Investigation of the Nature of Degradation Products of Dental Luting Cements by Atomic Absorption Spectrophotometry

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The aim of this study was to examine the nature of degradation products of dental luting cements, life base, temp bond, carboxylate cement and durelon. Disintegration studies were done using standard cement disks (20 mm in diameter × 1.5 mm thick). The cement disks were prepared according to the manufacturer's recommendations and immersed in 50 mL of water for 7 d. Co, Cu, Cr and Zn in the test solutions were determined by atomic absorption spectrophotometry. In the temp bond cement (ZnO eugenol), Zn is major constituent of the cement. But only minor constituent of the leachate; conversely, Co and Cu, only minor constituents of the cement. Zn and Co are major constituents of the durelon and carboxylate cements. Carboxylate cement was second lowest in loss of material in this study.

Key Words: Chemical structure, Dental luting cements, Degradation.

INTRODUCTION

Various types of luting cements are available for cementation of indirect restorations. These cements differ from one another in both mechanical and biological properties. *In vitro* tests, in particular, show considerable variation in rates of solubility and disintegration[1].

One of the most important properties which determine the durability of luting cements in the mouth is their resistance against dissolution or disintegration[2]. The chemical composition of the test medium of water, differs from oral fluids and thus there is no element of abrasion in the test[1]. The test only measures the extent of the decomposition of the matrix accurately when the degradation products are water-soluble. If they are insoluble, they adhere to the cement and can not be measured or transferred to the solution because there is no element of abrasion in the test[1]. The presence of excessively high amounts of soluble salts can result in absorption of water by the cement generating an osmotic pressure that can cause the cement to disintegrate[1].

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This investigation was designed to obtain more information about *in vitro* degradation rates of luting cements. The purpose of this study was to evaluate the nature of degradation products obtained by *in vitro* disintegration tests of some temporary and permanent cements.

EXPERIMENTAL

Representative brands of temporary and permanent cements were used in the tests (Table-1). The manufacturers' instructions were followed with respect to powder/liquid ratio and mixing procedure. The cement disks (20 mm in diameter × 1.5 mm thick) were prepared in the usual manner. Single disks of cement (1 h old) were immersed in 50 mL of water for 7 d.

TABLE-1
CEMENTS USED IN THIS STUDY

Materials	Chemical Nature	Lot No.	Company
Life base	Calcium hydroxide, zinc oxide	3-1071	Kerr, Orange, USA
Temp bond	Zinc oxide eugenol	3-1050	Kerr, Orange, USA
Carboxylate cement	Zinc oxide, magnesium oxide	1950471	Heraeus Kulzer, Dormagen, Germany
Durelon	Zinc oxide, magnesium oxide	150545	3M ESPE Dental Products, Seefeld, Germany

In the test, Co, Cu, Cr and Zn in solutions were determined by atomic absorption spectrophotometry (Perkin-Elmer orp, Analytical instruments, Norwalk, U.S.A.). The Flame method is based on the process whereby the light liberated by the burning of the sample by a flame is measured. Each element has a unique light spectrum. It is mostly used to determine elements such as Zn, Fe, Cu, *etc.* at ppm level. Before the sample is read, heavy metals have been prepared at different concentrations. Standard curves have been drawn. The quantity which meets at the drawn curves is the quantity in the sample[3,4].

The water of the sample solution (50 μL) is removed by drainage at 110 °C for 20-45 h. At 350-1200 °C for 20-45 h, the organic substances are removed by heating and at 2000-3000 °C for 3-10 h, they are atomized by heating.

Graphite works with argon gas and is used to determine the elements at ppb level. The chemical analysis of water-soluble materials going into solution shows that the erosion of cement is a complex phenomenon[5].

The data given in Table-2 for 4 common types of dental cements *i.e.*, life base, temp bond, carboxylate cement and durelon, show that the chemical composition of material leached differs considerably from that of the parent cements.

RESULTS AND DISCUSSION

In the dental life base and temp bond cement (ZnO eugenol), Zn is a major constituent of the cement, but only a minor constituent of the leachate; conversely, Co and Cu, which are only minor constituents of the cement, are major constituents of the leachate.

In the carboxylate cements (durelon and carboxylate cement), Zn and Co are major constituents of the cements (Table-2). In this study, carboxylate cement was second lowest in loss of material. Comparison of degradation products of used cements was shown in Fig. 1. These observations demonstrate that cements are not simple substances and that selective leaching of certain regions occur.

TABLE-2
DISINTEGRATION VALUES OF THE CEMENTS

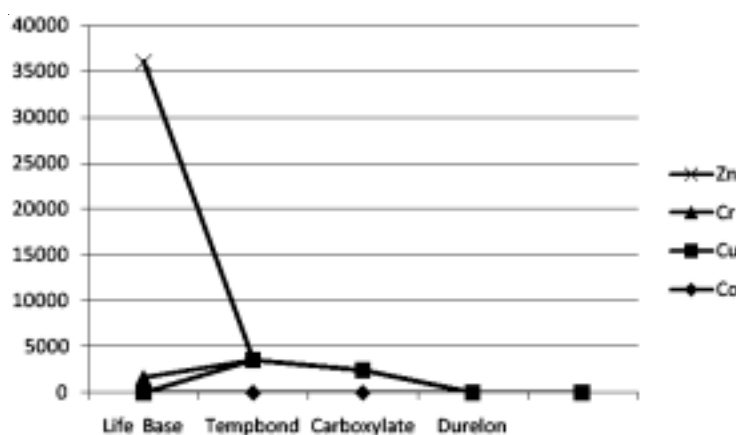| Cements | Material eluted (Mg/L) | | | |
| | Species | | | |
	Co	Cu	Cr	Zn
Life base	0.130	NS	1.628	34.456
Tempbond	0.091	3.532	NS	269.71
Carboxylate	0.057	2.462	NS	7101.9
Durelon	0.052	NS	NS	1290.9

NS = Non significant.

Fig. 1. Comparison of degradation products of used cements

The degradation process, which is mostly a sequence of absorption, disintegration and solution, was expressed by a time-constant[6]. The surface area of the specimen exposed to the medium appears to be a critical factor in the disintegration rate of certain cements[7]. One of the products of degradation *i.e.*, zinc hydroxide, is almost insoluble in a neutral solution so that the small concentrations of zinc ions in solution, which are estimated by the test, give no indication of the extent of the decomposition of the cement. Thus, the test seriously overestimates the durability of this cement[1].

A true indication of disintegration can only be obtained by weighing the specimen before and after the test and removing loose degradation products, zinc hydroxide and some zinc oxide filler[1].

In general, the dental silicate cement has a higher solubility and disintegration figure than zinc phosphate cement because it contains soluble sodium salt and hardens at a slower rate. It is, however, more stable under oral conditions. Zinc oxide-eugenol cement, exhibited the most rapid loss of material[8]. The stability of dental cement in a test solution can only be estimated once the cement has been fully hardened and the soluble reaction products are removed by water leaching. Such tests have shown, that in the long run, zinc oxide-eugenol cements are hydrolytically unstable[1]. Zinc oxide-eugenol cement is a low-strength base used as a temporary cement filling in the event that the patient will return at a later date for a semi-permanent restoration. The powder is mainly zinc oxide and the liquid is eugenol with olive oil used as a plasticizer.

A dental zinc oxide eugenol cement composition comprises of a combination of: 1.a) a putty-form base agent composition in which 5.0 to 50.0 % by weight of silicic acid having a mean particle size of 2 to 2000 millimicrons is contained in an eugenol-containing base agent composition, b) a putty-form setting agent composition in which 0.5 to 15.0 % by weight of an inorganic filler material having a solubility of up to 0.2 g/100 mL of water at 20 °C is contained in a zinc oxide-containing setting agent composition. 2. A cement composition, as defined in claim 1, which is an inorganic filler material, has a mean particle size of 2 to 2000 millimicrons. The non-eugenol-zinc oxide cements typically contain an aromatic oil and zinc oxide. Other ingredients may include olive oil, petroleum jelly, oleic acid and beeswax[9].

In this study, it is found that zinc oxide eugenol cement contains Co and Cu ions, respectively (0.091 and 3.532 mg/L).

The set mass of the cement consists of unreacted zinc oxide particles in a matrix of zinc eugenolate. It is well-documented that eugenol is able to penetrate dentin. In the literature, the diffusion rate of eugenol released from zinc oxide-eugenol (ZOE) increased to a peak after 1 day (about 0.3 nmol/min) and then decreased slowly to 0.08 nmol/min after 14 days[10]. Metals also have an allergenic potency. Ni, Co and Cr are recognized to be redoubtable sensitising agents, whereas only very few cases of allergic contact dermatatis are known to have Au, Pd, Pt, Ti, *etc.*[11].

Bis-eugenol, a white crystal at room temperature, probably does not mix with the test solution, because of its greater insolubility in water than eugenol. Even though a zinc eugenolate chelate between zinc oxide and the eugenol dimer is formed, the chelate has poor stability in moisture, resulting in the degradation of the 9:1 mixture. But the solubility and disintegration of the zinc oxide-eugenol with *bis*-eugenol met the ISO standard[12].

Nagasawa *et al.*[13] stated that a significant increase in disintegration was found for paste-mix type cements without eugenol at 28 d as compared to that at 7 d, whereas the paste-mix and powder-liquid type cements with eugenol did not show significant changes in disintegration values. This indicates that disintegration of the cements containing eugenol was least influenced in water over time after being

mixed. The major constituent in cement liquid for powder-liquid type cement or the accelerator used for paste-mix type cement, seems to be a factor affecting the disintegration in distilled water.

All dental cements set as the result of the replacement of protons in viscous, hydrogen bonded and acid liquids, such as phosphoric acid, eugenol or poly (acrylic acid), by metal ions supplied by simple or complex oxide powders. A metal salt is precipitated to form a cementing gel[1]. Zinc phosphate cement is composed of a zinc oxide powder and phosphoric acid[14]. The set cement is an anionic solid, where phosphate units are bound into a disordered 3 dimensional array by metal ions[15].

Hersek and Canay[16] found that after 8 months, the cement specimens were removed and the amount of solubility was measured using direct techniques. Scanning electron microscopy was used to evaluate surface topography after disintegration. The elements present in each cement were determined with energy-dispersive spectro-scopy. The zinc phosphate and zinc polycarboxylate cements demonstrated approximately equal solubility. Glass-ionomer cement exhibited significantly less solubility than both zinc phosphate and polycarboxylate cement.

Polycarboxylate cement is composed of a zinc oxide powder and polyacrylic acid. The zinc ions react with the carboxyl group of adjacent polyacrylic acid chains so that an ionically cross-linked structure is formed[17]. Glass-ionomer cement is composed of a fluorine-containing aluminosilicate glass powder and a liquid containing polyacrylic acid[14]. Metal ions become increasingly bound to the polyacid chain as the cement sets[15].

Some investigators[1,6,18] suggested that the elements detected in the zinc phosphate cement were Ca, Zn, Mg, Al and P. The elements detected in the polycarboxylate cement were Ca, Zn, Mg, Si and Sr; and the those that were detected in the glass ionomer cement were Al and Si.

The hardening reactions of conventional luting agents continue throughout the progression of the test and soluble reaction intermediates are formed. Consequently, zinc and magnesium are leached from both zinc phosphate and polycarboxylate cements and aluminium and silicon are lost from glass ionomer cement[6,19].

Wilson[1] stated that some oral fluids have an acidic character and thus causes the erosion of the cements. This acidity can be generated as the result of the action of certain *streptococci* and *bacilli* on sugars.

Kaplan *et al.*[20] investigated that the disintegration of 3 endodontic cements in water was determined quantitatively and qualitatively. Specimens were immersed in water for 48 h (GI), 7 (GII) and 45 d. The quantitative results had no correlation with the qualitative observations, which was probably due to the difference in the timing of the immersion of the materials.

There are some limitations to this test. The test medium is water and is therefore different to oral fluids. When evaluating the results of this laboratory study, it should be noted that there may be limitations to the direct application of *in vitro* result to *in vivo* situations. Further clinical testing and *in vivo* investigation are still required to

determine whether cement materials have the lowest degradation value. Iwaku *et al.*[21] suggested that the cements tested showed remarkably greater disintegration in the lactic acid solution than in the distilled water. Disintegration of the cements containing eugenol was least influenced in water over time after being mixed. The major constituent in cement liquid for powder-liquid type cement or the accelerator used for paste-mix type cement, seems to be a factor affecting the disintegration in distilled water[13].

Conclusion

Within the limitations of this study: (a) For the temporary cements, Zn is major constituent of the cement. (b) Durelon has the lowest value of disintegration of this study. (c) Zn and Co are major constituents of carboxylate cements. (d) These observations demonstrate that cements are not simple substances and that selective leaching of certain regions occurs.

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