THERAPEUTIC ROLES OF FLUORIDE RELEASED FROM RESTORATIVE DENTAL MATERIALS
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SUMMARY: Because topical fluoride is considered to be beneficial for oral health, fluoride release and recharge features have been added to various restorative dental materials. These materials act as a rechargeable reservoir that can release fluoride, be recharged with fluoride, and then re-release fluoride, thus ensuring the availability of fluoride over a longer period of time. The ability of these materials to deliver the optimal concentration of fluoride required for various therapeutic actions for dental health has resulted in their popularity. This paper reviews the fluoride releasing materials and the therapeutic effects of the released fluoride.

Keywords: Anticariogenic effects; Antimicrobial effects; Fluoride recharge; Glass ionomers.

INTRODUCTION
Although the role of systemic fluoride ions (F) for oral health has been controversial for 70 years, the topical application of F to the teeth is considered by many to be beneficial.1,2 The association of reduced tooth decay and a high drinking water F concentration was observed in Colorado, USA, in 1915.3 Tooth decay (dental caries) is the most common disease that damages the teeth by demineralizing the dental hard tissues in the presence of microorganisms and carbohydrates over a period of time.4,5 Tooth enamel is the hardest material in the human body6 and can be disintegrated by cariogenic bacteria.4 The prevalence of caries is on the rise in all populations around the globe regardless of age, sex, and ethnicity.7 Topical F administered in the oral cavity is considered to have a significant therapeutic role in the prevention of dental caries. There are a variety of mechanisms through which F acts to prevent or retard the progress of tooth decay including hindering demineralization, increasing remineralization, and inhibiting bacterial growth.8

Several media have been used for the administration of F including water fluoridation,9 and the use of F releasing varnishes and filling materials.3 The American Dental Association approved the use of F supplements (tablets, drops or lozenges) for children10 but their use has been criticized because of the risk of fluorosis and the topical rather than systemic mode of action of F. F releasing restorative materials, recommended for high caries risk patients and for root caries patients,9,11 have gained popularity in recent years.

Since the invention of alumino-glass silicate materials in 1972,12 a number of dental materials have been introduced, which are claimed by their manufacturers to have a significant capacity to release F in the oral cavity. However, these F releasing materials may vary in terms of the quantity of F released, and the
recharge and releasing pattern. This paper reviews the F releasing materials and the therapeutic effects of the released F.

**FLUORIDE RELEASING DENTAL MATERIALS**

In the current era, F release is considered to be a very important property of restorative dental materials and the F release property has been added to all the major groups of dental materials. However, there are clear variations in the F release and F uptake characteristics amongst these dental materials.

All the major groups of fluoride releasing dental materials and their quantitative ability to release F are shown in Figure 1.

![Figure 1. Fluoride releasing dental materials and their quantitative ability to release fluoride in oral cavity.](image)

F releasing restorative materials, acting as a F pool for oral tissues with the ability to replenish after release, can raise the F availability in saliva, plaque, and mineralized tissues. These materials have been classified into three categories depending on the amount of F released.

(i) **High fluoride releasing materials**: Includes glass ionomer cements (both conventional and resin modified glass ionomers).

(ii) **Intermediate fluoride releasing materials**: e.g., compomers, usually no burst release is present.

(iii) **Low fluoride releasing materials**: e.g., F releasing composites and F releasing amalgam.

Most current F releasing materials have the target of preventing recurrent caries, particularly in high risk caries patients. A brief description of F releasing restorative materials follows.

*Silicate cements*: Silicate cements (zinc silicate) were the first group of tooth colored filling materials that were popular due to their having better aesthetic properties than silver amalgam and the ability to release F in the oral cavity.
Silicates were reported to reduce the rate of caries to as low as 3% compared to the rate of 12% with amalgam restorations. An anti-caries effect was observed due to the F release and the development of a recurrent caries lesion was very rare. The major drawback with this group of materials was their high solubility in the oral cavity and a lack of chemical bonding with the tooth structure. These materials were used until the invention of glass ionomers and are now rarely used due to availability of more efficient materials.

**Glass ionomer cements:** A glass ionomer cement (GIC) is composed of two components: aluminofluorosilicate glass and polyalkenoic acids. The GIC materials set as a result of an acid-base reaction between the two components and the release of F and other ions occurs with acid attack on the glass particles. GICs have played an important role in restorative dentistry because of their unique properties, including direct chemical bonding to the natural tooth structures, F release, and F recharge, make them ideal material for a range of restorative procedures. The anticariogenic effects of F are delivered through a variety of mechanisms. The physical and thermal properties of these materials are similar to dentin. The major drawbacks of glass ionomers are their poor mechanical properties and the very long setting reaction, making them unsuitable for stress bearing applications in the oral cavity. These materials release a burst quantity of F initially followed by a decline in F release that remains consistent over a longer period. Glass ionomers are superior to all the other available restorative materials in F release and better, even in recharge, than the compomers and resin composites which exhibit a negligible amount of F recharge from external sources.

In order to improve the weak properties of the glass ionomers, a large number of modifications have been made to conventional glass ionomers, including resin modified, acid modified, and metal reinforced GICs, leading to the availability of a variety of modified GIC materials in the market (Figure 1). However, while almost all the modified types of GIC release F, their abilities to do this differ on a quantitative basis and in the release pattern.

**Resin-modified glass-ionomer cements:** The main purpose of modification in GICs is to improve the performance of these materials without compromising the F release characteristics. Resin or acid modification was targeted to control the sensitivity to moisture during the setting reaction and to improve the strength in the initial stages. Resin modified glass-ionomer cement (RMGIC) was synthesized by modifying polyacrylic acid by the addition of methacrylate and the components of a light activation system. Therefore, RMGICs exhibit a dual cure with an initial acid-base reaction followed by complete curing with light. RMGICs have the ability to release as much F as conventional GICs, but the formation of F complexes during the photochemical reaction may compromise the F release.

**Metal-reinforced glass ionomer cements:** Enamel is the hardest material in the oral cavity and stronger than the GIC. The main aim of metal reinforced GIC remains to improve the mechanical properties such as hardness, stiffness, and wear resistance. The metal reinforcement in glass ionomers may be done using two
approaches. Firstly, metallic particles, such as silver, may be physically incorporated in the glass particles. This modification of GIC improves the mechanical properties such as strength and toughness. Secondly, metal particles can be fused to the glass particles during sintering to create a cermet. Both types of metal reinforced systems release considerable amounts of F at first but the amount then drops off over time. However, less F is discharged from the cermets as a proportion of the glass particles is covered by metal thus reducing the surface area available for F release.\textsuperscript{3} With the silver admix type of metal modified cements, the material may not bind as well with the tooth surface, but the cement filler interface provides an additional surface area for F release. The physical and mechanical properties of these materials are better but the esthetic properties are poorer because of a change in color. The amount of cumulative F released from the various materials and cermets is shown in the Table\textsuperscript{3}.

<table>
<thead>
<tr>
<th>Type</th>
<th>14 Days (µg)</th>
<th>30 Days (µg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type II Glass ionomers</td>
<td>440</td>
<td>650</td>
</tr>
<tr>
<td>Type I Glass ionomers</td>
<td>470</td>
<td>700</td>
</tr>
<tr>
<td>Glass ionomer liners (conventional)</td>
<td>1000</td>
<td>1300</td>
</tr>
<tr>
<td>Glass ionomer liners (light cured)</td>
<td>1200</td>
<td>1600</td>
</tr>
<tr>
<td>Cermets</td>
<td>200</td>
<td>300</td>
</tr>
</tbody>
</table>

\textit{Giomers:} Giomers, a relatively new member of this group, were developed in an attempt to improve the physical, mechanical, esthetic, and biological properties of the existing glass ionomers. This is a hybrid material and the modification has been made in the filler component. The pre-reacted glass (PRG) fluoroaluminosilicate particles are added to poly acids forming a glass ionomer matrix construct followed by mixing with a resin matrix.\textsuperscript{24-27} The manufacturers of these materials have claimed they show better physical and mechanical properties, better biocompatibility, and more effective F release.\textsuperscript{24} Giomers can be classified between GICs and compomers as PRG technology. The fluoroaluminosilicate glasses are modified before their inclusion in a dimethacrylate resin matrix to allow release of F. However, a bonding system, similar to compomers, is required for the adhesion of giomers to enamel and dentin.\textsuperscript{28,29} Compared to conventional GICs and RMGICs, giomers produce a significantly better surface finish\textsuperscript{29,30} and have better mechanical properties.\textsuperscript{30} However, the F release with giomers is not any better than with GICs.\textsuperscript{13} On the basis of PRG technology there are two types of giomer materials;

\textit{(i) Fully reacted glass particles giomers (F-PRG):} Fluoridated glass particles are fully reacted using acid to form a broad glass ionomer hydrogel layer. An example of this type of giomer is Reactmer paste produced by ShofuInc, Kyoto Japan.\textsuperscript{21,27}
(ii) Surface reacted glass particles giomers (S-PRG): Fluoridated glass particles are surface reacted. An example of this type is Beautifil. Beautifil is used in combination with FL-Bond to get adhesion with the tooth enamel and dentine and is biocompatible and nontoxic to unexposed pulp.

This glass ionomer matrix, as present in Reactmer, contains complexes of F and is easily penetrated by water resulting in a considerably higher F release compared to compomers and resin composites. PRG technology results in an increased reactivity of the glass particles which form a wide glass ionomer hydrogel matrix layer which is responsible for the F release upon contact with water.

Polyacid-modified composites (Compomers): Polyacid-modified resin composites (compomers) are synthesized using the components of resin composites: bisphenolglycidyldimethacrylate (BISGMA) and GIC (ion leaching glass silicate fillers). Compomers initially set by photopolymerisation and this is followed by an acid-base reaction responding to water sorption. The polyacid modification is used to improve the aesthetic and mechanical properties in an attempt to merge the properties of GIC and resin composites in a single material.

In order to achieve clinically stable bonding, these materials need a bonding system using an acid etching technique. The abrasion resistance of compomers is better than that of glass ionomers. Most of the compomer materials show no initial burst release of F, but the level of F release remains relatively constant over a period of time. This is the major difference in the F release pattern between GIC or RMGIC and compomers. During the setting reaction of compomers, in the first phase, light activated polymerization takes place in the matrix which behaves like a composite. After curing and prior to the contact with water, F is bound to the filler particles that are surrounded by the polymerized matrix. Compomers release more F than composites but less than any GIC.

Resin composites: Resin composites have superior mechanical properties to the others with an improved resistance to wear but have no inherent adhesive properties and have a higher coefficient of thermal expansion. F release is the least in these materials. Because they lack the ability to adhere to the tooth structure, adhesion is gained micromechanically by using the acid etching technique. Resin composites may contain fluoro alum in fluoroaluminosilicate silicate glass in their composition but there is no reaction with acid during setting and no formation of a glass ionomer matrix layer which ultimately results in reduced F release. F release from composites predominantly occurs because of the dissolution of fluoridated salts and they are the least efficient F releasing materials.

Amalgam: Amalgam is a metallic compound which is used with mercury to restore the tooth. Amalgams showed excellent mechanical properties and are successful in stress bearing areas compared to other restorative materials. Amalgam has been investigated for a F release property using GIC lining and different media. A very small amount of F was released (0.02 ppm in 28 days) in de-ionized water and an even lower amount in artificial saliva.
SIGNIFICANCE OF FLUORIDE RELEASE FROM DENTAL MATERIALS

A beneficial therapeutic role of F in the prevention of caries and tooth decay has been reported in multiple studies.\(^8,21,36-41\) Rather than having a single mode of action, fluoride ions act in multiple ways to produce the therapeutic effects (Figure 2).

The main therapeutic effects and mechanisms of F release in the oral cavity are:

Effects on dental plaque: The most common oral diseases (dental caries and gingivitis) have a very strong association with dental plaque. Tooth brushing and dental floss are mechanical means of removing plaque and preventing these diseases. The F plays its role by chemical inhibition of pellicle and plaque formation on tooth surfaces by interference with ionic bonding and inhibition of microbial growth and metabolism.\(^9\) The fluoride ion also interfere the synthesis of intracellular enzymes (pyrophosphatase, acid phosphatase, and peroxidase) and inhibits ATPase which is required for bacterial colonization.\(^8\) A very low

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**Figure 2.** Summary of therapeutic effects of fluoride in the oral cavity.
concentration of F has been observed to produce these effects on plaque bacteria.42,43

Antimicrobial effects: The antimicrobial role of F is well documented in the scientific literature.8,36,39,44 Bacterial growth inhibition is directly related to fluoride ion release. The higher the release, the greater will be the effect.9 There are three key mechanisms for the antimicrobial activity; firstly, inhibition of bacterial metabolism and secondly, inhibition of bacterial growth and bacterial death. Lastly, F may also reduce the bacterial acid production and alter the surrounding environment effectively. However, the cariostatic characteristics of restorative materials are correlated with the concentration of released F.14 For example, a new restoration can release a sufficient amount of F to reduce the bacterial count in the plaque. In contrast, with an old restoration (one year or older), the F release is too low to affect the cariogenic bacteria, such as Lactobacilli and Streptococcus mutans, associated with the dental plaque.45

Effects on caries prevention: An optimal level of F (1 µg/mL) is required for caries inhibition and to attain remineralization potential in the oral cavity.46 To achieve the benefits, it is recommended to use material with a minimum long term F release rate of 2–3 µg/mL/day. The F release from any material declines with time. In order to maintain a consistent F supply for remineralization, the restorative material must be recharged with F from fluoridated toothpastes and mouth washes.9 An in vitro study by Torii et al.47 reported that the occurrence of secondary caries is inhibited around the F releasing restorations. There is a quantitative reduction in the cariogenic bacteria occupying the dentinal tubules in carious dentin with a consequent stopping or slowing down of the cariogenic process.48

Effects on dental hard tissues: The protection from F is provided to the tooth structure immediately adjacent to the F releasing restoration.49 F released from the restorative material has an effective zone of approximately 1 mm from the margin of the material.50 The F reduces the enamel solubility and enamel demineralization51 and, more importantly, enhances the remineralization of carious enamel.9 The hydroxyapatite crystals present in the dental hard tissue (enamel and dentin) can be transformed to fluorapatite crystals by replacing the OH- group with F-. The fluorapatite crystals are more resistant to acid attack than hydroxyapatite and this reduces the caries’ progression.9 In addition, F precipitates on the tooth surface in the form of calcium fluoride and this acts as a protective layer by releasing F in response to a drop in pH.36

The cariogenic process is a combination of the demineralization and remineralization phases.4 In vitro studies45,52 have reported that even a small amount of F (0.03–0.07 ppm) has the ability to transform the demineralization phase to the remineralization phase. However, F penetration may vary for different dental tissues, and a deeper penetration occurs in dentin and cement, compared to enamel, due to their having a more porous microstructure.53,54 The dentinal walls underneath F releasing GIC may contain up to 5,000–6,000 ppm F.53
MECHANISM OF FLUORIDE RELEASE

GIC are composed of F containing silicate glass particles and polyalkenoic acids that are set hard by an acid-base reaction of the powder particles and the liquid components. The attack by acid, produced by oral cariogenic bacteria, on the glass particles results in the leaching of different ions from the glass fillers including F. Glass ionomers release F in an aqueous medium in two stages. The first stage is of a F burst release, also called the short term reaction, which results from the rapid outer surface dissolution of the glass filler particles into solution. In the second stage, there is long term F release which is quite slow, but sustained, from inside the bulk of the cement. The initial release of a higher amount of F from the glass ionomers is probably due to the burst of F released as a result of the chemical reaction with the polyalkenoate acid. The maximum F release from GIC takes place during first four hours of the setting reaction.

FACTORS AFFECTING THE RELEASE OF FLUORIDE

The elution of F is a complex phenomenon which is still not fully understood. There are a number of factors influencing F release and the performance of dental restorative materials while in service. These factors may be related to the material’s chemistry (the setting reaction and the formation of a hydrogel layer), the content of F in the composition, and the environmental conditions (pH and temperature). In vitro, F discharge was related to the exposed surface area but not the weight. Similarly, radiant heat applied to GIC using a high-intensity fiber-optic quartz tungsten halogen light source, for various intensities and time intervals, had no effect on the F release. F release has been observed to be maximal in acidic and demineralizing regimes and to be lowest in a salivary medium which provides even better protection in cariogenic conditions. Various studies have shown that F release is affected by the different storage media, manipulative errors involving the powder to liquid ratio, the mixing, the curing time, and the amount of the exposed area.

RMGICs typically have the potential for releasing F in equivalent amounts to conventional glass ionomer cements but are affected by the F complex formation and its interface with polyacrylic acid and also by the kind and quantity of resin used for the photochemical polymerization. The amount of F release is also related to the thickness of the hydrogel layer formed on the glass particles during the setting reaction. The greater the thickness of the hydrogel matrix layer, the greater will be the F release. Poly acid modified materials (compomers) have strontium fluoridated glass particles with a very thin hydrogel layer formed on them resulting in a reduced F release with no burst release of F. Similarly, the thickness of the glass ionomer matrix layer also affects the recharge ability of material. For example, a thin layer results in a decreased F recharge ability and re-release. It has been claimed that gionmers produce a very thick layer of hydrogel on the glass filler particles which ultimately results in a greater F release. A wider hydrogel layer is formed in the gionmers than in the compomers. On the basis of a broader hydrogel layer, which may be considered as the major factor to control F recharge and re-release, it is expected that the gionmers will exhibit a more efficient
F recharging characteristic than the other resin matrix materials. These all factors are crucial when developing new materials or modifying existing materials. Understanding these parameters can help to improve the F release in new materials.

**FLUORIDE RECHARGE OF RESTORATIVE MATERIALS**

The F releasing dental materials not only release the F but also have the ability to take up F from a F rich environment. These materials are considered the F reservoir and once the F is depleted, it may be replenished by new fluorides from external sources like toothpastes, mouth washes, and topical F solutions. Topical F application can re-charge the glass ionomer restoration but the release after recharge is only short term and recharge must be accomplished daily to maintain an elevated level.

Compomers and composites can also recharge but their capabilities are less than with the resin modified and conventional glass ionomers whose recharge capabilities may be due to the porosities present in them. The pH of the topical application used for the recharge ability is also an important factor. Acidic F preparations may cause a degradation of the GIC materials and should be avoided. Although RMGICs are more resistant to surface attack they still get degraded when exposed to acids. The F release and recharge characteristics are based on the composition (fillers and F content), the setting reactions, and the biological situations around the restoratives. The ability to recharge the F of GICs is superior to that if the compomers and composites. It is clear that the GICs can release F and once placed in the oral cavity have a recharge ability to replenish their F for re-release. The F for recharging may come from the professional topical application of F varnish as well as from mouth washes, toothpastes, tea, and F-containing salts.

**CONCLUSIONS**

The available F releasing materials discharge sufficient F to produce therapeutic effects in the oral cavity. These materials have the potential to recharge their F content from F-containing mouth washes and toothpastes and can act for a long period as rechargeable reservoirs with a cycle of: recharge with F—release F—recharge with F. The F released from these dental restorative materials has a topical mode of action and systemic side effects are extremely rare.

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Therapeutic roles of fluoride released from restorative dental materials

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