Hydration mechanisms of mineral trioxide aggregate

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Abstract

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Aim To report the hydration mechanism of white mineral trioxide aggregate (White MTA, Dentsply, Tulsa Dental Products, Tulsa, OK, USA).

Methodology The chemical constitution of white MTA was studied by viewing the powder in polished sections under the scanning electron microscope (SEM). The hydration of both white MTA and white Portland cement (PC) was studied by characterizing cement hydrates viewed under the SEM, plotting atomic ratios, performing quantitative energy dispersive analyses with X-ray (EDAX) and by calculation of the amount of anhydrous clinker minerals using the Bogue calculation. **Results** Un-hydrated MTA was composed of impure tri-calcium and di-calcium silicate and bismuth oxide. The aluminate phase was scarce. On hydration the white PC produced a dense structure made up of calcium silicate hydrate, calcium hydroxide, monosulphate and ettringite as the main hydration products. The un-reacted cement grain was coated with a layer of hydrated cement. In contrast MTA produced a porous structure on hydration. Levels of ettringite and monosulphate were low. Bismuth oxide was present as un-reacted powder but also incorporated with the calcium silicate hydrate.

Conclusions White MTA was deficient in alumina suggesting that the material was not prepared in a rotary kiln. On hydration this affected the production of ettringite and monosulphate usually formed on hydration of PC. The bismuth affected the hydration mechanism of MTA; it formed part of the structure of C-S-H and also affected the precipitation of calcium hydroxide in the hydrated paste. The microstructure of hydrated MTA would likely be weaker when compared with that of PC.

Keywords: hydration, mineral trioxide aggregate, Portland cement.

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Introduction

Mineral trioxide aggregate (MTA) has been used in dentistry for the past decade. The material has been patented as being composed of ASTM (American Standards for Testing Materials) type 1 Portland cement (PC) with a 4 : 1 addition of bismuth oxide added for radio-opacity (Torabinejad & White 1995). This material has been manufactured as ProRoot MTA. The similarity of MTA and PC as regards the basic elemental composition has been reported (Estrela *et al.* 2000, Funteas *et al.* 2003, Asgary *et al.* 2004). The production of calcium hydroxide as a by-product of the hydration reaction of PC and MTA was only published recently (Camilleri *et al.* 2005). MTA had been likened to calcium hydroxide (Holland *et al.* 1999) and it was postulated that the mechanisms of action of MTA, PC and calcium hydroxide were similar (Holland *et al.* 2001); however, none of the publications demonstrated from where the calcium ions originated. Camilleri *et al.* (2005) showed that MTA and PC had the same constituent elements as verified by Energy Dispersive Analysis with X-ray (EDAX) under the Scanning Electron Microscope (SEM) and also had the same

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phase constituents verified by X-ray diffraction analysis except for the bismuth oxide present in MTA. Thus, on hydration both MTA and PC would be expected to produce calcium silicate hydrate gel and calcium hydroxide. This would explain the similar mode of action of MTA and calcium hydroxide (Holland *et al.* 1999, 2001).

Portland cement is composed of four main oxides, namely lime (CaO) 60–66%, silica (SiO₂) 19–25%, alumina (Al₂O₃) 3–8%, and ferric oxide (Fe₂O₃) 1–5%. The lime is obtained by decomposition of limestone (CaCO₃) and the other components are produced from shale. Added calcium sulphate typically amounts to 3–6%. White PC is similar to the grey version but raw materials low in iron and other colouring transition metals such as chromium and manganese are used.

Portland cement is manufactured by a clinkering process or the partial fusion of the raw materials. This process includes decarbonization of limestone at 400–600 °C, formation of dicalcium silicate, tricalcium aluminate and tetracalcium aluminoferrite between 800 and 1200 °C and production of tricalcium silicate at 1400 °C by reaction of dicalcium silicate with the free lime (Taylor 1997) The final clinker is composed of:

55% tricalcium silicate	3CaO·SiO ₂ (C ₃ S)
20% dicalcium silicate	2CaO·SiO ₂ (C ₂ S)
10% tricalcium aluminate	3CaO·Al ₂ O ₃ (C ₃ A)
10% tetracalcium aluminoferrite	4CaO·Al ₂ O ₃ ·Fe ₂ O ₃ (C ₄ AF

It is assumed that the hydration mechanism of MTA is similar to that of PC. However, there is a lack of precise knowledge of the hydration mechanism of MTA. The aim of this study was to report the hydration mechanism of MTA.

Materials and methods

White MTA (ProRoot White MTA; Tulsa Dental Products, Tulsa, OK, USA; Batch number: A 0405 000 001 00) and white PC (Castle White PC; BS EN 197–1: 2000, Type CEM 1; strength class 52,5N) were used.

Determination of mineralogy of unhydrated MTA

A polished section of uncured MTA was prepared by mixing MTA powder with a small amount of epoxy resin. The resulting hardened disk was remounted vertically in fresh resin and sawn and polished so that it could be viewed in vertical cross-section. This doublemounting procedure was adopted in case segregation of MTA particles had occurred before the epoxy had set. A thin conductive coating of evaporated carbon was applied to the sections prior to examination in the SEM.

The SEM used was an ISI SS40 (ISI, Tokyo, Japan), with an energy-dispersive X-ray system (SAMx Numerix, Levens, France) and a standard beryllium window X-ray detector. The beryllium window was used to absorb X-rays emitted from light elements. Quantitative analyses were carried out using X-ray standards obtained from minerals for each element, with the exception of bismuth. A bismuth standard was obtained using particles of bismuth oxide in the uncured MTA. Oxygen was calculated by stoichiometry. The sections were examined using backscattered electron imaging.

Microscopy of cured MTA and PC

Mineral trioxide aggregate was mixed with the liquid provided in capsules to produce a water-to-MTA ratio of 0.5. One gram of cement (Castle White PC, manufactured to BS EN 197-1: 2000, type CEM I, PC strength class 52,5N) was mixed with 0.5 g distilled water, to give a water/cement (w/c) ratio of 0.5. The pastes were compacted in a rectangular mould 30 mm by 5 mm and 10 mm deep using a stainless steel plugger. The two materials were cured at 37 °C for 30 days, in sealed plastic (polythene) containers. This temperature was used to simulate body temperature. After 24 h, when the pastes had set and started to harden, a drop of additional water was added to each container to ensure that adequate water was available for curing. Curing was carried out using a thermostatically controlled water bath (MGW Lauda M 20; Leica Microsystemes SA, Rueil-Malmaison, France). After the pastes had cured, fractured pieces were immersed in acetone for 4 days to remove any remaining water, and then dried in a vacuum desiccator for 4 h. The dried paste pieces were set in epoxy resin using vacuum impregnation. The hardened resin block was sawn (Labcut 1010, Agar Scientific, Stansted, UK) and ground under copious water irrigation using progressively finer grits of abrasive paper to produce a flat surface. Fresh resin was applied to the flat surface to fill pores not filled with resin when originally embedded. Finally, the hardened surface was reground and polished. A thin conductive coating of evaporated carbon was applied to the sections prior to examination in the SEM.

Analysis of hydration products was performed both qualitatively and quantitatively by:

1. Identifying and labelling of hydration products viewed under the SEM in back scatter mode.

2. Examining the sections in more detail by collecting a series of 50 quantitative analyses of the hydration products and plotting the data as atomic ratios. Atomic ratios were used rather than the absolute values as the proportion of water present could not be quantified. Plots of Al/Ca versus Si/Ca were drawn.

3. Performing semi-quantitative analyses by scanning areas of the hydrated cement, thereby representing 'average' compositions of each mineral.

4. Calculation of the quantity of the main mineral phases in the cements performed by the Bogue calculation (Bogue 1929). Using the Bogue calculation the percentage of each clinker phase was calculated from the amount of the original raw mineral. The calculation was worked out as follows:

- $C_3S = 4.0710CaO 7.6024SiO_2 1.4297Fe_2$ $O_3 - 6.7187Al_2O_3$
- $C_2S = 8.6024SiO_2 + 1.0785Fe_2O_3 + 5.0683Al_2$ $O_3 - 3.0710CaO$
- $C_3A = 2.6504Al_2O_3 1.6920Fe_2O_3$
- $C_4AF = 3.0432Fe_2O_3$

The ferrite phase was absent from the white cement. All the alumina was assumed to be present in the aluminate phase as C₃A; again the required amount of calcium oxide was allocated to the phase and was subtracted from the bulk composition. The proportion of C₃A was thereby determined. The silica was assumed to be present as C_2S . The required amount of lime was allocated and subtracted from the bulk composition. Any lime remaining was used to combine with the C₂S to form C_3S . This decreased the quantity of C_2S already determined above. These determinations were carried out on clinker. As the cement contained calcium sulphate allocations were also made for the calcium present in the gypsum. This calculation also required the level of uncombined lime in the clinker. This value was not available for MTA. Thus, mineral proportions for a range of free lime contents were calculated.

Results

Determination of mineralogy of unhydrated MTA

In polished section the un-cured MTA was found to consist of particles (<1 μ m to approx. 30 μ m, occasionally up to 50 μ m) containing impure tricalcium silicate (alite) and impure dicalcium silicate (belite). Particles (10–30 μ m) of bismuth oxide were numerous (Fig. 1). The particles comprising the bulk of the



Figure 1 Back scattered scanning electron micrograph of un-hydrated MTA showing bright particles composed of bismuth oxide and darker particles composed of cement.



Figure 2 Back scattered scanning electron micrograph of un-hydrated MTA showing details of individual particles: alite (a); belite (b); gypsum (g); bismuth oxide (Bi). Darker areas within some particles are due to indentations in the surface and not a uniform phase of low atomic number such as the aluminate phase.

material were composed of alite or belite or a mixture of both (Fig. 2). Scattered particles of limestone or hydrated lime, gypsum and potassium aluminium silicate (assumed to be clay or feldspar) were also present. The aluminate phase normally present in white PC was scarce.

Microscopy of cured PC and MTA

The cement paste in the hydrated white PC had a moderately dense microstructure, with numerous residual unhydrated cement grains (Fig. 3). Most of



Figure 3 Hydrated white Portland cement: general view, showing moderately dense hydrates with scattered un-hydrated cement grains (pc). Light grey material in the matrix is calcium hydroxide and the darker grey is mainly calcium silicate hydrate (C-S-HO).



Figure 4 Hydrated white Portland cement: detail showing unhydrated residual un-hydrated cement (bright grains); calcium hydroxide (CH, white amorphous), 'outer product' (op) – or undifferentiated product – calcium silicate hydrate and inner product – or in-situ hydration product – calcium silicate hydrate. The dashed line around the residual cement grain at lower right indicates the original extent of the cement grain.

the residual unhydrated cement grains had a dense rim of hydration product made up of pure calcium silicate hydrate (C-S-H). This hydration product was formed both within the original volume of the cement grain (inner product) and also outside the original volume of the cement grain (outer product). The hydration products were calcium silicate hydrate (C-S-H), calcium hydroxide (CH), monosulphate phase and ettringite (3CaO·Al₂O₃·3CaSO₄·31H₂O) (Fig. 4). The hydration products were examined in more detail by collecting a series of 50 quantitative analyses of the hydration products and plotting the data as atomic ratios. The plot of Al/Ca versus Si/Ca showed a typical plot of points representing C-S-H, CH and intermediate points representing mixtures (Fig. 5). Another group of data points, less well defined but still distinct, represented a mixture of C-S-H and monosulphate (AFm) phase. Another three points represented mixtures of C-S-H and ettringite (Aft) phase. The Si/Ca ratio of the C-S-H was approximately 0.55–0.60, and the Al/Ca ratio approximately 0.05.

In section, the hydrated MTA had numerous large spherical pores at low magnification (Fig. 6). At higher magnification, numerous unreacted bismuth oxide particles were visible. C-S-H and CH were both present, but not readily discernible in the backscattered electron image (Fig. 7). X-ray microanalyses showed that the C-S-H had taken up bismuth, while the CH had not. CH and C-S-H appeared to be more intimately mixed. Unhydrated cement grains were numerous, often with dense rims of hydration product similar to those in the white PC. In some instances, the dense rims were present but the residual unhydrated cement particle was not present resulting in hollow grains.

Detailed examination of hydration products using a series of 50 quantitative analyses and plotting the data as atomic ratios (Fig. 8) revealed the presence of a mixture of CH and CSH. There was very little ettringite or monosulphate present (Fig. 8). The Si/Ca ratio of the C-S-H was approximately 0.60 and the Al/Ca ratio approximately 0.05. The Bi/Ca ratio increased with C-S-H content. The C-S-H contained approximately 5.5% bismuth as Bi_2O_3 by weight, or approximately 5.0% bismuth. The determined bismuth content may be an underestimate due to the high mean atomic number of bismuth oxide compared with the other phases.

Semi-quantitative analyses of both hydrated MTA and PC is shown in Table 1. The aluminium content and sulphur levels in the MTA compared with the white PC were low. The Bogue calculation of the main mineral phases (Table 2) of both cements showed typical proportions of alite, belite and aluminate for the white PC as reported in textbooks (Taylor 1997) and a low level of aluminate phase in the MTA regardless of the assumed value for the free lime.

Discussion

Chemical analysis of MTA was performed by characterization of the various compounds on electron

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Figure 5 Plot of atomic ratios of Al/Ca versus Si/Ca of hydrated Portland cement. Lines represent mixtures of phases. Data points are classified according to the most likely interpretation of their position on the plot. Points described as 'Higher Al/Ca' appear to be mainly AFm phase (monosulphate).



Figure 6 Back scattered scanning electron micrograph of hydrated MTA showing numerous spherical air voids up to $300 \ \mu m$ across mostly infilled with epoxy resin and some part-filled with calcium hydroxide.

micrographs. The double mounting procedure was adopted to ascertain that a representative section of the powder was being analysed. Chemical analyses can also be performed using Energy Dispersive Analyses with X-ray (EDAX) and also X-ray Diffraction analyses (XRD). EDAX only identifies the constituent elements of the material under study. This can lead to misconceptions on the actual compound composition of the material (Camilleri *et al.* 2005). MTA was always believed to be a tri-oxide based on the results of chemical analyses performed by EDAX which showed three distinct elemental peaks (Torabinejad *et al.* 1995). In actual fact the material was found to be



Figure 7 Back scatter electron micrograph of hydrated MTA showing un-hydrated cement particles (pc), calcium hydroxide (CH). Rims of inner hydration product (ic) are seen, which do not contain un-hydrated cement. The cement grains seem to have reacted completely but leaving a void, or they were not firmly attached and fell out during specimen preparation. This is not typical of mature Portland cement paste.

composed mainly of calcium silicate (Camilleri *et al.* 2005). Compound composition identification can be performed by X-ray diffraction analyses. XRD only identifies crystalline phases; amorphous structures cannot be characterized using this technique. XRD is useful in performing chemical analyses of unhydrated cement as PC is crystalline (Camilleri *et al.* 2005).

The use of atomic ratios rather than the absolute values of each mineral was more useful as the proportion of water present cannot be quantified. This



Figure 8 Plot of atomic ratios of Al/Ca versus Si/Ca of hydrated MTA. Lines represent mixtures of phases; the only conclusive mixture indicated is a mixture of CH and C-S-H. Little ettringite or monosulphate is present, even as a minor constituent mixed with C-S-H.

Table 1 Semi-quantitative analyses of hydrated MTA and hydrated Portland cement

	Na ₂ O	MgO	AI_2O_3	SiO ₂	SO ₃	K ₂ O	CaO	TiO ₂	Bi_2O_3	Fe ₂ O ₃
White PC	0.0	0.3	4.3	23.4	2.9	0.1	68.4	0.2	0.0	0.4
Hydrated MTA	0.0	0.2	1.7	23.2	2.1	0.0	63.1	0.0	9.6	0.2

MTA, mineral trioxide aggregate; PC, Portland cement.

Table 2 Bogue calculations for different assumed free lime contents

	0% Free CaO			1% Free	CaO		2% Free CaO		
	C ₃ S	C ₂ S	C ₃ A	C₃S	C ₂ S	C ₃ A	C₃S	C ₂ S	C ₃ A
White PC	72	13	11	68	16	11	64	19	11
MTA	69	14	5	65	17	5	61	21	5

MTA, mineral trioxide aggregate; PC, Portland cement.

is a standard technique used to express X-ray microanalyses data. Depending on the atom ratios used, different hydrate phases can be differentiated; common ratios are Si/Ca v Al/Ca and Al/Ca v S/Ca.

Semi-quantitative analyses were obtained by scanning areas of the hydrated MTA and of the hydrated white PC. These analyses should be viewed as 'semi-quantitative' because the X-ray software assumes an homogeneous specimen in calculating the interelement effects. The specimen is evidently not homogeneous. An alternative method for quantitative determination of the chemical composition of the cements is by using X-ray fluorescence (XRF) analyses with a fused bead and a free lime determination using ethylene glycol extraction. This method is more accurate in estimation of the cement mineral proportions. The determinations carried out on the PC control sample were similar to values quoted in cement chemistry literature (Taylor 1997, Lea 1998). Thus, this method was suitable for determination of the mineral composition of MTA.

The Bogue calculation is a standard method of assessing the content of the main mineral phases in cement. Traditionally, the Bogue calculation was used to calculate the potential phase composition from the four main oxides, with the assumption that the main phases are strictly C_3S , C_2S , C_3A and C_4AF (Taylor 1997). The Bogue calculation requires a figure for the uncombined lime (free lime) in the cement. Free lime contents were not available for the MTA and PC samples in this study. The Bogue calculation is not intended to give an actual phase composition of the cement but it was used to supply the potential composition which is

possible to achieve under ideal conditions, assuming the pure phase compositions given. The composition of minerals in real cement differs from the assumed compositions of the Bogue calculations.

Mineral trioxide aggregate was composed mainly of tri- and di-calcium silicate. This is in agreement with previous publications on the compound composition of MTA (Camilleri et al. 2005). Tricalcium and dicalcium silicate compositions in the MTA were typical of those in white PC. The MTA had a lower level of aluminate phase than is normally reported for white PC. The deficiency of the aluminate phase was evident on viewing the electron micrographs. The aluminate phase in PC is required to act as flux during the manufacture of the cement. The flux is required to achieve adequate clinkering of the raw materials (Lea 1998). As MTA is deficient in the aluminate phase this indicates that the cement was very likely manufactured in a laboratory rather than in a rotary kiln. The lack of liquid phase inside a rotary kiln would have made it impossible to achieve proper clinkering.

On hydration the PC produced calcium silicate hydrate gel and calcium hydroxide. Production of monosulphate phase and ettringite was also evident. These reaction by-products were evident on the electron micrographs and also on the atomic ratio plots. The hydration of PC involves a number of chemical reactions, which take place simultaneously (Taylor 1997, Odler 1998, Moir 2003). In water, calcium silicates undergo hydrolysis producing calcium hydroxide and a less basic calcium silicate hydrate. On completion of hydration a calcium silicate gel with the approximate composition $C_3S_2H_3$ is formed. The trical-cium silicate and the dicalcium silicate reactions are as follows:

 $2(3CaO \cdot SiO_2) + 6H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + 3Ca(OH)_2$

 $2(2CaO \cdot SiO_2) + 4H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + Ca(OH)_2$

The resulting hydrate is poorly crystallized and produces a porous solid, which may be defined as a rigid gel. The silicate hydrate gel has typical calcium to silica ratio of approximately 1.7 which is lower than the 3 : 1 ratio in the tricalcium silicate. The excess calcium is precipitated as calcium hydroxide. The presence of calcium hydroxide makes the hydrated cement highly alkaline (pH 12.5). The tricalcium aluminate reacts with water in the presence of gypsum resulting in the formation of a high-sulphate calcium sulphoaluminate known as ettringite. The ettringite continues to form until all the sulphate ions are used up in the reaction. Once depleted, further hydration of tricalcium aluminate results in the conversion of ettringite into a low-sulphate sulphoaluminate (mono-sulfate).

The hydration mechanics of the PC were evident on the electron micrographs. The unreacted cement grain was coated by a rim of calcium silicate hydrate gel (C-S-H). The outer edge of this rim corresponded approximately to the original size of the cement grain. The dense hydration product comprising such rims is often relatively pure C-S-H. Inner hydration product is formed topochemically. Hydration products formed outside the original volume of the cement grain (outer product) is formed in the region originally occupied by water when the paste is first mixed. The hydration product in this region is formed mainly through precipitation from solution. The hydration of PC undergoes four stages namely the pre-induction period. the induction (dormant) phase, acceleration and postacceleration phase (Taylor 1997, Odler 1998, Moir 2003). In the pre-induction period (first few minutes) a rapid dissolution of ionic species occurs. As a result of hydrolysis of the tricalcium silicates a calcium silicate hydrate phase precipitates at the cement particle surface. Very little dicalcium silicate reacts at the initial stages of the reaction. Tricalcium aluminate dissolves and reacts with the calcium and sulphate ions present in the liquid phase producing ettringite that also precipitates on the cement particle surface. The preinduction phase is followed by the induction (dormant) period (first few hours). The hydration of all the clinker minerals progresses very slowly. The silicate hydrate coating on the unreacted cement grains retards further hydration and leads to the 'dormant period' a period of 1–2 h of relative inactivity where the cement is plastic and workable. In this way a barrier is formed between the nonhydrated material and the bulk solution causing a rise in the concentration of dissolved ions in the liquid phase in immediate contact with the nonhydrated material. An initial set is initiated when the calcium silicate hydrate coating breaks up resulting in continuation of the hydration process. The volume of the hydration products is more than twice that of the anhydrous cement. As hydration proceeds, the hydration products gradually fill in the spaces between the cement grains. Initially, during the dormant period, the cement grains are separate and the hydration products are mainly calcium hydroxide and ettringite. After an hour calcium silicate hydrate gel begins to form. Intergrowth of calcium silicate hydrate fibres causes stiffening while increase in the volume of the solids

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decreases the porosity of the paste. The ettringite deposited over the surface of the tricalcium aluminate further reduces the reaction of the tricalcium aluminate. Once the sulphate ions are depleted the ettringite laver breaks down and is converted to monosulphate. This is followed by the acceleration stage (3-12 h after)mixing) where the progress of hydration accelerates again and is controlled by the nucleation and growth of the resultant hydration products. The rate of tricalcium silicate hydration increases and more calcium silicate hydrate gel is formed. The hydration of dicalcium silicate also increases at this stage. Crystalline calcium hydroxide (portlandite) precipitates from the liquid phase. The calcium ion concentration thus declines in the liquid phase. Finally in the post-acceleration period the hydration rate slows down gradually as the amount of nonreacted material declines and the rate of hydration process becomes diffusion controlled. The silicate hydrate phase continues to be formed due to the continuing hydration of both the tricalcium and the dicalcium silicate. The supply of calcium sulphate becomes exhausted and as a consequence the ettringite phase formed in the early reaction starts being converted to monosulphate.

In the hydrated MTA the main reaction products were calcium silicate hydrate and calcium hydroxide. These hydration products were viewed on the back-scattered electron micrographs and their presence was shown on the atomic ratio plots. C_3A was difficult to discern in the SEM images; the low alumina content would explain why this was so. The low levels of tricalcium aluminate would also explain the low levels of ettringite and monosulphate found in hydrated MTA. Both ettringite and monosulphate are formed on hydration of the tricalcium aluminate in normal PC.

The bismuth was present both as unreacted filler in the hydrated MTA and also formed part of the structure of the C-S-H. The microstructure of the paste appeared to have been affected by the presence of bismuth; CH and C-S-H appeared to be more closely intermixed. The large areas of calcium hydroxide present in the PC were absent in the MTA sample. Additionally, MTA had dense rims with central voids which were not present in the control. The cement grain may have hydrated fully and left a central pore, or it may have fallen out during specimen preparation. Neither of these alternatives is normally a characteristic of mature cement paste.

Further research is warranted on the affects of bismuth oxide on MTA. Bismuth oxide, as Bi_2O_3 , is regarded as being soluble in acid (Lide 1998) but data

on alkali solubility is scarce. Evidently, it is soluble in alkali to some degree. The proportion of bismuth oxide that reacted in the hydrated MTA was probably controlled by the extent that bismuth could be accommodated within the C-S-H. Whether bismuth would continue to dissolve over an extended time, or whether the limit was reached within the 30 days curing time, is unclear. Studies on the biocompatibility of bismuth oxide have shown that bismuth oxide does not encourage cell growth (Camilleri *et al.* 2004).

The microstructure of the hydrated MTA would be likely weaker than that of the hydrated PC. The MTA contained larger spherical air voids and they are more numerous; the paste was also more porous, with a higher proportion of capillary pores.

Conclusions

Mineral trioxide aggregate was deficient in alumina suggesting that the material was not prepared in a rotary kiln as is customary for the manufacture of PC. On hydration this affected the production of ettringite and monosulphate usually formed on hydration of PC. The bismuth affected the hydration mechanism of the MTA; it formed part of the structure of C-S-H and also affected the precipitation of calcium hydroxide in the hydrated paste. MTA had a weaker microstructure when compared to PC.

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