ASSESSING THE ABILITY OF ACIDULATED FLUORIDE SOLUTIONS TO ETCH GLASS-BASED RESTORATIVE MATERIALS – A PILOT STUDY

Submitted as partial fulfilment for the degree of Doctorate in Clinical Dentistry (Prosthodontics)

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Chapter 1

LITERATURE REVIEW

1.1 INTRODUCTION

Topical fluorides have been used widely in dentistry for over fifty years, and are credited with having contributed greatly to the marked decline in caries prevalence recorded in most industrialized countries over the last three decades (Fejerskov, 1981). A wide variety of forms of topical fluoride have been developed in an effort to provide differing modes of action in caries control. For example, the low concentrations of fluoride in dentifrices and mouth rinses have been designed to provide prophylactic protection against caries across the population, though are effective only to a limited degree. More advanced rates of caries development have lead to the formulation of high fluoride concentration gels and varnishes subject to professional application on prescription. One such gel containing sodium fluoride in an acidulated base (called acidulated phosphate fluoride or APF), was widely used until it was found to etch glass-based restorative materials. Yet, such a formulation has been shown to provide a much higher level of fluoride uptake into tooth structure, (Pai, 1995) and to protect against strong acidic challenges such as dental erosion than its neutral counterpart. The studies to evaluate the latter effect were by Jones et al (2002) and Mok et al (2001) who reported the reduction in the loss of enamel surface to a significant extent with the application of acidulated topical fluoride gel prior to simulated endogenous and exogenous acid exposure.

The nature and rate of damage to glass-based restorative materials has had little investigation. Whether alternative forms of acidulation would eliminate this destructive effect of the acidulated gel has not been investigated. The objective in this project is to investigate both the above questions. This review of dental literature relevant to this area of investigation provides background information on both the nature and intended function of topical fluorides generally, and the nature of the glass-based restorative materials.

1.2 MECHANISM OF ACTION OF FLUORIDE IN INHIBITING THE CARIES PROCESS

1.2.1 The chemical process of dental caries

It is generally accepted that caries results from demineralization of the mineral phase of the tooth by bacterial acids within dental plaque. The plaque bacteria metabolize fermentable carbohydrates, producing organic acids such as lactic, acetic and propionic acids causing a fall in pH and increased enamel apatite solubility. These acids diffuse through the plaque into the enamel and dissolve apatite to produce calcium and phosphate ions at susceptible sites (Larsen and Bruun, 1994; ten Cate and Featherstone, 1996). Demineralization occurs when this mineral diffuses out of the tooth and into the oral environment (ten Cate and Featherstone, 1996), below the critical pH value for each patient. Critical pH is the pH at which the saliva is exactly saturated with respect to enamel apatites and it varies over a wide range. Its value is largely influenced by the concentration of calcium and phosphate in the saliva and plaque fluid (Larsen and Bruun, 1994). People with low concentrations of these ions in the saliva may have the critical pH as high as 6.5, whereas those with high salivary concentrations of the ions, may have a critical pH of 5.5 (Dawes, 2003). Dissolution of mineral in the plaque and in any calculus present adds to the concentration of calcium and phosphate whereby the critical pH is lowered (Fejerskov and Clarkson, 1996).

The reverse process in which the mineral is reabsorbed into the tooth and the damaged crystals are rebuilt is called remineralization. This process occurs once the level of saturation of calcium and phosphate ions at the tooth surface exceeds that within the tooth structure. The process of reversal of the demineralization balance to result in remineralization is aided by mild concentrations of acid ions, though is again reversed to the demineralization phase if the concentration of acid ions results in an under-saturation of calcium and phosphate ions. The presence of fluoride ions in the environment greatly assists the remineralization process to progress (Larsen and Bruun, 1994).

A series of buffer systems tends to counteract alterations of pH. These include the buffer systems of saliva (phosphate, bicarbonate and protein systems), the organic and inorganic material in plaque which has a buffering capacity approximately ten times that of saliva (Shellis and Dibdin, 1988), and the buffer system of calculus with a capacity in excess of 100 times that of saliva (Larsen and Bruun, 1994).

The caries process is also affected by the solubility of the tooth mineral. The variability in composition and the presence of foreign ions which are more reactive, particularly carbonate at approximately 2-5 % wet weight in the enamel crystal lattice, are responsible for the greater solubility of dental enamel (ten Cate and Featherstone, 1996; Clarkson et al, 1996).

1.2.2 The anti-caries mechanisms of fluoride

Fluoride is acquired into the enamel crystal lattice through the systemic route by ingestion of fluorides from various sources such as water, food and topical fluoride preparations. This process occurs mainly during the mineralization stage of enamel (pre-eruptively). This type of fluoride is permanently bound in the form of fluorhydroxyapatite and cannot be extracted unless the enamel crystal is dissolved (Larsen and Bruun, 1994). This pre-eruptive mechanism allows fluoride to act as a catalyst causing transformation of the highly soluble calcium-phosphate phases to the larger and more stable, less reactive and less soluble hydroxy and fluorapatite crystals. Fluoride also fills in the voids where hydroxyl ions are missing and becomes more strongly bonded to the lattice than hydroxyl ions, thus stabilizing the crystal lattice structure of enamel (Nikiforuk, 1985). Fluoride concentration in enamel is dependent upon fluoride intake during enamel development (pre-eruptively) and fluoride availability in the oral environment post-eruptively, called the topical effect (ten Cate and Featherstone, 1996).

Topical fluoride treatment or fluoride from other sources such as fluoride in saliva and water may also act directly on the tooth surface. This type of fluoride is taken up in enamel in the form of calcium fluoride and as adsorbed fluoride (loosely bound fluoride) (Larsen and Bruun, 1994). A small amount of liberated fluoride ion may also form a permanently bound fluorapatite following APF treatment (Nikiforuk, 1985).

The post-eruptive effect of fluoride on caries can simply be viewed as reducing the dissolution of tooth apatite, enhancement of remineralization of initial lesions and inhibiting demineralization of tooth surfaces by preventing plaque bacteria from producing sufficient acids that result in demineralization through bactericidal and bacteriostatic actions (Nikiforuk,1985). A review by Marquis (1995) described the effects of fluoride on bacterial metabolism through direct action in which fluoride acts as an enzyme inhibitor and also through binding of fluoride to heme to inhibit heme-based peroxidases. Indirect action includes the formation of metal-fluoride complexes, most commonly aluminium fluoride, and the most pertinent action is by its weak-acid effects. The latter effect is by enhancing bacterial membrane permeability to protons which compromises the function of F-ATPases in exporting protons, hence inducing cytoplasmic acidification and acid inhibition of glycolytic enzymes.

The remineralization process can occur at both the early and later stages of caries formation. When the pH falls during the caries attack, fluoride in the enamel surface and in the plaque is released, and together with the action of fluoride in saliva will stop further enamel dissolution. As the pH rises, partial remineralization occurs with formation of new larger and less soluble crystals, which contain more fluoride (as fluoridated hydroxyapatite) and less carbonate (Nikiforuk, 1985). Continuous exposure to fluoride may further increase the amount of new mineral at the lesion. During this demineralization-remineralization episode of the carious attack, fluoride acts by inhibiting mineral ion loss at the crystal surfaces and by enhancing this rebuilding or remineralization of calcium and phosphate in a form more resistant to subsequent acid attack (ten Cate and Featherstone, 1994). Plaque fluoride, particularly during acid attacks or after a topical application of fluoride in the form of gels, solutions or dentifrices may reach a high enough ionic concentration to exert an antibacterial effect (Nikiforuk, 1985). Fejerskov et al

(1981) and Beltran and Burt (1988) suggest that a continuous presence of low concentration of fluoride ions at the tooth surface provides maximal caries prevention.

An *in vitro* study by Marsh and Bradshaw (1990) that combined the influences of fermentable carbohydrate, pH and fluoride on the stability of complex oral microbial communities has demonstrated that a low concentration of sodium fluoride (1mmol/L; 19 ppm) is able to reduce the rate of acid production and the fall in the pH of dental plaque. Furthermore, the combination of a moderately low environmental pH (pH 5.0) and low fluoride level (1 mmol/L) able to prevent *Streptococcus mutans* growth, resulted in its proportions within the bacterial community remaining low.

1.3 DEVELOPMENT OF TOPICAL FLUORIDE

Topical fluorides have been regarded as important caries-preventive measures for more than 40 years. They have also been used for arresting or remineralizing established carious lesions in patients with high caries risk. Topical fluoride therapy refers to the use of systems containing moderate to large concentration of fluoride that are applied locally or topically to erupted tooth surfaces to prevent the formation of dental caries. This term encompasses the use of fluoride rinses, dentifrices, pastes, gels, varnishes and solutions that are applied in various ways (Stookey and Beiswanger,1995). The rationale for using topical fluoride agents is to increase the rate and concentration of fluoride acquisition to a level higher than that which occurs naturally (Nikiforuk, 1985).

The first clinical study of topical fluoride was reported in 1942 by Bibby using 0.1% sodium fluoride solution. He reported 35 per cent less caries development in the treated quadrant compared with the untreated control quadrant after two years, during which the test quadrant was cleaned and dried prior to application of the solution for 7 – 8 minutes three times a year. In 1946, Knutson and colleagues used two per cent sodium fluoride solution to paint the teeth as a caries preventive measure. A 20 to 40 percent caries reduction has been reported but this procedure proved not to be cost effective for the general population as the application needs to be repeated at least 15 to 20 minutes at a time in order to achieve a good effect.

Mouthrinses with fluoride solutions were developed in the 1950s in an effort to find simple, time saving and effective methods for fluoride applications. A concentration of 0.2 per cent sodium fluoride solution was used as a mouthrinse every week or every second week at schools in Scandinavia for nearly 25 years (Koch et al., 1994). However, this program has been largely withdrawn today with the introduction and increasing use of fluoride toothpastes. The rationale for this is that a better caries protection is developed with once or twice daily brushing the teeth compared with rinsing the mouth with a fluoride solution.

Fluoride varnishes were developed in the 1960s, based on the premise that a longer duration, higher concentration and more intimate contact between fluoride ions and enamel leads to a higher fluoride uptake by the enamel (Murray, 1989). Three materials that have been used in clinical trials are Duraphat, Elmex Protector (an amine fluoride 297 with self-polymerizing polyurethane varnish) and Epoxylite 9070 (disodium monofluorophosphate incorporated into a soft, flexible, polyurethane-based adhesive coating). The most thoroughly investigated and used varnish is Duraphat that contains 22.6mg F/ml sodium fluoride. The varnish is remarkably water tolerant and adheres to the tooth surface for up to 20 hours. A considerable amount of loosely bound fluoride is deposited into the enamel surface which is then slowly dissolved and influences the de- and remineralization processes (Koch et al., 1994). Currently, Duraphat (Colgate Oral Pharmaceuticals, Inc., Canton, Mass) is marketed in 5 per cent sodium fluoride varnish in a tube that contains 10 ml of product. However, Mok et al. (2001) noticed the inability of Duraphat to adhere to root surfaces unlike on enamel surfaces.

Bibby (1945) attempted the first study of fluoride dentifrice using 0.1 per cent sodium fluoride with conventional formulation but failed to show any anti-caries effect after two years. Initially, the manufacture of fluoride dentifrice faced a major problem in which the fluoride component reacted chemically with other ingredients causing no cariostatic effect. However, with the growing interest in fluoride dentifrice, a wide range of active fluoride ingredients have been tested in various chemical combinations. Today, most of the fluoride compounds are compatible with the toothpaste components and the two major salts used are sodium fluoride and sodium monofluorophosphate. The manufacturers have competed during the last decade by focusing on i) changing the F concentration ii) combining more than one fluoride component iii) adding other active agents to potentiate the fluoride effect (Koch et al, 1994). Generally, all studies have demonstrated caries decrease in the order of 30 per cent but the differences in design of the studies makes direct comparisons of findings invalid (Murray, 1989).

1.4 DEVELOPMENT OF ACIDULATED FLUORIDE

Enhancement of fluoride uptake by enamel was first reported by Bibby in 1947 by lowering the pH of the fluoride system. It was not until 1963 that Brudevold et al. developed an acidulated phosphate fluoride formula using 1.23 per cent fluoride solution in an effort to establish a composition providing maximal fluoride uptake to enamel while causing minimal demineralization. These investigators reviewed the various chemical reactions of fluoride with enamel (hydroxyapatite) and concluded that if the fluoride system was made acidic, it would enhance the rate of reaction of fluoride with hydroxyapatite. They also concluded that if the phosphoric acid was used as the acidulant to increase the concentration of phosphate present at the reaction site, it was possible to produce greater amounts of fluoride incorporation into the enamel surface as fluorhydroxyapatite with minimal formation of calcium fluoride and minimal loss of calcium phosphate.

Nikiforuk (1985) provides the formula for 1.23% APF solution at a pH of 3.2 as follows:

'Add 20 gram of sodium fluoride (reagent grade) to approximately 700ml of distilled water, in a 1 litre plastic-graduated flask. After it has dissolved, add 6.3 ml concentrated orthophosphoric acid (85% reagent grade), 5.9ml of concentrated hydrofluoric acid (50% reagent grade) and make up to 1 litre with distilled water. Mix very thoroughly. The stock solution must be kept in a screw-capped, polyethylene bottle (glass bottles should not be used because they can be attacked by the undissociated hydrofluoric acid (HF) molecules), and dispense in a small plastic container for use on patients. The stock and dispensing containers should be tightly capped when not in use. The solution is stable indefinitely. The pH should be reasonably well controlled. However, glass electrodes cannot be used with acid fluoride solution. Non-glass electrodes can be safely used.'

The increased uptake of fluoride and its penetration into the enamel from this formula at pH 3.2 is thought to be related to the fact that over 50 per cent of the fluoride available in the form of undissociated hydrofluoric acid (HF) which diffuses more readily than the charged species; F^- or HF^-_2 (Nikiforuk, 1985). HF also is a known glass solvent, indicating that its use in this formula is likely to contribute to etching of glass-based restorative materials.

1.5 TOPICAL FLUORIDE/ENAMEL REACTIONS

The reaction between enamel and concentrated topical fluoride results in the formation of complex calcium salts and other compounds depending on the topical reagents used and the conditions of the reaction. If a high fluoride concentration above 100 ppm is used at low pH (such as the APF), the results will be the formation of large quantities of calcium fluoride as follows (Nikiforuk, 1985):

$$Ca_{10}(PO_4)_6(OH)_2 + 20\,F^- \rightarrow 10CaF_2 + 6(PO4)^{3-} + 2(OH)^- \qquad (1)$$

With APF, a slight temporary dissolution of surface enamel mineral will occur resulting in formation of dicalcium phosphate (reaction 2) as well as calcium fluoride (reaction 1):

$$Ca_{10}(PO_4)_6(OH)_2 \rightarrow 6CaHPO_4 + 4Ca^{2+} + 2H_2O \qquad (2)$$

The reaction products will dissolve in saliva and release fluoride, calcium and phosphate ions. The fluoride ions are mostly (over 90%) incorporated into the enamel as calcium fluoride and are quite rapidly dissolved. There is only a small fraction of fluoride remaining in permanently bound form, presumably as fluorapatite (ten Cate and Featherstone, 1994).

1.6 COMPARISON OF ACID FLUORIDE VS NEUTRAL (NaF)

In 2002, Delbem and Cury carried out an *in vitro* study on 192 enamel blocks, which were obtained from 45 impacted human third molars. One hundred and forty four of them were treated with fluoride gel, acidulated or neutral for 1 or 4 minutes whereas another 48 blocks serve as a control group. Ninety six blocks of the fluoride treated group and 24 control blocks were submitted to a high cariogenic challenge. Enamel demineralization was then assessed by surface and cross-sectional microhardness using a Shimadzu HMV-2000 microhardness tester and fluoride concentration in the enamel blocks was determined after removing an enamel layer by etching acid. The results showed that acidulated phosphate fluoride (APF) treatment is more efficient in increasing the enamel resistance to demineralization than the neutral fluoride (Sodium fluoride gel). APF is also found to be more efficient than NaF gel in enamel fluoride uptake. The latter result was in line with that of Pai (1995), who carried out a study on comparative fluoride uptake into enamel from various topical fluoride agents, which include 1.23 per cent APF gel and NaF in the form of gel, mouthrinse and toothpaste in various concentrations. The fluoride uptake into the enamel using APF gels were found to be significantly higher and also to a greater depth than with the NaF with similar concentration of fluoride. Gao et al in 2000 had compared fluoride release/uptake of three different materials that were placed into three fluoride recharging agents. Materials placed in APF gel had showed significant fluoride ion release compared to sodium fluoride and calcium fluoride. However, the effect was transitory.

Mok et al (2001) studied the ability of fluoride gels and varnishes in providing protection against demineralization using *in vitro* models of wine assessors' erosion. The fluoride sources used in the study include NaF gel in 2.2 per cent concentration, Duraphat varnish, Fluor Protector varnish and 1.23% APF gel. All increased protection against erosive demineralization. Of the gels, the 1.23 per cent APF gel was found to be most effective in providing protection against erosion both to the enamel and roots of the teeth. NaF gel was found to only provide slight protection against erosion both to enamel and root surfaces.

Another similar study by Jones et al (2002) using an *in vivo-in vitro* model of endogenous dental erosion also produced similar findings. A 1.23 per cent APF and 2.2 per cent NaF neutral gel were coated on enamel tiles which were bonded on intra-oral appliance worn by subjects to facilitate pellicle and plaque formation prior to exposures to 0.06mol/L hydrochloric acid (HCl) which simulated the effects of gastric acid exposure (endogenous erosion). APF were found to greatly reduce the depth of demineralization of enamel compared with NaF gel, which also provides enamel protection but to a much lesser extent. A similar finding had also been reported by Kutler and Ireland in 1953.

1.7 DISADVANTAGES OF ACIDULATION

An *in vitro* study by Soeno et al. (2000) evaluated the surface changes of one microfilled (Silux Plus) and four hybrid (Clearfil AP-X, Litefil IIA, Palfique Estelite, Progress) resin-based composites (RBC) when they were exposed to APF agents (Fluorident Gel and Floden). One third of the disk specimens from each group were treated with Fluorident Gel for 30 minutes, another one third treated with Floden for 30 minutes while the rest one third of the specimens served as control. The surface roughness was evaluated using surface analyzer Surfcoder SE-30D and scanning electron microscope (S-3500N) was used for microscopic evaluation. The results showed a greater surface roughness (Ra) value of Clearfil AP-X, Litefil IIA and Progress compared to Silux Plus. Palfique Estelite exhibits a small Ra value with no statistical differences compared to Silux Plus. The results suggest that APF agents do cause surface roughness to RBC especially in those containing larger inorganic filler particles. Therefore, the selection of microfilled or submicron filled hybrid materials is useful both in achieving a smooth surface and greater resistance to etching by APF agents. Besides the type of fillers incorporated, this study also demonstrated that the polishing method after hardening of the material may also affect the surface textures of composite materials.

In 2000, Cehreli et al studied the effect of 1.23% APF gel on the surface characteristics and roughness of one high viscosity glass ionomer cement (HVGIC) and three polyacid modified resin composites (PMRC) materials compared with a resin-based composite and two resin modified glass ionomer cement (RMGIC). The materials used were Fuji IX GP (HVGIC), Dyract AP, F2000 and Compoglass F (PMRC), Vitremer and Fuji II LC (RMGIC) and Silux Plus (RBC). Among all groups, Fuji IX GP displayed the highest surface roughness. While the SEM images of Vitremer and Fuji II LC revealed no significant micromorphological changes after the APF treatment. Among PMRC materials, F2000 displayed the highest mean roughness (Ra value) after APF treatment. This study indicates that APF treatment increases the surface roughness of some of the cements to an extent which could contribute to plaque accumulation, produce surface staining of the materials and become an area to harbour the colonization of *Streptococcus mutans*.

A similar result was observed by Yip et al (1999) who carried out a study on surface roughness and weight loss of aesthetic restorative materials related to fluoride release and uptake. They found that there was a trend of increasing Ra values from the resin composite, to the PMRC, to the RM-GICs and to the conventional GIC after APF gel application. El-Badrawy and McComb (1998) have reported the same result with the APF gel, whereas neutral fluoride gel has shown minimal effects. De Witte et al (2003) also observed surface roughening of GIC and RM-GIC treated with neutral NaF solutions compared to specimens stored in water. However, Triana et al (1994) did not observe the etching effect of glass ionomer cement when a neutral fluoride gel was used.

1.8 RANGE OF GLASS-BASED RESTORATIVE MATERIALS

It is important to determine which restorative materials are most susceptible to APF etching, and why the potential for etching is present. The presence of glass based compounds is the most obvious risk factor, considering the information considered in the previous paragraphs. However it is important to consider other aspects of their structure which might also contribute to potential etching by APF gels.

1.8.1 Resin Composites

The major components of modern resin composites include (Ruyter,1988):

i) An organic resin matrix
ii) An inorganic filler
iii) A coupling agent

The resin matrix is the chemically active component of the composite. It is comprised of principal (higher molecular weight) monomers and diluent (lower molecular weight) monomers. The most commonly used of the principal monomers is Bis-GMA, which is the reaction product of bisphenol-A and glycidyl methacrylate. This highly viscous monomer due to the high molecular weight helps to reduce the polymerisation shrinkage. A few composites also use a urethane dimetacrylate rather than Bis-GMA which also has a high molecular weight. The lower molecular weight or low viscosity monomer is added to the composite formulation to overcome the excessive stiffness problem with even the addition of small amount of filler. This will reduce the viscosity of the material for better blending with the inorganic constituents and clinical manipulation. The examples of the low viscosity monomers are methyl metacrylate (monofunctional), ethylene glycol dimetacrylate and triethylene glycol dimetacrylate (both are difunctional). The latter is the most commonly used due to its better properties. Greater quantities of this type of monomer will give the composite materials lower viscosity but greater shrinkage on polymerization (Bryant, 1998).

The resin matrix also contains hydroquinone as polymerization inhibitors. This is essential to prevent premature polymerization for long shelf life of the composite. Activator/initiator systems are responsible to achieve the cure for composite material. This depends upon the type of reaction, which may be either chemical curing or visible light activated curing.

A variety of fillers have been included in composites to improve its properties. This may include lithium aluminosilicates, crystalline quartz, silicon dioxide and boron silicates. In many composites, quartz is partially replaced by heavy metal particles such as barium, strontium, zinc, aluminium or zirconium for radio-opaque property. The following are the effects of inorganic fillers on the properties of composite:

i) Provide better mechanical properties such as compressive strength, elasticity modulus and hardness

ii) Reduce coefficient of thermal expansion

iii) Improvement in aesthetics as glass can reflect the colour of the surrounding tooth structure

iv) Reduce contraction on setting

v) Reduce the heat evolved in polymerization

vi) The composite appears radio-opaque if using barium or strontium glasses

Commercial products can be classified into four groups based on the type and quantity of filler content as shown below in Table 1.1 (Combe, 1986):

Table 1.1: Classification of composite resin

Type	**Typical Particle Size (µm)**	**% (by weight) of filler**	**General comments**
Large particle	15-35	78	Good mechanical properties but difficult to polish due to surface roughens on abrasion of resin matrix. May attract plaque.
Fine Particle	1-8	70-86	Good mechanical properties with better finishing and polishing characteristics than above.
Microfine filled	0.04	25-63	Smooth surface is easy to get and maintain and does not attract plaque. However, mechanical properties are poorer, wear resistant may be poor with also greater shrinkage on setting and absorb more water due to lower filler content.
Blended filler	0.04 and 1-5	77-80	Developed in an effort to obtain the benefits of both filler types.

However, current nanotechnology has led to the development of nanofilled composite resin characterized by containing nanoparticles with the size between 5-75nm and nanoaggregates of 0.6-1.4μm. The latter are made of zirconia/silica or nanosilica particles (sized 5-20 nm) and they are treated with silane to bind to the resin. The distribution of the fillers (aggregates and nanoparticles) gives a high load, up to 79.5%. (Geraldi and Perdigao, 2003). This smaller particle size has improved the properties of the composite resin and can be used for both anterior and posterior restoration. They provide a better finished restoration, less curing shrinkage, less cusp wall deflection and reduces the presence of microfissures in the enamel edges (Meyer et al, 2003).

It is very important that the filler and the resin matrix are strongly bonded together to have an acceptable mechanical properties. This is achieved with the use of silane coupling agent of one form or another.

1.8.2 Glass Ionomer Cement (GIC)

Development of glass ionomer cement began in the early 1970s (Wilson and Kent, 1972). Since then, this material went through a lot of changes in terms of its variety of compositions to produce a better material with the ability to bond to dentine, release fluoride, provide improved radiopacity and clinically acceptable aesthetic. Research will still continue with the aim to improve physical properties and therapeutic potential. A variety of clinical application has been designed in which Type I is used for luting agents, Type II is for restorations whereas Type III is for liners and bases (Mount,1994). GIC is a powder-liquid system, the powder component consists of calcium fluoroaluminosilicate glass and the liquid usually water or tartaric acid diluted with water. The components of calcium fluoroaluminosilicate glass are shown below in Table 1.2 (Mount and Bryant,1998):

Table 1.2: Components of calcium fluoroaluminosilicate glass in powder component of GICs

Component	**Weight %**
SiO_2 (quartz)	29.0
Al_2O_3 (Alumina)	16.6
CaF_2 (fluorite)	34.2
Na_3AlF_6 (cryolite)	5.0
AlF_3	5.3
$AlPO_4$	9.9

The mixture of the glass is fused at a high temperature producing a molten mass which is then shock-cooled, ground and sieved to a powder with maximum particle size is 50µm for filling materials (for better translucency) while less than 20µm for the luting and lining materials (Mount and Bryant, 1998). Radiopacity is achieved with the incorporation of barium, strontium or lanthanum, by fusing metal to the glass particles (eg. in cermet powder) or by mixing with dental amalgam alloy or zinc oxide (Shen, 2003). Fluoride is one of the main components for promoting remineralization to the surrounding tooth structure besides its effect on the glass fusion temperature and working characteristics of GIC. It may also have some inhibitory effect on plaque formation (Mount, 1994).

In most of the current cements, the liquid is a 40-55% solution of 2:1 acrylic acid-itaconic acid copolymer in water or a copolymer of maleic acid and acrylic acid. These acids improve storage by increasing the reactivity of the liquid, decreasing the viscosity and provide less tendency for gelation compared with that in the original GIC which was quite viscous and tended to gel in time (Mount and Bryant, 1998). This is due to the use of about 50 per cent concentration of polyacrylic acid aqueous solution. Current GIC may have about 5-15% of tartaric acid in the liquid component in order to improve the handling characteristics, increase working time but it shortens the setting time (Shen, 2003). It also allows the use of lower fluoride content in the glass to provide more translucent set cement, hence improving aesthetics.

The resin-modified glass-ionomer materials consist of glass-ionomer components as described above with the addition of 15-25% resin, usually in the form of hydroxyethyl methacrylate (HEMA) with less than 1% polymerization groups and a photoinitiator. This explains the setting, which is partly by acid-base reaction and partly by a photochemical polymerization. The composition may vary as different manufacturers try to add or change its properties.

1.8.2.1 Setting reaction of GIC

The setting reaction of the GIC is through an acid-base reaction (van Noort, 1994):

$$\underset{\text{glass}}{MO.SiO_2} + \underset{\text{acid}}{H_2A} \rightarrow \underset{\text{salt}}{MA} + \underset{\text{silica gel}}{SiO_2 + H_2O}$$

When the powder and liquid are mixed to form a paste, the surface of the glass particles is attacked by the acid liquid causing diffusion-based adhesion between the glass particles and the matrix. About 20-30% glass is decomposed and calcium, aluminium, sodium and fluoride ions are released into the aqueous medium, which leads to the formation of a cement sol (dissolution stage). The next stage involves firstly the formation of calcium polysalts (occurs relatively rapid within 4-10 minutes from the start of mixing) and eventually aluminium polysalts that cross-link the poly(alkenoid acid) chains (Shen, 2003). Fluoride and phosphate ions form insoluble salts and complexes. The salts hydrate to form a gel matrix. An orthosilicic acid is formed on the surface of the particles by the sodium ions which then becomes a silica gel and assists in binding the powder to the matrix as the pH rises (Mount and Bryant, 1998).

1.8.3 Dental ceramics

Dental ceramics or porcelain are used to make denture teeth, fixed partial dentures, crowns and bridges which can be porcelain jacket crowns, porcelain bonded to metal, inlays, onlays, labial veneers and bridges. They can be classified according to their fusing temperatures in the laboratory (Combe, 1986):

i) high fusing	1290 to 1370°C
ii) medium fusing	1095 to 1260°C
iii) low fusing	870 to 1065°C

van Noort (2002) considered modern dental ceramics to fall into three categories, based on the nature of the supporting structure:

i) reinforced ceramic core systems (eg. alumina-reinforced PJC, glass-infiltrated high strength ceramic core systems, pure alumina cores and zirconium ceramics)

ii) resin-bonded ceramics

iii) metal-ceramics

The philosophy behind this is to provide a high strength supporting structure for the ceramic as well as achieving an aesthetic finish.

Silica (SiO_2) is the main component of most dental porcelain and can appear as quartz in crystallize form or as an amorphous glass called 'fused silica'. The tetrahedron backbone of 'fused silica' with a three-dimensional network of covalent bonds between them, require high-melting temperature. Glass modifiers or fluxes such as metal ions of sodium, potassium or calcium will interrupt some of the oxygen-silica bonds by associating with the oxygen atoms resulting in many linear chains of the silica tetrahedra and this can be melted at a lower temperature (Anusavice, 1996). A balance must be maintained between a suitable melting range and good chemical durability as too high concentration of glass modifiers will cause the glass to crystallize or devitrify. The chemical durability of the glass will reduce in terms of resistance to water, acids and alkalies.

Feldspar in dental porcelain is a mineral that occurs naturally and is composed of potash (K_2O), alumina (Al_2O_3) and silica (SiO_2). This is used in dentistry to make metal-ceramic crowns and many other dental ceramics and glasses due to its incongruent melting property. Anusavice (1996) described incongruent melting as a process by which one material melts to form a liquid plus a different crystalline material. The feldspar undergoes incongruent melting when heated up to temperatures between 1150°C and 1530°C to form crystals of leucite in a liquid glass.

Dental porcelain may also contain alumina (Al_2O_3), boric oxide (B_2O_3), pigment oxides, glazes and stains. Alumina has a high compressive, tensile and flexural strength therefore is used as a strengthening agent to hinder crack within the material (Combe, 1986). It can also alter the softening point and viscosity of glass. Boric oxide is a glass former and a ceramic flux and can lower the softening temperature of the glass. Pigment oxides are added to give the required shades to simulate natural teeth. Examples are the oxides of chromium, cobalt, nickel, titanium and iron (II) oxide. Glazes and stains may also be used to obtain the required aesthetic effects (Combe, 1986). The appearance of opacity may be achieved with the addition of zirconium, titanium or tin oxides.

1.9 THE RATE OF ETCHING OF GLASS-BASED RESTORATIONS BY APF GELS

An *in vitro* study by Wunderlich and Yaman (1986) evaluated the effect of commercial topical fluorides on the surface of porcelain-fused-to-metal restorations with a scanning electron microscope (SEM) and surface roughness tracings. Twenty five samples were immersed in 1.23% APF gel and 20 samples in 8% stannous fluoride (SnF) for 4 to 64 minutes. Three samples each were placed in 2% NaF, 0.05% SnF, 0.2% NaF solutions and 0.4% SnF gel for 5 days. Half of each of these samples were masked with electrical tape, modeling clay or baseplate wax to prevent contact with fluoride before the fluoride solution immersion. The surface roughness was measured using a Surfanalyzer 150 profile recorder. The roughness of the surfaces was already observed on samples exposed to 1.23 per cent APF gel in four minutes, whilst less in 8% SnF. A statistically significant difference in surface roughness was obtained between the test and control sides exposed to both, 1.23% APF gel and 8% SnF. The mean differences are increased with increase duration of the exposure. However, there were no significant differences in roughness on the surfaces exposed to the low concentration of stannous fluoride and to the two different concentrations of neutral sodium fluoride.

Anusavice (1996) also reported the surface roughness of glazed feldspathic porcelain is produced within four minutes of 1.23% APF gel application. A further 30-minute exposure to 1.23% APF gel appears to attack the filler particles of the glass and in 300 minutes, the porcelain surface showed a generalized severe degradation, which could lead to further breakdown of the structure.

1.10 SUMMARY OF THE ETCH SUSCEPTIBILITY FACTORS IN GLASS-BASED RESTORATIVES

The evidence available clearly points to the vulnerability of the glass component of restorative materials to attack by APF gels. The HF component of APF would appear to be the most likely culprit, though it is not known whether the ortho-phosphoric acid itself might contribute. This needs investigation.

While there is evidence that resin composite restorations with large glass or quartz filler particles might also suffer some etching effects, the more modern micro and submicron filled hybrid resins appear less likely to show this effect (Section 1.7). However, no similar study has been carried out to evaluate the most current nanofilled resin composites. Quartz has a structural elements common to glass, and thus appears to also be reactive to HF. It appears that the level of exposure of these particles has a major influence on whether they are susceptible to etch. For example, the smaller micro and submicron quartz particles do not appear to be affected to a significant extent by HF attack, and in RMGIC materials, the glass also appears to be largely unreactive.

Whether the matrix in GIC is also reactive is not certain. It does contain high concentrations of Strontium and Aluminium bound acrylates and some silicates; and may also be reactive to HF and H_3PO_4. This needs further investigation. It is clear that the resin composite material itself is resistant to both acids.

1.11 POSSIBLE ALTERNATIVE ACIDULATING SYSTEMS

The advantages of an acidulated topical fluoride system in increasing resistance of enamel and root cementum to the more highly acidic erosive challenges lead us to explore whether other methods of acidulation than the use of HF, and possibly H_3PO_4, might be feasible. Whilst the H_3PO_4 was included partly to provide sufficient phosphation in the system to inhibit possible dissolution of tooth mineral at the low pH (3.2), a lower concentration of phosphate ion may be necessary if used in association with a less strongly dissociating acid than HF. In fact, a less acidic form of phosphate ion might be able to fulfil this requirement if a weakly dissociating acid is used. The need to have no resulting demineralization of apatite is a critical requirement, as well as there being no etching of restorative materials.

A further factor which needs to be taken into account is the ability of fluoride itself to inhibit demineralization of apatite. Featherstone et al (1992) have pointed out that, to halve the dissolution rate of calcium in apatite by caries-producing acids, a ten-fold increase in fluoride concentration is needed. He points to the limit this imposes on fluoride concentration, which may be safely used in combating strong acidic challenges to apatite. Even so, with a weakly dissociating acid, this concentration of fluoride ion may be adequate to inhibit such demineralization.