$\qquad\quad | \qquad\qquad | \qquad\qquad |$$
$$\qquad\; COOH \qquad COOH \qquad COOH \qquad\qquad\qquad (Wilson\ (1977))$$
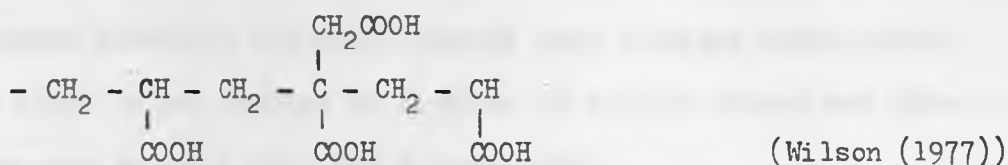
7.4.2 SETTING REACTION OF GLASS IONOMER CEMENTS

The setting reaction is essentially an acid-base reaction between
acid decomposible oxides i.e. aluminosilicate glass, which form the
powder and an aqueous solution of polyalkenoic acid. The acid base
nature of the reaction is demonstrated by the rapid increase in the
pH during the initial reaction which may be represented thus:

GLASS + POLYACID ⟶ POLYSALT + SILICA
(POWDER) (LIQUID)   GEL   GEL
                     (MATRIX)   (PARTICLE
                                 COATING)
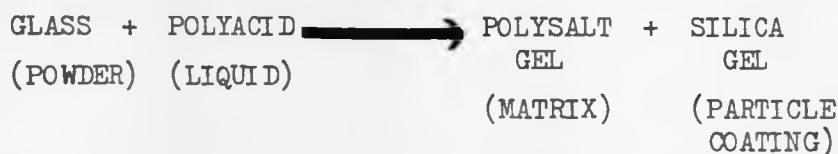
On mixing the powder and liquid, hydrated protons from the
polyacrylic acid attack the surface of glass powder resulting in
the liberation of positively charged ions Ca^{+2}, Al^{+3}, Na^+ and F^-
and PO_4^{-3} into aqueous phase where they react with polyanion chains
and begin to precipitate and gelation occurs resulting in an insoluble
polysalt gel, Wilson and Crisp (1974). The glass powder is degraded
to a hydrated siliceous gel.

Infra-red spectroscopy Wilson and Kent (1972) and chemical studies Crisp et al (1974) demonstrated that the precipitation of insoluble salt gel results from binding of multivalent cations to polyanion chains with the formation of ionic crosslinks. The gel matrix contains both covalent   and ionic bonds hence they are termed ionic polymer (ionomer) cements Wilson, (1978).

The glass ionomer cements have a double setting reaction.   Initially calcium carboxylates are formed as a firm gel which has the property of being carvable. Later the aluminium polycarboxylates are formed and the cement sets hard due to the high ionic potential of the trivalent aluminium ion which ensures much stronger crosslinking. This stage is not reached until after 30 minutes Wilson and Crisp (1975); Wilson and McLean (1977) and Wilson (1978).

TABLE 2

CHEMICAL COMPOSITION OF TYPICAL

GLASS IONOMER CEMENT

	% m/m
Si^{+4}	13.3
Al^{+3}	13.1
Ca^{+2}	17.3
Na^{+1}	1.6
P^{-3}	2.5
F^{-1}	22.7
O^{-2}	28.0

(Crisp, (1975))

FIGURE 2

SCHEMATIC REPRESENTATION OF SETTING REACTION OF GLASS

IONOMER CEMENT

A.D. Wilson (1977)

LIQUID
POLYACID
POLYACRYLIC, ITACONIC,
TARTARIC ACID

HYDROGEN
IONS

POLYANIONS

MATRIX
CALCIUM
ALUMINIUM
POLYSALTS.

GLASS CORE

SILICA JEL

Ca^{+2}
Al^{+3}
Na^{+}
PO_4^{-3}
F^{-}
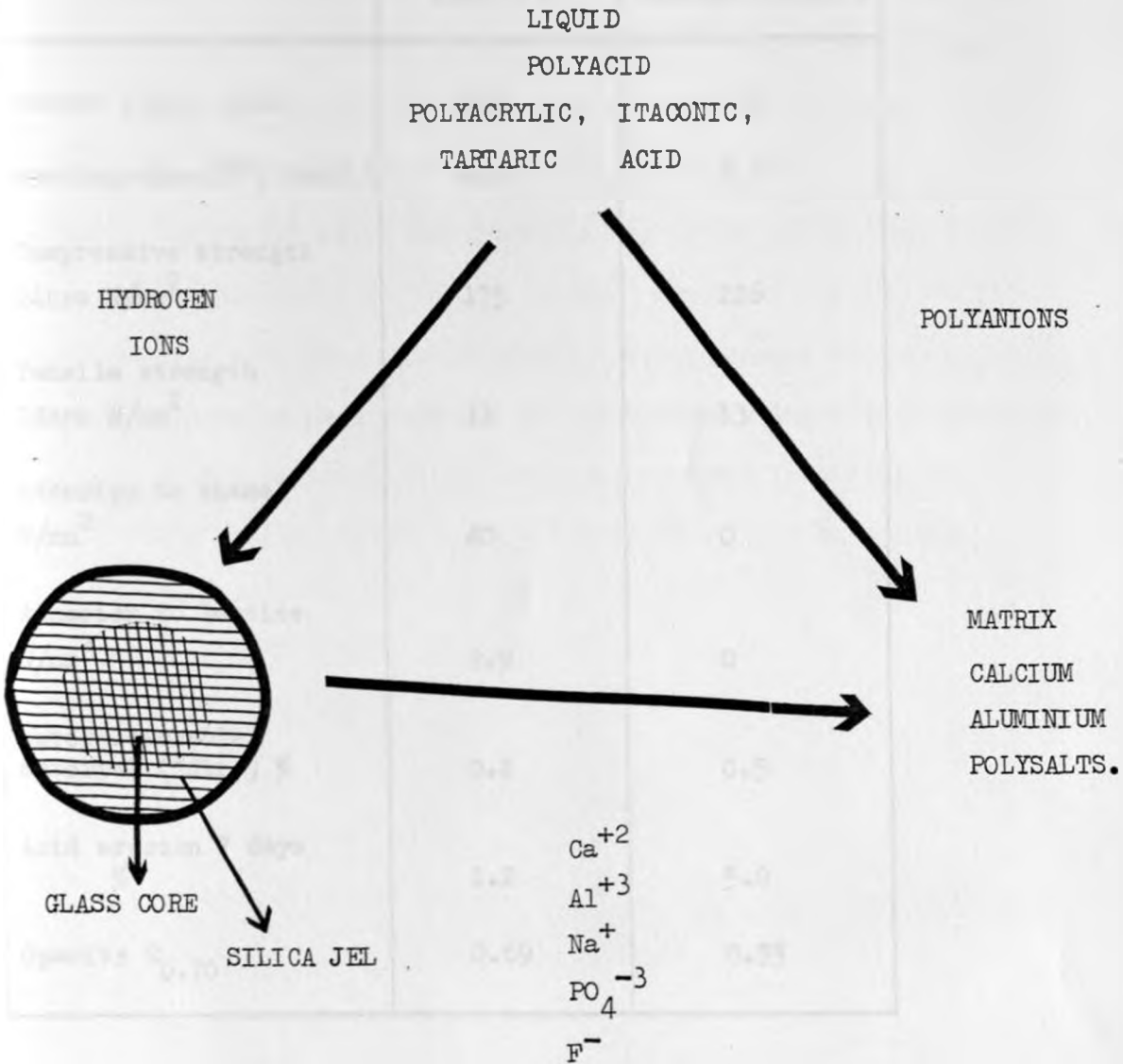
TABLE 3

COMPARISON OF PROPERTIES OF A GLASS IONOMER CEMENT AND

DENTAL SILICATE CEMENTS

PROPERTY	GLASS IONOMER (ASPA IV)	SILICATE (SUPER-SYNTREX)
Powder liquid g/ml	3.5	4.0
Setting time 37°C (min)	4.0	3.7
Compressive strength 24hrs N/nm^2	175	226
Tensile strength 24hrs N/nm^2	13	13
Adhesion to enamel N/nm^2	40	0
Adhesion to Dentine N/nm^2	2.9	0
Water-leachable material (24hrs) %	0.4	0.5
Acid erosion 7 days %	1.2	5.0
Opacity $C_{0.70}$	0.69	0.55

7.5 DISSOLUTION OF CEMENTS

The measurement of dissolution of dental silicate, and glass ionomer cements is difficult. This point has been made. Wilson and Batchelor (1968a) since cements are non homogenous they have two phases hence it is important that we consider what is meant by "solubility".

When sodium chloride is dissolved in water, being a single chemical species, solubility is the transfer of sodium chloride molecules from the solid to a dissolved state. In the case of cements however this is more complex because cements consists of two phases. Thus as in the case of silicate cement, Wilson (1968a) have shown how dissolution consists of the release of F^-, Al_2O_3, PO_4^{-3}, Na^+ and other species at different rates and quantities with the result that it is not possible to express solubility on the simple way appropriate for example sodium chloride. In the case of glass ionomer cements a number of studies have reported the continuous release of fluoride as a part of the dissolution process. Forsten and Paunio (1972), Tveit (1981), Forsten (1977). Others have said F^- release stops after six months.

7.6 STUDIES ON THE DISSOLUTION OF SILICATE CEMENT

Dissolution of silicate cement has been studies by several workers
and "in vitro" investigation of its solubility have been carried out
by various methods. Most workers have measured solubility by measuring
the weight of evaporated eluate resulting from immersion of a silicate
disc in the test medium for various periods of time. Paffenbarger et al
(1938) evaluated solubility of twelve brands of commercially available
cements for a period of five weeks. Other workers have used the same
method, Norman et al (1957); Jorgensen (1963); Eichner et al (1968).

Stralfors (1969) used an alternative method of measuring the
weight lost from a sample disc after immersion in test medium either
with or without some form of drying. A similar method had previously
been applied by Voelker et al (1916), Mathews et al (1935),
Naeslund et al (1933). This method does not take into consideration
the water absorbed during the trial which should be removed before
weighing. Much of the absorbed water is chemically bonded and can
only be removed at very high temperatures. Erikson (1970) tried
to remove the water by heating at 110°C for 4 days.

Hochstrasser (1961) found much higher values of dissolution
by measuring the depth of dissolution on the specimen disc. This is
probably because of the brushing away of the loose particles of
cement from the surface of the sample.

More recently Wilson and Batchelor (1967, 1968a) used a method
based on chemical analysis of the eluate for its constituents to
measure its solubility. Pulver and Rossington (1970) studied erosion
by measuring the amount of phosphate and silicate leached into solution
from major constituents of cement powder, liquid and gel matrix.

In an attempt to standardize testing conditions American Dental Association specification test has been helpful in the selection of commercial products. Several authors Wilson and Batchelor (1976), Jorgensen, (1963)(1970), claim that not all the cements meets the specifications. This claim probably arises from the fact that solubility involves many factors. Wilson (1976) suggested the inadequacy of the ADA specification test which is based on the solubility of test specimen for 24 hours only. Thus:

a) The ADA specification test gives a measure of soluble/ intermediates present while the cement is still hardening and where the matrix is still polymerizing. The relation of early vulnerability to aqueous attack and hardening state must be considered.

b) The specification test gives an imperfect account of the clinical durability and has little meaning if the products of hydrolysis are insoluble or volatile for example. Silicate cement has a higher solubility and disintegration values than phosphate cement in water. It is more stable in oral fluids. This is because it contains soluble sodium salt. Hence the solubility of silicate cement and phsophate cement cannot be compared.

Wilson and Batchelor (1967), Paffenbarger (1938) found that the solubility of various commercial brands differed considerably during the first week, while the quantity dissolved during the following weeks showed much less variations. The solubility decreases with time. They also found considerable difference between the composition of the eluate and the parent cement. Silica and alumina, major constituents of the cement, were only present in minor amounts in the eluate.

Sodium and phosphate were present in relatively large amounts. Hence the erosion of dental silicate cement has special significance.

There is thus a general agreement that the standard specification test needs to be supplemented by other tests of fully hardened cements for longer clinically significant periods of time and in media that simulate oral conditions. Wilson and Batchelor (1967b) stated that "solubility" a term frequently applied in dental specification test is a misnomer. Solubility strictly applies to pure chemical compounds in which excess solid is in equilibrium with a saturated solution of itself. Hence no heterogeneous solid, like the cement, can be termed to have a true solubility. Since the composition of the solution and cement differs the material going into solution expressed as a percentage of the cement as in ADA specification test has little scientific or clinical significance.

A number of workers have carried out studies on various aspects pertaining to the dissolution of the cement. They have examined a number of variables relating to the dissolution of dental silicate cements.

   A.   The effect of mixing variables.

         a)   Powder liquid ratio

         b)   mixing time

         c)   curing time (Specimen age)

         d)   curing temperature

   B.   The effect of immersion media i.e. addition of organic acid
         volume of liquid, frequency of change of solution.

   C.   The effect of shape of specimen.

   D.   The effect of addition of modifiers.

7.6.1   THE EFFECT OF MIXING VARIABLES ON DISSOLUTION OF SILICATE CEMENT

a)   POWDER:LIQUID RATIO

The manufacturers often claim that the formulations of cements are not too sensitive as to influence the manipulative variables such as powder:liquid ratio. Swartz et al (1968) investigated the effect of P/L ratio of three different cements in distilled water changed daily for 5 days. The solubility of certain cements was influenced more than others by alterations of P/L ratio. Correa thesis, reported an optimal P/L ratio producing a cement that will have minimum solubility. The P/L ratio that gave least solubility and standard consistency as determined by ADA Specification test were identical.

Measuring chemical resistance of cement by elution of phosphate and silicate Wilson et al (1967) found:

a)   a decline in the resistance to aqueous attack as the
P/L ratio decreased. This was more pronounced at lower
P/L values.

b)   the amount of phosphate,silicate,and sodium eluted into
solution increases as the powder:liquid ratio decreases

Similar investigations were carried out by Jorgensen (1970) for longer periods of time and found similar results.

b)   MIXING TIME

Swartz et al (1968) found that an increase in the mixing time and incorporation of the powder into the liquid in small increments did not alter the solubility of cement. Skinner and Phillips (1967) reported that a slight prolongation of mixing time led to an increase in the solubility. Jorgensen (1970) found no effect in the solubility as the mixing time is varied.

c)   CURING TIME (SPECIMEN AGE)

This is the time that elapses from spatulation to the time when specimen contacts the immersion medium. Jorgensen (1970) examined this variable by placing test specimen in immersion media at different times after mixing i.e. 5, 10, 15, 30, 60 minutes 24 and 48 hours for 24 hours. Wilson and Batchelor (1967b) investigated the same variables by measuring the elution of phosphate and silicate from the cement which had been protected from media for various time intervals. Both these workers showed that solubility was affected by the age of cement. The solubility decreased rapidly during the 1st hours after mixing. These findings corroborates with those of previous workers like Dausch et al (1940), Manly et al (1951), Norrah et al (1957) and Charbaneau (1962).

The setting reaction of cement is not complete after the initial set. The reaction is completed when the phosphate is precipitated and the silica has completely polymerized. Hence increasing the curing time before contact with the immersion medium enables these mechanisms to proceed to completion.

7.6.2 EFFECTS OF DIFFERENT IMMERSION MEDIA ON THE DISSOLUTION OF SILICATE CEMENT

The effects of immersion media on solubility of dental silicate cement were demonstrated by early workers. Voelker et al (1916) observed that silicate cement was three times more soluble in Lactic acid than in water Rosthj (1929) noted that silicate cements were more soluble in Lactic acid than in acetic acid. Naeslund (1933) reported very high solubility of silicates in citric acid. These studies involved a limited number of specimens.

Paffenbarger et al (1938) indicated that the life of a silicate restoration in the mouth varied greatly. A clinical survey by Hanschel and Weatherel (1947) showed that most disintegration occurs adjacent to the gingival margin areas due to increased acidity resulting from the disintegration of plaque accumulated in these areas. The rate of disintegration is influenced by the rapidity and efficiency with which salivary mechanism buffers the adherent food debris, the amount of carbohydrate intake and the level of oral hygiene, i.e. presence of bacteria.

Norman et al (1957) found a dramatic increase in the solubility of silicate cements using buffered solutions of acetic, lactic and citric acid at pH 4 and 5. The pH of the storage medium also increased. This finding concurred with that of Paffenbarger et al (1938) who also noted a decrease in solubility with time. The observation was probably due to the buffering effect of the solvent by the products of dissolution. Similar results were reported by other workers like De Freitas (1968), Erikson (1970), Pulver and Rossington (1970), Swartz et al (1968), Jorgensen (1970) and Wilson and Batchelor (1967a, 1967b). The notable findings by all these workers were:

a)   products of dissolution showed large quantities of silica and phosphates and lesser quantities of Al^{3+}, Ca^{+2}, Na^{+}, Mg^{+2}, Zn^{+2} and F^{-}. De Freitas (1968) did not find any zinc in the eluate.

b)   There was no difference in the products of dissolution of a given material with various media. Hence it can safely be concluded that there is no single constituent material that is particularly vulnerable by specific acid.

c)   There is a decrease in the rate of dissolution of silicate

cement after 24 hours with all organic acids except citric

acid. This can be attributed in part to some activity of the

citrate ion itself and that various organic ions may be more

destructive than others. All the above findings correlate

with the in vivo observations of Hanschel and Weatherel (1947).

Eichner (1968) expressed solubility as a function of time. He plotted

a logarithmic graph from his experimental data. He suggested a mathe-

matical expression that would fit the resulting curves.

Log S = log S_o + n log t

where   S   is the solubility

                S_o is the solubility at 24 hours

                n   is the slope of straight line.

The above mathematical expression shows that solubility decreases

exponentially with time.

Wilson and Batchelor (1967a) suggested that the greater solubility

observed in silicate cement in organic acid is due to the ability of

organic acid anions to form stable compound complexes with some metallic

cations. They further pointed out the disadvantages of gravimetric

methods of estimation of dissolution of cement in organic acids:

a)   positive attack by acid of the gel matrix is obscured by

washing away of considerable amount of salt found in young

cement.

b)   eluted material cannot be determined gravimetrically by

evaporation due to the presence of test medium. The material

lost by the test medium may be obscured by inhibition of

water during weighing.

7.6.3 THE EFFECT OF SIZE OF SPECIMEN

Norman et al (1963) showed that since the weight of the test specimen varied considerably, the rate of solubility of silicate cement was governed primarily by the surface area. He suggested that solubility of cement should be reported as the amount of dissolved residue per unit area of exposed surface rather than as a weight loss per unit volume of weight. A cube and a disc of the same volume of cement does not have the same surface area Eichner (1968). The surface area:volume rates of a disc is much higher, hence difference in the solubility of a cube and a disc might be expected. Tests of solubilities of three cements surprisingly showed no difference in their solubilities. Studies of solubility of silicate cements by chemical analysis methods using specimens of different sizes by Wilson (1971) showed that the amount of material eluted from the specimens is more related to the surface area than to the volume. From the above studies it is clear that there exists some controversy on the effects of surface area to volume ratio with regard to solubility of cements.

7.7 FLUORIDE RELEASE FROM SILICATE AND GLASS IONOMER CEMENTS

The addition of fluoride in the manufacture of cements is primarily to lower the fusion temperature Wilson (1977), to improve the workability Wilson (1974) and cohesive strength by complex ion formation. Several workers have demonstrated a reduction of recurrent caries around silicate and glass ionomer cement restorations. Voelker et al (1944) studied recurrent caries around silicate and amalgam. Laswell (1966) carried out a comparative study on recurrent caries around amalagam, silicate and composite restorations. He found the incidence of recurrent caries to be 9.2% amalgam, 8% composite, 3.8% silicate restorations. Minoguchi (1967) found that in a five year observation period there was less recurrent caries with fluoride containing amalgam than with conventional amalgam, however the addition of fluoride into amalgam has an undesirable effect on the physical properties of amalgam, i.e. reduction in compressive strength. Kidd (1978) demonstrated a similar cariostatic effect of fluoride in glass ionomer cements in vitro.

The cariostatic effect has been considered to be the consequence of the release of fluoride from the silicate and glass ionomer cement and consequent uptake of part of the fluoride by adjacent enamel. Several workers like Phillips and Swartz (1957), Norman et al (1961) have demonstrated the effect of fluoride on tooth structures. They have shown that there is a decrease of enamel solubility when exposed to fluoride containing material. Hence there is an uptake of released fluoride by the enamel. Hallsworth (1969) showed that there is a higher fluoride content in enamel around a silicate restoration than a more distant enamel tissue. Legrand (1974), Crisp, Lewis and Wilson (1975), Phillips (1969) and Lind (1974) made similar observations.

The question has arisen whether it is possible to obtain fluoride release from virtually insoluble material. Phillips (1969) considered the release of fluoride to be a direct result of dissolution. Forsten (1972 suggested that the release of fluoride is not dependent on dissolution of the bulk of the restoration. Fluoride release is governed by

a) the solubility of fluoride containing compounds in the restoration

or b) diffusion of fluoride ions through the material.

Both Forsten (1972) and Norman (1960) observed some fluoride release from composite filling materials though to a lesser extent.

The solubility of glass ionomer cement in oral fluids is less than that of silicate cement, Kent, Lewis and Wilson (1973), hence one should expect less fluoride release from glass ionomer cement than silicate cement. Moldonado et al (1978), and Forsten (1977) found that glass ionomer cement releases slightly more fluoride than silicate cements. More recently Tveit et al (1981) studied the release of fluoride from amalgam, silicate and glass ionomer cement and found five times more fluoride release from the silicate cement than from glass ionomer. It was also suggested in this study that the release of fluoride is dependent on dissolution and electrochemical disintegration (corrosion) of the material. These two findings contradict some of the earlier findings.

The duration of fluoride release is uncertain. Forsten (1972) reported that continued release of fluoride did not decrease very much with time. Moldonado et al (1978) observed an initial high release of fluoride for the first few days then a gradual decrease. Causton (1981) reported a fluoride release for the first six months only and decreases to insignificant levels thereafter.

7.8 DISSOLUTION AND EROSION OF GLASS IONOMER CEMENTS

Much less work has been done on the dissolution of glass ionomer cements than the silicate cements. The release of fluoride which is a dissolution process has been studied extensively in glass ionomer cements and silicate cements because of their anticariostatic effect.

Freshly mixed glass ionomer cement in their hardened state contains residual water in their gel matrix. Elliot et al (1975) showed that glass ionomer cement contains 20% by weight of residual water. He also demonstrated that if the cement is maintained in a state of low relative humidity the water is lost from the system until a hygrometric equilibrium is established at ambient temperature. The loss of water can be measured by weight changes of cement disc exposed at a particular relative humidity at a constant temperature. Elliot et al (1975) and Crisp et al (1980) showed that the rate of loss of water is greatest during the first 24 hours and a state of equilibrium is attained within 2–3 days. Causton (1981) showed that not all the water is lost from glass ionomer cement. Samples stored in 0% relative humidity showed a continued loss of weight, although at a slower rate than occurs initially. This indicates that some water is bound tightly to the gel matrix. Hence the presence of two types of water "loose" water and "tight" water. This concured with Elliot et al (1975) who demonstrated that temperatures of upto $200^{o}C$ is required to remove the total quatity of water.

The proportion of bound water increased with curing time of specimen before desorption. Causton (1981) showed that the desorption coefficient fell as the length of storage time increased, the decrease being proportional to $\log_e t_s$ (where t_s is the storage time). A similar relationship was demonstrated by Crisp et al (1976). When

examining the effect of desorption coefficient of water on other properties of cement.

MacLean and Wilson (1977) demonstrated that glass ionomer cement is more resistant to acid attack. This is because it consists of both ionic and covalent bonds Crisp (1980). The insoluble matrix resulting from covalent bonds take time to form. Hence exposure of the cement to water too soon may upset the completion of this reactions.

8. PROGRAMME OF WORK

This is a two part study on the dissolution and erosion of
commercially available silicate 'Biotrey' cement and glass ionomer
cement 'Chemfil'.

A. Various factors that influence the dissolution of silicate
cement have been studied. In this study, the effect of volume
of media, and surface area:volume ratio of specimen on
dissolution was investigated.

Standard discs of test material were suspended in different
volumes of aqueous solution in closed vessels for given
periods of time.

Specimens of different surfacea area:volume ratios were similarly
suspended in standard volumes of aqueous solution in closed
vessels for 5 days unchanged and 5 days changed daily.
Dissolution was measured gravimetrically by evaporating the
aqueous solution and weighing the eluate.

B. The dissolution and erosion of glass ionomer cement 'Chemfil'
was investigated by analysis of organics released, using
facilities made available by the Water Research Laboratory,
Elder Way, Stevenage, Herts. A brief study on thermogravimetry
of glass ionomer cements was conducted using samples of test
material prepared under different conditions.

A total of five experiments were undertaken using standard
discs of material under test.

9. INVESTIGATION

9.1 MATERIALS

The materials investigated in this study were.:

1) "BioTrey" silicate cement, a craze resistant filling material
for restoration of anterior teeth. The cement is produced
by the Amalgamated Dental Trade Distributors Ltd., London,
England.

The Batch Numbers used were as follows:

POWDER	LIQUID
YF 10	UM 4 YD
RC 21	UM 4 WL

2) "DeTrey" Chemfil cement a glass-ionomer restorative material
consisting of a blend of alumino silicate glass and polyacrylic
acid. The material is produced by A.D. International Ltd.,
De-Trey Division, Weybridge, Surrey, England.

The Batch Numbers used were:

POWDER

AF 50	BB 110
AA 100	AL 56
BB 160	AA 15

9.1.1 MIXING OF MATERIAL UNDER TEST

a) SILICATE CEMENT

The manufacturers instructions recommend a powder to liquid
ratio of 1.4g – 2.0g to 0.4ml at ambient temperature of $23^{\circ}C$. A powder
to liquid ratio of 1.2gm to 0.5gm was used throughout the investigation.

b) GLASS IONOMER CEMENT

The manufacturers recommendation of P/L ratio of 6.8:1 was used
throughout the investigation.

9.2 METHOD

9.2.1 PREPARATION OF TEST SPECIMENS

(a) PREPARATION OF STANDARD DISC

All the investigations on Silicate and Chemfil Cements were conducted with the use of standard discs of these materials, except in cases where surface area to volume ratio was studied.

The preparation of standard discs was as follows:

The required material was weighed out as in 9.1.1a and 9.1.1b.

A split steel ring of 2.0cm internal diameter and 1.5cm thickness was placed on a cellulose acetate sheet supported on a flat glass slab. Freshly mixed material as in 9.1.1 was placed in the ring to slightly overfill it immediately after mixing. A 15mm length of dental floss was inserted into the material through the split in the ring.

A second cellulose acetate sheet was placed over the top of the ring. A glass slab was then placed over the set up and gently hand pressure was applied. The excess material escaped from the top surface of the ring.

Three minutes after mixing ceased, the discs still covered by cellulose acetate sheets were transfered into an oven held at $37^{o}C$ and allowed to set for 1 hour.

After this time the cellulose acetate sheet was removed and the disc carefully pressed out of the ring. Excess material was removed from the disc with a sharp scalpel. The disc and the floss was then weighed to an accuracy of 0.0001g.

(b) PREPARATION OF DISCS OF VARIOUS SURFACE AREA:VOLUME RATIOS

Rings of heights 2.0mm, 5.0mm, 10.0mm and 20.0mm were cut from rubber tubing of internal diameter 15.0mm.

Freshly mixed cement was packed into the rings as in 9.2.1a above. The discs were not removed from the rings after curing.

The rubber tubing was chosen in preference to perspex glass tube because it gave a better seal at the periphery of the discs.

The resulting discs had similar exposed surface areas but different volumes of materials.

9.2.2 MEASUREMENT OF DISSOLUTION OF CEMENT

The disc of material under test were suspended in 50ml of dissolution media in weighed 100ml beakers. The beakers had tightly fitting lids. They were placed in an oven held at $37^{\circ}C$. In cases where the effect of volume of dissolution media was being investigated beakers of larger sizes were used. They were sealed with cellulose acetate sheets.

Specimens were withdrawn from the dissolution media at the end of the experimental period, brushed gently with a small soft camel hair brush and rinsed with deionized water. The rinsings were collected in the beaker.

The dissolution medium was then evaporated in the beakers in an oven held at $70^{\circ}C$. The beaker with the eluate was cooled to room temperature in a dessicator containing dried silica gel for 24 hours. The beakers and the eluate were weighed to an accuracy of 0.01mg (0.0001g). This process of heating, cooling and weighing was repeated until constant weight of residue was reached.

The measurement of dissolution in the present investigation was determined by evaporation to dryness of the liquid in which the disc had been immersed and then weighing the solid residues.

A control run of media without a disc was operated alongside each of the experiments. The dissolution of a specimen was the weight of the residue less the weight of the residue in the control.

9.2.2a. THE EFFECTS OF SURFACE AREA:VOLUME RATIO

The effects of surface area:volume ratio was investigated by preparing a series of discs of heights 2mm, 5mm, 10mm and 20mm as described in 9.2.1b.

Each of the discs was suspended in 50ml of solution such that both end surfaces of the discs were exposed to solution.

The dissolution of the specimen was investigated with the water changed daily, and unchanged for 5 days.

9.2.2b. THE EFFECT OF VOLUME OF THE MEDIA

A series of 5 standard discs of specimen were prepared as in 9.2.1a above.

The discs were suspended in various volumes of media 25ml, 50ml, 100ml, 250ml, 400ml and 1000ml in weighed beakers of different sizes, for 5 days, and 30 days unchanged.

The dissolution was investigated as is described above in 9.2.2.

A control was run in parallel with each series of specimens.

9.2.2c. THE EFFECT OF ADDITION OF FLUORIDE

A 10% solution of sodium fluoride (0.1M) was prepared by dissolving 4.199gm of sodium fluoride in 1 litre of deionized water. The solution was further diluted to give solution of 0.01M, 0.05M solutions.

A series of 5 standard discs were immersed in weighed 100ml beakers containing 50ml of the fluoride solution, and placed in an incubator held at $37^{o}C$ for 5 days unchanged and 30 days unchanged.

A control weighed beaker containing 50ml of the fluoride solution (without a disc) was run along side the experimental specimen.

The dissolution of the cement in fluoride solution was the amount found in the experimental run less that found in the control.

9.2.3 'CHEMFIL' GLASS IONOMER CEMENT

The manufacturers instruction for powder:liquid ratio of 6.8:1 was used throughout the investigation. The required amount of powder was weighed out using a chemical balance and transfered to a thick mixing glass slab measuring 15cm by 8cm. The required amount of liquid was measured out using a calibrated pipette. The powder was gradually incorporated into the liquid in three equal portions using a plastic spatula. The total mixing time was one minute at room temperature $22 \pm 2^{o}C$ and relative humidity of $51 \pm 2\%$. The specimen was thereafter treated as in 9.2.1a.

9.2.3a. RELEASE OF ORGANIC SPECIES FROM GLASS IONOMER CEMENT

Discs of 'Chemfil' glass ionomer cements was prepared as in 9.2.1a. They were immersed in 25ml, 100ml and 250ml of deionized water at pH 6.7 and phosphate solutions containing 0.98gm PO_4^{-2} 1^{-1} at pH 7. These were held at $37^{o}C$ for perios of time ranging from one to six weeks.

After the predetermined time the discs were removed and rinsed. The resulting solution including the rinsings were subjected to analysis for Total Organic Content (TOC). The analysis was done on a Carlo Erba Strumenzione Type 400P TOC monitor. The basis of this instrument is catalytic hydrogenation of organic species followed by their estimation with a flance ionization detector. The instrument does not respond to carbonates or bicarbonates.

9.2.3b. THERMOGRAVIMETRIC ANALYSIS OF 'CHEMFIL' GLASS IONOMER CEMENT

The following samples with different histories were prepared for thermogravimetric analysis.

Sample A   = Discs prepared by mixing the cement according
                  to standard procedures then cured at $37^{\circ}C$ for
                  1 hour.

Sample B,C,D = As 'A' but stored at room temperature for 1, 7 and
                  21 days respectively.

Sample E   = As 'A' but immersed in deionized water held at
                  $37^{\circ}C$ and changed daily for 5 days. The samples were
                  then dried at room temperature for 12 hours prior
                  to analysis.

Sample F   = As 'E' but the solution was not changed for 5 days.

Sample G   = As 'A' but immersed in phosphate solution containing
                  0.98gm PO_4^{-2} l^- held at pH 7 for 5 days unchanged.
                  The sample was similarly dried for 12 hours at room
                  temperature prior to analysis.

A Stanton Redcroft Type TG 750 apparatus was used for analysis. Each of the samples to be analysed was ground using a pestle and mortar.

Approximately 10mg of the sample was loaded into the thermogravimetric
balance pan. The temperature was set to rise at the rate of 5°C/min.
The temperature and the gravimetric changes were recorded simultaneously
on the same chart. The analysis of all the samples was carried
out either in static air and in   white spot grade Nitrogen
flowing at the rate of 4.5 ml/min.

FIGURE 3

SAMPLES OF TEST MATERIALS

FIGURE 4

PREPARED SPECIMENS OF TEST MATERIAL
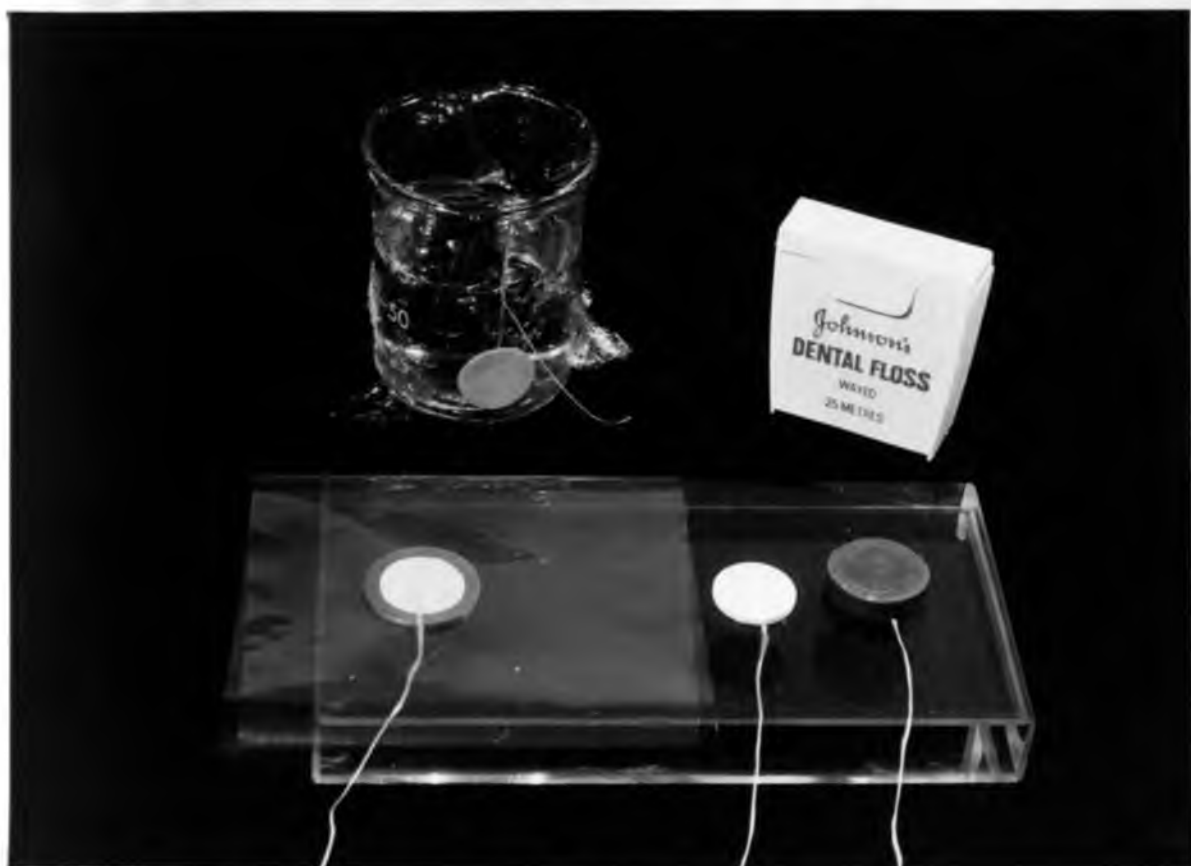
10 RESULTS

10.1 THE EFFECT OF SURFACE AREA:VOLUME RATIO OF SPECIMEN ON DISSOLUTION OF 'BIOTREY' SILICATE CEMENT

All the specimen used in the test had similar exposed surface
areas but different volumes hence dissolution is expressed as milligrams
of eluate. The data for the dissolution of silicate cement discs of
different thickness for a five day test period is given in Table 4.
Table 5 shows the daily and cummulative dissolution of silicate
cement specimen of different thickness for a five day test period.
Figure 5 shows the dissolution plotted against the thickness whereas,
Figures 6 and 7 show the daily and cummulative dissolution plotted
against time,Figures 10 and 11 show the relationship between dissolution
and logarithm of time and square root of time respectively. The
relationship between the ratio of dissolution at a definite time and
at an infinite time versus the square root of time is shown in
Figure 12. Figure 13 shows the relationship of dissolution with
the square of the thickness of the disc. It is observed that there
is a linear function between dissolution of silicate cement and
logarithm of time, square root of time and also the square of the
thickness of disc.

10.2 THE EFFECT OF VOLUME OF SOLUTION ON DISSOLUTION OF BIOTREY SILICATE CEMENT

The data presented in Table 6 shows the dissolution of standard
specimen of silicate cement disc immersed in different volumes of
deionized water for 5 days and 28 days 'unchanged'. The relationship
between the volume of solution and the dissolution of cement is
shown in Figure 8 where the dissolution is plotted against the
volume of solution.

10.3 THE EFFECT OF ADDITION OF FLUORIDE ON THE DISSOLUTION OF 'BIOTREY' SILICATE CEMENT

The data presented in Table 7 shows the dissolution of silicate in different concentrations of fluoride solution for a test period of 5 days and 28 days unchanged. Figure 9 shows the relationship between the molarity of fluoride solution and the dissolution of cement. The dissolution of cement is plotted against the concentration of fluoride in the solution.

10.4 THE RELEASE OF ORGANIC SPECIES FROM 'CHEMFIL' GLASS IONOMER CEMENT

The amount of organic species leached out of standard discs of glass ionomer cement is shown in Table 8. Duplicate runs were conducted for each test series and a control was run alongside each test series. The amount of the organics leached out of standard specimen was obtained by subtracting the control value from the mean of the two samples. The data is presented in Figures 14 and 15 where the amount of organic species leached out into different volumes of solutions is plotted against the time. The error bars indicate the scatter of the data obtained and are derived by subtraction of the control value from each of the values in the same test series.

10.5 THERMOGRAVIMETRIC ANALYSIS OF 'CHEMFIL' GLASS IONOMER CEMENTS

The percentage weight loss of Chemfil glass ionomer cement samples of different histories and under different thermogravimetric conditions are shown in Tables 9 and 10. Thermogravimetric analysis of the specimen was carried out in static air and slow flowing Nitrogen. Some of the data in Table 9 and 10 are presented in Figures 16 and 17 showing the relationship between the weight loss and temperature change in both static air and slow flowing Nitrogen.

TABLE 4

THE EFFECT OF SURFACE AREA/VOLUME RATIO ON DISSOLUTION
OF SILICATE (BIOTREY) CEMENT

Medium : Deionized water Experimental period : 5 days		
Dissolution (mg) from 2mm thick discs	Mean	6.7
	S.D.	0.854
Dissolution (mg) from 5mm thick discs	Mean	8.5
	S.D.	0.634
Dissolution (mg) from 10mm thick discs	Mean	9.4
	S.D.	0.341
Dissolution (mg) from 20mm thick discs	Mean	10.5
	S.D.	0.707

TABLE 5

THE EFFECT OF SURFACE/AREA VOLUME RATIO ON THE DISSOLUTION OF SILICATE (BIOTREY) CEMENT

Number of specimens : 5

Dissolution Media : Deionized water

Experimental time : 5 days daily change

		Day 1	Day 2	Day 3	Day 4	Day 5
Dissolution (mg) from 2mm thick disc	Mean	6.9	1.4	1.2	0.8	0.6
	S.D.	1.135	0.350	0.469	0.320	0.096
	Cumulative Dissolution	6.9	8.3	9.5	10.3	10.9
	S.D.	1.135	0.791	0.6825	0.604	0.589
Dissolution (mg) from 5mm thick disc	Mean	7.0	1.8	1.6	1.5	1.4
	S.D.	0.512	0.282	0.665	0.666	0.042
	Cumulative Dissolution	7.0	8.8	10.4	11.9	13.3
	S.D.	0.512	0.390	0.473	0.508	0.452
Dissolution (mg) from 10mm thick disc	Mean	8.8	2.5	2.1	1.8	1.6
	S.D.	1.530	0.129	0.698	0.690	0.270
	Cumulative Dissolution	8.8	11.3	13.4	15.2	16.6
	S.D.	1.530	0.977	0.902	0.838	0.753

TABLE 6

THE EFFECT OF VOLUME OF MEDIUM ON DISSOLUTION OF
BIOTREY SILICATE CEMENT

Number of Specimens : 5

Medium : Deionized water

Mean weight of disc : 1.0529g

		EXPERIMENTAL PERIOD	
		5 Days	28 Days
Dissolution (mg) in 25ml	Mean S.D.	6.4 0.200	6.3 0.364
Dissolution (mg) in 100ml	Mean S.D.	8.7 0.697	11.8 1.178
Dissolution (mg) in 250ml	Mean S.D.	11.2 1.30	15.9 0.620
Dissolution (mg) in 400ml	Mean S.D.	13.0 0.234	18.1 0.671
Dissolution (mg) in 1000ml	Mean S.D.	17.8 0.690	27.8 1.047

TABLE 7

THE EFFECT OF ADDITION OF FLUORIDE ON DISSOLUTION OF SILICATE (BIOTREY)
CEMENT

Number of Specimens : 5 Mean weight of specimen : 1.0704 g Standard Deviation : 0.085 Medium : Fluoride Solution			Experimental Time	
			5 Days	28 Days
Concentration of F⁻ Solution 0.01M	Dissolution (mg)	Mean	33.96	38.2
		S.D.	3.20	2.8
		Control	23.2	24.0
0.05M	Dissolution (mg)	Mean	104.9	99.2
		S.D.	2.9	3.40
		Control	106.7	107.1
0.1M	Dissolution (mg)	Mean	183.0	178.2
		S.D.	1.71	3.1
		Control	212.0	210.9

TABLE 8

ORGANIC RELEASE FROM GLASS IONOMER CEMENT 'CHEMFIL'

Number of Specimen : 2 Mean weight of specimen : 1.0094g Standard Deviation : 0.0214		Experimental Period			
		2 Days	7 Days	21 Days	42 Days
Medium Deionized Water	Organic (mg) in 25ml	0.300	0.151	0.108	0.142
	Organic (mg) in 100ml	0.305	0.185	0.165	0.01
	Organic (mg) in 250ml	0.163	0.363	0.200	0.0
Phosphate Buffer	Organic (mg) in 25ml	0.053	0.185	0.185	-
	Organic (mg) in 100ml	0.09	0.355	0.09	-
	Organic (mg) in 250ml	0.075	0.538	0.165	-

TABLE 9

THERMOGRAVIMETRIC ANALYSIS OF 'CHEMFIL' IN STATIC AIR

TEMPERATURE $^{\circ}K$	PERCENTAGE WEIGHT LOSS						
	A	B	C	D	E	F	G
295	0	0	0	0	0	0	0
323	10.0	4.5	7.0	6.0	11.8	13.2	16.5
373	12.0	10.0	12.0	8.5	16.0	18.0	19.2
423	12.5	10.5	12.5	9.0	17.0	19.5	21.0
473	13.0	11.5	13.0	9.5	18.5	20.0	21.5
523	14.0	12.0	13.5	10.0	21.0	20.5	22.0
573	15.0	12.0	14.0	10.5	22.5	21.5	22.8
623	21.5	14.0	15.5	12.0	26.0	22.5	24.0
673	24.0	15.5	23.0	17.5	33.0	31.0	32.0
723	25.0	18.5	25.0	20.5	34.0	32.0	32.5
773	25.6	19.0	27.0	21.0	35.0	32.5	33.0
823	26.5	19.0	28.0	21.5	36.0	33.0	33.8
873	27.0	19.5	29.5	22.5	36.2	33.5	34.2
923	29.0	20.5	30.0	22.8	37.0	34.0	35.0
973	29.5	22.0	30.5	23.5	38.0	34.0	36.0

A   = Disc mixed according to standard procedure then
           cured at $37^{\circ}C$ for 1 hour.

B,C,D = As 'A' but stored at room temperature for 1, 7 and
           21 days respectively.

E,F   = As 'A' but immersed in deionized water for 5 days
           changed daily and 5 days unchanged respectively.
           Dried at room temperature for 12 hours.

G   = As 'A' but in phosphate solution for 5 days unchanged.
           Dried at room temperature for 12 hours.

TABLE 10

THERMOGRAVIMETRIC ANALYSIS OF 'CHEMFIL'IN NITROGEN

ATMOSPHERE

TEMPERATURE $^{\circ}K$	PERCENTAGE WEIGHT LOSS						
	A_1	B_1	C_1	D_1	E_1	F_1	G_1
295	0	0	0	0	0	0	0
323	7.0	6.0	4.5	6	11.2	13.0	12.0
373	9.0	8.5	7.5	8.5	14.5	16.0	16.0
423	9.8	9.0	8.0	9.0	15.5	17.0	17.0
473	10.0	9.8	8.7	9.8	16.0	17.0	17.5
523	10.2	10.0	9.0	10.0	16.5	17.0	17.8
573	11.0	10.0	9.5	10.0	17.0	17.0	17.8
623	12.0	10.5	11.8	10.5	17.8	19.0	17.8
673	17.2	17.8	16.8	13.5	24.0	24.5	19.5
723	18.2	18.5	19.5	17.8	25.8	26.4	27.0
773	18.9	18.5	20.0	18.5	25.8	27.5	27.5
823	19.5	18.5	20.5	18.5	26.0	28.0	27.5
873	20.5	19.0	21.0	19.0	26.5	28.0	28.0
923	21.7	19.5	21.5	19.0	27.0	29.0	28.0
973	22.0	19.5	22.0	19.0	27.5	29.0	28.0

$A_1, B_1, C_1, D_1, E_1, F_1, G_1$ as A,B,C,D,E,F,G in Table 9

TABLE 11

ELUTION OF PHOSPHATE AND SILICA FROM CEMENT

DISC INTO DEIONIZED WATER

SPECIE ELUTED	EXPERIMENTAL PERIOD (HRS.)				
	1	6	24	48	$M_{inf.}$
Phosphate ion (mg)	2.15	3.60	4.80	5.35	5.40
$\dfrac{M_t}{M_{inf}}$	0.46	0.59	0.89	0.99	
Silica (SiO_2) (mg)	0.20	0.40	0.90	1.40	1.60
$\dfrac{M_t}{M_{inf}}$	0.13	0.25	0.56	0.88	

Dental Silicate Cement. II Preparation and Durability.
Wilson et al (1967b)

Dental Silicate Cement. III Environment and Durability.
Wilson et al (1968)

FIGURE 5

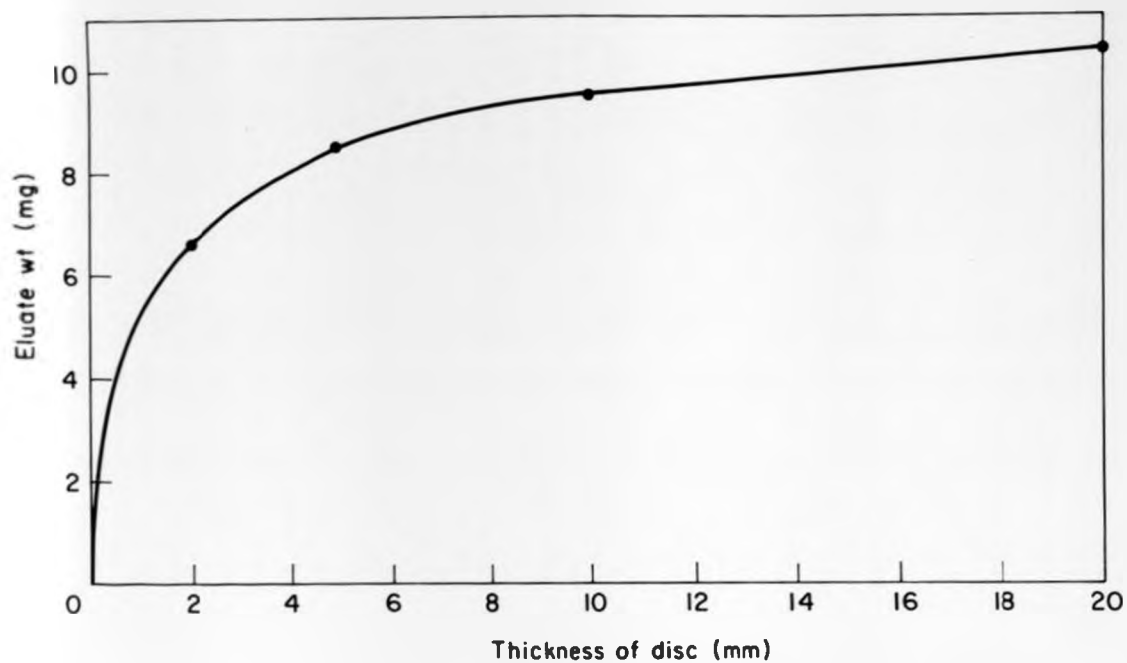DISSOLUTION OF SILICATE CEMENT AS A FUNCTION OF THE THICKNESS OF THE DISC
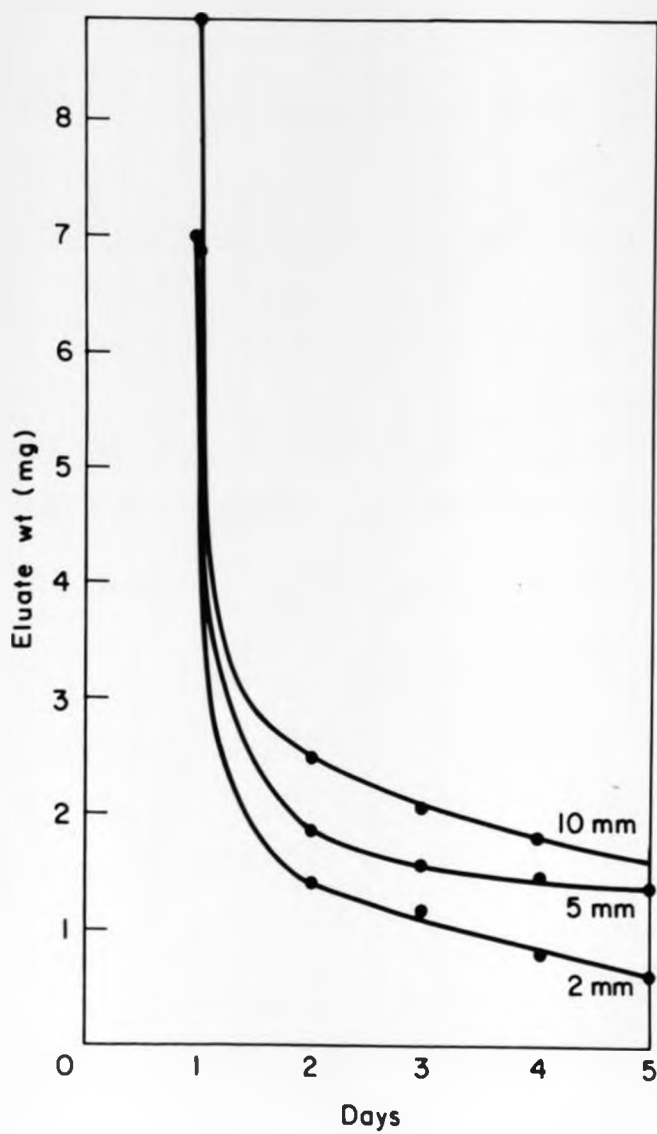
FIGURE 6

DAILY DISSOLUTION OF SILICATE CEMENT AS A FUNCTION OF IMMERSION TIME

FIGURE 7

CUMMULATIVE DISSOLUTION OF SILICATE AS A FUNCTION OF IMMERSION TIME

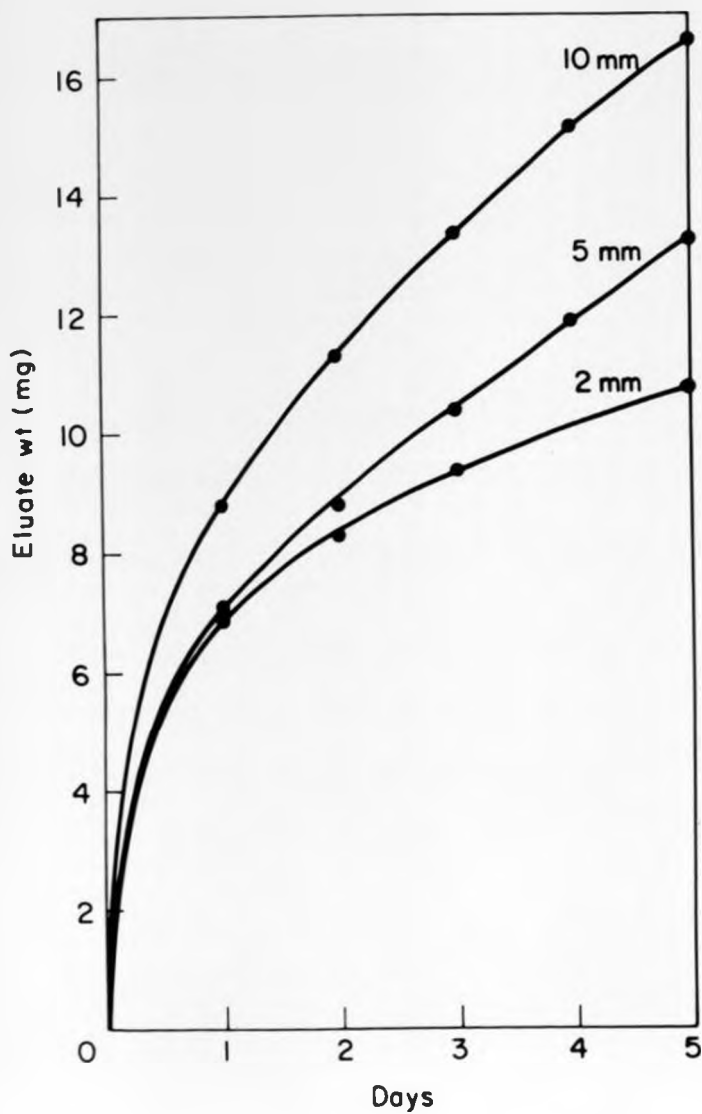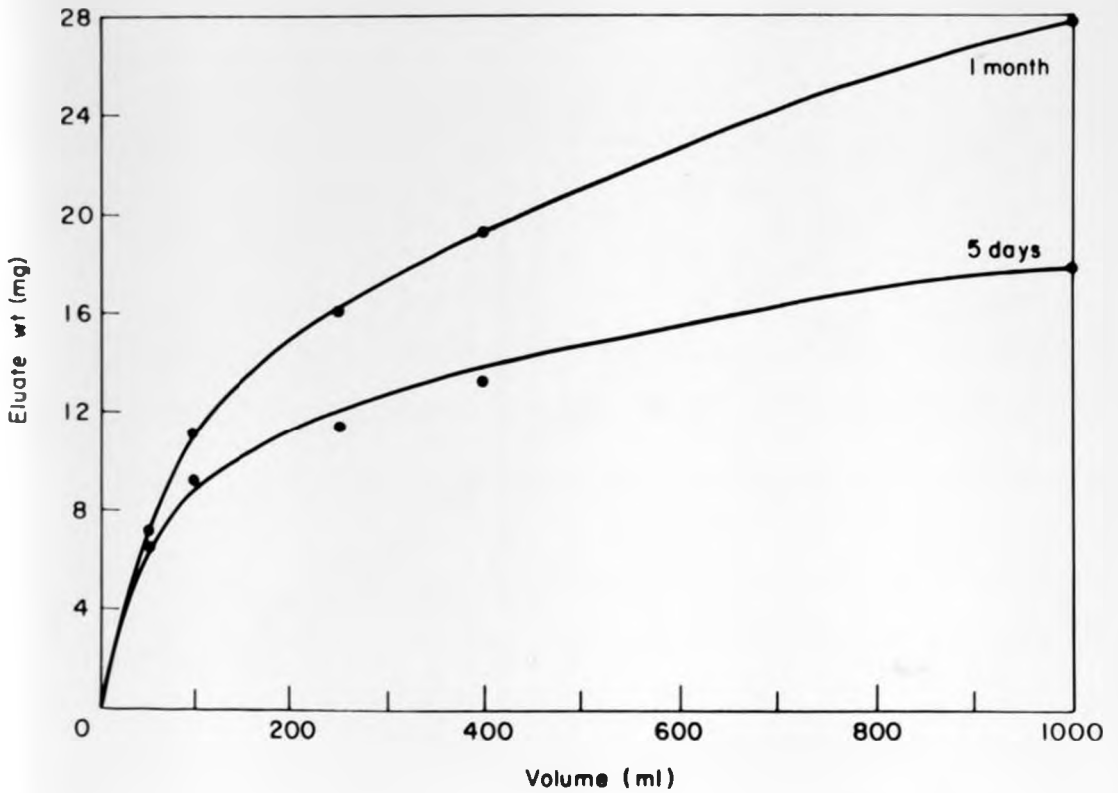# FIGURE 8

DISSOLUTION OF SILICATE CEMENT AS A FUNCTION OF THE VOLUME OF SOLUTION
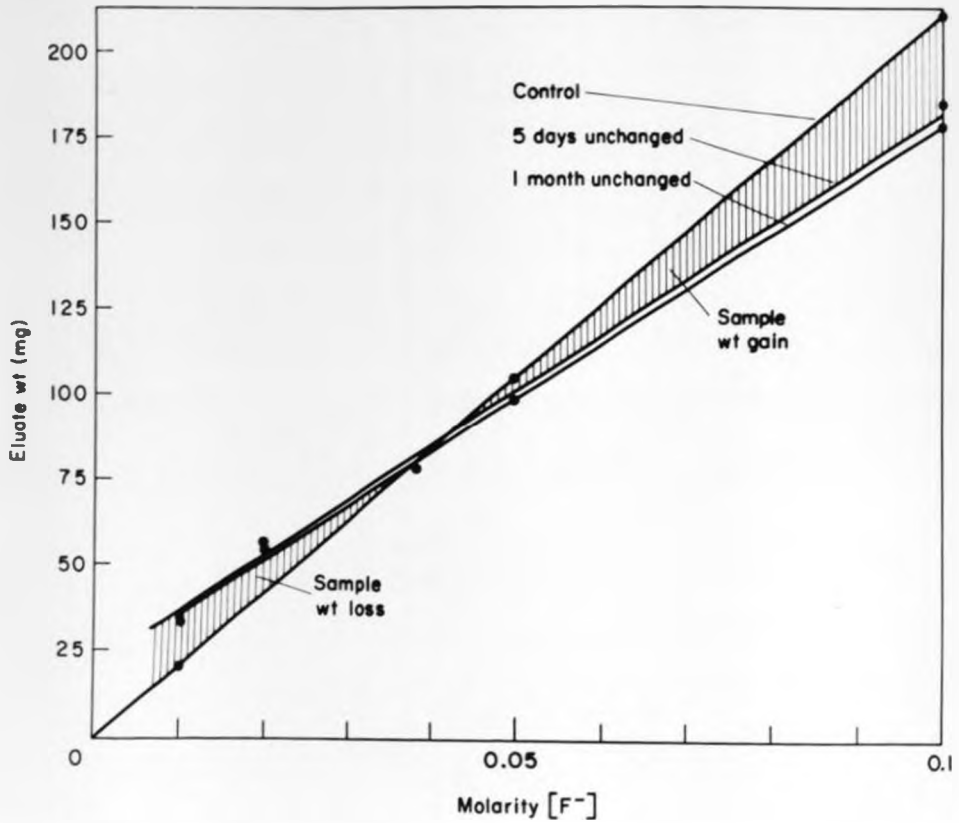
FIGURE 9

DISSOLUTION OF SILICATE CEMENT AS A FUNCTION OF FLUORIDE CONCENTRATION
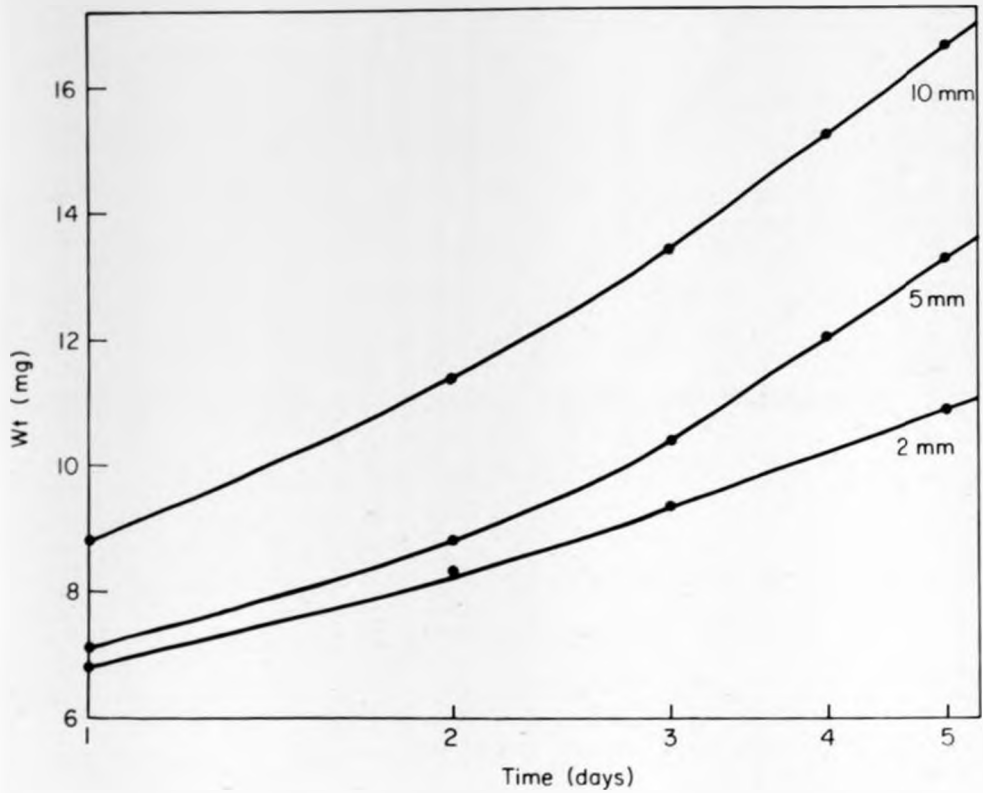
FIGURE 10

DISSOLUTION OF SILICATE CEMENT AS A FUNCTION OF LOGARITHM OF IMMERSION

TIME

FIGURE 11

DISSOLUTION OF SILICATE CEMENT AS A FUNCTION OF THE SQUARE ROOT OF

TIME OF IMMERSION

FIGURE 12

THE RATE OF DISSOLUTION OF SILICATE CEMENT AT A DEFINITE TIME M_t AND

AT INFINITE TIME M_{inf} AS A FUNCTION OF THE SQUARE ROOT OF TIME

A — 2mm Disc

B — 5mm Disc
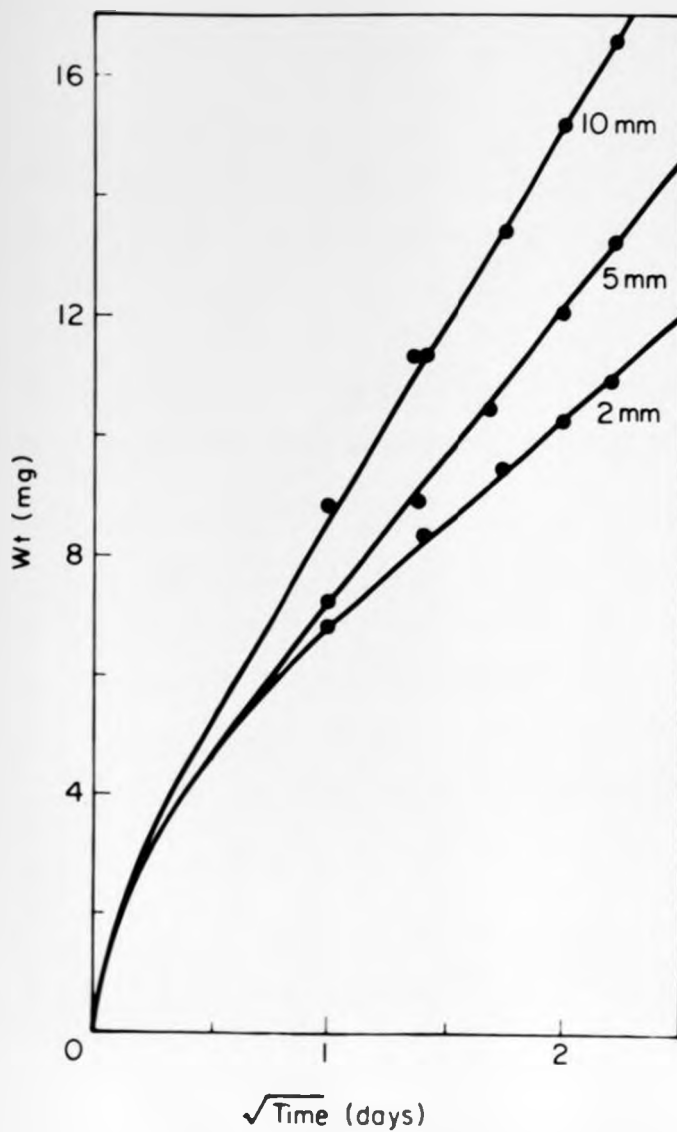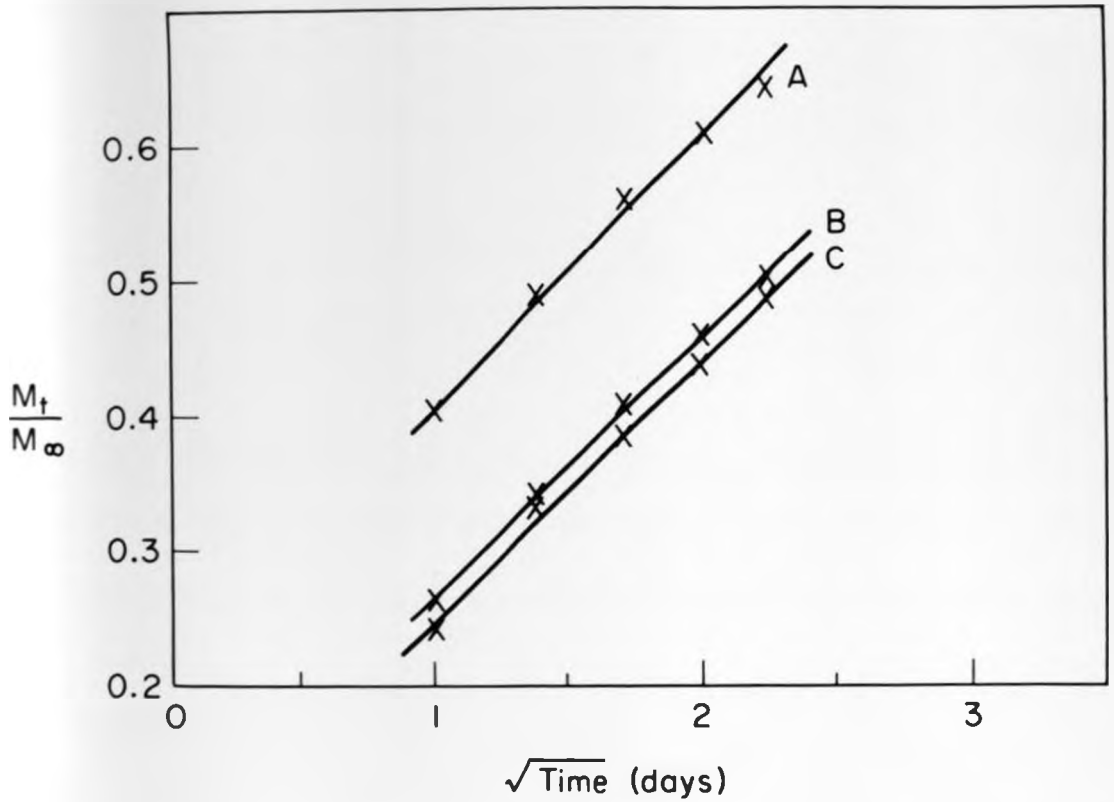
C — 10mm Disc

FIGURE 12

THE RATE OF DISSOLUTION OF SILICATE CEMENT AT A DEFINITE TIME M_t AND

AT INFINITE TIME M_{inf} AS A FUNCTION OF THE SQUARE ROOT OF TIME
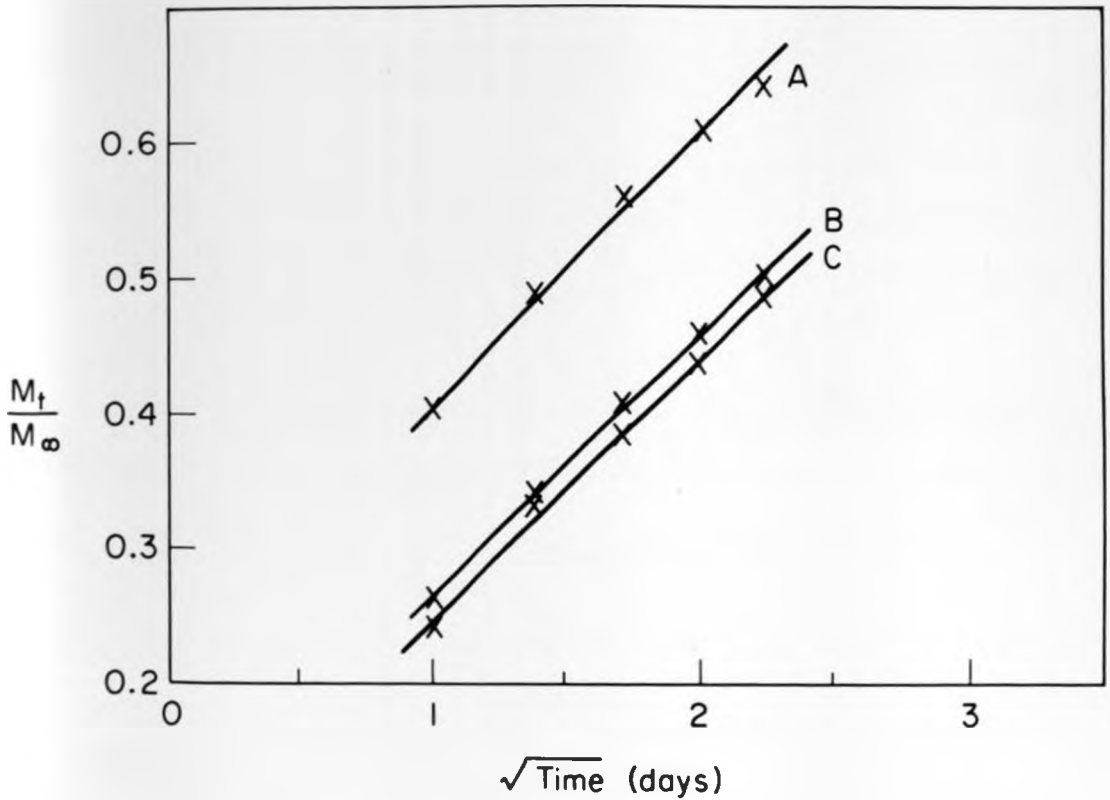
A - 2mm Disc

B - 5mm Disc

C - 10mm Disc

FIGURE 13

DISSOLUTION OF SILICATE CEMENT AS A FUNCTION OF THE SQUARE OF THICKNESS

OF DISC
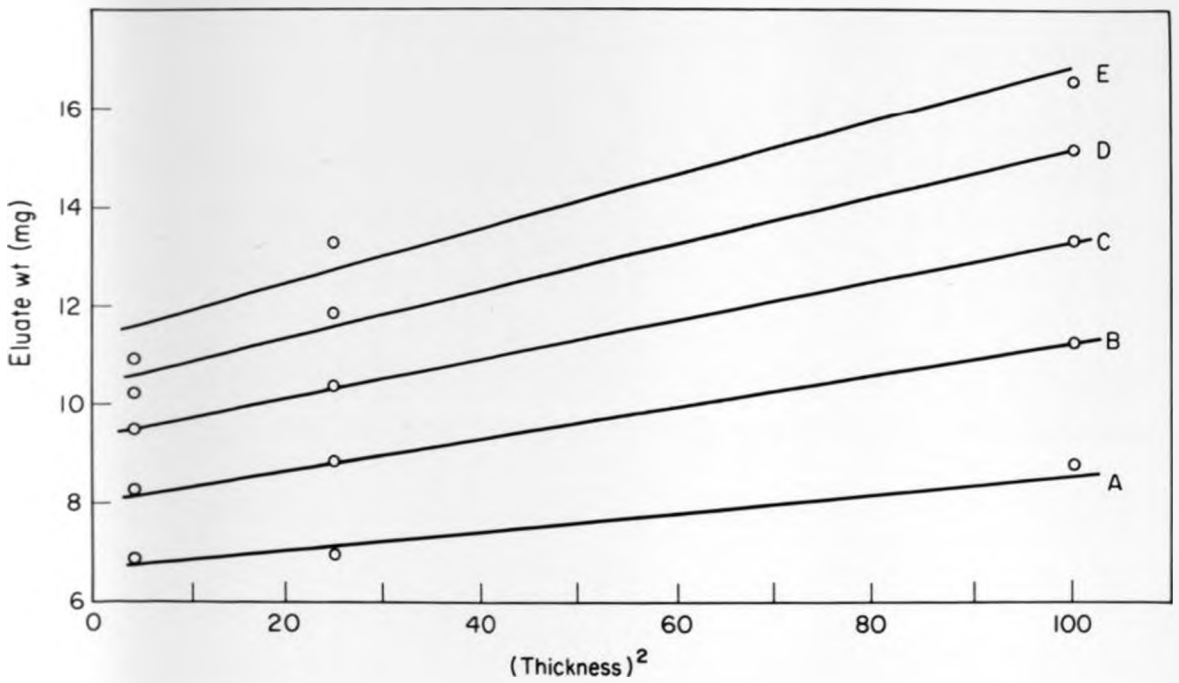
A — Dissolution after 1 day

B — Cummulative dissolution after 2 days

C — Cummulative dissolution after 3 days

D — Cummulative dissolution after 4 days

E — Cummulative dissolution after 5 days

FIGURE 14

THE RELEASE OF ORGANIC SPECIES FROM GLASS IONOMER CEMENT IN DEIONIZED

WATER AS A FUNCTION OF TIME
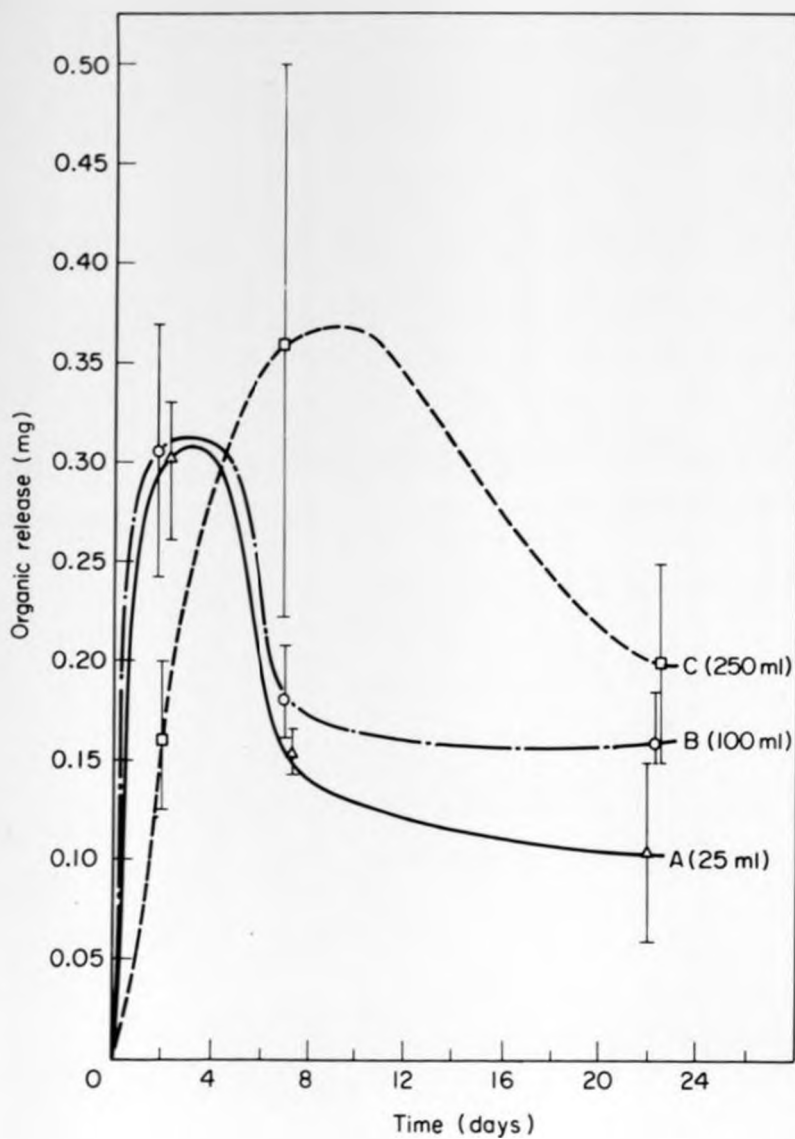
THE RELEASE OF ORGANIC SPECIES FROM GLASS IONOMER CEMENT IN PHOSPHATE BUFFER SOLUTION pH 7 AS A FUNCTION OF TIME
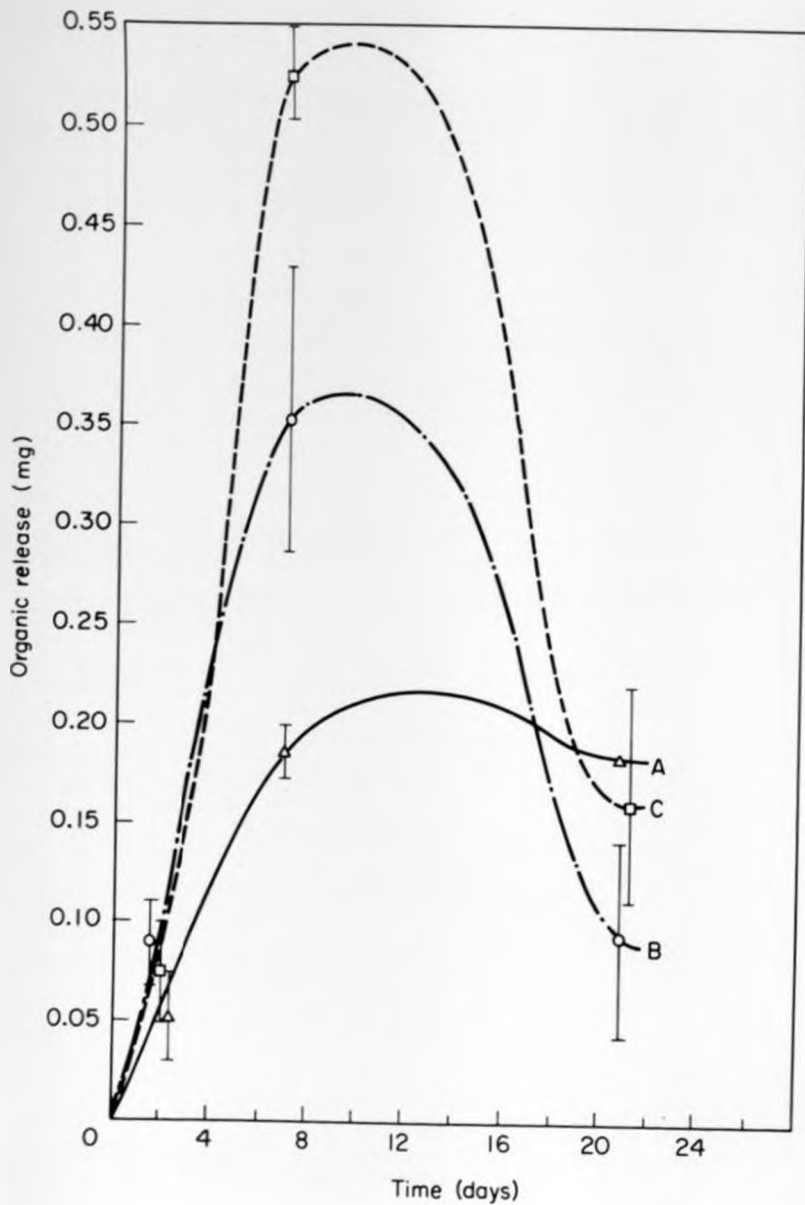
A — 25ml Phosphate solution

B — 100ml Phosphate solution

C — 250ml Phosphate solution

FIGURE 16

THERMOGRAVIMETRIC ANALYSIS OF GLASS IONOMER CEMENTS. I.

C   = Disc mixed according to standard procedure then
        cured at 37°C for 1 hour and stored at room temperature
        for 7 days. Analysis in static air.

C_1 = As 'C' but analysis in slow flowing Nitrogen.
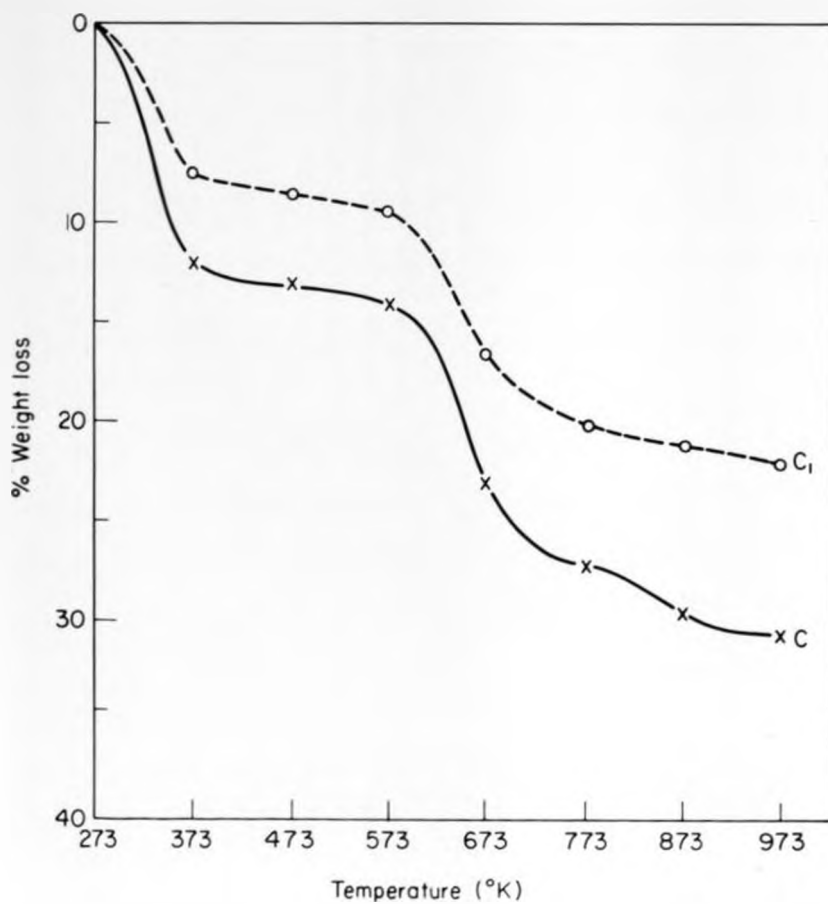
FIGURE 17

THERMOGRAVIMETRIC ANALYSIS OF GLASS IONOMER CEMENTS. II.

A = Disc prepared according to standard procedure
then cured at $37^{\circ}C$ for 1 hour.

E,F = As 'A' but immersed in deionized water for 5 days
changed daily and 5 days unchanged respectively.
Dried at room temperature for 12 hours, and
analysed in static air.

G = As 'A' but immersed in phosphate solution for 5 days
unchanged. Dried at room temperature for 12 hours.

E_1, F_1, G_1 = As 'EFG' but analysed in slow flowing Nitrogen.
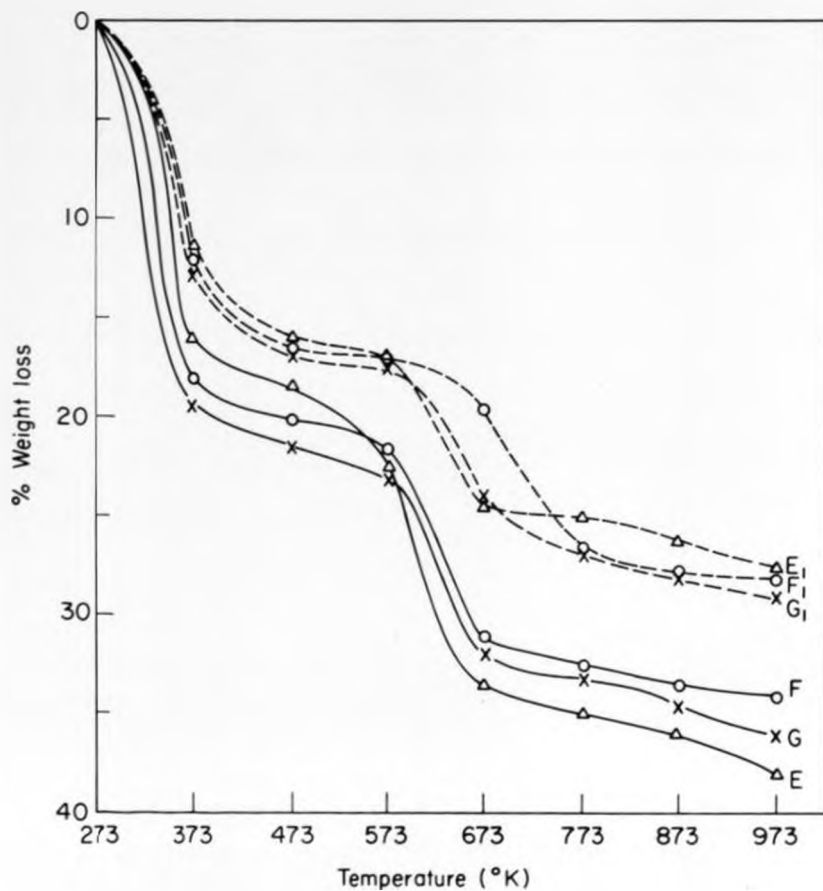
11. DISCUSSION

11.1 THE EFFECT OF SURFACE AREA:VOLUME RATIO OF SPECIMEN ON DISSOLUTION OF 'BIOTREY' SILICATE CEMENT

The solubility of a restorative material in oral conditions is of the utmost importance when under consideration for clinical application. Dental silicate cements, though an excellent material in many ways, generally suffer from a high solubility in oral conditions. In spite of this, they continue to be used clinically, and in addition provide a 'model system' for examining the behaviour of cements in general. Factors that influence the dissolution of silicate cement and indeed any other cements can be divided into intrinsic and extrinsic factors. The former relates to the cement itself and the manner of its preparation, whereas the latter concerns the environment in which the cement specimen is placed. The 'eluate weight' method was used in this study to examine the various aspects of dissolution of silicate cement.

The results as shown in Table 4   in the section 10.1 on the effects of surface area:volume ratio of specimen on the dissolution of silicate cement confirm and extend the findings of earlier work by Tan (1981). From the results of this work, it is observed that increasing the depth or thickness of the specimen, results in a corresponding increase in the amount of material lost from a constant surface area. This suggests that the material lost from the specimen into the solution is derived from the surface of the material, as well as from the bulk. The loss of material from the bulk probably occurs through the fissures on the specimen. These fissures may be seen on the surface of the specimen with a microscope. Similar findings have been reported by Cranfield (1980) in respect of fluoride release. The release of fluoride is of course one facet of the

overall dissolution process. These findings concur with those of Wilson (1971) as well as Tan (1981). However it does not support the findings by Eichner (1968) who maintained that the surface area of the specimen, alone determined the solubility of a cement.

11.2   THE EFFECT OF VOLUME OF SOLUTION ON THE RATE OF DISSOLUTION OF 'BIOTREY' SILICATE CEMENT

It was suggested Tan (1981) that extrinsic factors such as frequency of change of solution and composition of solution could affect the rate of dissolution of cements. It has been confirmed in this study that extrinsic factors have a significant influence on the dissolution of cements as shown in Figure 8. The variation of the rate of dissolution with the volume of solution used, shows the importance of this parameter. The effect is valid both for a short test period, i.e. 5 days, as well as for a longer test period, i.e. 28 days. This is an important distinction because Wilson (1967) has shown that the relative rates at which different species are eluted from the cement disc change considerably with time. Soluble leachants like phosphate salts are lost in the early stages, while other species leach out in the later stages. This occurs when most of the more soluble leachants have dissolved out. Using volumes of 10mls, 20mls, and 50mls of test solution, Wilson (1971) found no significant effect on the elution of phosphate salts. This is probably due to the fact the sodium dihydrogen phosphate salt in the matrix is so soluble that it is well below its saturation level in the eluate for the volumes of solution used.

11.3 THE EFFECT OF ADDITION OF FLUORIDE TO THE SOLUTION ON DISSOLUTION
OF 'BIOTREY' SILICATE CEMENT.

Wilson (1967) has shown that phosphate ions are released from
silicate cement into solution, in which it is immersed, as the
specimen dissolves. Numerous studies have demonstrated that fluoride
ions are also released into the solution in the process of dissolution.
Forsten (1972, 1977), Legrand (1974).

One aspect that has been demonstrated for silicate cement is
that dissolution is a quasi-equilibrium process in that these materials
not only release phosphate, fluoride and other ions into the surrounding
solution, but can also take them up from such solutions. Tan (1981)
showed that phosphate ions could be released into the solution and
could be taken up by the specimen as well. The results of the present
work, displayed in Figure 9, shows that similar effects operate for
fluoride ions. The fluoride ions are released into the solution when
specimens are immersed in a weak fluoride solution i.e. $0.01M.F^-$.
Conversely, it is shown that fluoride ions are taken up by the specimen
from solution when specimens are immersed in solutions of higher
concentrations, i.e. $0.1M.F^-$.

The results obtained in the study, in conjunction with those of
earlier workers, shed some light on the discrepancies noted in most
of the published data on dissolution of silicate cement. Since no
two workers or groups of workers appear to have employed the same
conditions i.e. volume of solution, composition of solution or frequency
of change of solution, it is hardly surprising that differences in
the results even in the rankings exist. The observations made in
this study leads to a number of important conclusions.

a) The ranking of the performance of materials such as the silicate cement may only be valid if all the samples are investigated under near identical conditions.

b) Deionized water which has been used in most of the tests is not a satisfactory medium for testing the dissolution of materials. This is because the pH, which is initially near neutral, and its ionic strength i.e. the content of dissolved salts will change quite considerably during the test period. This is due to the species being leached out from the specimen leading to changes in both these parameters. It is quite possible that species might be leached out from the cement into the surrounding solution and subsequently reabsorbed.

There are a number of theoretical models that have been devised in order to explain the phenomena of dissolving solids. Though the basis of these models are outside the scope of this study, three of the main models that exist will be applied to the results of this study. These models postulate:-

a) The dissolution of a specimen is directly proportional to the logarithm of the time for which the specimen was in contact with the solution.

b) The dissolution of the specimen is directly proportional to the square root of time for which specimen was immersed in solution.

c) The ratio of the amount of material leached out of the specimen after a definite time period "M_t" to the amount of material leached out at an infinite time 'M_{inf}' is proportional to the square root of time the specimen was immersed in the solution. Kydonius (1980) has discussed these models at some length and has shown how types of dissolving systems obey one or the other of the models above.

Some systems obey one model in their early stages of dissolution and another model at subsequent stages. These models appear to be applicable to simple dissolution systems. The dissolution of silicate cement is a complex one. It involves the leaching out of several species at different rates. The release of these species follows different laws. An attempt has been made in this study to relate the data from dissolution of silicate cement to these models. This is shown in Figures 10, 11 and 12. The extent to which the data is linearized by the type of treatment can be seen. While no single model results in a perfect linearization, all three models applied give regions of linearity over part or indeed most of the dissolution time period.

Bearing in mind the effect of M_t/M_{inf} versus the square root of time 't' it was decided to retrospecitvely apply this treatment to previously published data. The release of individual species, phosphate and silica from publications of Wilson et al (1967b, 1968) are shown in Table 11. From these data M_t/M_{inf} versus the square root of time plots were drawn (though these are not reproduced here). From these plots it was found that the ratio of amount of species eluted at a definite time 'M_t' and at an infinite time 'M_{inf}' is approximately a linear function to the square root of time of immersion. This treatment should not be ignored in future 'in vitro' experimental work on dissolution of dental cements. This relationship may not be quite apparent in freshly mixed cement. This is due to super imposition of the effect of chemical setting reactions, which rapidly change the level of soluble ions in the cement in a complex manner.

The weight loss method used in this study to measure the dissolution of silicate cement is a simple one. However, it is a valid method in contrast to that used by other workers such as Erikson (1970) and Eichner (1968), who applied the 'disc weight loss' method. Their methods have been shown to be erroneous because of simultaneous absorption of water by the specimen. The 'weight loss' in the present study is the aggregate of all the species eluted from the specimen. Each of the species eluted follows a different pattern of release, hence it is an approximation to apply a single equation to the sum total amount of species released.

While the present work has highlighted important factors affecting the rate of dissolution of silicate cement, it could not provide much insight at the molecular level. It seems clear that phosphate ions Tan (1981) and fluoride ions as shown in this study attain some sort of equlibrium, which can be tilted either way according to the species in the surrounding solution. The phosphate ion originally introduced into the cement as an acid, i.e. linked with hydrogen ion, can associate with many other species present in the cement including Aluminium, Calcium, and Sodium ions. In most cases a range of salts exists i.e. Na_3PO_4, $NaHPO_4$, $Na_3H_2PO_4$ and even more complex species such as hydroxyapatite are known to form. The concentration of phosphate and fluoride ions in human saliva is relatively lower than those at 'cross-over' points on silicate cement. Hence, clinically, silicate cement exposed to saliva will lose both these ions and other constituents either, into solution, or, into the surrounding tooth substance. It would seem possible that, under certain conditions, if the balance of ionic concentrations is favourable that there could be a gain of fluoride ions by the cement from the tooth structure.

11.4   RELEASE OF ORGANIC SPECIES FROM 'CHEMFIL' GLASS IONOMER CEMENT

The glass ionomer cements developed by Wilson et al (1969) are known to have superior properties to silicate cement not least in respect of their solubility. The "wash out" phenomenon clinically observed in silicate cement is not found in these materials. Nevertheless, an 'in vitro' study of the nature and extent of the solubility of these materials is largely lacking. This is, in some measure, due to experimental problems. Several workers Forsten (1972, 1977), Tveit (1981) have studied one facet of dissolution of glass ionomer cements, namely the release of fluoride. The availability of fluoride electrode makes such a study experimentally easy. But this apart, no study of their overall solubility appears to have been made. McCabe (1982) has attempted to do this by "disc weight loss" method. Insufficient details of this work are available at the present time. However the method of "disc weight loss or gain" is hampered by the property of water uptake by glass ionomer cements. Tan (1981) has shown that for silicate cements such water uptake is not only considerable but also dependent on the 'history' of the sample, that is it's curing procedure, the nature of solution in which it was immersed as well as the time of immersion. While not condemning his technique, it is felt that good evidence is lacking McCabe's paper to show that this factor was controlled.

→   In the present study, the release of organic species from discs of glass ionomer cement into deionized water and phosphate solution has been investigated. The technique developed allowed monitoring of organic concentrations in water at the parts per million (ppm) level. This technique uses very specialized equipment. The Carlo Erba T.O.C. (Total organic content) apparatus detects only organic carbon. Thus carbon from carbonates and bicarbonates is not detected,

however, it must be added that if the carbonates present are converted, for example, by photosynthetic action into organic matter then the detectable carbon content increases. This instrument cannot be used to differentiate one organic compound from another. The organic species detected in this study might either be tartaric acid, polyacrylic acid (PAA) or a salt of either of the acids. As far as is known there are no other organic species present in this material.

It was recognised early in this study, in experiments using artificial saliva as an immersion medium, that contamination was a problem and would be a major source of error. The experiments using artificial saliva were abandoned since the organic species leached out would contain a "background count" of contaminants. Such formulations of artificial saliva also favoured bacterial growth. In the investigation carried out, controls were used throughout the experiment. The levels of organics detected in the controls gave cause for concern, once again highlighting the problem of contamination. It is also to be borne in mind that samples had to be transported by train to the Water Research Laboratories. These often stood for 1, 2 or even more days prior to analysis. There was little that could be done to prevent this. Under laboratory conditions, dust contamination would probably have made some contribution to the background contamination levels. The circumstances allowed only two runs in each series of experiments to be carried out and analysed.

The procedure decided upon was to take the mean of the two values obtained from each series and subtract the value obtained in the control run. The mean values of organic species in each volume of solution used are shown in Table 8. It is observed that organic

species are released from glass ionomer cements in detectable amounts.

Figures 14 and 15   shows the organic species leached out of

cement plotted against time for the different volumes of deionized

water and phosphate solution used. The error bars show the

scatter of the data for each series. It is observed from these

graphs that the trend is consistent. It appears that organic species

are released from glass ionomer cement and reach a maximum concentration

then subsequently decline. The reason for this decline is not

well defined, however it appears that reabsorption of the organic

species by the cement sample occurs. This follows the same lines

as reabsorption of fluoride and phosphate ions in silicate cements.

Alternatively, if the species released were tartaric acid or

polyacrylic acid, it is possible that on release it formed a thin

film on the walls of containing vessel. It is also possible that,

due to slow curing, the polyacrylic acid (PAA) leached out into

solution and reacted with metal cations to form an insoluble species.

This insoluble species was then either precipitated onto the surface

of the cement or reabsorbed into it.

11.5 THERMOGRAVIMETRIC ANALYSIS OF GALSS IONOMER CEMENTS

A very limited study of the thermogravimetric analysis of glass

ionomer cement has been published previously. Elliot et al (1975),

Hornsby thesis (1975). The data presented in this study appears to

have been obtained in static air. The aim of this aspect of work was

to learn to what extent cement history and thermogravimetric conditions

affected the water loss.

Samples of different histories as shown in Section 9.2.3b were

subjected to thermogravimetric analysis in air and in Nitrogen flowing

at the rate of 4.5ml/min. General feature resulting from the analysis is very rapid weight loss (presumably due to water loss) at temperatures between $295^{\circ}K$ to $373^{\circ}K$, followed by a relatively inert portion over the range $373^{\circ}K$ and $573^{\circ}K$ after which a further weight loss sets in again. At higher temperatures most organics tend to lose weight by a charring process. Such charring is in effect oxidation. The oxygen for this derives from both the air and the oxygen included in the organic molecules themselves. There is no way in which the latter process can be hindered. However thermogravimetric apparatus can be operated in a Nitrogen atmosphere thereby precluding oxidation of species. The effect of substitution of Nitrogen is interesting in that while the overall shape of the TG curves remains basically unchanged, progressively less overall weight of the samples is lost. Most of the difference in weight loss occurs above $373^{\circ}K$, where oxidation in any case would be low. This aspect must be persued further and has important implications in defining 'loosely bound' and 'tightly bound' water as both Wilson (1975) and Hornsby (1976) have done. Tan (1981) has shown that silica loses water continuously upto very high temperatures and it is possible that the major portion of the weight loss above $473^{\circ}K$ is almost entirely due to this species. It is observed in this study that at $373^{\circ}K$ 75% of the weight lost for glass ionomer cement is found when samples are analysed in static air. Comparison of results from experiments with flowing and static air would further illuminate such effects. An alternative would be to run the samples on a TG and the gases passed through a tightly sealed gas chromatograph chamber where they are analysed. This would determine the nature of substance being lost.

The weight change of the specimen that had been immersed in deionized water and in phosphate solution was greater than that of specimens stored at room temperature. There was a greater weight change in specimens stored in phosphate solution than those stored continuously in deionized water for 1 week. By comparison, the specimens, in deionized water changed daily for 1 week had the least weight change. It is true that fluoride has been released and that this would be replaced by oxygen or hydroxyl group. The resulting specimen would undoubtedly have different Thermogravimetric characteristics. The extent of fluoride substitution would hardly reach the 1% level as many studies of fluoride ion release have shown. It would be of interest to study samples immersed in solutions for longer periods of time.

The implications of these findings must be considered in assessing the value of 'disc weight loss' method as a mean of investigating glass—ionomer cement solubility. Such an approach, as used by Eichner (1968), Erikson (1970) for silicates, has been to a large extent discredited. More recently MCabe (1982) has reported the use of the same method for following weight loss of glass ionomer cements. The question is raised once again as to the extent to which variable amounts of water uptake or variation in the temperature at which it is lost affect such data.

12 CONCLUSIONS

The study undertaken in this project has led to a number
of conclusions:

12.1 TESTING THE DISSOLUTION OF CEMENTS

It is clear that the volume of the surrounding, the surface
area:volume ratio of specimen and the frequency of change of the liquid,
affect the rate of dissolution of silicate cement. This finding
has implications for previously published work on this material.
There are suggestions that these findings are not only valid for
silicate cements but also glass-ionomer cements.

12.2 THE RELEASE AND UPTAKE OF FLUORIDE

The presence of fluoride in dental cements such as   silicate
is significant. The release of fluoride exert a cariostatic effect
on the enamel, however it is now seen that if fluoride were absent
in the cement it could abstract fluoride from the enamel. This
would accelerate tooth decay or breakdown.

12.3 RELEASE OF ORGANIC SPECIES FROM GLASS IONOMER CEMENTS

Glass ionomer cement has been shown to release a very limited
amount of organic material, the nature of this is not known. The
organics released under the conditions of the present work are most
probably reabsorbed into the cement. Under "in vivo" conditions this
would not be the case. They would most probably pass into the
body through the digestive system.

12.4 WATER LOSS FROM GLASS IONOMER CEMENT

The manner of water loss from these materials coupled with their
known uptake of 12% or more of water, renders the "sample weight loss"
method of analysis of dissolution highly unsuited for use with these

12.5   SUGGESTIONS FOR FURTHER WORK

a)   METHOD OF INVESTIGATION OF DISSOLUTION OF CEMENT:

The findings in this study on the methods used to investigate
the dissolution of cements calls for a tighter definition and control
of conditions under which such materials are tested.

b)   IDENTIFICATION OF SPECIES

A study should be extended to identify which organic species
is/are present in the eluate of glass ionomer cements. Trace amounts
of organic material especially those unsaturated or monomeric have
been thought or been associated with carcinogenic properties.

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14. ACKNOWLEDGEMENTS

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