

# Fluoride-Releasing Dental Restorative Materials: An Update\*

## SUMMARY

*The fluoride ion has a well-established beneficial role in dentistry in protecting the teeth from assault by caries. It is known to contribute to the dynamic mineralisation process of the natural tooth mineral, and also to become incorporated with the mineral phase, forming a thin layer of fluorapatite. This is more resistant to acid attack than the native hydroxyapatite, hence protects the tooth against further decay. Other recently discovered aspects of the role and uptake of fluoride will also be discussed.*

*One of the widely used dental restoratives, the glass-ionomer dental cement, is able to release fluoride in a sustained manner that may continue for many years, and this is seen as clinically beneficial. The closely related resin-modified glass-ionomer cement, and also the polyacid-modified composite resin ("compomer") are able to do the same. There are also fluoride-containing conventional composite resins able to release fluoride.*

*These various materials are reviewed and the way in which they release fluoride are described, as well as the effectiveness of the release at the levels involved. Studies of effectiveness of fluoride release from these various classes of material are reviewed, and shown to suggest that release from conventional and resin-modified glass-ionomers is more beneficial than from composite resins. This is attributed to 2 causes: firstly, that it is not possible to replace the lost fluoride in composites, unlike glass-ionomers, and secondly because the other ions released from glass-ionomers (calcium, phosphate) are able to contribute to local remineralisation of the tooth. The absence of these other ions in fluoridated composites means that remineralisation is able to occur to a lesser extent, if at all.*

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## The Role of Fluoride against Dental Caries

Fluoride has been known to have a role in the prevention of dental caries since early observations in the 1930s linked fluorosis in patients with low levels of tooth decay<sup>1</sup>. Over the years, this subject has been studied intensively and it is now known that fluoride acts topically rather than systemically<sup>2</sup>. It has also been established that long term exposure of the teeth to fluoride is the most effective way to exploit this topical effect and to minimise dental caries<sup>3</sup>.

Dental caries arises from 3 interacting factors, namely (i) the presence of fermentable sugars in the mouth, (ii) the occurrence of bacteria in dental plaque, and (iii) the presence of teeth, in particular their mineral phase<sup>4</sup>. Bacteria in the plaque metabolise the sugars, producing a cocktail of weak organic acids, of which by far the most abundant is lactic acid<sup>5</sup>. These acids attack the mineral component of the tooth, hydroxyapatite, leading to loss of structure. As decay develops, so the relative amount of mineral phase is reduced, leaving behind only collagen, which discolours and takes on a leathery texture<sup>4</sup>.

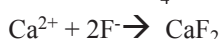
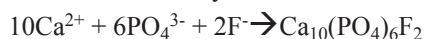
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Dental caries can be viewed as a disturbance to the demineralisation-remineralisation balance in the hydroxyapatite phase of the tooth<sup>2</sup>. A healthy tooth surface is maintained by a balance between dissolution of hydroxyapatite into saliva (demineralisation) and precipitation of hydroxyapatite from the saliva onto the tooth surface (remineralisation). Under healthy conditions, these 2 chemical processes occur at the same rate, and the net effect is that the mineral phase of the tooth is maintained in a functioning and fully intact form.

The presence of lactic acid at the tooth surface alters this balance, enhancing the rate of demineralisation relative to that of remineralisation<sup>2</sup>. Consequently hydroxyapatite is lost from the mineral phase and the tooth decays.

Fluoride's principal role in inhibiting decay is now considered to be its effect on the remineralisation process<sup>6,7</sup>. Specifically, it promotes this process, thereby re-establishing the mineral phase of the affected tooth<sup>2,6-9</sup>. Remineralisation involves inducing hydroxyapatite crystals to grow by precipitation of  $\text{Ca}^{2+}$  and  $\text{PO}_4^{3-}$  ions from saliva onto the surface of the mineral phase<sup>10</sup>. The mechanism is complex, involving dynamic activity mainly between the tooth and the saliva. Fluoride ions appear to influence this process by 2 possible mechanisms, namely substitution of hydroxyl ions into hydroxyapatite and formation of calcium fluoride<sup>11</sup>. Both take place in solution close to the tooth surface, but lead to the formation of substances of low solubility, which consequently precipitate onto the tooth surface.

The 2 reactions may be summarised as:



Reaction (ii) generates a slight excess of hydroxyl groups in solution, which would otherwise have precipitated as hydroxyapatite, and which are alkaline. However, they are readily buffered *in vivo*. They may also be useful in neutralizing the organic acids produced by the oral bacteria. Reaction (ii) precipitates an insoluble species that can act as a nucleation site for hydroxyapatite growth and thus promote remineralisation of the biomineral.

The initial precipitate appears to be amorphous, but seems to generate crystals at a reasonable rate and this contributes to remineralisation. The new mineral phase includes some fluoride, mainly as a thin surface layer. Molecular dynamics calculations have shown that these layers are no more than 3 atom layers thick<sup>9</sup>. The new precipitated phase is less soluble than the fluoride-free hydroxyapatite, but this difference in solubility is no longer considered to be the principal mechanism by which fluoride inhibits caries<sup>12</sup>.

Uptake of fluoride by hydroxyapatite has been shown to follow 2 different kinetic models, depending on concentration. At very low concentrations, of the order

of  $3 \times 10^{-5}$  mg/L (30 ppb), under both static and stirred conditions, it was found to follow pseudo-first-order kinetics<sup>13</sup>, i.e.

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t$$

where  $q_e$  is the equilibrium uptake (in concentration units),  $q_t$  is the uptake at time  $t$ , and  $k_1$  is the first-order rate constant.

At higher concentrations of fluoride ion, i.e. in the range 100-1000 ppm and static conditions, uptake has been shown to follow pseudo-second-order kinetics<sup>14</sup>. This means it follows the equation:

$$t/(q_t) = 1/[k_2(q_e)^2] + t/(q_e)$$

where  $k_2$  is the second order rate constant.

It is not straightforward to relate kinetics of adsorption to the mechanism, but in this case, it does seem that the pseudo-second-order process relates to a change in mechanism, in this case the deposition of  $\text{CaF}_2$ . Because of the low but finite solubility of  $\text{CaF}_2$ , under low concentration conditions, i.e. in the ppb range, any calcium fluoride remains soluble, its solubility in water being  $1.6 \times 10^{-5}$  g/cm<sup>3</sup> at 20°C<sup>15</sup>. Hence at low concentrations of fluoride ion, little or no  $\text{CaF}_2$  precipitates out of solution. This would favour the  $\text{F}^-/\text{OH}^-$  exchange mechanism of remineralisation at the hydroxyapatite surface. Under higher concentration conditions, by contrast,  $\text{CaF}_2$  is insoluble and is precipitated so that the alternative remineralisation process is able to occur as well. This is consistent with the change in kinetics at higher concentrations<sup>14</sup>.

## Modern Restorative Materials

Modern dental restoratives are based on either composite resin or glass-ionomer systems<sup>16</sup>, each with their own subsets of material<sup>17</sup>. Briefly, they are classified as follows:

(i) *Composite resins*. These are based on large organic monomers, mainly bisphenol glycidyl methacrylate (bis-GMA) or urethane di-methacrylate, plus other lower viscosity monomers, such as tri-ethylene glycol di-methacrylate (TEGDMA). They are filled with inert particulate filler of varying particle size, which are bonded to the organic matrix by silane coupling agents. Modern composite materials are typically single paste systems that polymerize by photo-initiation.

The resulting material has excellent aesthetics, but does not bond to the tooth surface. Instead, it needs bespoke bonding agents<sup>18</sup>, the subject of which is beyond the scope of the present article. Composite resins are not inherently fluoride-releasing, but can be made so by adding fluoride compounds<sup>19</sup>.

(ii) *Polyacid-modified composite resins*. These materials were developed in an attempt to make a composite resin

with the fluoride-releasing capability of conventional glass-ionomer cements<sup>17</sup>. They are composed of the same type of components as conventional composite resins, i.e. large monomer molecules, diluents, and particulate inorganic fillers. In addition, they contain acid-functional monomers and small amount of reactive alumina-silicate glass as filler<sup>20</sup>. The primary setting reaction is polymerization, brought about by the photo-sensitive initiators on application of light of the appropriate wavelength from a dental curing lamp. Following this, in the mouth, they are able to draw in small amounts of water, and this triggers the acid-base reaction, and makes the fluoride originally present in the glass filler available for transport to the outside of the restoration<sup>20</sup>. There is also some diminution in mechanical properties of these materials on exposure to moisture<sup>21</sup>, indicating that the acid-base reaction does not contribute to strength. The fluoride-releasing nature of these restoratives means that they have become widely used in children's dentistry<sup>20</sup>.

(iii) *Glass-ionomer cements.* Conventional glass-ionomers are based on a calcium (or strontium) fluoroaluminosilicate glass powder, which is reacted with a polyalkenoic acid, typically poly(acrylic acid) to make a cement<sup>16,17</sup>. This material sets rapidly to form a porcelain-like substance that adheres to the tooth structure, and can release fluoride, as well as other ions (calcium or strontium, sodium, silicate and phosphate)<sup>22</sup>. The physical properties and appearance of the set cement are considered acceptable for most clinical applications, though the overall aesthetics is less good than the composite resins.

The ability of these materials to release ions is important as this process is involved in the development of long-term durable bonds with the tooth. Studies have shown that ions can move from the cement and from the tooth into the interfacial region to create an ion-exchange layer that proves highly durable in clinical service<sup>23,24</sup>.

Mechanical properties of set cements are acceptable for many clinical applications, as shown by the range of conditions treated using the ART technique<sup>25</sup>. This technique, involving removal of caries by hand-held scoops only, and no dental drill, is only possible with glass-ionomers, as it requires a material capable of forming natural adhesive bonds to the tooth. Despite these successes, many authorities are cautious about the wide use of glass-ionomers in restorative dentistry<sup>26</sup>, and these materials are often used mainly in children's dentistry<sup>27</sup>, where their ability to release fluoride is considered particularly advantageous.

(iv) *Resin-modified glass-ionomers.* Resin-modified are similar to conventional glass-ionomers in that they contain a basic ion-leachable glass powder, and also a water-soluble polymeric acid<sup>28</sup>. However, they also contain the water-soluble organic monomer 2-hydroxyethyl methacrylate, HEMA. An initiator system is also required,

in order to bring about addition polymerization of the HEMA, and this is typically a photo-initiator sensitive to blue light at 470 nm<sup>28-30</sup>.

Certain brands of resin-modified glass-ionomer contain modified polymers which are based on poly(acrylic acid) but contain a minority of branches that are terminated in vinyl groups. These undergo co-polymerization with the HEMA when irradiated with blue light, so that the set material contains organic cross-links when cured, in addition to the ionic cross-links formed by the acid-base reaction<sup>30</sup>. Like conventional glass-ionomers, resin-modified glass-ionomers are able to form strong adhesive bonds to both enamel and dentine<sup>29</sup>. They also release fluoride.

Resin-modified glass-ionomers were originally designed for use as liners and bases in dentistry though they have since been formulated for use as complete restoratives<sup>30</sup>. In addition, they can be used for core build-up and for luting, though in the latter application, they are not photocured but are prepared with a 2-part initiator that forms free radicals when the components are mixed. This means that they are able to set in the dark. They are widely used, particularly in paediatric dentistry as alternatives to amalgam<sup>27</sup>.

It has been suggested that the presence of HEMA in these materials compromises their biocompatibility<sup>31</sup>. Studies have shown that HEMA is released from resin-modified glass-ionomers, especially in the first 24 hours<sup>32</sup>, and it is able to diffuse through the dentine and affect the pulp, where it has been found to be cytotoxic<sup>33</sup>. There is also the possibility of systemic effects, including contact dermatitis<sup>34</sup> and sensitisation<sup>35</sup> on dental personnel. Safety precautions have been recommended when using these materials<sup>31</sup>, mainly ensuring good ventilation of the work place and avoiding the intake of HEMA vapour from the uncured resin-modified glass-ionomer material.

(v) *Giomers and glass carbomers.* 2 other tooth-coloured materials are available in modern clinical dentistry that are claimed to be innovative, namely the giomers and the glass carbomers. In fact, these are each types of established material, as already described.

Giomers are a type of flowable composite resin, but contain as at least part of their filler, pre-reacted ionomer glass treated with poly(acrylic acid)<sup>36</sup>. As such, they are moderately fluoride-releasing<sup>37</sup>, due to the pre-reaction at the glass surface of the filler particles, but in all important particulars they are composite resins. Their fluoride release has been associated with their anti-bacterial characteristics<sup>38</sup>.

The other type of modern material, the glass carbomer, is a type of complex glass-ionomer cement<sup>39</sup>. It is based in glass-ionomer cement chemistry, but has been modified in order for the set cement to promote mineralisation within the tooth<sup>40</sup>. The glass carbomer contains nano-scale particles of powder and also

hydroxyapatite and fluorapatite as secondary fillers. The reactive glass powder is modified with dialkyl siloxanes, and the liquid is aqueous poly(acrylic acid). The manufacturers recommend treating the newly placed material with a high-energy dental curing lamp, though the material does not set by photo-polymerization. Rather, the lamps exert a heating effect<sup>40</sup>.

Glass carbomers are designed for use as either restorative materials or as fissure sealants, and as part of their function when placed, they promote mineralisation. This partly arises from the presence of calcium fluorapatite nanocrystals, which act as nucleating agents, and partly from the presence of hydroxyapatite, which is a source of mineralising ions. The setting of glass carbomers has been shown to resemble that of glass-ionomers closely, especially in the behaviour of aluminium. This element is present in the glass powder in 4-co-ordination, but changes to 6-co-ordination in the matrix of the set material<sup>39</sup>.

## Fluoride Release Patterns

In terms of fluoride release, glass-ionomers have been studied the most, and are inherently fluoride-releasing, as a result of the composition of the glass component. For this reason, their release will be considered first in this section, followed by the various types of composite resins.

(i) *Fluoride release from glass-ionomers.* Fluoride release is considered one of the important clinical advantages of glass-ionomers of both types (conventional and resin-modified)<sup>38</sup>. This release has been shown, for conventional glass-ionomers, to last for at least 5 years<sup>39</sup>. Release occurs by 2 mechanisms, a relatively rapid dissolution process from the surface layers and a slower process that relies on diffusion of the fluoride ions through the bulk cement<sup>38,41</sup>. Having diffused through the cement, these ions are released into the surrounding aqueous solutions. The latter process is identified from kinetics based on the square root of time,  $t^{1/2}$ .

The overall process of fluoride release has been shown for both conventional and resin-modified glass-ionomers to follow the equation<sup>43</sup>:

$$[F]_c = [F]_t/(t + t_{1/2}) + \beta t^{1/2}$$

The first term is the early dissolution process, sometimes called "early washout", though it continues for some time, possibly up to 4 weeks following exposure of the glass-ionomer cements to the aqueous medium<sup>43</sup>. The second term, in  $t^{1/2}$ , is the one describing the diffusion part of the process. The term  $[F]_c$  is the cumulative fluoride release at time  $t$ , the term  $[F]_t$  is the total amount of fluoride available for release,  $t_{1/2}$  is the time to release half of this total amount and  $\beta$  is a constant. The experimental

results show an excellent fit with this equation, with a correlation coefficient of 0.9987 for Ketac Fil (ESPE, Seefeld, Germany)<sup>43</sup>.

Amounts of fluoride released are relatively low, even in the early stages of release. They have often been quoted relative to the surface area of the cement specimens, i.e. as  $\mu\text{g}/\text{mm}^2$ <sup>26</sup>, which is not helpful in determining likely local concentrations *in vivo*. Another complicating factor is that *in vitro* studies have typically been carried out into deionised water<sup>43</sup> or even tap water<sup>42</sup>, and fluoride release is suppressed in both artificial saliva<sup>44</sup> and real saliva<sup>45</sup>.

Of the studies that have quoted fluoride concentrations, Creanor et al<sup>46</sup> found a fall from 15-155 ppm at 24 hours to 0.9-4 ppm at day 60. In another study, Perrin et al<sup>47</sup> showed that after 1 year, the steady state fluoride release was in the range 0.5-7 ppm. The high early value has been confirmed in several other studies<sup>48-51</sup>.

Fluoride release from conventional glass-ionomers has been demonstrated *in vivo*<sup>45</sup>. Immediately after placement of between 1 and 6 restorations the fluoride concentration in unstimulated saliva was found to rise from a baseline of around 0.04 ppm to between 0.8 and 1.2 ppm. After 1 year, the level was found to be 0.3 ppm, almost 10 times greater than the baseline values, thus demonstrating that sustained release of fluoride also occurs *in vivo*<sup>51</sup>.

Conventional glass-ionomers not only release fluoride, they are also capable of taking it up under appropriate conditions. This phenomenon has been called "fluoride re-charge"<sup>41</sup> and was first suggested by Walls in a review of conventional glass-ionomer cements for clinical dentistry<sup>54</sup>. Since this time, there have been numerous studies to demonstrate the effect experimentally.

For example, Preston et al studied re-fluoridation by exposing glass-ionomers to a 500 ppm fluoride solution 13 times over a 2-year period, and showed that on each occasion fluoride release increased following re-charge<sup>55</sup>. Similarly Goa et al<sup>56</sup> demonstrated that conventional glass-ionomers designed for use in the ART technique released increased amounts of fluoride following exposure to a re-charge fluoride solution. Increased fluoride release following exposure to fluoride solutions has been confirmed in numerous other studies<sup>57-61</sup>. It has also been shown for glass-ionomers following exposure to fluoridated toothpastes<sup>62</sup> and fluoride gels<sup>63</sup>.

These studies have typically measured fluoride uptake indirectly. Fluoride uptake has been assumed to occur when the glass-ionomer specimens were exposed to the fluoride solutions because of the enhanced release when they were moved into pure water. 2 studies that have measured fluoride uptake directly have given extra insights into the process. Both studies used similar approaches, measuring reduction in fluoride concentration in recharge solutions in the presence of specimens of hardened glass-ionomer cement.



The first of these studies showed that potassium fluoride solutions corresponding to 100 and 1000 ppm fluoride ion uptake by immature cements followed pseudo-first order kinetics<sup>64</sup>, i.e.

$$\ln(q_e - q_t) = \ln(q_e) + k_1 t,$$

where  $q_e$  is the equilibrium uptake,  $q_t$  is the uptake at time  $t$ , and  $k_1$  is the first order rate constant. The cements employed had been cured at 37°C for only 10 minutes prior to exposure to fluoride solution, and most of the uptake was complete with a few hours<sup>64</sup>. Subsequent exposure of the specimens to water showed that they released very little of the fluoride taken up in their first 24 hours in water.

The second study examined the effect of maturation on fluoride uptake<sup>65</sup> (Tab. 1). 4 commercial restorative grade glass-ionomers were used and the fluoride concentrations of solutions containing a small specimen were determined after 24 hours. The storage solution was nominally 1000 ppm in fluoride, but measurement showed it actually to be  $978.0 \pm 5.7$  ppm. Specimens of cement that had been matured for 1 month prior to exposure to this fluoride solution made little or no difference to this concentration, as shown in the table. This contrasted substantially with the results for specimens cured for 24 hours, leading to the conclusion that, as maturation proceeds, glass-ionomers lose their capacity to take up fluoride, at least from neutral solutions. This in turn suggests that glass-ionomers are less effective at undergoing fluoride recharge than has been widely assumed, and that in clinical conditions there is no effective recharge at all for the majority of glass-ionomer restoration's service life.

Table 1. Fluoride concentration of storage solutions after 24 hours (ppm) (Standard deviations in parentheses)<sup>65</sup>

Material	Cure time	Fluoride concentration at 24 hr/ppm	Equivalent uptake/ppm
None	-	978.0 (5.7)	0.0
Fuji IX Extra	24 hr	880.0 (17.6)	98.0
	1 month	965.2 (4.7)	12.8
Fuji IX Fast	24 hr	902.4 (4.5)	77.6
	1 month	983.6 (2.3)	-5.6
Ketac Molar Quick	24 hr	892.4 (7.8)	87.6
	1 month	982.2 (5.1)	-4.2
Chemflex	24 hr	911.1 (3.1)	66.9
	1 month	965.4 (8.8)	12.6

Studies have shown that Na, Al, P and Si are also released in neutral conditions<sup>22</sup>, either as free positively charged ions ( $\text{Na}^+$ ,  $\text{Al}^{3+}$ ) or as negatively charged oxy-ions

(e.g.  $\text{PO}_4^{3-}$ ,  $\text{SiO}_3^{2-}$ ). Under acidic conditions, calcium (as  $\text{Ca}^{2+}$  ions) is also released<sup>22</sup>. All ions, including fluoride, are released in greater quantities in acid than in neutral conditions, and this is associated with increased rates of overall degradation of the glass-ionomer as indicated by increases in roughness and decreases in hardness on storage in acid<sup>66</sup>. Resin-modified glass-ionomer cements have also been shown to release increased levels of fluoride and other ions under acidic conditions<sup>67,68</sup>.

As active caries typically has a pH of about 4.9<sup>69</sup>, the ability to release increased amounts of fluoride may be advantageous<sup>67</sup>. Greater amounts of fluoride have been suggested to have an increased preventative effect *in vivo* for these materials. However, under acidic conditions, there is greater likelihood of the fluoride being complexed and not available as free  $\text{F}^-$  ions. The reduced pH, with extra  $\text{H}^+$  ions available, may lead to the formation of un-dissociated HF, and the increased release of  $\text{Al}^{3+}$  leads to the possibility of the occurrence of such complexed species as  $\text{AlF}^{2+}$ ,  $\text{AlF}_2^{+70}$  or even  $\text{AlF}_4^{-71}$ . Experimental results with a fluoride ion selective electrode have suggested that under acidic conditions almost all of the fluoride is complexed in some way<sup>22</sup>.

A study to examine the effect of such complexation confirmed the absence of free fluoride in acid extracts from glass-ionomer cements, despite the overall higher levels of fluoride released compared with neutral conditions<sup>72</sup>. Exposure of these solutions to synthetic hydroxyapatite powders showed rapid depletion in fluorine levels, demonstrating that the mineral is capable of taking up fluoride readily, whatever state (free or complexed) it is in solution<sup>72</sup>. It was also found that, despite the increased levels of aluminium released into acidic solutions, there was no significant amount of aluminium deposited onto the hydroxyapatite surface. This, in turn, suggests that the aluminium does not become involved in the remineralisation process<sup>72</sup>. Overall, this study confirmed the suggestion of Forss<sup>67</sup> that increased fluoride release under acidic conditions is probably of clinical benefit.

(ii) *Fluoride release from composite resin materials.* Composite resins are not inherently capable of releasing fluoride, but may become so if appropriate fluoride-containing compounds are added to them. These include inorganic salts (e.g.  $\text{NaF}$  or  $\text{SrF}_2$ ), fluoridated glasses or organic fluoride compounds. Longer-term sustained release requires only sparingly soluble fluoride salts, such as  $\text{SrF}_2$  or  $\text{YbF}_3$ , or leachable glass fillers<sup>43</sup>. Fluoride release from these substances requires water to diffuse into the composite resin, a process that is slow, due to the hydrophobic nature of the resin polymer system<sup>73</sup>. It is, however, accelerated by the presence of hydrophilic or ionic additives<sup>74</sup> so that it occurs at a sufficient rate to promote the release of fluoride from the restoration.

The amount of fluoride released by composites tends to be much lower than that released by glass-ionomer cements of either type. It is also lower than that released by polyacid-modified composite resins. This may be because the simple water uptake/dissolution process is less effective at providing fluoride than the mechanisms in glass-ionomers or compomers; or it may reflect lower fluoride loadings in the composite formulation<sup>55,75,76</sup>.

Fluoride release tends to show no "early burst" from composite resins, and also there appears to be little capacity for fluoride recharge in most systems, though recharge has been demonstrated for an experimental composite system<sup>77</sup>. On the other hand, fluoride has been shown to be released over long periods of time, at least a year having been reported in a number of studies<sup>78,79</sup>.

Kinetics of fluoride release from composite resins are less clear than those of glass-ionomers<sup>59</sup>. Systems have shown a variety of types of behaviour, including fluoride release directly proportional to time and approximately proportional to the logarithm of time or to the inverse square root of time,  $t^{-1/2}$ <sup>79,80</sup>.

Like fluoridated composite resins, polyacid-modified composite resins shown no initial burst of fluoride<sup>52,81,82</sup>, but deliver a sustained release that continues for considerable periods of time<sup>45,52</sup>. Fluoride release has been shown<sup>59</sup> to follow the kinetic equation:

$$[F]_c = [F]_i t / (t + t_{1/2}) + \alpha t$$

Values of the constant,  $\alpha$ , vary with the material and can be considered as a measure of the driving force for the release process<sup>26,83</sup>.

Levels of fluoride release from polyacid-modified composite resins vary with brand, and can be comparable with those of conventional glass-ionomer cements in certain cases<sup>26</sup>. There is, though, a fundamental difference in fluoride release between these 2 materials as polyacid-modified composite resins have to take up moisture to promote the secondary setting reaction before fluoride can be released from the filler<sup>20</sup>, and is able to move out of the material. In some brands of polyacid-modified composite resin, fluoride levels are augmented with added fluoride salts, such as  $\text{YbF}_3$ , but even in these materials there has to be diffusion of water into the material to dissolve out the fluoride salt, and this process takes a finite time. These delayed processes mean that polyacid-modified composites may release very little fluoride when newly placed<sup>83</sup>, even if they are eventually capable of releasing amounts of fluoride that match those of conventional glass-ionomers in the long term (up to 3 years)<sup>81,83</sup>.

The final group of composites, the giomers, have also been studied for their fluoride release behaviour. It has been confirmed that they can release fluoride for extended periods of time<sup>52,84</sup>, though, like other types of composite, there is no early burst of release. Amounts of fluoride released are lower than for other composites, and this may be a reflection of the relatively small amount of available fluoride within these materials. Studies suggest

that neither polyacid-modified composites nor giomers are capable of any significant fluoride recharge<sup>85</sup>.

## Clinical Effects of Fluoride Release

Fluoride is provided to individuals mainly from fluoridated oral health care products, including toothpastes, and drinking water. Fluoridated toothpastes contain high amounts of fluoride, generally at least 1000 ppm but possibly up to 5000 ppm<sup>86</sup>, though this level is diluted on application, and clears from the mouth after about an hour<sup>87</sup>. Drinking water typically provides fluoride at concentrations of around 0.7 - 1.0 ppm<sup>88</sup>, and this also clears fairly quickly after consumption. However, regular exposure to these fluoridated substances may result in long-term changes in the baseline fluoride concentration in saliva<sup>89</sup>, with increases from around 0.02 ppm to between 0.10 and 0.20 ppm having been measured in some subjects<sup>90</sup>. As we have already seen, fluoride levels attributable to release from glass-ionomer cement rose following placement of restorations, but only to 0.8-1.2 ppm immediately, to 0.3-0.5 ppm after 6 weeks<sup>47</sup> and 0.3 ppm after 1 year<sup>53</sup>.

Restorative materials therefore contribute only small additional amounts of fluoride, compared with toothpastes and drinking water. Against that, it is sustained, and of the same order as the shift in concentration due to sustained use of fluoridated oral care products. It also occurs close to the tooth surface, which increases its chances of having positive effects.

In principle, fluoride may have antibacterial properties and there is certainly evidence that, even at low concentrations, sufficient is released from restorative materials to reduce bacterial growth and interfere with bacterial metabolism<sup>91,92</sup>. However, this has not always been found, and results seem to be sensitive to precise details of the experiments and the release conditions<sup>93,94</sup>. In general, it seems that the level of fluoride release, even from conventional glass-ionomers, is too low to have a consistent effect on the dental plaque, leading to the conclusion that such effects are minor compared with the effect of fluoride on the mineral phase of the tooth<sup>26</sup>.

Studies of precipitation of fluoride suggest it forms a calcium fluoride-like layer on the surface of the mineral phase of the tooth<sup>95</sup>. This layer facilitates the precipitation of mineral phase, fluorapatite or fluoro-hydroxyapatite, thus promoting remineralisation and preventing further loss of mineral phase<sup>96</sup>. The literature is unclear what this calcium fluoride-like precipitate is, but the solubility of calcium fluoride as estimated from its solubility product ( $3.9 \times 10^{-11} \text{ mol}^2 \text{ dm}^{-6}$  at  $20^\circ\text{C}$ <sup>15</sup>) suggests that this it is not  $\text{CaF}_2$ , because this substance would not precipitate until the fluoride concentration exceeded 8.0 ppm. The substance may be a mixed hydroxide-fluoride

salt,  $\text{CaF}(\text{OH})$ , but whatever it is, it has the effect of substantially increasing the fluoride concentration within the tooth mineral. *In vivo* studies have shown that, as a depth of 10  $\mu\text{m}$  with enamel surfaces exposed to fluoride, the interior concentration of fluoride rises to of the order of 300-600 ppm<sup>97</sup>. *In vivo* studies of fluoride uptake from glass-ionomers have shown significant increases in fluoride levels in both primary and permanent enamel<sup>91,98</sup>. Greater amounts of fluoride have been shown to be taken up by dentine and cementum<sup>99-101</sup>, this difference being attributed to the greater porosity and different microstructures of these latter tissues<sup>26</sup>.

An important consideration in the potential anti-caries effects of fluoride release by restorative materials is the occurrence of gaps between the filling material and the cavity wall<sup>102</sup>. These gaps are typically filled with fluid through which fluoride can be transported and interact with the mineral phase of the cavity wall. Other ions can also dissolve in these gap fluids<sup>103</sup> eventually leading to the growth of crystalline substances<sup>104</sup>. Concentrations in these gap fluids may be relatively high, i.e. in the range 5 to 80 ppm, and this would certainly be enough for substantial remineralisation to be promoted and further caries to be prevented<sup>79,103</sup>.

Whatever the precise mechanism, fluoride-releasing materials appear to have some capacity to reduce the damage inflicted by caries progression. For example, glass-ionomers showed reduced lesion dimensions *in vivo* in a study using premolars extracted for orthodontic reasons<sup>105</sup>, and experimental fluoridated composites were shown to reduce the extent of enamel demineralisation compared with a non-fluoridated composite control<sup>103</sup>. However, there have been only a few clinical studies on the effectiveness of fluoridated restoratives against caries and what data that have been obtained are somewhat contradictory. Consequently there remains doubt as to whether these materials release sufficient fluoride to prevent or inhibit caries *in vivo*, and there is a need for properly conducted clinical studies to examine this question. Given what is known about release levels and the effect of small, sustained increases in fluoride concentration in saliva, it would be surprising if these materials did not have beneficial effects. For the moment, though, supporting evidence is not available and work needs to be done to address this question.

## Conclusions

This article has reviewed that range of modern restorative materials available to the clinician. They range from those materials that release relatively high levels of fluoride, at least initially, i.e. conventional glass-ionomers and resin-modified glass-ionomers, to those that release only low levels of fluoride, namely the fluoridated

composite resins. They include the relatively new proprietary materials giomers and glass carbomers, which are shown to be specialised types of composite resin and glass-ionomer respectively.

The interaction of fluoride with the tooth mineral (hydroxyapatite) is reviewed. Findings are presented to demonstrate that low levels of fluoride are able to promote remineralisation *via* precipitation of fluorapatite or a calcium fluoride-like substance, both of which lead to increased crystallisation and incorporation of fluoride into the mineral phase.

Despite these known remineralisation mechanisms, the current literature remains unclear as to whether fluoride-releasing restoratives are clinically beneficial. The physico-chemical studies discussed suggest that it is likely that they are, but so far clinical studies have not confirmed this point. Rather, they have come to conflicting conclusions about the effectiveness of these materials. Further clinical studies are needed to answer this question unambiguously, as it is important clinically, especially for groups such as children and special care patient groups with poor oral hygiene.

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