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Chemical and structural changes in zinc polycarboxylate cements after immersion in dilute organic acid solutions

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The behaviour of zinc polycarboxylate cements in contact with dilute aqueous solutions of organic acids at concentrations close to those existing in buccal medium, was studied. The organic acids were acetic, citric, tartaric and lactic acids, at 0.01 M and 0.001 M. The elution of zinc and magnesium was 10–1000 times greater in acid than in pure water, and correlated with the concentrations and the dissociation constants, pK_1, of the acids tested. In all cases, important water losses were observed. In the 0.01 M acids, the cement structure collapsed to form a viscous, compact and homogeneous layer on the cement surface. In this layer, the polymeric carboxylic chains were regenerated from the zinc and magnesium polycarboxylate cement. Comparison with pure water showed that even the smallest concentration of the weak acids greatly modified the cement behaviour. This could explain the well-known differences in erosion processes between theoretical erosion predicted by standard specification tests and the *in vivo* situation. © *1998 Chapman & Hall*

1. Introduction

In buccal medium, dental cements are subjected to different kinds of constraints. Particularly, they must be resistant to solubility and disintegration processes. ISO (International Standards Organisation), ADA (American Dental Association), and AFNOR (Association Française de NORmalisation) specification tests have been established for dental cements immersed in water. The validity of these procedures is doubtful [1, 2]. Differences between *in vitro* disintegration tests and *in vivo* applications have been pointed out [3, 4]. Few studies on erosion processes of dental cements have been carried out using organic acids, despite their presence in buccal medium [5, 6]. The source of these acids can be both alimentary (citric, acetic and tartaric acids) and bacterial (lactic acid). The aim of this study was to evaluate the reactions of polycarboxylate cements placed in contact with dilute organic acids and in particular to study the chemical and structural alterations they undergo.

2. Materials and Methods

Two commercial polycarboxylate dental cements were prepared according to the manufacturers' instructions: Bondalcap (Ivoclar) and Bondex (Espe). The former cement being predosed, the powder and the liquid were mechanically mixed in an electronic vibrator (Vibramat plus, 4000 vibrations/min, 5 s). By this procedure, highly reproducible samples were obtained [7]. The latter cement was manually mixed. The composition of the cements are indicated in Table I.

All samples were pressed into cylindrical form (4.7 mm diameter, 15.0 mm length) of constant surface and volume, stored 48 h in a controlled atmosphere (37 °C and 100% RH) to ensure that the cements were stabilized [8], and then weighed. The control samples were placed in contact with 100 cm^3 water and the test samples in a 0.01 M or 0.001 M aqueous solution of acetic, citric, lactic or tartaric acid (Aldrich Chemical). All manipulation was performed under sterile conditions to avoid bacterial contamination. The samples were stored for 1 wk at 37 °C in an electronically regulated stove. The cements were then washed with distilled water and equilibrated at 37 °C and 100% RH atmosphere for 48 h and then weighed and analysed. The eluates from the experiments carried out with water and with the 0.01 M acid solutions were evaporated (70 °C, 48 h), and the dried residues were weighed and analysed. The weight of the dried residues in the eluates from the 0.001 M acid solution was below the detection limit.

The amounts of eluted zinc and magnesium were determined by atomic absorption spectrophotometry (AAS) on a Philips Pye-Unicam SPS Spectrometer using an air/acetylene flame. The pH was measured with a WTN pH 95 pHmeter with a double inner

TABLE I Composition of cements studied

Cement	Powder (P) % (wt/wt)		Liquid (L)	P/L ratio
Bondalcap	90.0 10.0	ZnO MgO	Polyacrylic acid	5
Bondex	78.3 7.6 14.1	ZnO MgO Dried polyacrylic acid	Water	7.5

standard (sensibility ± 0.01 pH). Scanning electron micrographs were obtained with a Leica Cambridge Stereoscan 360 microscope. Samples were vacuum-dried, gold-plated for secondary electron imaging (SEI) and carbon-plated for back-scattered electronic diffusion imaging (BSI). SEI and BSI were obtained using a 432 pA current intensity, and an electron dispersive X-ray mapping (EDXM) image, focused on ZnK_α, was obtained using a 22 nA current intensity.

X-ray diffraction diagrams (XRD) were obtained with an IBM PC computer-controlled Philips diffractometer, (100 scans, 3°–35°, 1600 points, acquisition delay 500 ms) using a CuK_α anticathode ($\lambda = 0.154\ 18$ nm) with a nickel filter.

Infrared absorption spectra were recorded on an FT-Bomen DA8 spectrometer, driven by a VAX3100 computer, in the 4000–400 cm^{-1} range. Samples were 1% (wt/wt), diluted in KBr (Aldrich Chemicals, spectroscopic grade) and pelletized under 9 $kN\,cm^{-2}$ pressure (pellet diameter 13 mm, thickness 0.2 mm).

Differential scanning calorimetry (DSC) was performed on a DSC4 Perkin–Elmer calorimeter. Indium was the calorimetric and thermometric reference, and all measurements were performed under nitrogen flow on 3 mg pelletized samples. The heating rate was 20 °C min^{-1}.

Thermogravimetric analysis was performed using a Setaram thermobalance, Ugine-Eyrand system, B 601 model, controlled with an RT 64 regulator.

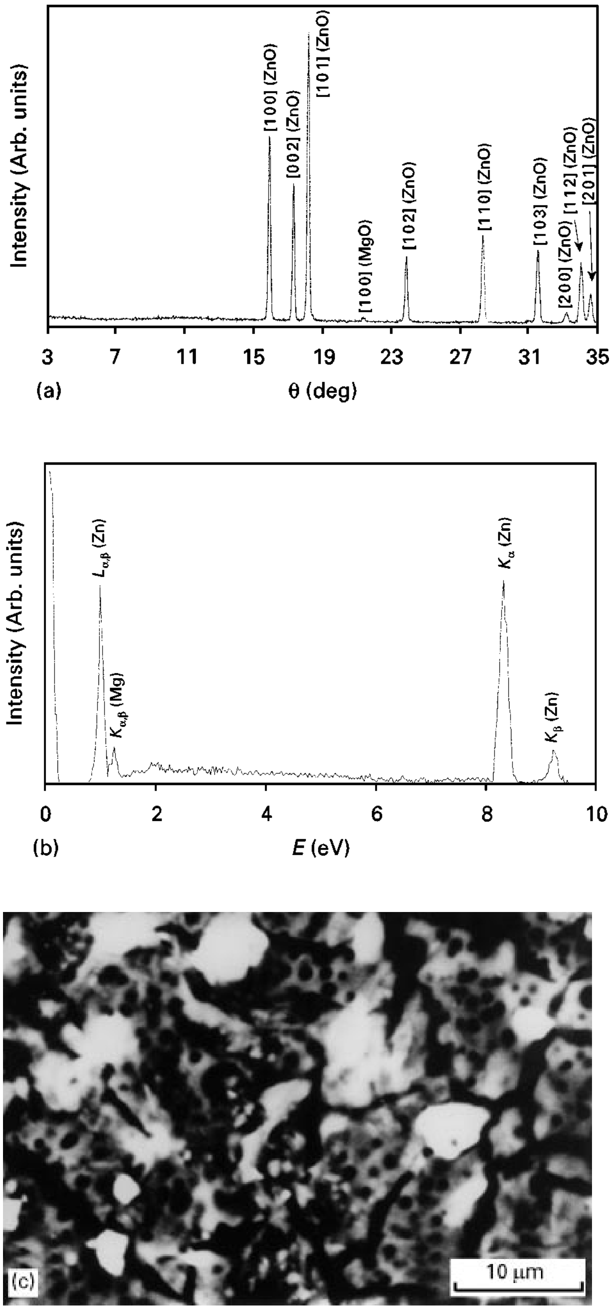


Figure 1 Characterization of the Bondex control sample: (a) X-ray diffraction pattern, (b) X-ray emission spectrum, (c) BSI.

3. Results

3.1. Cements immersed in water

X-ray diffraction patterns of both cements (Fig. 1a) only showed the presence of crystallized ZnO and MgO. The X-ray emission spectra (Fig. 1b) showed that zinc and magnesium were the only atoms present (detection for $Z > 9$). Therefore, if additives like Al_2O_3, SnF_2, SiO_2, CaO, iron or titanium were present, they represented less than 1%. BSI showed macroscopic heterogeneity (Fig. 1c). Diffusion analysis showed white spots corresponding to areas with a high zinc and magnesium content, a grey background with low zinc or magnesium content and black parts (bubbles and fissures) which did not contain any zinc or magnesium. There were two types of bubbles: (i) numerous microbubbles (0.5–1 μm diameter) and (ii) macrobubbles (5 μm diameter) which were scattered throughout the cements; they were more numerous in Bondex than in Bondalcap. This is exemplified by the SEI in Fig. 2a and b, which show the surface and cross-section of a Bondalcap sample after contact with water. Despite this minor difference, the composition and structure of the two commercial cements was found to be similar and their reactions with the different acids led to the same results.

3.2. Cements immersed in dilute organic acids

Table II summarizes the measurements and analyses of the cements and the eluents. The mass loss of the cements was always higher than the total amount of zinc and magnesium eluted.

The comparison between cements immersed in water and those in contact with the 0.001 M acids

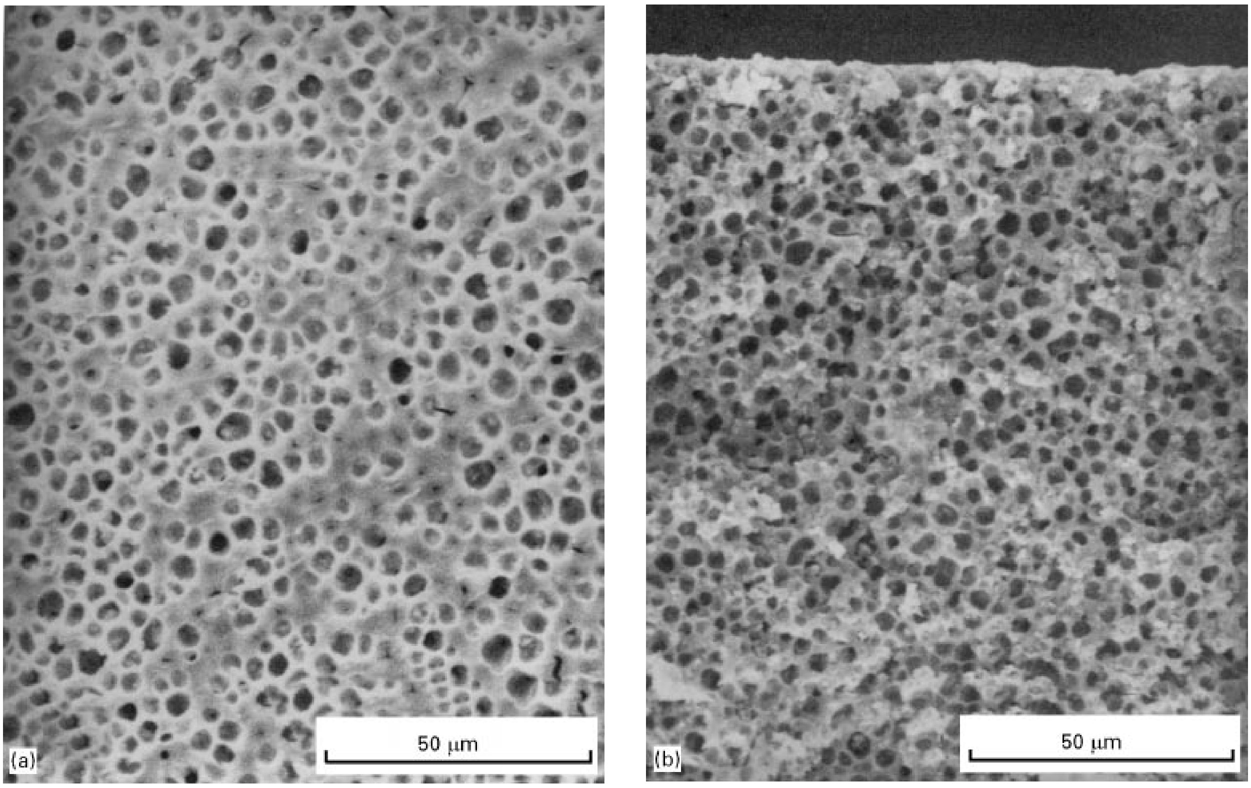


Figure 2 SEI of Bondalcap cement after contact with water for 1 wk: (a) surface, (b) cross-section.

showed no significant difference, except in the case of citric acid. The surface and cross-section showed the same aspect as for the water-immersed cements (Fig. 2a and 2b). After contact with 0.001 M citric acid, the surface of the cements showed a different aspect (Fig. 3a and b); the structure of the cement surface was replaced by a new structure, consisting of ovoid cavities situated side by side (average diameter, 21 μm). Only a thin layer (1–2 μm) of the material was concerned by this transformation.

Contact of cements with 0.01 M organic acids led to the formation of a viscous cement layer at the surface, henceforth called "gangue", with a more pronounced colour than the corresponding cement, i.e. orange for Bondalcap and yellow for Bondex. This gangue covered the entire cement core. After drying (25 °C, 0% RH), it became rigid and brittle. Fig. 4a–h show secondary electron images of the surfaces and of the cross-section of Bondalcap samples after contact with 0.01 M diluted acids. The gangue surface was smooth, even at very high magnification (× 10 000), with no trace of the type of particles observed by Matsuya *et al.* [6], which probably were bacteria. The aspect of the gangue was similar for these cements, but its thickness varied with the nature of the acid. Roughly, its thickness was 35 ± 5 μm when acetic acid was employed, 80 ± 12 μm with citric acid, 29 ± 8 μm with lactic acid and 55 ± 7 μm with tartaric acid. Cross-section views showed that the gangue was homogeneous: neither microbubbles nor unreacted zinc (or magnesium) oxide particles could be observed, even with high magnification. The gangue had less

TABLE II Cement mass loss, pH of solutions, amounts of zinc and magnesium eluted and mass of eluted dried residues after immersion of Bondalcap (Bp) and Bondex (Bx) polycarboxylate dental cements in pure water or organic acid solutions

Solution	Mass loss ($mg\,cm^{-2}$)		pH_{t0}[a]	pH_{t1}[b]		Eluted Zn ($mg\,cm^{-2}$)		Eluted Mg ($mg\,cm^{-2}$)		Mass of eluted dried residues ($mg\,cm^{-2}$)	
	Bp	Bx		Bp	Bx	Bp	Bx	Bp	Bx	Bp	Bx
Pure water	20.3	16.9	6.57	5.76	5.44	0.005	0.011	0.030	0.032	0.0	2.8
0.01 M acetic acid	41.5	25.7	3.20	4.09	3.93	5.70	6.48	0.66	0.73	19.1	15.2
0.001 M acetic acid	34.6	20.6	3.68	5.74	5.85	0.61	0.60	0.19	0.11	ND[c]	ND
0.01 M citric acid	74.3	65.3	2.48	3.09	3.14	18.9	22.9	2.94	2.68	44.2	38.9
0.001 M citric acid	39.3	23.3	3.03	5.56	4.90	2.75	1.92	0.137	0.250	ND	ND
0.01 M lactic acid	29.4	32.8	2.78	3.49	3.42	8.25	6.30	1.13	0.74	19.8	22.8
0.001 M lactic acid	18.0	19.0	3.43	5.05	5.16	0.636	0.614	0.167	0.139	ND	ND
0.01 M tartaric acid	54.9	48.0	2.52	3.00	3.07	20.0	16.1	2.11	1.49	35.1	39.4
0.001 M tartaric acid	20.5	24.2	3.06	4.95	5.68	2.18	1.84	0.282	0.186	ND	ND

[a] pH of solutions before contact with cements.
[b] pMH of solutions after 1 wk contact with cements at 37 °C.
[c] Not determined.

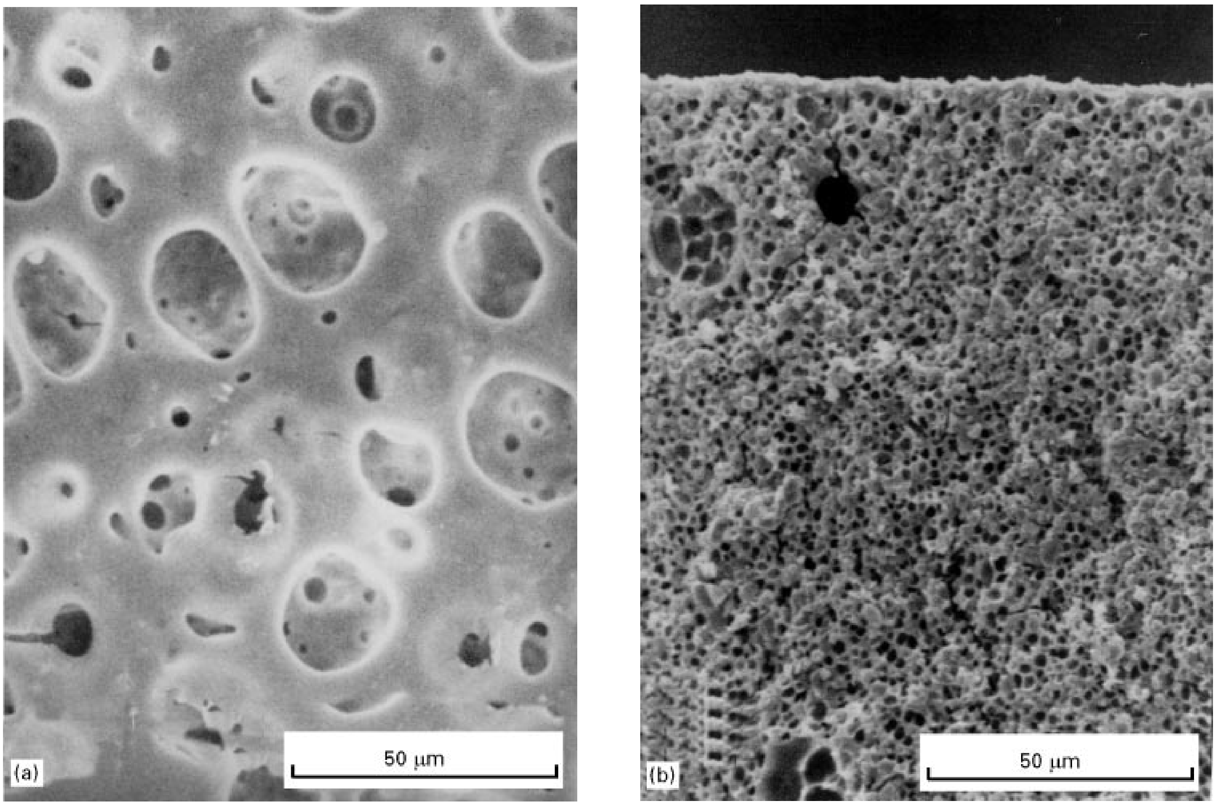


Figure 3 SEI of Bondalcap cement after contact with 0.001 M citric acid one week: (a) surface, (b) cross-section.

zinc than the bulk of the cement, as was shown by the EDXM technique (Fig. 5a and b). The infrared spectrum of the gangue indicated a shoulder at 1720 cm^{-1} (Fig. 6).

4. Discussion

4.1. Cement structure

X-ray emission analysis showed that the white areas in Fig. 1c correspond to unreacted zinc oxide particles,

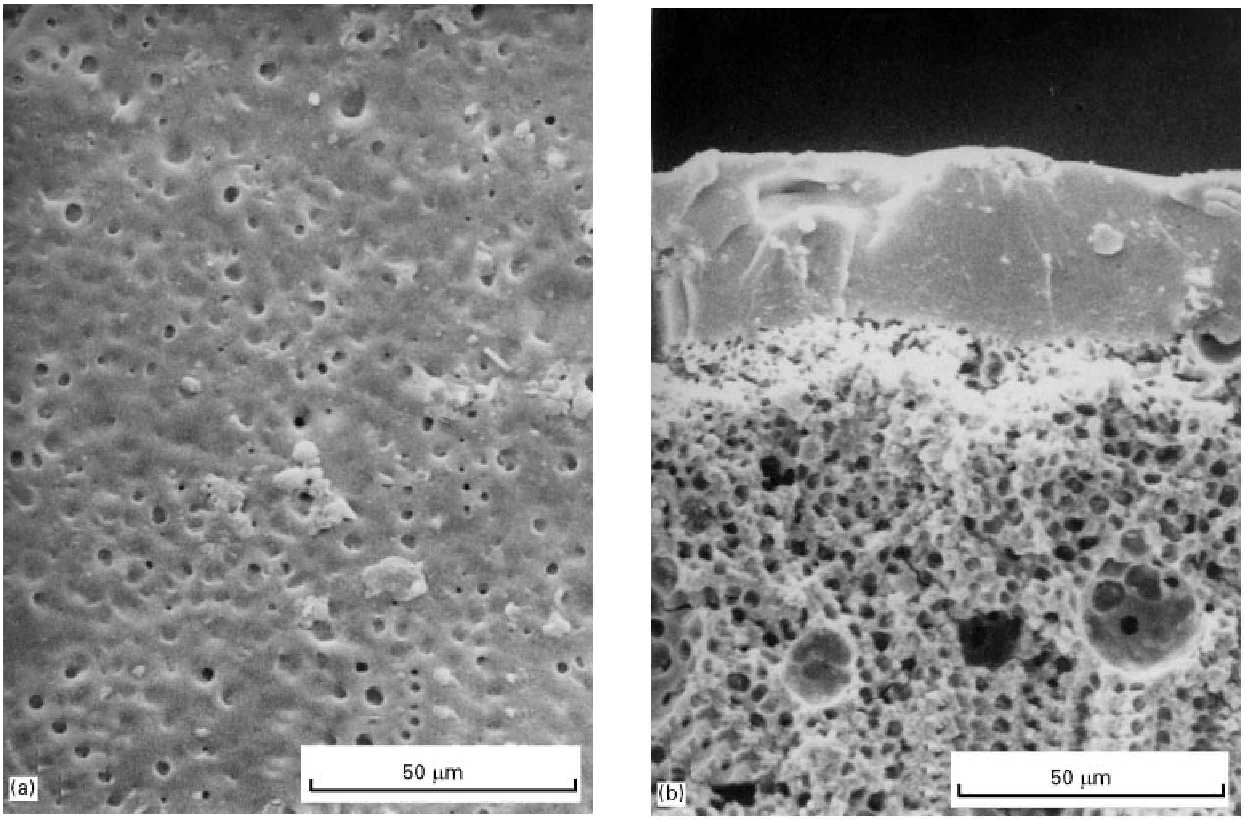


Figure 4 Set of Bondalcap cement after 1 wk contact with 0.01M acetic acid: (a) surface, (b) cross-section; citric acid: (c) surface, (d) cross-section; lactic acid: (e) surface, (f) cross-section; tartaric acid: (g) surface, (h) cross-section.

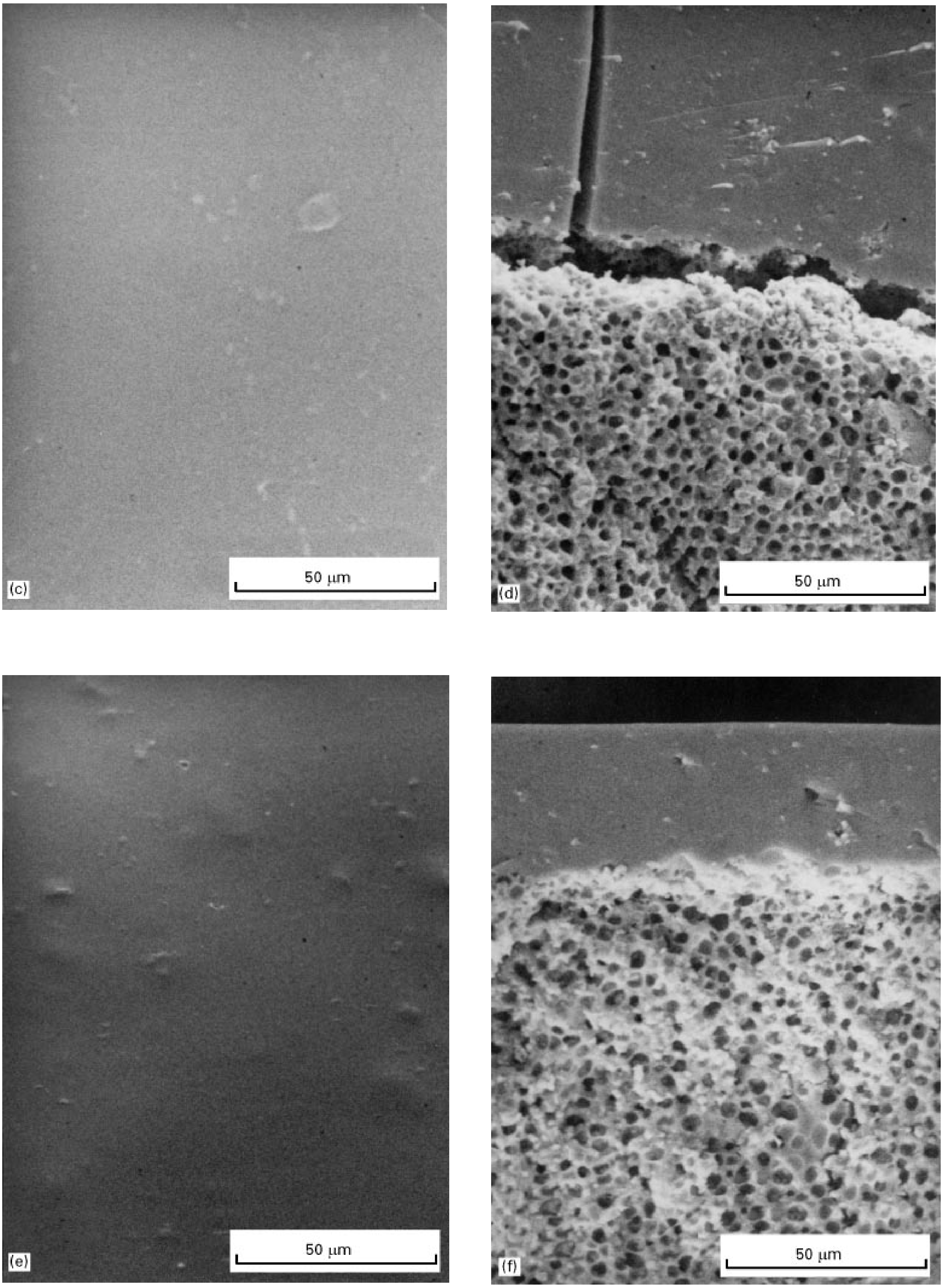
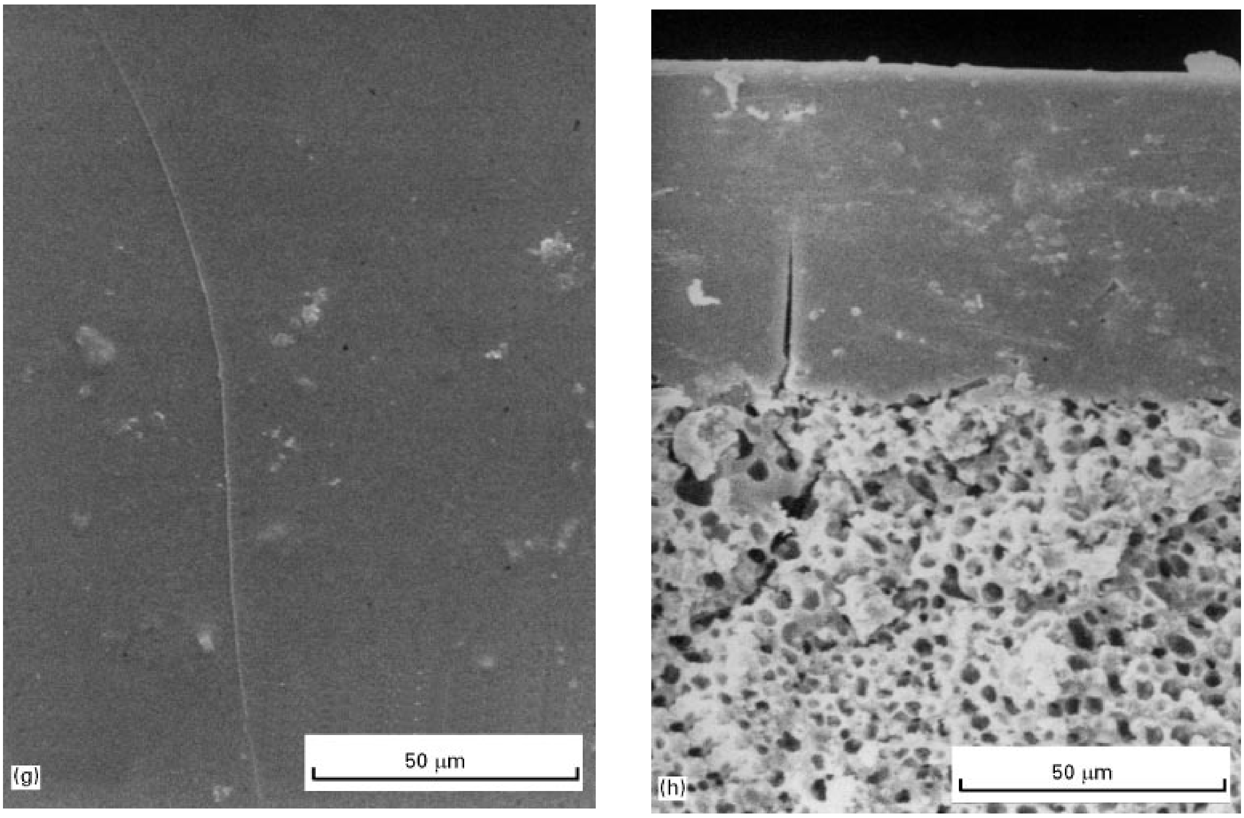


Figure 4 Continued

the grey background to the organic matrix and the black discs to bubbles. These results are in good agreement with the theory that zinc polycarboxylates are composite cements which have a "core–link structure" [9]. Polycarboxylate cements are constituted of unreacted zinc oxide and magnesium oxide particles surrounded by an organic–inorganic zinc and magnesium polycarboxylate matrix [10]. Water is another component of the cement, present as (i) free water (occlusal cavities), (ii) adsorbed water, and (iii) bound water associated with the organic–inorganic matrix [11]. In the polycarboxylate matrix, zinc and



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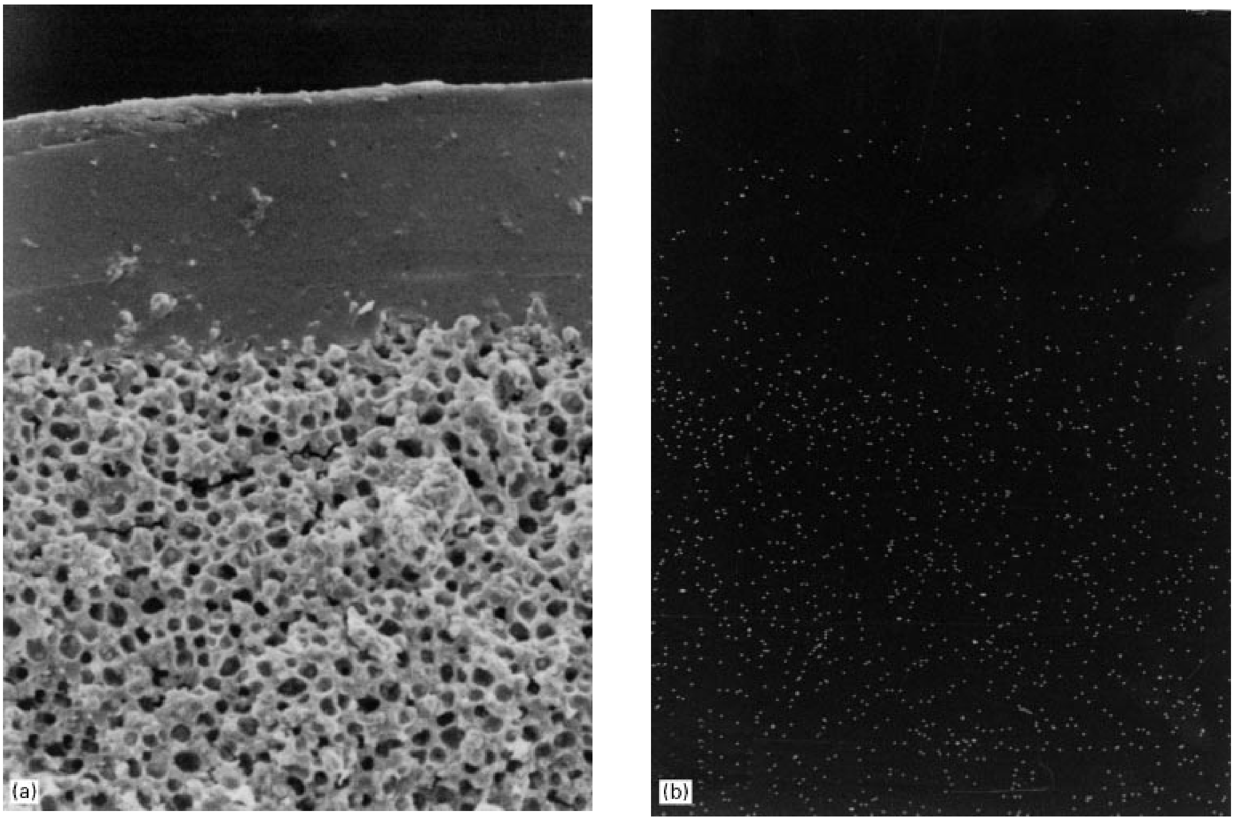

Figure 5 Cross-section SEI of the Bondex cement after contact with 0.01 M citric acid for 1 wk: (a) SEI, (b) ZnK_α imaging.

magnesium atoms are divalent and hexacoordinated [12] with the carboxylic functions of the surrounding polymeric chains. Some bonds are bridging and others are chelating [13]. These bonds are weak, as is shown by the values of the formation constants of zinc polyacrylate ($pK = 3.3$) and magnesium polyacrylate ($pK = 1.8$) [14]. Numerous water molecules are also present, either coordinated to the cations or polarized around the carboxylic groups [15, 16].

Bondalcap and Bondex are very similar cements: unreacted oxide particles are typically 2–3 μm diameter

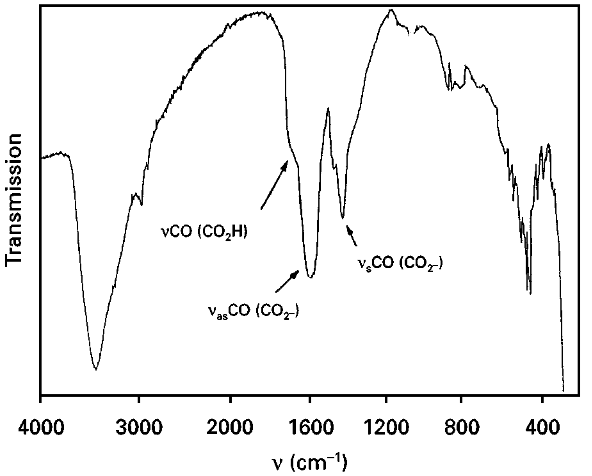

Figure 6 Infrared spectrum in the 1200–2000 cm^{-1} region of the gangue of the Bondex cement in 0.01 M citric acid.

and occlusal water represents roughly 10% (wt/wt) (when cements are stored in a 100% RH atmosphere). These cements only differed in the bubble size distribution; this is probably due to the fact that Bondalcap was prepared mechanically and Bondex manually [7]. This difference had no impact on the behaviour of the cements under our experimental conditions.

4.2. Behaviour of the dental cements in pure water

The results presented in Table I show that the average amounts of cations eluted from the cements in pure water was 0.008 mg cm^{-2} for zinc and 0.031 mg cm^{-2} for magnesium. These values are consistent with those reported by Crisp *et al.* [17]. The fact that almost four times more magnesium was eluted from the cements than zinc (average Zn/Mg = 0.26) is intriguing, because there was more zinc than magnesium initially present in the cements (average Zn/Mg ratio = 12.9). This phenomenon cannot be explained by the formation constants of the polycarboxylates because that for magnesium polycarboxylate is 32 times greater than that for zinc polycarboxylate. Rather, the excess magnesium in the eluate necessarily originated from the residual oxides. Indeed, the solubility of MgO (6.2 mg l^{-1}) is about four times greater than the solubility of ZnO (1.6 mg l^{-1}) [18].

Hydrolysis of the residual oxides occurs in water according to

$$MO + 5H_2O \rightarrow M(OH)_2(H_2O)_4 \qquad (1)$$

where M represents Zn or Mg, both of which are hexacoordinated, four water molecules being associated with the metal.

The observed mass loss of the cements (mean value 18.6 mg cm^{-2}) was far greater, however, than the combined amount of zinc and magnesium oxide loss (mean value 0.050 mg cm^{-2}, calculated from the zinc and magnesium elution values, Table I). The mean weight of dry residues in the eluate was estimated to be 0.4 mg cm^{-2}. If the mass loss of the cements had been due to dissolution of the organic matrix itself, the weight of the dry residues would have been much greater. Consequently, the mass loss can only be attributed to desorption of absorbed water.

4.3. Behaviour of the dental cements in 0.001 M diluted organic acids

The results given in Table II show that when cements are in contact with 0.001 M acid, the amount of zinc and magnesium eluted was 10- to 100-fold greater than when they were in water. Elution in citric acid was greater, followed by tartaric acid, lactic acid and acetic acid. This rank order is in good agreement with the values of their dissociation constants, pK_1, at 25 °C (Table III).

In acid, erosion of the cements was due not only to residual oxide dissolution but also to dissociation of the zinc and magnesium polycarboxylate matrix as shown by the ratio of eluted zinc to magnesium (Fig. 7). The Zn/Mg polycarboxylate matrix probably dissociated because more zinc was eluted than magnesium. The cations could come from the matrix by proton exchange according to

$$R(CO_2)_2M + 2H^+ \rightarrow R(CO_2H) + M^{2+} \qquad (2)$$

where R represents the chain bearing the carboxylate groups in the cement.

In an acid environment, this reaction leads to an increase in pH, as observed experimentally. Fig. 8 shows a clear correlation between cationic elution and variations in proton concentration. The increase of zinc and magnesium content in solution was seven times greater (in meq l^{-1}) than the corresponding

TABLE III Acid constants pK_a

Acid	pK_1	pK_2	pK_3
Acetic	4.8		
Citric	3.1	4.8	6.4
Lactic	3.9		
Tartaric	3.2	4.8	

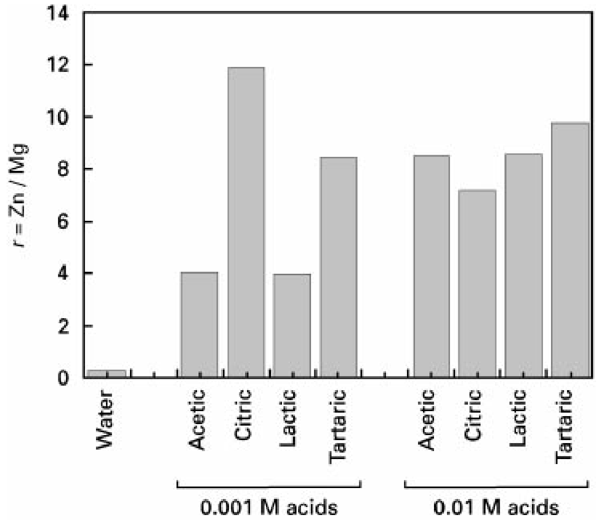

Figure 7 Mean value of the ratio of zinc to magnesium eluted from the cements as a function of the type of acid.

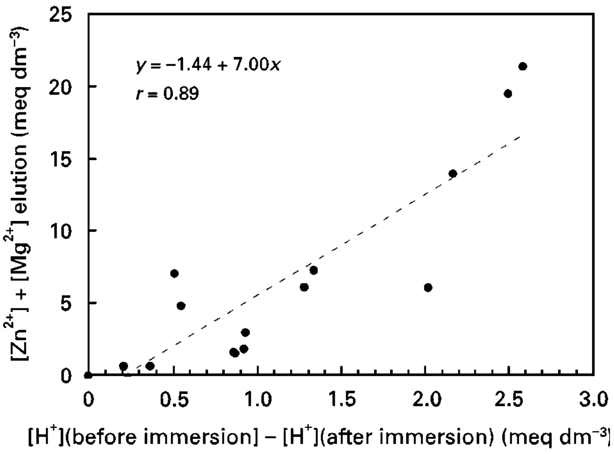

Figure 8 Cationic ion concentration versus $[H^+]$ variation in the various eluants before and after immersion of the cements (values for pure water were taken to be 0).

decrease in proton concentration. This fact indicates that some other mechanism is involved which compensates for proton losses.

A first possible source of the protons is hydroxide formation according to

$$M^{2+} + H_2O \rightarrow MOH^+ + H^+ \qquad (3)$$

which is favoured by an increase in pH. However, because the constants corresponding to this reaction are high ($pK_{Mg} = 11.4$ and $pK_{Zn} = 9.0$), this mechanism cannot explain the source of the protons.

Given the presence of complexing organic ligands in solution, a second possible source of protons is a donor–acceptor exchange reaction. Depending on the nature of the acid, different situations can be envisaged.

(i) With acetate and lactate

$$2LH + M^{2+} \rightarrow L_2M + 2H^+ \qquad (4)$$

where $L = CH_3CO_2^-$ (acetate) or $CH_3CH(OH)CO_2^-$ (lactate). The dissociation constant, pK, of these complexes being about 1 for zinc and magnesium, a simple calculation gives the following reaction constants: pK (acetate) = 8.6 and pK (lactate) = 6.8 (identical for both zinc and magnesium).

(ii) Complex formation with citrate leads to several chemical species, the following reaction predominates

$$2CiH_4 + M^{2+} \rightarrow (H_3Ci)_2M + 2H^+ \qquad (5)$$

The pK is 4.8 for zinc and 6.2 for magnesium.

(iii) Complexation with tartrate is calculated according to the following predominant reaction

$$2TaH_2 + M^{2+} \rightarrow (TaH)_2M + 2H^+ \qquad (6)$$

The pK is 6.1 for zinc and 7.4 for magnesium.

4.4. Behaviour in 0.01 M diluted organic acids

Zinc and magnesium elution in 0.01 M acid solutions was approximately ten times greater than in 0.001 M acids. Elution depended on the nature of the acid; the same rank order was observed in the 0.01 M acids as for the 0.001 M acid solutions. Elution was strongly correlated with pH changes, as shown previously (Fig. 8) and can be explained by the exchange reaction according to Reaction 2. The pH increase is retarded by the mechanisms explained by Reactions 3–6.

Protons/ion exchange appeared to be more important than hydroxide formation and led to carboxylate group re-acidification. The infrared spectra of the gangue (Fig. 6) exhibited a shoulder at 1720 cm^{-1}, characteristic of the δ_{CO} stretching vibration of CO_2H indicative of the presence of carboxylic groups. This re-acidification occurs in such a way that the magnesium and zinc bridging bonds in the matrix disappear, leading to a decrease of the mechanical cohesion of the matrix. The cement surface becomes viscous and the gangue appears. Fig. 3a shows a Bondalcap sample surface exposed to 0.001 M citric acid where a partially elaborated gangue appeared.

Cement losses are proportional to gangue thickness as shown by Fig. 9. Fig. 10 shows that mass losses are positively correlated with the dried elution solution masses.

The ratio of eluted zinc to magnesium reached a maximum mean value of 8.7, only weakly dependent

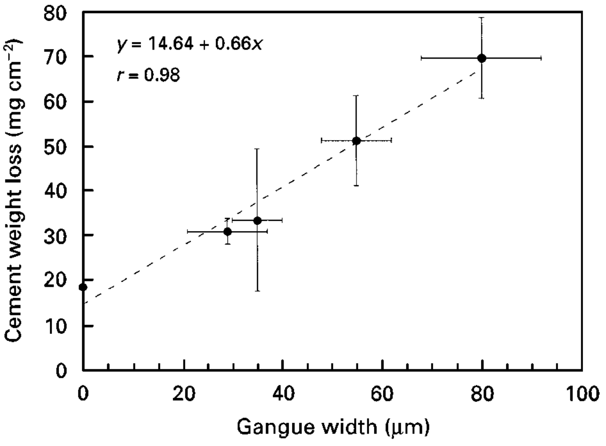

Figure 9 Cement weight loss (measured on samples equilibrated at 100% RH) versus the average gangue width.

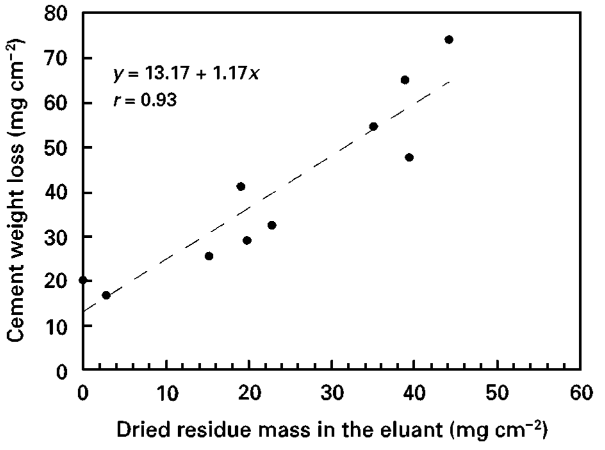

Figure 10 Cement weight loss (measured on samples equilibrated at 100% RH) versus dried residues in the eluant.

on the nature of the acid (Fig. 7), and smaller than their mean ratio in the cements before immersion (which is equal to 12.9). Some zinc cations remained in the gangue linked to polymeric chains whose acidity increased as zinc and magnesium were exchanged with protons.

5. Conclusion

The present report illustrates the importance of taking into account the presence of organic acids in buccal medium when analysing zinc polycarboxylate dental cement erosion.

Elution of zinc and magnesium is 10–100 times greater in 0.001 M acid solutions than in pure water and increases 10-fold when the acid concentration is multiplied by 10. Elution depends on the type of acid and decreases according to the following order: citric > tartaric > lactic > acetic.

The mass loss of the cements in pure water, as well as in dilute acid, can mainly be explained by: (i) water departure (occlusal and surface water), and (ii) residual oxide (ZnO and MgO) dissolution. Dissolution of the organic part of the cement (the Zn/Mg organic matrix) is negligible. Cation departure by protonation of carboxylate groups in the polymeric chains partly occurs only when the cement is in contact with 0.01 M acid. When cationic loss is high, the matrix tends to lose its rigidity: it becomes viscous and forms a compact, homogeneous layer at the cement surface. The thickness of this layer, called "gangue", is directly related to the acidity of the eluent.

The difference in behaviour of polycarboxylate dental cements in pure water and acid, even very dilute, could be a part of the explanation of known discrepancies between *in vitro* experiments (involving conventional standard tests of erosion in pure water) and *in vivo* investigations.

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