

Decay-Inhibiting Restorative Materials: Past and Present

CE 2

Abstract: Clear differences exist in the fluoride release characteristics and setting reactions of glass-ionomer cements and compomers. Differences in decay inhibition associated with specific materials are less clear. Furthermore, resin added to glass ionomer cement formulations and acids added to composite resins make it difficult to distinguish composite resins from compomers and glass ionomer cements, all of which have reported fluoride release. Optimal fluoride release from a dental restorative depends on several conditions, including oral flora, saliva, diet, mineral content of the dental tissues, and marginal seal of the restoration. Presently, *in vitro* and *in vivo* studies suggest that materials which behave similarly to silicate cements in their setting reactions and hydration characteristics will behave as decay-inhibiting restoratives. Until optimal fluoride release from dental restoratives can be quantified, dental clinicians are encouraged to consider clinical outcomes as the best test for decay inhibition. Nearly a century of clinical findings support the anticariogenicity of silicate cements. This article reviews fluoride release and anticariogenicity of restorative materials using silicate cement as a model with a well-defined mechanism for preventing secondary caries. The behavior of newer materials is compared to silicate cement for predicting decay inhibition.

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Learning Objectives:

After reading this article, the reader should be able to:

- explain how composition, setting reaction, and water content affect fluoride release from dental restoratives.
- distinguish between glass ionomer cements, resin-modified glass ionomer cements, compomers, and composite restorative material classifications.
- predict the decay-inhibiting potential of new restorative materials based on historical perspectives.
- use a more complete spectrum of restorative materials targeted toward patient needs in the area of caries control.

Throughout the first half of the 20th century, silicate cement was the most widely used esthetic restorative material.¹ Although the use of silicate cement has been all but discontinued in modern dental practice, this material warrants discussion because its anticariogenic properties have been clinically observed and its mechanism well defined.² This article reviews the composition, setting chemistry, and clinical behavior of silicate cements, drawing comparisons to modern esthetic materials and helping dentists understand categorical material differences based on setting chemistry.

Many of today's "fluoride releasing" materials are in part comprised of silicate cement components, but only a few have clinically demonstrated anticariogenic properties.^{1,3-8} The historical perspectives reflected here might identify characteristics that would be useful in predicting caries-related clinical outcomes.

Although the composition, chemistry, and anticariogenic properties of silicate cements are well described in the dental literature, confusion exists regarding mixtures containing components of silicate cement but lacking a cement-setting reaction. For clarity, this review will first define cements and other mixtures according to their setting chemistry using terminology recommended by McLean, Nicholson, and Wilson in 1994.⁹

Product Definitions Based on Setting Chemistry

Silicate cement consists of a basic glass and phosphoric acid solution. Setting of silicate cements is the result of an acid-base reaction between the components.

Glass ionomer cement consists of aluminosilicate glass used in silicate cements and an acidic polymer which sets by an acid-base reaction between the components.

Resin-modified glass ionomer cement (systematic name, resin-modified glass polyalkenoate) is a material that sets partly by an acid-base reaction and partly by light- or chemically activated polymerization such that the acid-base setting reaction creates a hard solid within a clinically acceptable time (ie, a few minutes).

Figure 1A—
Pretreatment view of
root caries; teeth
Nos. 12 and 13.



Figure 1B—
Posttreatment view
of glass ionomer
cement buildups, GC
Fuji IX™ GP.



Although the use of silicate cement has been all but discontinued in modern dental practice, this material warrants discussion because its anticariogenic properties have been clinically observed and its mechanism well defined.

Polyacid-modified composite resin is a mixture of acid-decomposable glass, possibly with some polymeric acid, but with insufficient amounts to promote an acid-base reaction in the dark.

Review of Chemistry and Setting Reactions

Silicate cement powder is a ceramic prepared by the fusion of silica (SiO_2) and alumina (Al_2O_3) in the presence of a fluoride flux with perhaps various calcium compounds.^{2,8} Around 1900, it was discovered that the addi-

tion of fluoride flux resulted in fusing an “esthetic” aluminosilicate glass with improved translucency. After approximately 30 years of clinical use, the remarkably infrequent occurrence of contact caries adjacent to “esthetic” silicate cement restorations was reported by Volker et al.⁹ Work by Phillips and Swartz attributed caries-resistant enamel to the incorporation of fluoride, and in 1967, a retrospective study of silicate restorations confirmed their anticariogenicity.^{10,11}

Aluminosilicate glasses are alkaline and when exposed to acids, their outer surfaces release aluminum, calcium, and fluoride ions. In the case of silicate cements, calcium and aluminum ions react with phosphoric acid, creating an aluminum and calcium phosphate matrix that binds the partially reacted glass particles together.² This matrix includes soluble fluoride salts that do not contribute structurally to the cement and are leachable from the matrix without detriment to the cement. Leached fluorides have been shown to react with surrounding tooth enamel as well as inhibit carbohydrate metabolism in associated plaque.^{2,12-15} This results in long-term fluoride release and consequent decay inhibition.

Glass-ionomer cements employ aluminosilicate glass containing fluoride fluxes that are very similar to silicate cement.^{2,15} The principal chemical difference between silicate and glass ionomer cement is the acid component. In place of phosphoric acid, a mixture of various polyalkenoic acids has been substituted. The matrix of glass ionomer cement, therefore, is comprised of aluminum and/or calcium cross-linked polyalkenoic acid salts (ie, polyalkenoates). Aside from the setting reaction, calcium contained in the tooth unites chemically with polyalkenoic acids, resulting in glass ionomer cement adhesion to dentin and enamel.¹⁶ Glass ionomer cements resemble silicate cements in their long-term fluoride release and caries-inhibition characteristics.^{2,15} Figures 1A and 1B illustrate glass ionomer cement buildups in a caries active patient scheduled to receive full-coverage cast restorations on teeth Nos. 12 and 13.

Water and Its Effect on Fluoride Release

Water is an inherent component of both silicate and glass ionomer cements. Water that is created as a product of the acid-base reaction, as well as water originally contained in

the acid component, creates aqueous phases.^{2,15,16} These aqueous phases remain in the set cement, existing in the form of hydrogels that allow ion movement within the cement and ion exchange between the cement and its environment.^{2,16,17} These hydrogels also minimize dimensional change on setting of silicate and glass ionomer cements. Loss of water, or desiccation of the hydrogel, results in volume loss and crack formation and is detrimental to the integrity of both silicates and glass ionomer cements.¹⁵ Similarly, excessive hydration of early setting water-containing cements results in fluid movement that washes away matrix-forming ions, limiting the physical properties of the end product.¹⁶ The sensitivity of these cements to excessive hydration and dehydration is perhaps the greatest factor affecting their clinical performance.^{2,16}

Figure 2A—
Pretreatment view of cervical lesions on teeth Nos. 5 and 6.



Figure 2B—Post-treatment view of cervical restoration on tooth No. 5 restored with resin-modified glass ionomer cement and cervical restoration on tooth No. 6 restored with polyacid-modified resin. (Courtesy of W.W. Brackett, DDS, MSD; UNMC College of Dentistry).



To offer practitioners command of the initial setting of glass ionomer cements, polyalkenoic acids were modified by the addition of polymerizable resin side chains, allowing the formation of a resinous scaffold through light curing.¹⁸ Subsequently, chemically activated resin-modified glass ionomer cements were developed for clinical applications not suited to light curing. Resin modification dramatically reduced water movement into and out from the glass ionomer cement

matrix while having minimal effects on hydrogel formation and leachable fluoride. Within this resinous scaffold, the characteristic acid-base cement setting reaction was identified, indicating that the matrix formation and fluoride release mechanisms of silicate cement and resin-modified glass ionomer cement remained comparable.^{2,9,16-18} Figures 2A and 2B illustrate pretreatment and posttreatment views of tooth No. 5, restored using a resin-modified glass ionomer cement (GC Fuji II™ LC).

Composite resins differ from dental cements in that they undergo setting solely through polymerization of resin monomers.^{2,18,20} Composite resins contain glass filler particles that do not react with the resins to form either a salt matrix or hydrogel. Shortly after the development of resin-modified glass ionomer cements, efforts were made to graft acidic components of polyalkenoic acids onto composite resin monomers with the hope of creating composite resins that set through both polymerization and acid-base reactions.^{19,20} This hybridization of composite resins formed a new class of material termed “polyacid-modified composite resins.” Later, manufacturers identified these restorative resins as “compomers,” instilling the notion that the characteristics of “composites” and “ionomers” existed simultaneously. Figures 2A and 2B illustrate pretreatment and posttreatment views of tooth No. 6, restored using a polyacid-modified composite resin (Compoglass™).

Although compomer manufacturers claim to have identified an acid-base setting reaction that occurs subsequent to polymerization, no salt matrix has been identified, and the absence of hydrogels likely accounts for their lower fluoride release.^{14,18,20,21} Fluoride release from compomers is most likely a surface effect resulting from degradation of the aluminosilicate glass filler particles exposed to the oral environment. Clear differences exist in fluoride release patterns of silicate, glass ionomer cement, and resin-modified glass ionomer cements when compared to compomers.²¹ The ability of enamel to resist demineralization and/or exhibit remineralization results from transfer of ions contained in the restorative material and saliva into the dental tissues. Such ionic movement will occur very slowly in restorative materials that do not inherently contain water. Based on these differences, it is not surprising that the fluoride release from compomers is significant-

Table 1—Proposed Nomenclature and Classification of Some Currently Marketed Materials

Restorative Glass Ionomer Cements	Restorative Resin-Modified Glass Ionomer Cements	Polyacid-Modified Composite Resins
Alpha Fil ^{®a}	GC Fuji II [™] LC ^b	Compoglass ^{™,c}
Chemfil Superior ^c	Photac-Fil ^{®d}	DYRACT ^{™,e}
Cyber-Fil Alkenoate ^d	3M [™] Vitremer [™] Core Buildup/Restorative ^f	DYRACT AP ^{™,e}
GC Fuji II ^{™,h}		3M [™] F-2000 Compomer Restorative System ^f
GC Fuji IX [™] GP ^h		FREEDOM ^g
GlasIonomer Cement Type II ⁱ		Hytac Aplitip ^{®j}
Hi-Dense TC ⁱ		Ionosit Fil ^{®,a}
Ketac-Fil ^{®k}		
Ketac Molar ^{®l}		
Ketac-Silver ^{®l}		
MIRACLE MIX ^{®,h}		

^a DMG, Hamburg, Germany; marketed by Zenith Dental, Englewood, NJ 07631

^b Ivoclar Vivadent, Amherst, NY 14228

^c Dentsply Detry GMBH, Konstanz, Germany

^d Moyco Union Broach, York, PA

^e Dentsply/Caulk[®], Milford, DE 19963

^f 3M Dental Products, St. Paul, MN 55144

^g Southern Dental Industries, Ltd, San Francisco, CA 94105

^h GC America, Alsip, IL 60803

ⁱ SHOFU[®] Dental Corporation, Menlo Park, CA 94025

^j ESPE, Norristown, PA 19404

ly lower than fluoride release from silicates, glass ionomer cements, and resin-modified glass ionomer cements.^{2,20-22}

To boost fluoride release, soluble fluoride salts have been added to some polymers that absorb water but do not form hydrogels. Although these polymeric materials release fluoride after water sorption, the release is short lived and accompanied by indefinite softening of the material as a result of the plasticizing effect of the water on the polymer matrix.^{2,21-25}

Both glass ionomer cements and resin-modified glass ionomer cements have demonstrated the ability to function as fluoride reservoirs. Fluoride release from all glass ionomer cements is highest in the first few days after placement, then lessens. Aging glass ionomer cements exposed to topical fluoride show rapid fluoride uptake followed by controlled release in addition to sustained release of inherent fluoride. Compomers do not behave as fluoride reservoirs.²¹

Beneficial effects of fluoride release from restorative materials are related to many factors, including oral flora, saliva, diet, mineral-

ization characteristics of the tooth, and marginal integrity of the restoration. Presently, there are no data to quantify therapeutic fluoride-release levels. In the largest clinical study to date, restoration failure as a result of secondary caries was reported for 20,000 restorations. The recurrent caries incidence around amalgam restorations was 12%, whereas the incidence for silicate restorations was only 3%.¹¹ Materials known to resemble silicate cements in their fluoride composition and setting chemistry are most likely to mimic silicate cements in their anticariogenic effect. Until in vivo data such as these are reported for other fluoride-releasing materials, implications of fluoride release might be placing caries-prone patients at risk.

Summary and Conclusions

Dental cements are the end product of an acid (liquid)-base (powder) reaction that forms a salt matrix binding together partially unreacted powder particles. The matrix of aluminosilicate cements contains water in the form of hydrogels. Aluminosilicate cement powders release fluoride and other

ions during setting. Fluoride ions remain unbound in the matrix; therefore, they do not contribute structurally to the cement and are available for exchange with dental tissues.^{1,2,16-18,21} Diffusion-controlled fluoride release from the cement matrix results in additional fluoride movement from the unreacted aluminosilicate glass through the hydrogels. Similarly, hydrogels facilitate the movement of fluoride ions from the oral environment into the cement matrix according to the concentration gradient. Acid-base setting similarities and resultant hydrogels likely explain the similarities in fluoride release and ionic exchange mechanisms of silicate cements, glass ionomer cements, and resin-modified glass ionomer cements.

Ionic exchange between aluminosilicate-based dental cements and adjacent teeth has been shown to result in remineralization.

Ionic exchange between aluminosilicate-based dental cements and adjacent teeth has been shown to result in remineralization; in one in vivo study, hypermineralization of carious dentin was confirmed radiographically.^{26,27} Composite resin materials that harden by polymerization might contain aluminosilicate glass and/or added fluoride salts, but have not demonstrated ionic exchange with surrounding dental tissues.

In identifying the plausibility of ionic exchange between restorative materials and dental tissues, dentists are advised to consider the following:

- cement-forming ions are liberated by acid-base reactions that require mixing of components, generally a powder and liquid;
- acid-base reactions proceed slowly compared to polymerization reactions;
- cement hardening is a protracted process; and
- acid-base reactions produce a salt and water that can exist in the form of hydrogels, which are confirmed when desiccation of the set product is observed.

Additionally, if the product is polymerizable (contains resin) and requires visible-light activation, mix the components in the absence of light and test for hardening. Cements will

harden in the absence of light. This test, however, is limited because it will not distinguish between chemically activated composite resins and glass ionomer cements. Ultimately, it is left to the clinician to watch product labels, advertisements, and material safety data sheets to check for appropriate terminology describing the material.⁹

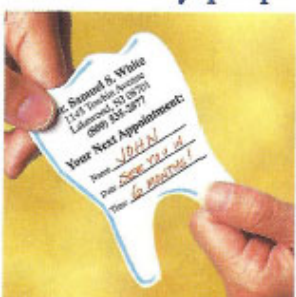
Table 1 classifies some currently marketed materials often identified as "ionomers." These materials have been separated into categories based on the definitions used in this review. The evolution of dental materials that contain aluminosilicate glass has far outpaced our ability to make clinically based performance determinations. The purpose of this categorization is to distinguish differences in setting chemistry. With all other factors being equal, the clinical behavior of decay-inhibiting restoratives has been best predicted on the basis of chemical composition and setting similarities. As fast-paced efforts continue to improve the physical properties of anticariogenic materials, our ability to predict clinical outcomes will become increasingly important for our patients, our practices, and ultimately, our profession.

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