The Chemistry of Dental Cements

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1 Introduction

The ancient art of dentistry and the need for dental materials arose from man's attempt to combat and repair the effect of dental diseases, which are largely associated with the development of civilization.[1] Exodontics, the extraction of teeth, and prosthetics were known to the civilization of Antiquity; examples of Greek exodontic instruments and Etruscan gold bridgework have been found.[2]

Much of dentistry, especially modern dentistry, is concerned with the restoration of the function and appearance of teeth following the lesions caused by caries. Restoration takes the form of the complete replacement of teeth, prosthetics; or conservation of the natural dentition, conservative dentistry. The latter includes the art of the restoration of eroded teeth using a filling material or a cemented inlay or crown.

The subject of dental materials forms an essential part of restorative dentistry. It is not merely a specialized branch of materials science, itself a complex amalgam of the chemical and physical sciences and technologies, but combines also the elements of cosmetic art, biological science, and clinical practice. It remains an art as well as a science and the requirements of one may impinge on those of the other. Thus basic chemistry cannot always be dissociated from biological and aesthetic requirements and this adds to the complexities of research. The development of restorative dentistry has been related to the availability of suitable materials. The search for these has continued throughout the history of dentistry and has been largely dependent on general advances in science and technology.

The requirements for dental restorative materials are demanding. Since they are prepared by the clinician in the surgery they must have good manipulative properties and adequate working time allied to the ability to set and harden rapidly once placed in position. They should, ideally, adhere to tooth material. Moreover, dental restorative materials are required to function in the sensitive but hostile environment of the mouth. Thus they should be bland towards living tissues, yet be able to withstand the aggressive action of acids generated from sugars by micro-organisms. No one material meets all these requirements

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[1] G. Toveradet, 'A Survey of the Literature of Dental Caries', Nat. Head Sci. Res. Council, Washington, Publication 225, 1952; P. J. Brekhus and W. D. Armstrong, *J. Amer. Dent. Assoc.* 1936, **23**, 1459.

[2] B. W. Weinberger, 'History of Dentistry', Mosby, St. Louis, U.S.A., 1948, vol. 1.

and all have limitations of performance and application. For this reason a wide variety of dental restorative materials have been formulated.

2 Dental Cements

One of the most important classes of materials used in dentistry is that of the dental cements. These materials, which are prepared directly in the surgery, are used for many purposes and depending on their formulation they may be used to attach prefabricated crowns and inlays to teeth, to line cavities for the protection of dental pulp against chemical and thermal insult, and even for the direct filling of cavities.

All dental cements are based on the hardening reaction between a powdered solid and a viscous hydrogen-bonded liquid. The plastic pastes formed by mixing these components set rapidly to hard salt-like gels.[3] The liquids, which may be water-based or organic, act as acids or proton donors. The cement powders are essentially amphoteric or slightly basic substances which act as proton acceptors in the cement-forming reaction. They may be simple oxides, such as zinc oxide, or complex aluminosilicate glasses containing appreciable amounts of fluoride. The essential cation in these powders—zinc in the zinc oxide cements and aluminium in the aluminosilicate cements—are cations with a small ionic radius and high ionic potential and are known in glass science to have a network-forming capacity. Beryllium and magnesium, occasionally found in minor amounts in both powder and liquid, also have a network-forming capacity. This capacity decreases with increasing basicity of the cation, and is greatest for cations of high charge and small ionic radius.

The most versatile powder for cement formation is zinc oxide which when treated with a wide range of organic and inorganic proton-donating liquids yields a whole family of cements.[4] Their development is closely bound up with dentistry. Historically, the first was invented by Sorel in 1855.[5] In this cement zinc oxide powder was combined with an aqueous solution of zinc chloride to form a cementitious mass. Its use in dentistry was recommended by Feichtinger in 1858[6] but it did not prove to be a success (another Sorel cement based on magnesium oxide and solutions of magnesium chloride is still used in the building industry).[7] Subsequent development of zinc oxide cements in the 1880's followed two courses. In one, the Sorel's liquid was replaced by aqueous solutions of phosphoric acid, giving rise to the zinc phosphate cement;[8] and in the other,

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[3] A. D. Wilson in 'Scientific Aspects of Dental Materials', ed. J. A. von Fraunhofer, Butterworths, London, 1975, Ch. 4.

[4] A. D. Wilson in 'Scientific Aspects of Dental Materials', ed. J. A. von Fraunhofer, Butterworths, London, 1975, Ch. 5.

[5] E. Sorel, *Compt. rend.*, 1855, **41**, 784.

[6] J. W. Mellor, 'A Comprehensive Treatise on Inorganic and Theoretical Chemistry', Longman, London, 1929, Vol. IV, p. 546.

[7] E. Sorel, *Compt. rend.*, 1867, **65**, 102; E. S. Newman, *J. Res. Nat. Bur. Standards*, 1955, **54**, 347.

[8] C. S. Rostaing, G.P.N. 6045/1878; G.P.N. 11 253/1880; C. N. Peirce, *Dent. Cosmos.*, 1879, **21**, 696.

various organic liquids were substituted, eugenol proving the most successful.[9] These traditional cements were fully developed by the end of the 19th century: thereafter the subject stagnated until recent years when a number of research studies have been conducted. Liquid chelating agents, other than eugenol, have been reported,[10,11] 2-ethoxybenzoic acid being the most notable.[11] A practical cement based on aqueous solutions of poly(acrylic acid) has also been developed as a practical material.[12]

Not all dental cements are based on zinc oxide. The traditional dental silicate cement utilized instead an aluminosilicate glass powder.[13,14] This cement and the zinc phosphate cement are the only dentally useful ones found in a large family of cements based on reactions between oxides and phosphoric acid solution.[15] The dental silicate cement remained unique until recently when another cement based on aluminosilicate glasses was discovered. This cement, which utilizes aqueous solutions of poly(alkenoic acids), has been termed by Wilson and Kent[13,16] a glass-ionomer or ASPA cement; ASPA is an acronym of *A*lumino-*S*ilicate *P*oly*A*crylic Acid.

Undoubtedly the most important recent development in dental cement technology has been the emergence of a new class of cement, the ionic polymer cement system where anionic polyelectrolytes are employed as cement forming liquids. The ionic polymer cements are at present represented by the zinc polycarboxylate cement of Smith[4,12] (which uses a zinc oxide powder) and the glass-ionomer cement of Wilson and Kent.[13,16] This field of dental science is one where further developments are to be expected.

The range of dental cements is summarized in Table 1. Despite their diverse nature certain features are common to all. The cements themselves fall within Wygant's definition of reaction cement,[17] a term applied to cements other than those which set by hydraulic action. Dental cements may be more closely defined as *acid–base reaction cements*. The cement-forming liquids are acidic, viscous hydrogen-bonded liquids capable of donating protons, exemplified by eugenol and phosphoric acid. The powders are amphoteric oxides, either zinc oxide or aluminosilicate glass, which act as proton acceptors. The cement-forming reaction is essentially an acid–base interaction between these two components, the gel-salt formed, in the liquid phase, acting as a binding matrix. General equations for the cement-forming reaction may be written as follows:

[9] J. S. King, *Dent. Cosmos*, 1872, **14**, 193; L. C. Chisholm, *Dent. Register*, 1873, **27**, 517; J. F. Flagg, *Dent. Cosmos*, 1875, **17**, 465; D. D. Smith, *ibid.*, 1878, **20**, 521; J. Wessler, *Deutsch. Mschr. Zahnheilk*, 1894, **12**, 478.

[10] T. H. Nielsen, *Acta. Odont. Scand.*, 1963, **21**, 159.

[11] G. M. Brauer, E. E. White, and M. G. Mashonas, *J. Dent. Res.*, 1958, **37**, 547.

[12] D. C. Smith, *Brit. Dent. J.* 1968, **125**, 381; B.P.N. 1 139 430/1969.

[13] A. D. Wilson in 'Scientific Aspects of Dental Materials' ed. J. A. von Fraunhofer, Butterworths, London, 1975, Ch. 6.

[14] T. Fletcher, B.P.N. 3028/1878; *Brit. J. Dent. Sci.*, 1879, **22**, 74; P. Steenbock, G.P.N 174 557, B.P.N. 15 176/1903; B.P.N. 15 181/1904; C. G. Voelker, *Dent. Summ.*, 1916, **36**, 177.

[15] W. D. Kingery, *J. Amer. Ceram. Soc.*, 1950, **33**, 239, 242.

[16] A. D. Wilson and B. E. Kent, *J. Appl. Chem. Biotech.*, 1971, **21**, 313; *Brit. Dent. J.*, 1972, **132**, 133; B.P.N. 1 316 129/1973.

[17] J. F. Wygant in 'Ceramic Fabrication Processes' ed. E. D. Kingery, M.I.T. Press, Cambridge, Mass., 1958, Ch. 18.

Table 1 *Classification of dental cements*

Cement	*Oxide powder (proton acceptor)*	*Liquid* (proton donor)*	*Cementing* (gel-salt)*	*Active Filler*
Zinc Phosphate	Zinc oxide and magnesium oxide	Phosphoric acid, aqueous solution	Zinc and magnesium phosphate	Zinc oxide and magnesium oxide
Zinc Carboxylate	Zinc oxide and magnesium oxide	Poly(acrylic acid)	Zinc and magnesium polyacrylate	Zinc oxide and magnesium oxide
Silicate	Complex fluorine-containing aluminosilicate glass	Phosphoric acid, aqueous solution	Aluminium phosphate and calcium fluoride	Complex fluoroalumino-silicate glass core sheathed by a siliceous hydrogel
Glass Ionomer	Complex fluorine-containing aluminosilicate glass	Poly(alkenoic acid) aqueous solution	Calcium and aluminium polyalkenates	Complex fluoroalumino-silicate glass core sheathed by a siliceous hydrogel
Zinc oxide eugenol	Zinc oxide	Eugenol	Zinc eugenolate	Zinc oxide
Zinc oxide eugenol/2-ethoxybenzoic acid	Zinc oxide	Eugenol/2-ethoxy-benzoic acid	Zinc eugenolate and 2-ethoxybenzoate	Zinc oxide

*Principal phase

$$\underset{\substack{\text{proton}\\\text{acceptors}}}{MO} + \underset{\substack{\text{proton}\\\text{donors}}}{H_2A} = \underset{\substack{\text{salt-gel}\\\text{matrix}}}{MA} + H_2O \tag{1}$$

$$\underset{\substack{\text{proton}\\\text{acceptors}}}{MO\,xSiO_2} + \underset{\substack{\text{proton}\\\text{donors}}}{H_2A} = \underset{\substack{\text{salt-gel}\\\text{matrix}}}{MA + xSiO_2} + H_2O \tag{2}$$

where M represents the cement-forming cation and A the cement-forming anion; for convenience of representation both M and A are taken to be bivalent.

The cement-forming reaction is one where hydrogen bridges in the liquid phase are progressively replaced by more rigid metal ion bridges, a process which causes the liquid to gel and the gel to harden. This generalized account of cement-formation is in accord with the views of Wygant[17] who has emphasized that maintenance of some continuity of structure is essential for cement-formation. This criterion can only be satisfied by amorphous systems since these possess structural flexibility and, indeed, the matrices of all dental cements are now known to be essentially amorphous. There is other experimental confirmation of Wygant's view. I.r. spectroscopic studies[18] on zinc oxide eugenol cements have shown that there is a structural affinity between the associated eugenol dimer in the liquid and the bisligand zinc eugenolate chelate in the matrix of the set cement. Electrical conductivity and permittivity studies on the dental silicate cement[19] have indicated that setting and hardening processes proceed with significant discontinuities.

The metal ions in dental cements Al^{3+} and Zn^{2+}, derived mainly from the powder but in some cases also from the liquids, are small ions of high ionic potential having some glass-forming ability. The same may be said of the phosphate group in dental silicate cements. Both phosphoric acid and poly-(acrylic acid) solutions used in dental cements will form glasses on heating. These observations are not coincidences but reflect the fact that the same structural considerations apply to cement gels as well as to glass structures.

The properties of dental cements are shown in Table 2. All set very rapidly and with certain exceptions are strong materials. Indeed the dental silicate cement is the strongest inorganic cement known and its strength is an order of magnitude greater than that of Portland cement.

3 Phosphate-bonded Cements

Cements based on the hardening reaction between a metal oxide or silicate and a concentrated solution of phosphoric acid can be formulated to set within a few minutes and to develop strength rapidly. This property makes them suitable for dentistry. There are two main types: the dental zinc phosphate cement employed for luting crowns and inlays, and the dental silicate cement used for the aesthetic filling of front teeth. Until quite recently they remained the materials of choice for these applications but the advent of the composite resins and ionomer cements has greatly reduced their usage.

[18] A. D. Wilson and R. J. Mesley, *J. Dent. Res.*, 1972, **51**, 1581.
[19] A. D. Wilson and B. E. Kent, *J. Dent. Res.*, 1968, **47**, 463.

Table 2 *The properties of typical examples of the various dental cements*[a]

	Phosphate bonded		*Ionomer*		*Non-aqueous*		
	Zinc phosphate	*Silicate*	*Zinc polycarboxylate*	*Glass-ionomer*	*Simple ZOE*	*Reinforced ZOE*	*Reinforced ZOE/EBA*
Powder/liquid proportion (g/ml^{-1})	4.2	4.0	3.6	3.5	2.6	2.4	6.2
Setting time, 37°C/min	4.25	3.75	3.25	4.0	3.75	3.75	6.0
Compressive strength, 24 h/MN m^{-2}	128	226	85	175	13	39	91
Tensile strength, 24 h/MN m^{-2}	8	13	12	12	1.6	3.5	8
Modulus of elasticity, 24 h/GN m^{-2}	13	18	6.2	9.0	—	—	
Opacity, C .70	1.0	0.50	1.0	0.69	1.0	1.0	1.0
Adhesive to Enamel/MN m^{-2}	0	0		4.0	0	0	0
Adhesive to Dentine/MN m^{-2}	0	0		3.0	0	0	0

(*a*) B. E. Kent, B. G. Lewis, and A. D. Wilson, *Brit. Dent. J.*, 1973, **135**, 322.

Phosphoric acid solutions used in phosphate cements have concentrations ranging from 45 to 60 % w/w as H_3PO_4 (Tables 3 and 4). The structures of these solutions is believed to be one where the phosphate groups are hydrogen bonded

Table 3 *Chemical composition of some zinc phosphate cements*[a,b]*/% w/w*

Powder			
ZnO	89.4	90.3	88.9
MgO	3.2	9.6	8.0
Al_2O_3	6.8	—	1.5
SiO_2	0.6	—	1.6
	100.0	99.9	100.0
Liquid			
Total phosphate (as H_3PO_4)	57.1	54.7	61.4
Al	2.4	2.5	3.1
Zn	5.6	4.7	—
H_2O	to 100.0	to 100.0	to 100.0

(*a*) B. Axelsson, *Odont. Revy*, 1965, **16**, 126; (*b*) A. D. Wilson, G. Abel, and B. G. Lewis, *Brit. Dent. J.*, 1974, **137**, 313.

Table 4 *The chemical composition of some dental silicate cements*[a]*/% w/w*

Powder			
SiO_2	41.6	38.8	31.5
Al_2O_3	28.2	29.1	27.2
CaO	8.8	7.7	9.0
Na_2O	7.7	8.2	11.2
F	13.3	13.8	22.0
P_2O_5	3.3	3.0	5.3
ZnO	0.3	2.9	—
H_2O	2.2	1.6	3.1 (by difference)
Less O for F	−5.6	−5.8	−9.3
	99.8	99.3	100.0
Liquid			
Total phosphate (as H_3PO_4)	48.8	49.3	50.7
Al	1.6	1.9	1.5
Zn	6.1	4.2	8.7
Water	to 100.0	to 100.0	to 100.0

(*a*) A. D. Wilson, B. E. Kent, D. Clinton, and R. P. Miller, *J. Materials Sci.*, 1972, **7**, 220.

to the water liquid lattices.[20] Experimental evidence[21–23] shows that there are other species present in solution in addition to H_3PO_4 and $H_2PO_4^-$, namely the hydrogen bonded dimer $H_6P_2O_8$ and the triple ion $H_5P_2O_8^-$. N.m.r. studies[21] suggest that more highly polymerized forms are also present such as $(H_3PO_4)_3$ and $(H_3PO_4)_4$.

Phosphoric acid solutions used for cement formation contain aluminium or zinc or both (Tables 3 and 4). Whereas zinc is present as a simple salt in solution[24,25] aluminium forms a variety of complexes with phosphoric acid.[21,24,26,27] At low Al : P ratios multi-ligand complexes are present corresponding to the formulae $Al(H_3PO_4)_n$, where $n = 2, 3$, or 4, (the state of protonation is unknown). As the Al : P ratio is increased other complexes are formed *i.e.* $Al,H_2PO_4^{2+}$, $Al,(H_2PO_4)_2^+$, and $Al,H_3PO_4^{3+}$. There is some evidence for the existence of dinuclear aluminium complexes at higher Al : P ratios and the formation of such species may play an important role in cement-forming reactions.

A. Dental Zinc Phosphate Cement.—The zinc phosphate cement has long been used in dentistry for cementing crowns and inlays and is still widely used[4] owing to a combination of good manipulative properties and strength. The cement appears to have originated in 1878—1880[8] and was prepared as a paste from strongly ignited zinc oxide and phosphoric acid in concentrated aqueous solution. In this simple form the cement proved clinically unsatisfactory. The cement was only accepted in dentistry when, as reported by Fleck in 1902,[28] improved forms became available. Cement formulations have remained essentially unchanged since the early 20th century. Typical modern compositions are given in Table 3.[29]

The chief problem with the zinc phosphate cement has always lain in the excessive vigour of the cement-forming reaction. Indeed, when plain zinc oxide powder and a simple aqueous solution of phosphoric acid are mixed together they react very rapidly and with the generation of much heat to form a crystalline mass which has little value as a cement. The reaction may be moderated in two ways. Firstly, by incorporation of zinc and aluminium salts in the liquid, and secondly by deactivating the zinc oxide powder, which is highly dispersed and so very reactive, by sintering. Sintering has the effect of consolidating the powder to a denser form of reduced surface area and reactivity. This

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[20] J. R. van Wazer, 'Phosphorus and its Compounds'. Interscience Publishers Inc. New York, 1958, Vol. 1, pp. 486—491.

[21] J. W. Akitt, N. N. Greenwood, and G. D. Lester, *J. Chem. Soc. (A)*, 1971, 2450.

[22] M. Selvaratnam and M. Spiro, *Trans. Faraday Soc.*, 1965, **61**, 360.

[23] K. L. Elmore, J. D. Hatfield, R. L. Dunn, and A. D. Jones, *J. Phys. Chem.*, 1965, **69**, 3520.

[24] A. D. Wilson and R. J. Mesley, *J. Dent. Res.*, 1968, **47**, 644.

[25] J. A. R. Genge, A. Holroyd, J. E. Salmon, and J. G. L. Wall, *Chem. and Ind.*, 1955, 357.

[26] R. F. Jameson and J. E. Salmon, *J. Chem. Soc.*, 1954, 4013.

[27] A. Holroyd and J. E. Salmon, *J. Chem. Soc.*, 1956, 269; J. E Salmon and J. G. L. Wall, *J. Chem. Soc.*, 1958, 1128; N. Bjerrum and C. R. Dahm, *Zeit. Phys. Chem. Bodenstein Festband*, 1931, 627.

[28] H. Fleck, *Dent. Items*, 1902, **24**, 906.

[29] B. Axelsson, *Odont Revy*, 1965, **16**, 126; A. D. Wilson, G. Abel, and B. G. Lewis. *Brit. Dent. J.*, 1974, **137**, 313.

process can be enhanced by the incorporation of other oxides in the sinter and magnesium oxide, sometimes supplemented by silica, is used for this purpose in preparing zinc phosphate cement powders. Zhuravlev *et al.*,[30] who studied the chemistry of the process, found that magnesium oxide reacts with zinc oxide to form a solid solution of zinc oxide in magnesium oxide and the powder cakes. Similarly, silica reacts with zinc oxide to form the mineral willemite, a variety of zinc orthosilicate.

Although the cement has been in existence for nearly 100 years, little is known about the cement-forming reaction and microstructure. The reaction may be presumed to be one of acid–base between zinc oxide and phosphoric acid with formation of zinc phosphate salt matrix. The general features are probably similar to those found in the dental silicate cement-forming reaction, which has been studied in detail (see Section 3B). There is always an excess of zinc oxide over phosphoric acid in zinc phosphate cement mixes and the set cement consists of zinc oxide particles embedded in a zinc phosphate matrix. At one time the matrix was thought to consist entirely of hopeite—crystalline zinc orthophosphate tetrahydrate, $Zn_3(PO_4)_2, 4H_2O$.[31] This view is now known to be an oversimplified one. Only when a plain zinc oxide and phosphoric solution are mixed together are hopeite crystallites formed in the vigorous reaction, and then as a non-cementitious mass. In practical dental cements,[32,33] where the reaction is attenuated by incorporation of aluminium in the liquid and magnesium oxide in the powder, a glassy matrix of amorphous zinc orthophosphate is produced. However, this matrix is not completely stable and crystallites of hopeite develop at the surface in the presence of free water. There is a period of inhibition which is related to the speed of the reaction. Surface crystallization is an unfavourable process for it destroys any bond that may have been formed between the cement and the tooth and consequently this type of dental cement is a non-adhesive one.

The phosphoric acid concentration of the cement liquid is an important parameter that determines many cement properties. An increase in the phosphoric acid concentration ratio retards the setting reaction.[33] No explanation has been advanced for this observation; possibly it is related either to a deficiency of water in the system (to aid transport of ions and hydrate reaction products) or to the fact that the H_3PO_4 concentration decreases as the phosphoric acid concentration increases owing to dimerization (see p. 272 and ref. 22). The compressive strength of this cement and its resistance to aqueous attack increases with phosphoric acid concentration. Inspection of the phase diagram[34] for $ZnO–P_2O_5–H_2O$ shows that when excess ZnO is present and the phosphoric acid concentration is less than 73.1 % w/w (as H_3PO_4) then the zinc phosphate species formed is $Zn_3(PO_4)_2, 4H_2O$. If this species is related to that in the cement,

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[30] V. F. Zhuravlev, S. L. Volfson, and B. I. Sheveleva, *J. Appl. Chem.* (*U.S.S.R.*), 1950, **23**, 121.

[31] A. Dobrowsky, *Chem. Tech.* (*Berlin*), 1942, **15**, 159.

[32] G. E. Servais and L. Cartz, *J. Dent. Res.*, 1971, **50**, 613; L. Cartz, G. Servais, and F. Rossi, *J. Dent. Res.*, 1972, **51**, 1668; S. Crisp, H. J. Prosser, I. K. O'Neill, and A. D. Wilson, *J. Dent. Res.*, 1978, in the press.

[33] H. K. Worner and A. R. Docking, *Austral. J. Dent.*, 1958, **3**, 215.

[34] J. E. Salmon and H. Terry, *J. Chem. Soc.*, 1950, 2813.

then its volume fraction in the matrix will increase as the phosphoric acid content of the liquid increases, with a limit at 73.1 % w/w H_3PO_4.

The properties of the cement may be briefly described. It has good manipulative properties and sets rapidly to a cement which can attain a compressive strength of 100 N mm^{-2} in 24 h. However, it suffers from a number of disadvantages, it is brittle, weak in tension, soluble in acids, opaque, and irritant to living tissues. Moreover, it is not adhesive either to enamel or dentine.

B. The Dental Silicate Cement.—Until quite recently the dental silicate cement was the most important of all the dental cements. However, alternative and superior materials are now available for the aesthetic restoration of front teeth and its use has declined considerably. The early history of the cement is obscure. It may have originated as early as 1878, but successful versions were not developed until 1903—1905[14,35] and the first modern type did not appear until 1908.[36]

Apart from the recently introduced glass-ionomer cement, the dental silicate cement is the only major dental cement not based on zinc oxide powder. The powder is, in fact, a type of calcium aluminosilicate glass which is ion-leachable in acid solution. All current glasses are prepared using a fluoride flux, and are, in consequence opal glasses containing phase-separated droplets of fluorite. The liquid component resembles that of the zinc phosphate cement and is a concentrated aqueous solution of phosphoric acid containing metal salts. The chemical compositions of some typical examples are given in Table 4.[37] When these two components are mixed together a rapidly setting cement is formed which develops a strength of *ca.* 250 MN m^{-2} in 24 h. The set cement has the valuable quality of translucency which is not possessed by zinc oxide cements. This property is of cosmetic importance, making the cement suitable for the aesthetic restoration of front teeth.

Despite its prominence in aesthetic restorative dentistry for more than 70 years the correct chemistry of its setting and structure remained unknown until quite recently. The accepted view was that setting resulted from the formation of silica gel, *i.e.* a setting mechanism similar to that found in the silicate cements formed by mixing sodium silicate and acid solutions. However, this is not so and the true mechanism of set was established by Wilson and his co-workers[37] using several techniques: wet-chemical methods,[38] i.r. spectroscopy,[39] electron-probe micro-analysis (EPMA),[37,40] electron microscopy,[37] electrical conductivity,[19] and pH measurements.[41] The following account is based on this work.

Before describing the cement-forming reaction it is appropriate to discuss the nature of the unusual glasses used for these cements. Their role is to supply metal ions to the liquid (at an appropriate rate) and this they are able to do be-

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[35] M. Morgenstern, *Ost-ung. Vjschr Zahnheilk*, 1905, **21**, 514.
[36] F. Schoenbeck, *U.S.P.*, N. 897 160/1908.
[37] A. D. Wilson, B. E. Kent, D. Clinton, and R. P. Miller, *J. Materials Sci.*, 1972, **7**, 220.
[38] A. D. Wilson and B. E. Kent, *J. Dent. Res.*, 1970, **49**, 7, 21.
[39] A. D. Wilson and R. J. Mesley, *J. Dent. Res.*, 1968, **47**, 644.
[40] B. E. Kent, K. E. Fletcher, and A. D. Wilson, *J. Dent. Res.*, 1970, **49**, 86.
[41] A. D. Wilson and B. E. Kent, *J. Dent. Res.*, 1969, **48**, 212.

cause they have the unusual property, for a silicate glass, of being acid decomposible. This is because they are aluminosilicates characterized by a high aluminium content (the Al : Si ratio approaches unity). A simple silicate, such as silica, is a macromolecule based on a three-dimensional network of [SiO_4] tetrahedra linked by Si—O—Si bridges and is impervious to acid attack. The behaviour of aluminosilicates is different. In these materials Al^{3+} can isomorphically replace Si^{4+} ions in the network (up to a maximum of 1 : 1) which thus consists of [AlO_4] and [SiO_4] tetrahedra linked by Al—O—Si bridges. Replacement of Si^{4+} by Al^{3+} increases the negative charge on the network, which has to be balanced by network dwelling cations such as Ca^{2+} and Na^+. This glass structure is susceptible to acid attack, since positively charged hydrogen ions can penetrate and disrupt the negatively charged network by attacking the Al^{3+} sites and severing the Al—O—Si links. Al^{3+}, Ca^{2+}, and Na^+ ions are liberated and orthosilicic acid, which polymerizes to silica gel, is formed.

The cement-forming reaction, which occurs in a number of overlapping stages, is essentially an acid–base interaction between the glass powder and the acidic liquid. In the first stage of the reaction H_3PO_4 ionizes to $H_2PO_4^-$ (detectable by i.r. spectroscopy[39]) and the hydrogen ions released attack the glass powder. Al^{3+}, Ca^{2+}, Na^+, and F^- are liberated from the glass leaving behind an ion-depleted layer of silica gel at the surface of the glass particles (as indicated by i.r. spectroscopy[39] and EPMA[37,40]). This decomposition is a rapid one. The liberated ions—Al^{3+}, Ca^{2+}, Na^+, and F^- ions—migrate, possibly as fluoride complexes, into the aqueous phase of the cement paste where they accumulate together with $H_2PO_4^-$, Zn^{2+}, and Al^{3+} ions already present in the liquid. As the pH of the system increases the ionic species precipitate as salts. The solubilization and precipitation of these ionic species is illustrated by Figure 1. The principal reaction is the formation of an insoluble aluminium phosphate salt, the gel matrix. Associated side reactions are the precipitation of calcium fluoride and formation of soluble sodium dihydrogen phosphate. When about 50 % of the total phosphate has precipitated the cement sets sharply. A schematic representation of this reaction is depicted in Figure 2.

Precipitation of ions continues long after the cement has set and strength and hardness also continue to increase[37] (Figure 3). The hardening process is largely controlled by increases in pH. Initially there is only a small increase in the apparent pH of the system from an initial figure of 0.8 to 1.7 at set, despite the extent of the interaction between the powder and the liquid because of the buffering action of phosphoric acid solution in the region of its pK, (2.1). The subsequent considerable increase in hardness over the following 24 h is accompanied by a much larger increase in apparent pH (from 1.7 to 5.0—5.5) which completes the precipitation process despite little further interaction between powder and liquid. In this pH region there is no buffering reaction.

Electrical conductivity measurements[18] indicate that slow diffusion reactions continue for several months and that the ionic character of the cement slowly diminishes; these changes are accompanied by small increases in cement strength.[42] The possibility of slow hydration reactions cannot be ruled out.

[42] G. C. Paffenbarger, I. C. Schoonover, and W. Souder, *J. Amer. Dent. Assoc.* 1938, **25**, 32.

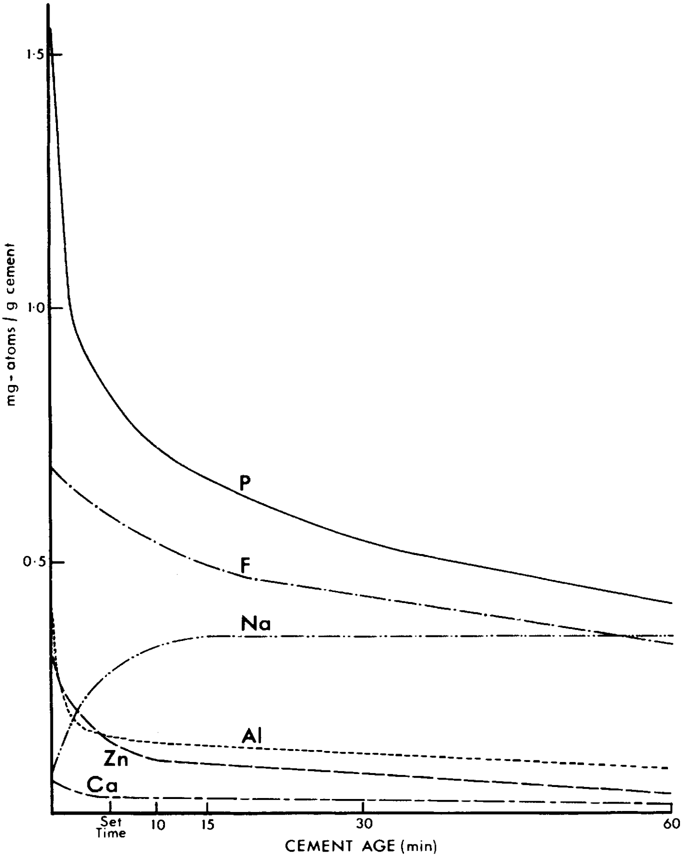

Figure 1 *The extraction and precipitation of ions in a setting dental silicate cement shown as soluble ion/time curves*

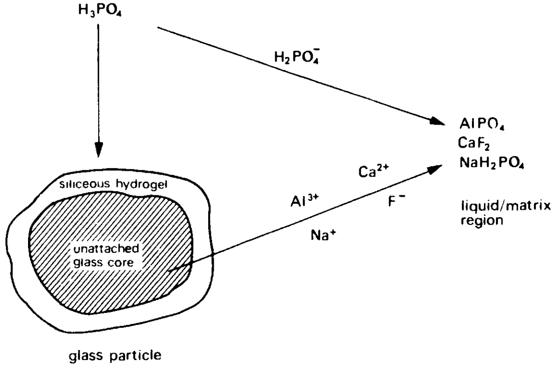

Figure 2 *Schematic representation of the cement-forming reaction of a dental silicate cement*

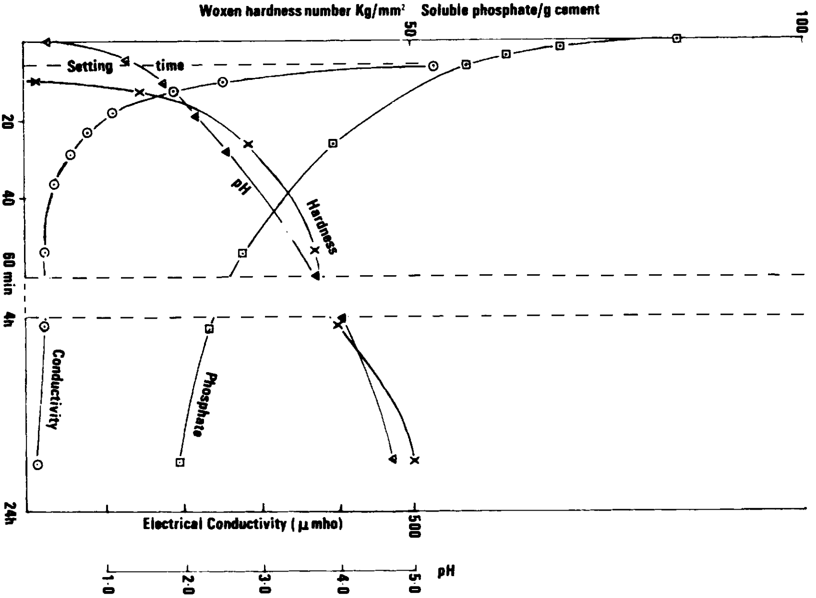

Figure 3 *Variation of soluble phosphate, pH, electrical conductivity, and hardness, with the age of the dental silicate cement*
(Reproduced by permission from *J. Mater. Sci.*, 1972, **7**, 220)

The microstructure of the set cement has been established using electron and optical microscopy[37] and electron probe microanalysis (EPMA) [37,40] the latter technique giving the spatial location of the elements and identifying regions where the various reactions occur. The set cement has a composite structure with acid-attacked glass particles embedded in an amorphous and particulate matrix. EPMA studies[37,40] show that the matrix contains aluminium, calcium, sodium, phosphorus, and fluorine, but not silicon, and that aluminium tends to be associated with phosphorus and calcium with fluorine (Figure 4). The matrix appears to consist principally of amorphous aluminium orthophosphate (a conclusion confirmed by i.r. spectroscopic data[39]) containing isolated areas of crystallites: fluorite, CaF_2, and augelite, $Al_2(OH)_3PO_4$.[37] However, the presence of aluminium fluorophosphates cannot be discounted since n.m.r. studies[21] on phosphoric acid solutions containing aluminium and fluoride ions have shown that fluoro-alumino-phosphate complexes containing direct Al–F links, are formed as well as alumino-phosphate complexes.

The properties of dental silicate cements, like those of the zinc phosphate cement, are sensitive to the phosphoric acid concentration of the liquid.[43] The setting time of cements increases with the acid strength of the liquid: slightly, in the range 50—60 % w/w H_3PO_4 and very sharply above 68 % w/w H_3PO_4 (Figure 5). This phenomenon is paralleled by an observed sharp increase

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[43] A. D. Wilson, B. E. Kent, R. F. Batchelor, B. G. Scott, and B. G. Lewis, *J. Dent. Res.*, 1970, **49**, 307.

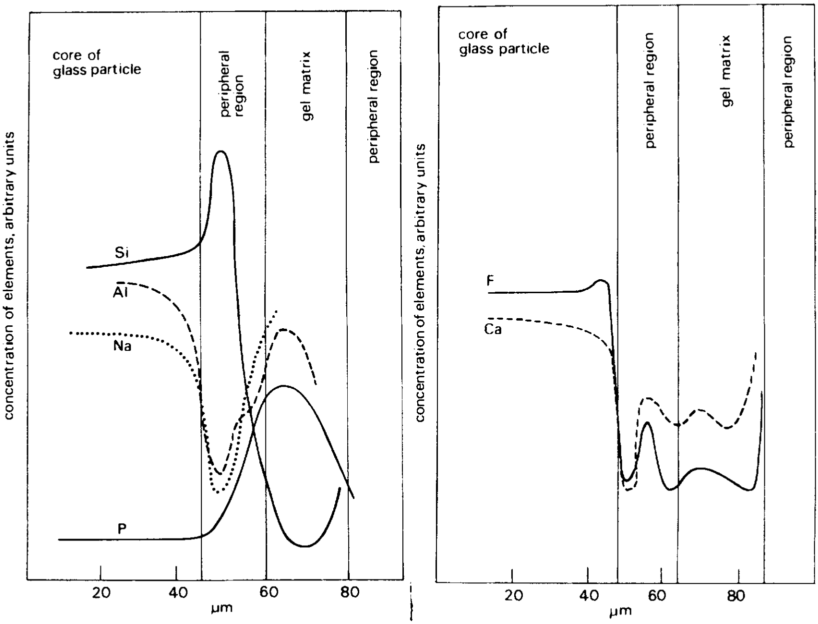

Figure 4 *Distribution of elements across the boundary of a glass particle* (Reproduced by permission from *J. Materials Sci.*, 1972, **7**, 220)

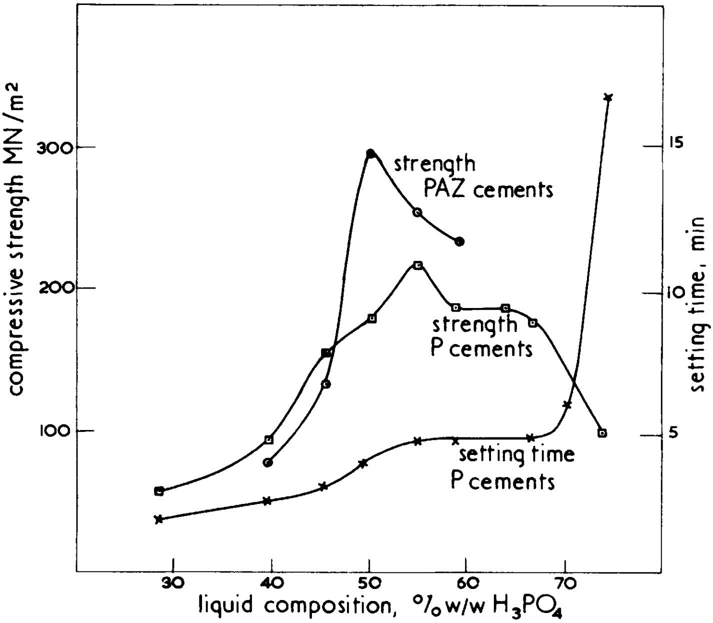

Figure 5 *Effect of phosphoric acid concentration in the liquid on the setting time and compressive strength of dental silicate cements: P, plain phosphoric acid; PAZ, phosphoric acid solutions containing aluminium and zinc*

in the viscosity and reduction of water vapour pressure of such solutions. Moreover, cements prepared with liquids containing more than 60 % w/w H_3PO_4 absorb water. These observations indicate that retardation of the setting reaction in this situation would be due to a deficiency of water which is required to transport ions and hydrate reaction products (*e.g.* aluminium phosphates and silica gel).

The compressive strength of this cement, like that of the zinc phosphate cement, is sensitive to the phosphoric acid concentration of the liquid. However, the form of the strength/acid concentration curve is different, with a maximum strength corresponding to an optimum acid concentration (Figure 5). This concentration lies between 49 and 55 % w/w (total phosphate calculated as H_3PO_4), the exact concentration depending on whether metal ions are present or not. The form of this curve requires some explanation. Decrease of cement strength with decreasing acid concentration, *i.e.*, increasing water content, observed at acid concentration below the optimum, is explained by the weakening effect of water present in the matrix in excess of that required to solvate the aluminium phosphate and silica hydrates. Decrease of strength with increasing acid concentration above the optimum can be explained by reference to the Al_2O_3–P_2O_5–H_2O phase diagram.[26] The phase diagram indicates that when excess Al_2O_3 is added to phosphoric acid solutions in the concentration range 0—65.3 % w/w (as H_3PO_4) the stable aluminium phosphate hydrate formed is $AlPO_4$, $3.5H_2O$. Above 65.3 % w/w H_3PO_4 another hydrate, $AlPO_4$, $2H_2O$ is formed. If the former species is superior to the latter as a cementing hydrate, the effect of phosphoric acid concentration is explained. The optimum phosphoric acid concentration would tend to be less than 65.3 % w/w (as H_3PO_4), since water is required for silica gel formation.

4 Ionic Polymer Cements

The ionic polymer cements,[44,45] which include the most recent dental cements, are based on acid–base reactions between aqueous solutions of poly(alkenoic acids) (40—50 % w/w) and certain acid-decomposible metal oxides,[12,46,47] aluminosilicate glasses,[16,48] and minerals.[49] In the setting reaction liberated cations become bound to polyanions in the aqueous phase to form a hard polysalt gel. These materials are of interest as they are intermediate between a filled organic polymer and an inorganic cement. They are novel in that the gel-matrix contains both covalent C—C and ionic bonds and so can properly be termed ionic polymer (or ionomer) cements.[44]

Many of these cements are weak, hydrolytically unstable and of little practical utility. However, hydrolytically stable cements are formed from zinc and copper

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[44] A. D. Wilson and S. Crisp, *Brit. Polymer J.*, 1975, **7**, 279.

[45] A. D. Wilson and S. Crisp in 'Ionic Polymers', ed. L. Holliday, Applied Science Publishers, London, 1975, Ch. 4.

[46] K. A. Hodd and A. L. Reader, *Brit. Polymer J.*, 1976, **8**, 131.

[47] S. Crisp, H. J. Prosser, and A. D. Wilson, *J. Materials Sci.*, 1976, **11**, 36.

[48] A. D. Wilson, *Brit. Polymer J.*, 1974, 6, 165; D. A. Wilson and S. Crisp, 'Organolithic Macromolecular Materials', Applied Sciences Publishers, London, 1977, Ch. 4.

[49] S. Crisp, A. D. Wilson, J. Elliot, and P. Hornsby, *J. Appl. Sci. Biotech.*, 1977, **27**, 369

oxides,[12,46,47] special aluminosilicate (ASPA) glasses,[16,48] and the minerals willemite and muscovite.[49] Of these cements those of zinc oxide, the so-called zinc polycarboxylate cements[12] and of calcium aluminosilicate glasses, the ASPA (or glass-ionomer) cements,[16,48] are of importance as the find practical applications for dentistry. These cements are notable for being bland towards living tissues and adhesive towards enamel, dentine, and base metals. Thus, stainless steel orthodontic buttons can be directly attached to teeth. Traditional dental cements are not adhesive and often irritant towards living tissues. Ionic polymer cements have certain features in common with the alginate impression materials, which are formed by an aqueous ionic reaction in solution between alginic acid and metal salts.

A. Ion Binding and Gelation.—Ionic polymer cements stiffen and set as the result of the neutralization of an aqueous solution of a poly(alkenoic acid) and the formation of an insoluble gel of multivalent metal polysalts. There are underlying molecular phenomena associated with these physical changes. During neutralization there are changes in the molecular configuration of the polymer chains, which extend as they acquire negative charges, causing the viscosity of solutions to increase.[50] Chemical gelation is also associated with the phenomenon of ion-binding.

Ion-binding. This is a phenomenon chiefly to be found in polyelectrolyte solutions. Polymer chains containing a high density of charged functional groups exert a considerable attraction on counter-ions which tend to remain in the proximity of these chains. These interactions can give rise to configurational and solvation changes. Generally, as in the case of ionic polymer cements, the chains are polyanions and the counter-ions are cations. There are a variety of binding situations which are determined by the nature of the cation and the polyanion, *i.e.* size, configuration, charge, charge distribution, polarizability, *etc.* A distinction may be made between non-specific long range electrostatic attractions, 'ionic atmosphere binding', and specific short range attractions, 'site ion-binding'.[51,52] Specific ion binding may be identified by a number of techniques which have been reviewed by Strauss.[52]

The strength of ion-binding depends on the acid strength,[53] molecular configuration,[54] and the number and distribution of ionized carboxy acid groups on the polymer chain. Ion-binding is most marked in polyelectrolyte solutions, where the co-operative effect of electrical charges strung along the polymer chain exerts a considerable influence over the counter-ion. Multivalent cations are more

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[50] A. Katchalsky and H. Eisenberg, *J. Polymer Sci.*, 1951, 6, 145.

[51] H. Morawetz, *Fortschr. Hockpolym. Forsch.*, 1958, **1**, 1; M. L. Miller, 'The Structure of Polymers', Reinhold, New York, 1966, Ch. 12.

[52] U. P. Strauss, in 'Polyelectrolytes', ed. E. Selegny, M. Mandel, and U. P. Strauss, Reidel Publishing Co., Dordrecht-Holland/Boston, U.S.A., 1974, p. 79.

[53] V. Crescenzi, A. de Cherico, and A. Ripamonti, *Ricercia Sci.*, 1959, **29**, 1424; V. Crescenzi, V. De Rosa, and D. Maldarella, *ibid.*, 1960, **30**, 1680.

[54] N. Muto, T. Komatsu, and T. Nakagawa, *Bull. Chem. Soc. Japan*, 1973, **46**, 2711; N. Muto, *ibid.*, 1974, **47**, 1122.

strongly bound than univalent cations[55] and chelation greatly enhances bond strength.[56]

There are several different solvation states associated with the formation of ion-pairs, the ions may be in direct contact or separated by one or more layers of water of solvation. According to Ikegami,[57] whereas unionized poly(acrylic acid) has no water of solvation, there are two hydration regions associated with a fully ionized polyacrylate chain: an intrinsic sphere of primary hydration surrounding each carboxylate group and a cylindrical sheath of secondary water produced by the co-operative action of the carboxylate groups along the chain. These hydration states are affected by the nature of the cation. Multi- and bi-valent cations can partly or wholly displace both primary and secondary water, the extent of this disruption depends on the nature of the cation and the degree of ionization of the polyacid chain. By contrast, Li^+, Na^+, and K^+ ions only penetrate the secondary hydration region with the minimum disruption of solvated water.

Gelation. Ion-binding and desolvation of salt bridges result in the gelation of polyelectrolytes by precipitation. Examples are the precipitation of naturally occurring polyacids, alginic and pectic acids, by calcium ions,[58] and the gelation of aqueous solutions of poly(acrylic acid) by multivalent cations.[55,59] Wall and Drenan[59] have attributed this type of gelation to the formation of salt-like cross-links but recognised that there were factors other than coulombic interactions, and indeed configuration changes and desolvation of ions play a role. Ikegami and Imai[55] consider that precipitation of a polyelectrolyte does not occur if the ion-pair formed remains hydrated—excepting a salting-out effect at high cation concentrations. Precipitation at low concentration of cations can only occur if a hydrophobic salt bridge is formed and thus formation of this type of ion-binding is accompanied by desolvation, which can be observed by volume changes. Univalent ions, *e.g.* Na^+, are only weakly bound and do not precipitate poly(acrylic acid) solutions except at high concentrations. More strongly bound bivalent ions, such as Ca^{2+}, even when present in low concentration, will precipitate poly(acrylic acid) that has been ionized to the extent of 25 %. However, the highly hydrated Mg^{2+} ions although strongly bound will not precipitate poly(acrylic acid) until ionization is appreciable (60 % or more) and water is displaced from the salt bridge. Such observations indicate that the formation of 'contact ion-pairs', rather than 'solvent-separated' ion-pairs, is necessary for gelation.

Although numerous investigations have been made of ion-binding in dilute solution, extrapolation of these results to the situation pertaining to cement gel must be treated with caution. Studies of ion-binding in concentrated solutions

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[55] A. Ikegami and N. Imai, *J. Polymer Sci.*, 1962, **56**, 133.

[56] F. T. Wall and S. J. Gill, *J. Phys. Chem.*, 1954, **58**, 1128; A. M. Kotliar and H. Morawetz, *J. Amer. Chem. Soc.*, 1955, **77**, 3692; H. P. Gregor, L. B. Luttinger, and E. M. Loebl, *J. Phys. Chem.*, 1955, **59**, 34.

[57] A. Ikegami, *J. Polymer Sci.*, 1964, **A2**, 907; A. Ikegami, *Biopolymers*, 1968, **6**, 431.

[58] I. Michaeli, *J. Polymer Sci.*, 1960, **48**, 291; D. A. Rees, *Chem. and Ind.*, 1972, 630; G. R. Seeley and R. L. Hart, *Macromolecules*, 1974, **7**, 706.

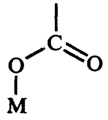
[59] F. T. Wall and J. W. Drenan, *J. Polymer Sci.*, 1951, **7**, 83.

and in gels present some difficulties, and are rare. The only technique that has been used in this connection is i.r. spectroscopy. Leyte *et al.*[60] have used this method to study ion-binding between alkali and alkaline earth metal ions and poly(alkenoic acid) and have concluded that the binding is purely ionic and nonspecific in character. Crisp *et al.*[47,61] have applied the attenuated total reflectance technique to study ionomer cement gels formed by the reaction of metal oxides and silicates with poly(acrylic acid) solutions. The frequency shifts of the symmetric and asymmetric stretching bands of the carboxylate group were used to determine the type of bonding. The binding of Na^+, Mg^{2+}, Ca^{2+}, and perhaps Zn^{2+} ions to poly(acrylic acid) were found to be purely ionic (Table 5). The evidence for covalent character in the $Zn^{2+} \ldots {}^-OOC$ linkage is inconclusive. The Al^{3+} and Cu^{2+} apparently form both ionic and complex forms. Structure (1) may be assigned to the Al^{3+} complex and either structure (1) or structure (2) to the Cu^{2+} complex.

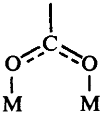
Table 5 CO_2^- *stretching frequencies*/cm^{-1} *of some metal polyacrylates*[a]

Metal	*Asymmetric stretch*	*Symmetric stretch*	*Structure*
Na^+	1540	1406	Ionic
Mg^{2+}	1535	1403	Ionic
Ca^{2+}	1533	1404	Ionic
Zn^{2+}	1540	1398	Ionic
Al^{3+}	1600, 1530	1390	Ionic, structure (1)
Cu^{2+}	1605, 1545	1405	Ionic, structure (1) or (2)
H^+	1690	1435	

(*a*) S. Crisp, H. J. Prosser, and A. D. Wilson, *J. Materials Sci.*, 1976, **11**, 36.



(1)



(2)

B. Poly(alkenoic acid) solutions.—Both types of ionic polymer cement used in dentistry, the zinc polycarboxylate cement and the glass-ionomer cement, use similar liquids—concentrated aqueous solutions of poly(alkenoic acids). These solutions are prepared directly by aqueous polymerization of alkenoic acids using ammonium persulphate as the initiator and propan-2-ol as a chain transfer agent.[45] The first liquids used in ionomer cements were 40—50 % w/w solutions of poly(acrylic acid), molecular weight range (M_w) 20 000—50 000[16,42,62] (Table 6).

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[60] J. C. Leyte, L. D. Zuiderweg, and H. J. Vledder, *Spectrochim. Acta*, 1967, **23a**, 1397.

[61] S. Crisp, M. A. Pringuer, D. Wardleworth, and A. D. Wilson, *J. Dent. Res.*, 1974, **53**, 1414.

[62] B. W. Bertenshaw and E. C. Combe, *J. Dent.*, 1972/73, **1**, 13; 1976, **4**, 87.

A number of alternative poly(alkenoic acid)s have been synthesized and include the homopolymers of maleic and methacrylic acid and copolymers of acrylic acid with other alkenoic acids, particularly itaconic acid.[63-65]

Table 6 *Composition of some glass-ionomer cements*[a-d]

Powder composition/% w/w

Fusion mixture	*Oxide glasses*			*Fluorine-containing glasses*		
	A	*B*	*C*	*D*	*E*	*F*
SiO_2	35.9	30.8	21.9	35.0	32.2	29.0
Al_2O_3	30.6	26.1	37.2	29.7	27.3	16.6
CaO	33.5	43.1	40.9	26.2	3.0	—
CaF_2	—	—	—	9.1	37.5	34.3
Na_3AlF_6	—	—	—	—	—	5.0
AlF_3	—	—	—	—	—	5.3
$AlPO_4$	—	—	—	—	—	9.9

Liquid composition

1. 50.0% w/w poly(acrylic acid), $\bar{M}_w$ = 23 000
2. 47.5% w/w poly(acrylic acid), $\bar{M}_w$ = 23 000 and 5.0% w/w tartaric acid.
3. 47.5% w/w poly(acrylic/itaconic acids), $\bar{M}_w$ = 23 000 and 5.0% w/w tartaric acid.

(*a*) A. D. Wilson and B. E. Kent, *B.P.* 1 316 129/1973; (*b*) A. D. Wilson, *Brit. Polymer J.*, 1974, **6**, 165; (*c*) A. D. Wilson and S. Crisp, *Brit. Polymer J.*, 1975, **7**, 279; (*d*) A. D. Wilson and S. Crisp, 'Organolithic Macromolecular Materials', Applied Science Publishers, London, 1977, Ch. 4.

The 2:1 acrylic acid–itaconic acid copolymer is superior to poly(acrylic acid) in that its viscosity in 50 % w/w aqueous solution is much less than that of poly(acrylic acid) and, moreover, does not increase with time and thus cause gelation. At first sight it appears surprising that the copolymer which has a higher COOH : total C ratio than poly(acrylic acid), and thus more propensity to form hydrogen bonds, should yield aqueous solutions which are less viscous and more stable. Three reasons for this behaviour may be advanced. Firstly, poly(itaconic acid) is known to form seven-membered rings with intramolecular hydrogen bonds[66] so reducing the propensity for intermolecular hydrogen bonds to be formed. Secondly, a random copolymer will not have the stereo-regularity of a homopolymer and so have less tendency to form a regular cross-linked array. Thirdly, some pendant groupings on the copolymer chains are more bulky than those present in poly(acrylic acid), thus increasing steric effects.

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[63] S. Crisp, B. G. Lewis, and A. D. Wilson, *J. Dent. Res.*, 1976, **55**, 299.

[64] A. Jurecic, B.P. 1 304 987/1973; S. Crisp, A. J. Ferner, B. G. Lewis, and A. D. Wilson, *J. Dent.*, 1975, **3**, 125; ESPE, B.P., 1 382 881, 1 382 882/1975; J. A. Barton, jun., G. M. Brauer, J. M. Antonucci, and M. J. Raney, *J. Dent. Res.*, 1975, **54**, 310.

[65] S. Crisp, B. G. Lewis, and A. D. Wilson, *J. Dent. Res.*, 1975, **54**, 1173.

[66] B. E. Tate, *Adv. Polymer Sci.*, 1967, **5**, 214.

C. Ion-Leachable Powders.—The zinc oxide powder used in zinc polycarboxylate cements is specially prepared by heating it either alone or with magnesium oxide (up to 10 % w/w) to 1100—1300°C for several hours.[45] This process is required to deactivate the powder and retard the setting reaction. These metal oxide powders[63,67] are generally similar to those used in zinc oxide cements (see Section 3A).

The formulation of the glasses used in the glass-ionomer cement is a far-more complex topic. Like the dental silicate cement, the glass-ionomer cement employs ion-leachable glasses as the powder component. These glasses are unusual; they are essentially calcium aluminosilicates characterized by a high Al : Si ratio, higher even than that found in the dental silicate cements, and are decomposed to silica gel by mineral acids.

There are two basic glass formulations used in this type of cement; these are (*a*) SiO_2–Al_2O_3–CaO and (*b*) SiO_2–Al_2O_3–CaF_2. Also compositions intermediate between these two main types may be used. In practice more complex formulations are used which incorporate auxiliary fluxes in the fusion mixture, *e.g.* Na_3AlF_6, $AlPO_4$, $Ca,(PO_4)_2$, and Na_2CO_3.

A number of advantages accrue from the use of a fluoride flux in glass preparation:

(i) temperature of fusion is lowered to 1000—1200°C;

(ii) release of fluoride during the cement-forming reaction improves workability, and these glasses, unlike simple oxide glasses, can form workable pastes with plain poly(alkenoic acid) solution,

(iii) fluoride appears to enhance the strength of cements (see Table 7), and

(iv) in dental applications topical release of fluoride from cement confers a cariostatic property on adjacent dental enamel.

Table 7 *Effect of fluoride in a glass on the strength of glass-ionomer*[a]

	Glass composition (atomic ratios)	
	A	*C*
Si	2.0	2.0
Al	2.0	2.0
Ca	2.0	2.0
O	9.0	8.8
F	0	0.4
Powder/liquid ratio/g ml^{-1}	2.5	2.5
Compressive strength 24 h/MN m^{-2}	74	125

(*a*) A. D. Wilson, *Brit. Polymer J.*, 1974, 6, 165.

These glasses vary in appearance from clear to opal. The microstructure of one of the opal glasses (Glass F, Table 6) has been studied in detail, [63] and found

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[67] B. W. Bertenshaw and E. C. Combe, *J. Dent.*, 1972/73, 1, 65.

[68] T. I. Barry, R. P. Miller, and A. D. Wilson, 'XI Conference on the Silicate Industry', Budapest, 1973, p. 881.

to be complex. There is a main calcium aluminosilicate matrix interspersed with phase-separated droplets. The droplets themselves are of complex morphology with an inner core of fluorite sheathed by a layer of calcium aluminosilicate (of higher calcium content than that of the surrounding matrix).

The glasses are ion-leachable and for the same reasons as those advanced for the acid-decomposible nature of those used for dental silicate cements (Section 3B p. 274). The reactivity of these glasses, towards acids, varies and in general depends on the $Al_2O_3 : SiO_2$ ratio. Obviously the higher the Al : Si ratio the higher will be the negative charge on the aluminosilicate network and hence the greater will be its susceptibility to acid attack. Since poly(acrylic acid) is weaker than phosphoric acid, the $Al_2O_3 : SiO_2$ ratio in glasses intended for glass-ionomer cements is greater than that in those for dental silicate cements.

D. Setting Reactions in Ionomer Cements.—Experimental investigations on the setting reaction of zinc polycarboxylate cements are limited; however, an i.r. spectroscopic study confirms that zinc oxide interacts with poly(acrylic acid) solution to form zinc polyacrylate salt.[47]

More extensive studies have been made on the glass-ionomer cements. The setting reaction between an ion-leachable glass (Glass F, Table 6) and a poly(acrylic acid) solution has been followed using chemical[69] and i.r. spectroscopic methods.[61] The cement-forming reaction takes place in a number of overlapping stages: the acid-attack on the glass when ion-leaching occurs, the initial precipitation and gelation, and long-term reactions—diffusion and hydration processes. Firstly, on mixing the glass powder and poly(acrylic acid) solution an immediate reaction occurs. Changes in the i.r. spectra (Table 8) are consistent with the loss of hydrogen ions from the poly(acrylic acid) solution ($COOH \rightarrow COO^-$) and the decomposition of the aluminosilicate glass network to silica gel. (EMPA[68] indicates that this attack occurs in the surface regions of the glass particles). Al^{3+}, Ca^{2+}, Na^+, F^-, and PO_4^{3-} ions are released from the glass and as the reaction continues they accumulate in solution (Figure 6) together with ionizing poly(acrylic acid) chains: concurrently, the pH of the aqueous phase increases. When these processes reach a certain point, the second stage of the cement-forming reaction is initiated as cations and anions begin to precipitate and gelation occurs (Figure 6), in this example after 10 min at 23 °C. The precipitation of an insoluble salt gel can be seen to result from the binding of multivalent cations to ionized poly(acrylic acid) chains (see Section 4A) with formation of desolvated ionic cross-links (salt bridges). As the reaction proceeds, more cations become bound, the number of cross-links increases and the salt gel hardens.

Although both calcium and aluminium are major constituents of the glass, i.r. spectroscopic[61] and chemical results[69] (Table 8, Figure 6) show that gelation or intial set results from the formation of calcium polyacrylate alone. According to i.r. spectroscopic data aluminium polyacrylate is not formed for about one hour, *i.e.* after set, although the cement used was prepared at a low powder/liquid ratio (1.5 g ml^{-1}) and consequently set more slowly than that used in the

[69] S. Crisp and A. D. Wilson, *J. Dent. Res.*, 1974, **53**, 1408, 1420.

Table 8 *Some changes occurring in the i.r. spectra (ATR) of a setting glass-ionomer cement*[a]

Species	*Band*/cm^{-1}	*Mode*	*Components*		*Fresh Paste*/5 min	*Set Cement*	*Hardened Cement*/24 h
			Powder	*Liquid*			
COOH	1700	C=O, stretch	—	Strong	Strong	Attenuated	Weak
COO$^-$(Al)	1600	COO$^-$, asym. stretch	—	—	—	Appears	Strong
COO$^-$(Ca)	1540	COO$^-$, asym. stretch	—	—	Appears	Enhanced	Strong
Silica gel	1050	Si—O, stretch	—	—	Appears	Enhanced	Strong
Glass	940		Strong	—	—	—	—

(*a*) S. Crisp, M. A. Pringuer, D. Wardleworth, and A. D. Wilson, *J. Dent. Res.*, 1974, **53**, 1414.

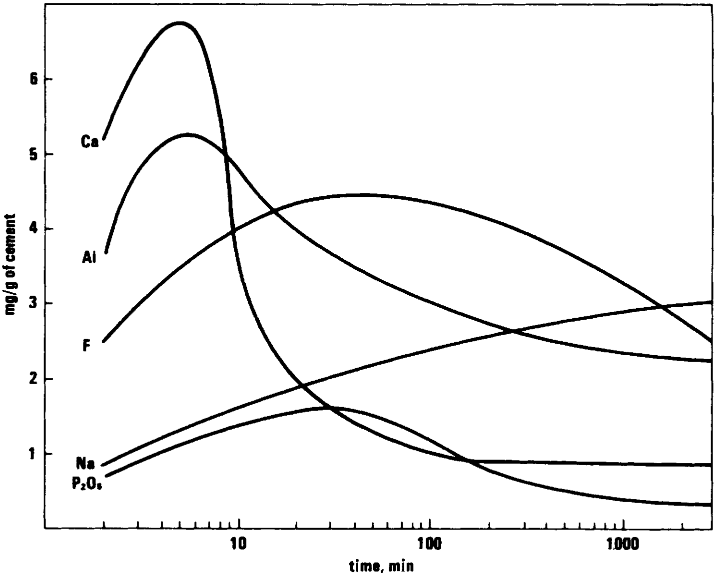


Figure 6 *The extraction and precipitation of ions in a setting glass-ionomer cement shown as soluble ion/time curves*
(Reproduced by permission from *J. Dent. Res.*, 1974, **53**, 1420)

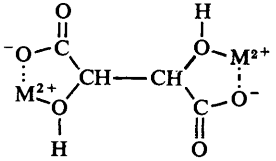
chemical studies (3 g ml^{-1}). At this stage of the reaction the cement is flexible and elastomeric. Subsequently, as the cement hardens to a rigid mass, aluminium, as well as calcium polyacrylate is formed (Table 8), and in the fully set cement both salts are present in equal amounts. Several reasons have been advanced to explain the delayed formation of aluminium polyacrylate. Differences in the morphology between Ca^{2+} and Al^{3+} ions in the glass surface may result in differential leaching. The aluminium ion, which is fully hydrated, is less mobile than the calcium ion. There is an increased entropy factor necessary for the formation of aluminium polyacrylate arising from the more demanding steric requirements for the binding of aluminium ions to polyacrylate chains.

The rheological changes accompanying these chemical processes are of clinical importance and can be affected by the chemical composition of the cement. Dental cements should be easy to mix, remain workable while being manipulated into position, and then set rapidly. Cements which steadily increase in stiffness are not desirable. Ideally, the paste should remain fluid and plastic right up to the moment of set, *i.e.* the set should be sharp, and thus combine maximum working time with minimum setting time. In this connection the presence of complexing agents in glass-ionomer cements plays a significant role.

The fluoride ion is important in controlling rheological parameters and setting characteristics and Crisp and Wilson[66] have shown that the fluoride ion aids the extraction of cations from the glass powder. The release of fluoride ions also improves workability; the cement paste prepared from the 1150 °C glass is workable while that from the 1300 °C glass is not. Simple oxide glasses are also known to yield unworkable pastes with simple poly(acrylic acid) solutions.

These observations suggest that the formation of fluoride complexes plays an important role in the cement-forming reaction and aluminium is known to form a whole series of complexes ALF^{2+}, AlF_2^+, *etc.* The effect of complex formation will be to aid the extraction and transport of cations and to prevent their premature binding to polyanion chains.

Other complexing agents notably tartaric acid, can play a similar role, when incorporated in the liquid.[70] Such an addition improves ease of manipulation, prolongs working time and sharpens the set of the cement paste. Indeed, powders of simple oxide glasses not containing fluoride, which yield intractable and slowly setting pastes when combined with plain polyacid solutions, give workable cements when tartaric acid is added to the liquid. It has been suggested that the formation of metal–tartaric acid complexes aids the extraction of cations from the glass and, also, temporarily prevents them binding to the polyanion chains, thus preventing premature gelation and sharpening the set. In effect this amounts to the acid-base reaction taking place, initially, between the glass and tartaric acid and not between the glass and the polyacid. A further suggestion has been made that tartaric acid bridges pairs of metal ions as shown in structure (3).



(3)

This molecular unit may be more effective than a simple metal ion in bridging polyanion chains by reason of it having some flexibility.

E. Cement Structure.—Little is known about the structure of the zinc polycarboxylate cement. The binding of zinc ions to polyacrylate chains is, as indicated above, almost purely ionic.[47] Since nearly all the water contained in the cement is 'evaporable' and not tightly bound,[71] the structure of the cement may be similar to that of the fused zinc polyacrylate cement of Nielsen.[72] The structure of this cement was studied using *X*-ray diffraction and i.r. transmission spectroscopy, and measuring various mechanical and rheological properties.[72] It was concluded that pendant half-salt, in-chain di-salt, and a cross-chain di-salt structure were present in the material (Figure 7).

The microstructure of the glass-ionomer cement has been established

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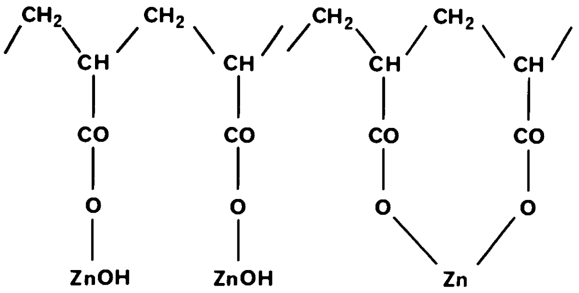
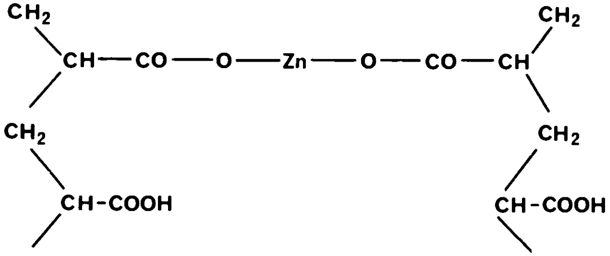
[70] A. D. Wilson, S. Crisp, and A. J. Ferner, *J. Dent. Res.*, 1976, **55**, 489; S. Crisp and A. D. Wilson, *J. Dent. Res.*, 1976, **55**, 1023.

[71] J. M. Paddon and A. D. Wilson, *J. Dent. Res.*, 1977, **56**, Special issue A, A175.

[72] L. E. Nielsen, *Polymer Preprints*, 1968, **9**, 596; J. E. Fields and L. E. Nielsen, *J. Appl. Polymer Sci.*, 1968, **12**, 1041.



Pendant half-salt In-chain di-salt



Cross-chain di-salt

Figure 7 *Proposed molecular structure for zinc polyacrylate salts*

(see Figure 8 on page 293).[68] Although chemically different the structure resembles that of the dental silicate cement: the matrix is particulate and the glass particles are degraded in the surface regions to silica gel. The composition of the matrix is quite different and composed of calcium and aluminium polyacrylates and unlike that of the dental silicate cement is adhesive to tooth structure and base metals.[73]

As indicated previously, the binding of Ca^{2+} ions to polyacrylate chains is purely ionic whereas that of Al^{3+} ions involve some complex formation. However, the exact molecular structure remains the subject of speculation; possibly there are structures present similar to those found in Nielsen's salt. In addition, since aluminium and calcium will be six-co-ordinate then there will be ligands, in addition to the polymer—COO^- groups, such as H_2O, OH^-, and F^-. Studies on the hydration states of these cements indicate that about half the water is 'non-evaporable' and tightly bound which suggests that ligand water is present in these cements. Structures of the type illustrated in Figure 9 have been postulated.[48]

This cement is adhesive towards base metals, tooth enamel (apatite), and

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[73] P. Hotz, J. W. McLean, I. Sced, and A. D. Wilson, *Brit. Dent. J.*, 1977, **142**, 41.

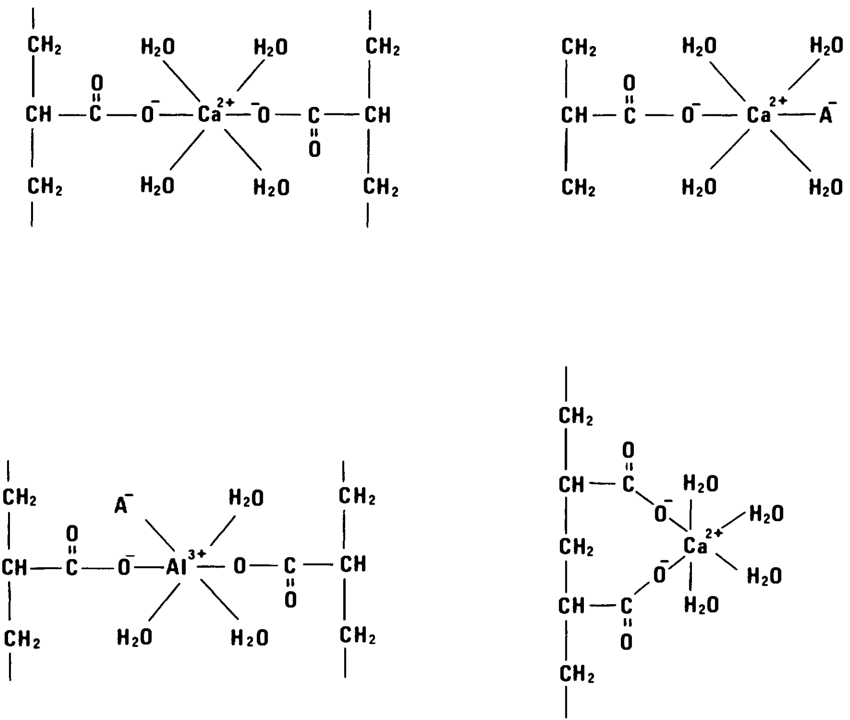

Figure 9 *Some postulated molecular structures present in the glass-ionomer cement*

dentine (collagen).[73] It does not adhere to chemically unreactive surfaces such as porcelain, gold, and platinum. Adhesion to oxide surfaces is believed to be by hydrogen and metal ion bridges formed between cement carboxylate groups and oxygen anions.

5 Non-aqueous Zinc Oxide Dental Cements

Zinc oxide can be treated with a large number of proton donating organic liquids to form cements, some of which are of practical use. These organic liquids include eugenol[9] and the 2-methoxy phenols,[74] the β-diketones,[10] other chelating agents,[10] and certain monocarboxylic acids,[75] which include 2-ethoxybenzoic acid.[11] Cements based on eugenol are the oldest and remain the most important in this class. They were developed in the years 1872—1875 when various combinations of phenolic compounds with zinc oxide were being explored for cement formation.[9] This cement has retained its popularity in dentistry as a temporary filling material and cavity base lining, to the present day. Although weak and

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[74] G. M. Brauer, H. Argentar, and G. Durany, *J. Res. Nat. Bur. Stand. Sect. A*, 1964, **68**, 619.

[75] E. W. Skinner, E. J. Molnar, and G. Suarez, *J. Dent. Res.*, 1964, **43**, 915; E. J. Molnar, *U.S.P.* N. 3 028 247/1962.

hydrolytically unstable it has ideal working properties, is easy to use and is tolerant towards living tissues. As with many dental cements its structure and setting reaction have only recently been elucidated.

The two components of the zinc oxide cement merit some discussion. Eugenol is a dimeric liquid, where the molecules are connected in pairs by an intermolecular phenolic hydrogen bridge. A second hydrogen bond (intramolecular) forms a five-membered ring (see Figure 10).

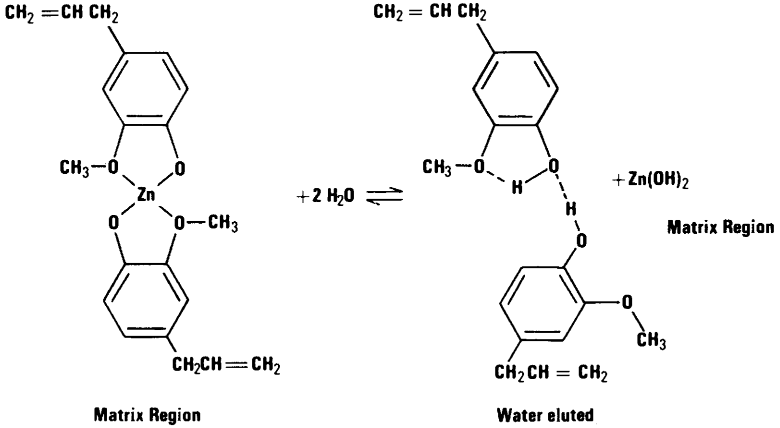

Figure 10 *Hydrolysis of zinc eugenolate to eugenol and zinc hydroxide showing the molecular structures of zinc eugenolate and eugenol*
(Reproduced by permission from *J. Dent. Res.*, 1973, **52**, 253)

The hydrogen bonds are dissimilar and are to be distinguished in the i.r. spectrum of eugenol (which exhibits H—O stretching frequencies at 3460 and 3520 cm^{-1} [18,76]) (Table 9); guaiacol has a similar structure (Table 10). Although Gerner *et al.*[76] consider the intramolecular bond in eugenol to be weaker than in the intermolecular bond, this conclusion is doubtful as the Badger–Bauer[77] formulae used, strictly only applies to linear hydrogen bonds.[78] In fact, dipole measurements[79] have shown that the intramolecular hydrogen bond in guaiacol is much stronger than would be expected from such calculations.

The zinc oxide powder is in a reactive form and is prepared either by oxidation of zinc metal or low temperature ignition of zinc salts. Increasing the ignition temperature deactivates the zinc oxide.[80] The paste, prepared by mixing the two components, sets to a friable cement consisting of zinc oxide particles

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[76] M. M. Gerner, B. A. Zadorozhnyi, L. V. Ryabina, V. N. Batovskii, and V. I. Sharchilev, *Russ. J. Phys. Chem.*, 1966, **40**, 122 (translated from *Zhur. fiz. Khim.*, 1966, **40**, 231).

[77] R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, 1937, **5**, 839.

[78] L. P. Kuhn and R. A. Wires, *J. Amer. Chem. Soc.*, 1964, **86**, 2161.

[79] J. H. Richards and S. Walker, *Trans. Farad. Soc.*, 1961, **57**, 399.

[80] D. C. Smith, *Brit. Dent. J.*, 1958, **105**, 313.

Table 9 *I.r. spectral differences between eugenol and a zinc oxide eugenol cement**[a]

Eugenol	*Deuterio-eugenol*	*Cement*	*Assignment*
3520, 3460	2600, 2560	Absent	O—H or O—D stretching
1370	1333	1319	Ring stretching coupled in eugenol with O—H or O—D in-plane deformation
1269	1269	1266, 1287	C—O stretching, aromatic O—CH_3 (split in cement)
1209	963	Absent	O—H or O—D in-plane deformation
794	Reduced	Absent	Probably an i.r. inactive mode activated by coupling with O—H out-of-phase deformation
480—450	< 400	Absent	O—H out-of-plane deformation (broad background absorption)

*Absorption bands given as cm^{-1}

(*a*) A. D. Wilson and R. J. Mesley, *J. Dent. Res.*, 1972, **51**, 1581.

Table 10 *I.r. spectral differences between guaiacol and a zinc oxide guaiacol cement**[a]

Guaiacol	*Deuterio-guaiacol*	*Cement*	*Assignment*
3490, 3440	2590, 2550	Absent	O—H or O—D stretching
1357	1332	1319	Ring stretching, coupled in guaiacol with O—H or O—D in-plane deformation
1208	951	Absent	O—H or O—D in-plane deformation
650—500	Not detected	Absent	O—H out-of-plane deformation (broad background absorption)

*Absorption bands given as cm^{-1}

(*a*) A. D. Wilson and R. J. Mesley, *J. Dent. Res.*, 1972, **51**, 1581.

embedded in a salt-like matrix.[81] The reaction is accelerated in the presence of moisture[80,82] or by the addition of zinc salts.[80,83]

The setting reaction between zinc oxide and eugenol is accompanied by changes in i.r. spectra as phenolic hydrogen is progressively replaced by Zn. Bands associated with phenolic OH groups diminish and ultimately disappear; similar observations have been made for the reactions between zinc oxide and deuterio-

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[81] A. D. Wilson, D. J. Clinton, and R. P. Miller, *J. Dent. Res.*, 1973, **52**, 253.
[82] R. F. Batchelor and A. D. Wilson, *J. Dent. Res.*, 1969, **49**, 883.
[83] W. Harvey and N. J. Petch, *Brit. Dent. J.*, 1946, **80**, 1.

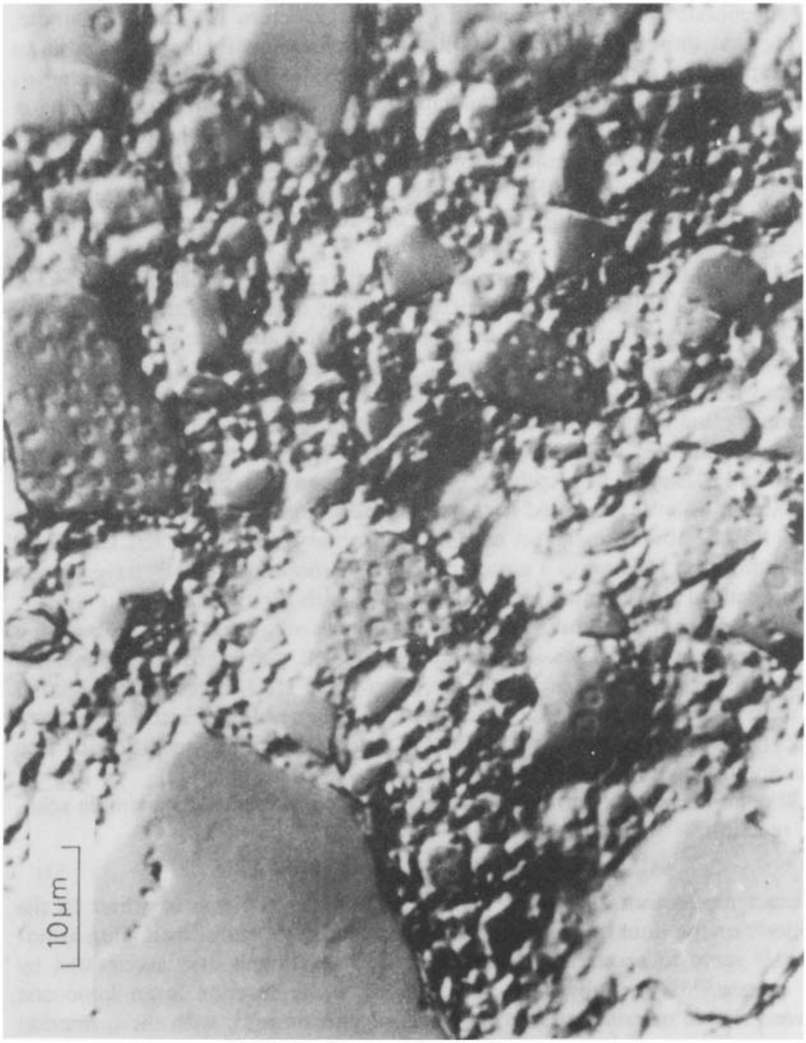

Figure 8 *The microstructure of the glass-ionomer cement* (Crown Copyright)

eugenol, guaiacol and deuterio-guaiacol[18] (Tables 9 and 10). These are the only spectral changes that occur in these cement-forming reactions and indicate that phenolic salts are formed. Copeland *et al.*[84] in 1955 reported that the cement matrix of the zinc oxide–eugenol cement has the empirical molecular formulae $Zn(C_{10}H_{11}O_2)_2$ and its *X*-ray diffraction pattern corresponds closely to that of zinc eugenolate salt. They proposed a chelate structure for zinc eugenolate, arguing that only phenolic bodies with methoxy groups in the *ortho* position were capable of cement formation with zinc oxide. The structure is seen as electrically neutral with two eugenolate ligands enclosing a central zinc ion (Figure 10). Wilson and Mesley[18] have pointed out that the i.r. spectra of eugenol and zinc eugenolate are remarkably similar; the only spectral differences are associated with the loss of OH groups, which is in accordance with the similarity between the dimeric structure of eugenol and the bisligand chelate structure of zinc eugenolate.

However, these workers in commenting on the work of Copeland *et al.*, have pointed out that although the three principal *X*-ray diffraction lines (at 17.0, 8.8, and 7.0 Å) are present in both the matrix material and zinc eugenolate salt, there were numerous minor differences. Indeed, the value of *X*-ray diffraction data may be doubtful for El-Tahawi and Craig[86] have shown that the zinc eugenolate matrix material is mainly amorphous. Gerner *et al.*[76] consider that the co-ordinate $Zn—OCH_3$ link is weak, but this conclusion is not definitive since Wilson and Mesley[18] consider that it is based on incorrect assignments.

Although water is generated in the cement forming reaction, thermal analysis shows it to be absent in the set cement,[18] an observation which has led to the speculation that H_2O plays a structural role. Wilson and Mesley[18] have argued that the central zinc ion may be six-co-ordinate, with the two eugenolate ligands in a square planar configuration with H_2O molecules occupying the two remaining diametrically opposed sites. It was further argued that since only one H_2O molecule is available for each zinc ion, then these H_2O molecules are shared and serve to bridge individual chelate molecules (Figure 11). Permittivity studies[86] support this view as they provide evidence for the initial generation of free water and its subsequent removal during the course of the reaction.

Although the cement-forming processes may be represented as a simple acid-base reaction:

$$2C_{10}H_{11}OOH + ZnO = (C_{10}H_{11}O_2)_2Zn + H_2O \qquad (3)$$

the exact mechanism has yet to be established. The addition of water to the powder[80] or the liquid,[87] or an increase in humidity of the surrounding atmosphere,[82] serve to accelerate the reaction. The reaction is also accelerated by zinc acetate.[80,83] The observations suggest that the reaction is an ionic one between simple or complex zinc ions and eugenolate ions, with the formation

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[84] H. I. Copeland, G. M. Brauer, W. T. Sweeney, and A. F. Forziati, *J. Res. Nat. Bur. Stand. Sect. A.*, 1955, **55**, 133.

[85] M. Braden and R. L. Clarke, *J. Dent. Res.*, 1974, **53**, 1263.

[86] H. M. El-Tahawi and R. G. Craig, *J. Dent. Res.*, 1971, **50**, 430.

[87] R. Viellefosse, H. Vayson de Pradenne, and J. P. Zumbrunn, *Rev. Odont-Stromat*, 1958, **5**, 488.

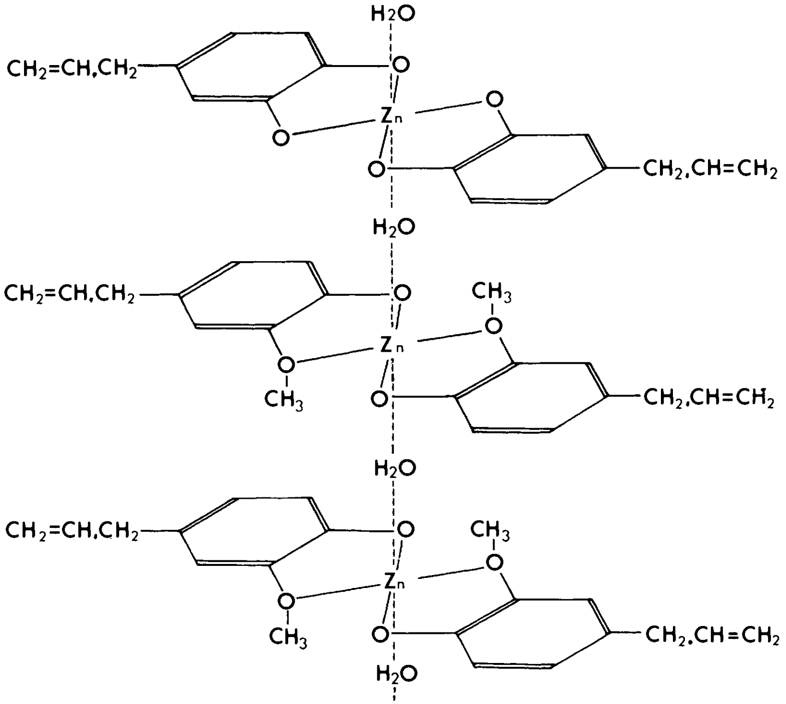

Figure 11 *Proposed* H_2O*-bridged structure for the zinc oxide eugenol cement matrix*

of zinc eugenolate. Zinc ions can be provided by addition of a zinc salt, *e.g.* zinc acetate which, therefore, acts as an accelerator. In the absence of zinc salts, zinc ions can be generated by the action of water on zinc oxide to convert it to a hydrate, which can then provide zinc in ionic form, as $Zn\ OH^+$ in $Zn(H_2O)_3\ OH^+$. In the absence of water the reaction is inhibited. However, once the reaction is initiated it becomes autocatalytic, since the reaction generates water. The rate of set depends on the nature of the zinc oxide used[80] and the temperature of ignition used in preparing the zinc salt is also important. Zinc oxide becomes progressively deactivated as this temperature is increased and when ignited to above 1000 °C the cement-forming reaction is totally inhibited.

The microstructure of zinc eugenolate cements may be briefly described. Studies using electron microscopy[81] have shown that the set cement consists of zinc oxide particles covered by outgrowths of zinc eugenolate which form a loosely connected matrix. The zinc eugenolate matrix develops in the region of the paste originally occupied by the eugenol liquid. At one time the zinc eugenolate matrix was considered to be crystalline. However, recent work indicates that the matrix is mainly amorphous, although small amounts of crystalline material are formed in cements accelerated by zinc acetate.[85] The friable nature of this cement has been attributed to its voided structure, poorly inter-connected matrix, and the inherent weakness of zinc eugenolate domains where the mononuclear ligands are joined by water bridges only. This cement can only be used as a temporary filling material because the matrix is hydrolytically unstable.[81,88] The CH_3O—co-ordinate link of the zinc eugenolate chelate is weak and the chelate hydrolyses into eugenol and zinc hydroxide. The zinc eugenolate is washed away from the zinc oxide particles and from the matrix. Some residual coherence is imparted to the hydrolysed cement by plate-like growths of zinc hydroxide which are relics of zinc eugenolate domains (Figure 10). The hydrolysis of zinc eugenolate may be regarded as a reversal of the original cement-forming reaction.

Other phenolic substances have cement-forming capability provided certain structural conditions are met. While simple phenol does not form a cement certain methoxyphenols, other than eugenol, do.[74] These are all 2-methoxyphenols: 2-methoxyphenol (guaiacol), 4-propenyl-2-methoxyphenol ('iso-eugenol' an isomer of eugenol) and 4-n-propylmethoxyphenol. The more acidic 4-propenyl-2-methoxyphenol reacts somewhat faster than eugenol since the propenyl group withdraws electrons from the aromatic ring. The 3-methoxyphenols, for geometric reasons, cannot form chelate rings with zinc ions and certain 2-methoxyphenols which have substituents adjacent to the methoxy and hydroxy groups cannot form cements, either because of the steric effects of these groups, which interfere with the chelation reaction. Examples include two isomers of eugenol, 3-allyl- and 5-allyl-2-methoxyphenols, and 5-n-propyl-2-methoxyphenol.

Other liquid chelating agents in addition to the phenols are capable of cement formation.[10] These include salicylaldehyde, 7-n-propyl-8-hydroxyquinoline and, more particularly, a whole range of β-diketones for which diketones, the substituent groups adjacent to the keto groups are important. Thus acetylacetone, which has methyl groups, readily forms a cement with zinc oxide whereas others, which contain bulky alkyl groups, do not.

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[88] A. D. Wilson and R. F. Batchelor, *J. Dent. Res.*, 1970, **49**, 593.