The hydration chemistry of ProRoot MTA

Qiu LI[1,2] and Nichola J. COLEMAN[3]

[1] *State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Wuhan 430070, China*
[2] *Green Building Materials Manufacturing and Engineering Research Centre of MOE, Wuhan University of Technology, Wuhan 430070, China*
[3] *School of Science, University of Greenwich, Chatham Maritime, Kent, ME4 4TB, UK*
Corresponding author, Nichola J. COLEMAN; E-mail: nj_coleman@yahoo.co.uk

'Tooth-coloured' ProRoot MTA is an endodontic cement comprising an 80:20 wt% mixture of white Portland cement (WPC) and bismuth oxide. The setting reactions within this cement system are not currently well understood. Accordingly, this research monitors the early hydration chemistry of ProRoot MTA by X-ray diffraction, solid state nuclear magnetic resonance and Fourier transform infrared spectroscopies, and isothermal calorimetry. The initial rate of hydration is rapid with 40% having reacted within the first 24 h; it then slows considerably such that within 3 days the hydration reactions are 58% complete and only increase by a further 1% within one week. The relatively fast reaction of alite to form C-S-H gel and portlandite, and the development of the calcium aluminosulphate phases, are as would be anticipated for the hydration of pure WPC. These findings confirm that bismuth oxide is an inert additive which does not participate in the hydration reactions.

Keywords: Mineral trioxide aggregate, Nuclear magnetic resonance spectroscopy, Cement hydration

INTRODUCTION

Mineral trioxide aggregate (MTA) is a commercial Portland cement-based dental restorative which has been used as a root-filling material since 1995. It is supplied as five 1 gram sachets of powder with accompanying 0.35 gram ampoules of sterile water which are mixed manually. The principal component of 'tooth-colored' ProRoot MTA (Tulsa Dental Products, USA) is white Portland cement (WPC) to which is added 20 wt% bismuth oxide (Bi_2O_3) to enhance radiopacity[1,2].

The main components of WPC are the impure phases: 'alite' (Ca_3SiO_5); 'belite' (β-Ca_2SiO_4); 'aluminate' ($Ca_3Al_2O_6$); and 'ferrite' ($Ca_2(Al/Fe)O_5$)[3]. Up to 5% of gypsum ($CaSO_4\cdot2H_2O$) is also ground into the cement to regulate the setting of the aluminate phase. When mixed with water, alite and belite react to form a poorly crystalline calcium silicate hydrate (C-S-H) gel phase, of approximate formula $Ca_3Si_2O_7\cdot3H_2O$, and portlandite ($Ca(OH)_2$). Alite and belite comprise isolated Q^0 silicate tetrahedra which become hydrated and condense to form Q^1 dimers. Ongoing condensation reactions give rise to short silicate chains with Q^1 end-groups, Q^2 mid-chain tetrahedra and Q^2(1Al) mid-chain silicate species which are linked to one silicate tetrahedron and one substituted aluminate tetrahedron[4].

The initial reactions of the aluminate and ferrite phases with gypsum and water yield ettringite (aka 'AFt', $6CaO\cdot Al_2O_3\cdot3SO_3\cdot32H_2O$) and its Fe-substituted counterpart. The ettringite subsequently converts to 'monosulphate' (aka 'AFm', $4CaO\cdot Al_2O_3\cdot SO_3\cdot12H_2O$) and water which are thermodynamically more stable[3].

The setting reactions of ProRoot MTA have been investigated using a range of instrumental techniques, including powder X-ray diffraction (XRD), Raman and infra-red spectroscopies, scanning electron microscopy and energy dispersive X-ray analysis[5-10]. Despite 20 years of clinical application, some fundamental aspects of the hydration chemistry of ProRoot MTA are not well understood. In particular, the impact of bismuth oxide on the hydration reactions of the cement remains a matter of dispute. Camilleri reports that bismuth oxide alters the hydration mechanism of WPC in ProRoot MTA and that bismuth is chemically incorporated into the C-S-H gel phase[7]. Conversely, this claim is refuted by Darvell and Wu on the basis that bismuth oxide is highly insoluble and has no known reactions under the alkaline conditions encountered during Portland cement hydration[2]. Additionally, a recent study of a model experimental cement comprising 80 wt% WPC and 20 wt% bismuth oxide using XRD and magic angle spinning nuclear magnetic resonance spectroscopy (MAS NMR) indicates that bismuth oxide is unlikely to participate in the cement hydration process of MTA[4].

Understanding the fate of bismuth oxide in MTA formulations is of key importance as the potential substitution of bismuth for silicon in the C-S-H gel phase would influence the chemical stability, physical durability and also the cytotoxicity of the material. In this respect, the principal objective of this study was to monitor the initial hydration chemistry of ProRoot MTA by XRD, Fourier transform infrared spectroscopy (FTIR), solid state ^{29}Si and ^{27}Al MAS NMR and isothermal conduction calorimetry. The extent of hydration was also determined quantitatively by ^{29}Si MAS NMR after 6, 24, 72 and 168 h.

MATERIALS AND METHODS

Preparation of materials
White ProRoot MTA (Dentsply, Tulsa, OK, USA, lot 11004158, expiry date October 2014) samples were

prepared according to the manufacturer's instructions by mixing the supplied powder and sterile water on a glazed ceramic slab for 30 s. The resulting pastes were hermetically sealed in polypropylene containers and cured at 37°C for either 6, 24, 72 or 168 h. Each sample-type (*viz.* MTA-6, MTA-24, MTA-72 and MTA-168) was prepared in triplicate. Prior to analysis by XRD, ^{29}Si and ^{27}Al MAS NMR and FTIR, the hydration reactions were quenched by solvent exchange with propan-2-ol. This was achieved by immersion of 5 mm fragments of the pastes in four consecutive 50 cm^3 washings of propan-2-ol in a sonic bath for 30 min. The samples were then dried to constant mass in a vacuum desiccator.

XRD analysis

Powder XRD was performed on the anhydrous ProRoot MTA powder, (labelled 'MTA') and on all hydrated specimens using a Bruker D8 diffractometer with Cu Kα=1.5406 Å, a step size of 0.019° in the 2θ range from 10 to 45° and a measuring time of 2 s per step. X-ray diffraction data were compared with JCPDS files using DIFFRAC.EVA software (supplied by Bruker).

FTIR

FTIR spectra were obtained for bismuth oxide (*ex.* Sigma-Aldrich, UK), anhydrous ProRoot MTA powder and all hydrated specimens using a Perkin Elmer Paragon spectrometer. Spectra were obtained in transmission mode from pressed KBr discs between 500 and 4,000 cm^{-1} wavenumbers.

MAS NMR

MAS NMR spectra of anhydrous ProRoot MTA powder and all hydrated samples were recorded on a JEOL JNM-ECX 300 MHz spectrometer. ^{27}Al spectra were collected with a pulse delay of 0.5 s, an acquisition time of 0.01024 s and 8,000 scans. ^{1}H-^{29}Si cross polarization (CP) MAS NMR spectra were obtained with a contact time of 10^{-3} s, a pulse delay of 5 s, an acquisition time of 0.0256 s and 68,000 scans. Single pulse ^{29}Si MAS NMR spectra were obtained with a pulse delay of 5 s, an acquisition time of 0.02048 s and 120,000 scans. All spectra were collected with a spin rate of 6 kHz. ^{29}Si and ^{27}Al chemical shifts were referenced to tetramethylsilane and the aluminium hexaquo-ion, respectively. The raw data were processed by Delta software (provided by JEOL) to obtain spectra which were then analyzed and deconvoluted using Igor Pro software.

Deconvolution and quantitative analysis of ^{29}Si MAS NMR spectra

The ^{29}Si MAS NMR spectrum of each hydrated cement was analyzed by a method reported by Love *et al.*[11] in which the signal from the unreacted alite that obscures the resonances of the early Q^1 hydration products is subtracted from the spectrum prior to deconvolution. In the case of each hydrated cement paste sample, the intensity of the ^{29}Si MAS NMR spectrum of the anhydrous WPC was adjusted such that the Q^0 signal of alite was of equal intensity to that of the sample.

This WPC background spectrum was then subtracted from that of the sample paste prior to deconvolution using iterative fitting of the ^{29}Si resonances to Voigt lineshapes. (It should be noted that the sharp signal from belite at −72 ppm persists in the subtracted spectrum, as the hydration of belite is considerably slower than that of alite.). The relative abundance of the various Q^n species and degree of hydration were then calculated from the subtracted and deconvoluted spectra[12].

Isothermal conduction calorimetry

The rate of heat evolution during the hydration of ProRoot MTA was monitored by isothermal conduction calorimetry using a Thermometric 2277 TAM calorimeter at 37.5°C. The analysis was carried out in duplicate, and in each case, ~0.1 g of accurately weighed paste was placed in the calorimeter immediately after mixing. Power (*i.e.* rate of heat evolution) data were collected every second for 88 h. The rate of heat evolution per unit kilogram of ProRoot MTA was then calculated by dividing the power data by the original mass of the sample.

RESULTS AND DISCUSSION

Powder XRD analysis

Qualitative powder XRD data were collected for anhydrous ProRoot MTA and for all hydrated specimens to confirm the initial composition of the material and to determine whether any bismuth-bearing product phases had formed during the hydration reactions (Fig. 1). XRD analysis indicates that the principal constituent phases of anhydrous ProRoot MTA are bismuth oxide (Bi_2O_3), alite (Ca_3SiO_5), belite (β-Ca_2SiO_4) and tricalcium aluminate ($Ca_3Al_2O_6$). Trace quantities of hemihydrate ($CaSO_4 \cdot 0.5H_2O$) and anhydrite ($CaSO_4$) are also present. According to its Material Data Safety Sheet, ProRoot MTA comprises 75% Portland cement, 20% bismuth oxide and 5% gypsum. During Portland cement manufacture, the heat generated during the grinding process commonly dehydrates gypsum to hemihydrate and anhydrite, which accounts for the presence of these phases and absence of gypsum in this material.

As hydration proceeds the reflections for alite diminish rapidly as this phase reacts to form C-S-H gel and portlandite. The concomitant development of the reflections of portlandite is clearly observed; however, those of the C-S-H gel are not apparent as this phase is very poorly crystalline. The rapid reduction of the peaks corresponding to the aluminate phase also indicates that this phase is readily consumed during the early stages of hydration. The reflections for bismuth oxide persist throughout the 7 day hydration period, and no other bismuth-bearing phases are detected.

FTIR spectroscopy

FTIR spectra of bismuth oxide, anhydrous ProRoot MTA and the hydrated specimens are shown in Fig. 2 and the corresponding FTIR spectra expanded in the 200 to 2,000 cm^{-1} region are shown in Fig. 3. The spectrum
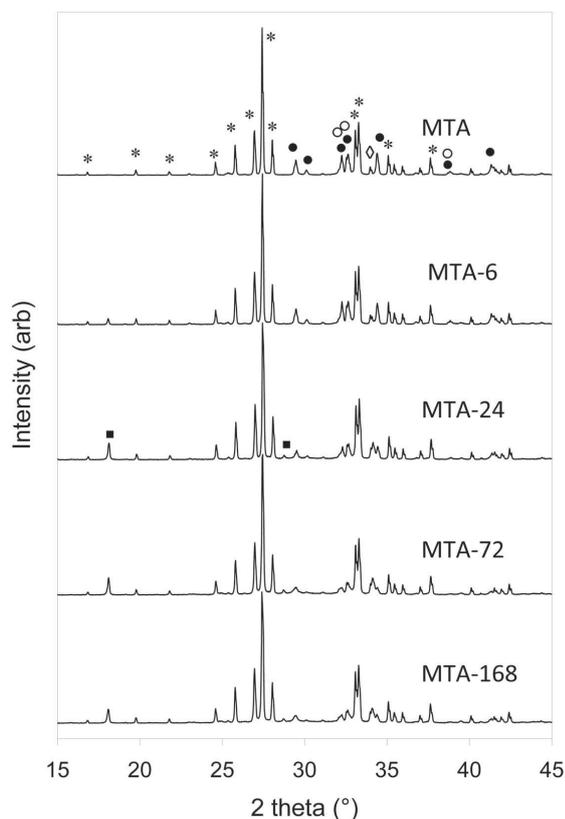
Fig. 1 Powder X-ray diffraction data for anhydrous and hydrating ProRoot MTA.
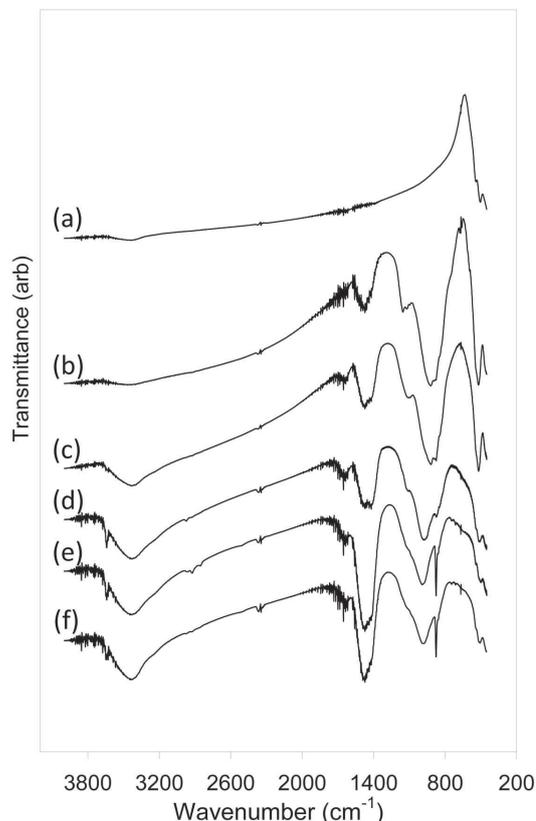Key: ● C_3S; ○ C_2S; ◊ C_3A; ■ CH and * Bi_2O_3.

Fig. 2 FTIR spectra of (a) bismuth oxide, (b) anhydrous ProRoot MTA, (c) MTA-6, (d) MTA-24, (e) MTA-72, (f) MTA-168.

of bismuth oxide contains two unresolved bands at 511 and 547 cm^{-1} which arise from Bi-O vibrations, a weak signal from adsorbed water stretching at 3,450 cm^{-1} and atmospheric water rotations in the 1,425–1,850 and 3,600–3,900 cm^{-1} regions (Figs. 2(a) and 3(a)).

The FTIR spectrum of ProRoot MTA (Figs. 2(b) and 3(b)) obtained in this study is similar to those reported by other researchers[5,6]. The combination band centerd at 935 cm^{-1} and the signal at 525 cm^{-1} are, respectively, assigned to Si-O stretching and bending modes of the silicate tetrahedra of alite and belite[13]. The sharp Si-O bending signal obscures the weaker bands arising from the bismuth oxide Bi-O vibrations. Sulphate stretching modes from anhydrite and hemihydrate give rise to the signals at 1,115, 1,155 and 1,160 cm^{-1}, and the band at 1,450 cm^{-1} is attributed to carbonate stretching vibrations. The carbonate signal indicates that calcium carbonate is present in ProRoot MTA. Minor proportions of calcium carbonate phases commonly occur in Portland cements and are formed from the atmospheric hydration and carbonation of residual free lime (CaO) in the mixture.

As hydration proceeds, the sharp signal at 525 cm^{-1} arising from SiO_4 bending modes of alite and belite diminishes rapidly as the alite phase is consumed (Figs.

2(c–f) and 3(c–f)). The progressive condensation of the hydrating silicate chains of the C-S-H gel phase is denoted by the shift in the signal maximum of the Si-O stretching combination band from 935 to 995 cm^{-1} during the 7 day hydration period. Within the first 6 h of hydration, the multiple sulphate stretching signals of hemihydrate and anhydrite are replaced by that of sulphate in ettringite at 1,110 cm^{-1} (Figs. 2(c) and 3(c)). Bending and stretching modes of hydrogen-bonded hydroxyl groups and of structural and bound water associated with the cement hydration products give rise to broad bands at 3,450 and 1,640 cm^{-1}, respectively; and the stretching modes of O-H species in portlandite are assigned to the sharp signal at 3,640 cm^{-1}. Calcium carbonate, from further atmospheric carbonation during sample preparation is indicated by the development of carbonate stretching at 2,900 and 1,450 cm^{-1} and bending at and 875 cm^{-1}. The FTIR spectra of the hydrated ProRoot MTA pastes do not provide any evidence of the formation of any additional bismuth-bearing product phases.

^{29}Si MAS NMR spectroscopy
^{29}Si MAS NMR spectroscopy can be used to determine the co-ordination environment and the extent of
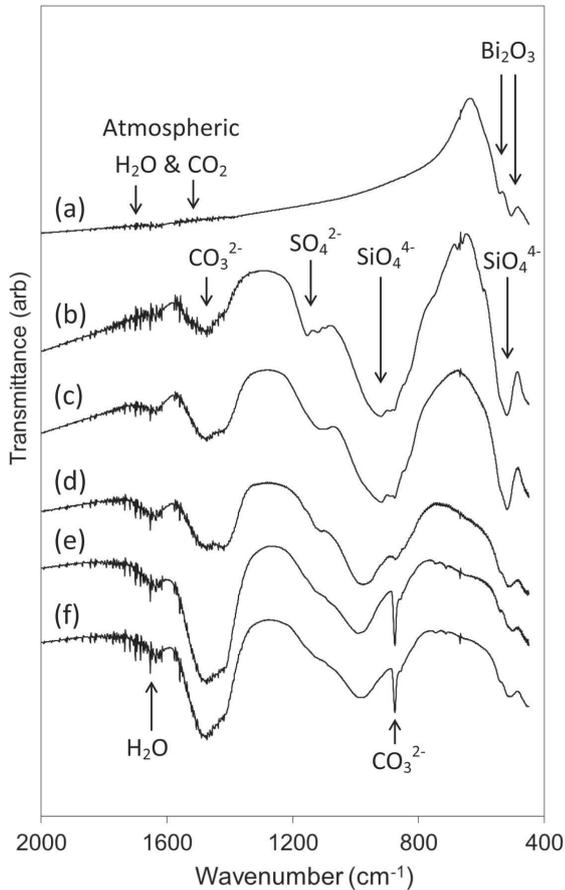
Fig. 3   Expanded FTIR spectra in the 200–2,000 cm^{-1} region for (a) bismuth oxide, (b) anhydrous ProRoot MTA, (c) MTA-6, (d) MTA-24, (e) MTA-72, (f) MTA-168.

Fig. 4 ^{29}Si MAS NMR spectra of anhydrous and hydrating ProRoot MTA.

polymerization of silicate species in mineral phases[14]. Isolated Q^0 silicate species have a chemical shift range of −65 to −75 ppm, Q^1 species resonate between −78 and −82.5 ppm, and Q^2 silicates give rise to signals in the range −84 to −87.5 ppm[11,12,15]. Replacement of silicon for aluminium in a neighbouring tetrahedron increases the chemical shift by approximately 5 ppm per Al substitution.

The ^{29}Si MAS NMR spectra of anhydrous ProRoot MTA and the hydrated samples are given in Fig. 4. The spectrum of ProRoot MTA closely resembles those of other white Portland cements reported in the literature[4,16]: the sharp signal at −72 ppm arises from a single Q^0 resonance of belite and the broad underlying signal between −65 and −79 ppm is assigned to the various Q^0 environments of alite[17]. As hydration progresses, signals corresponding to silicate species in the C-S-H gel appear and intensify in the Q^1 and Q^2 regions of the ^{29}Si MAS NMR spectra at the expense of the Q^0 alite signal. The spectra of the hydrating ProRoot MTA samples are similar to those of other hydrating white Portland cements, and do not provide
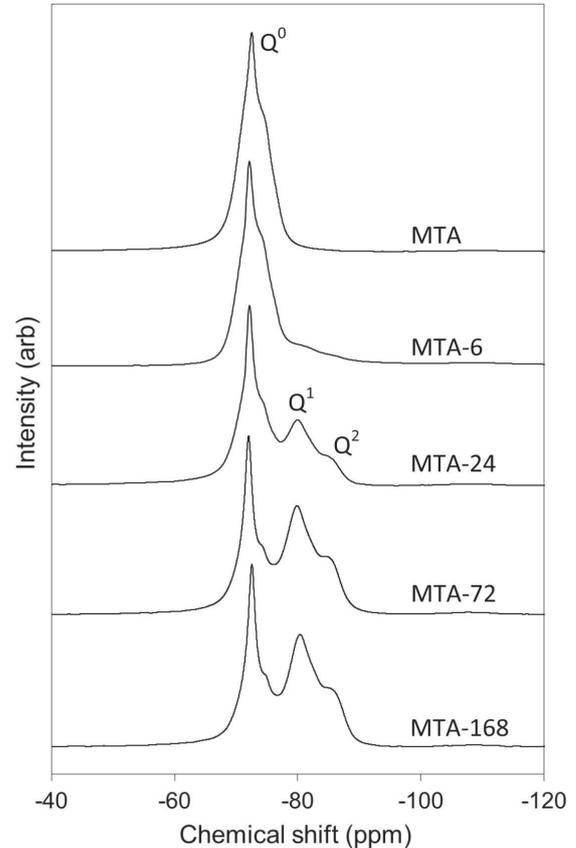
any indication that bismuth has been incorporated into the silicate system of the C-S-H gel phase.

^{1}H-^{29}Si CP MAS NMR spectroscopy
^{1}H-^{29}Si CP MAS NMR spectroscopy can be used to distinguish between anhydrous and hydrated silicate species in mineral phases, as anhydrous species do not appear in the spectrum[14]. The chemical shift ranges for ^{1}H-^{29}Si CP MAS NMR spectroscopy are concurrent with those given in the previous section for single pulse ^{29}Si MAS NMR spectroscopy; however, the intensities of the resonances obtained using this technique are not proportional to the relative abundance of the various Q^n species within the sample.

The ^{1}H-^{29}Si CP MAS NMR spectra of the hydrating ProRoot MTA samples are presented in Fig. 5. These spectra were collected to determine the chemical shifts of the early Q^1 hydration products, as these signals are partially obscured by those of alite and belite in the corresponding single pulse ^{29}Si MAS NMR spectra (Fig. 4). Within 6 h of hydration, Q^1 resonances are detected at −80 ppm, and the Q^n signals are seen to spread into the Q^2 region and intensify as hydration continues. After 1 week of hydration, the ^{1}H-^{29}Si CP MAS NMR spectrum of ProRoot MTA comprises partially resolved Q^1 and Q^2
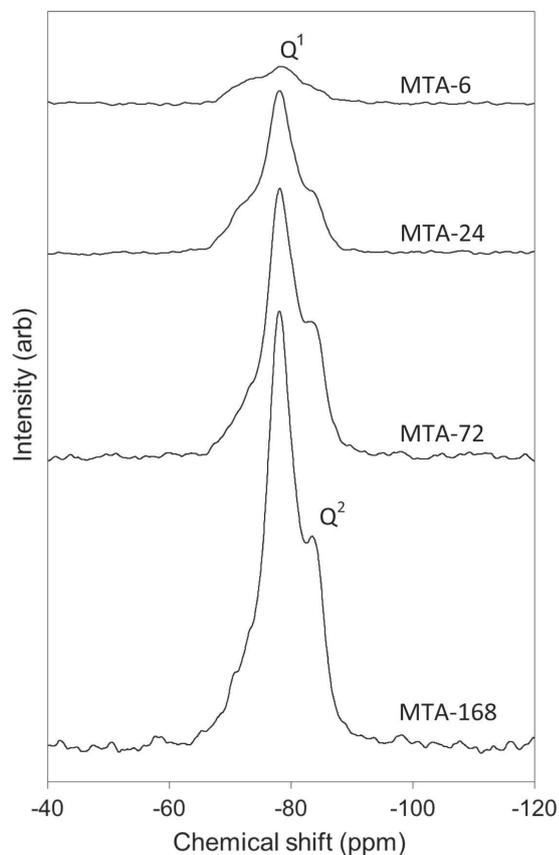
Fig. 5 ^{1}H-^{29}Si CP MAS NMR spectra hydrating ProRoot MTA samples.

Deconvolution and analysis of ^{29}Si MAS NMR spectra
The subtracted, deconvoluted and calculated ^{29}Si MAS NMR spectra of the hydrated ProRoot MTA samples are shown in Fig. 6, together with the residues (*i.e.* the differences between the subtracted and calculated spectra) which are plotted above the corresponding spectra. The small residues confirm the validity of this method for the deconvolution and analysis of these data. In addition to the resonances from the hydration products, each subtracted spectrum contains a proportion of the residual Q^0 signal from belite at −72 ppm.

The relative abundance of Q^n species and degree of hydration of the hydrated cements are listed in Table 1. The observed increase in degree of hydration as a function of time for ProRoot MTA is comparable to that reported for white Portland cement cured under similar conditions, with both systems achieving approximately 60% hydration within the first week[16].

^{27}Al MAS NMR spectroscopy
^{27}Al MAS NMR spectroscopy can be used to examine the co-ordination environments of aluminium phases in cements, zeolites, clays, glasses and ceramics[14,17-19].
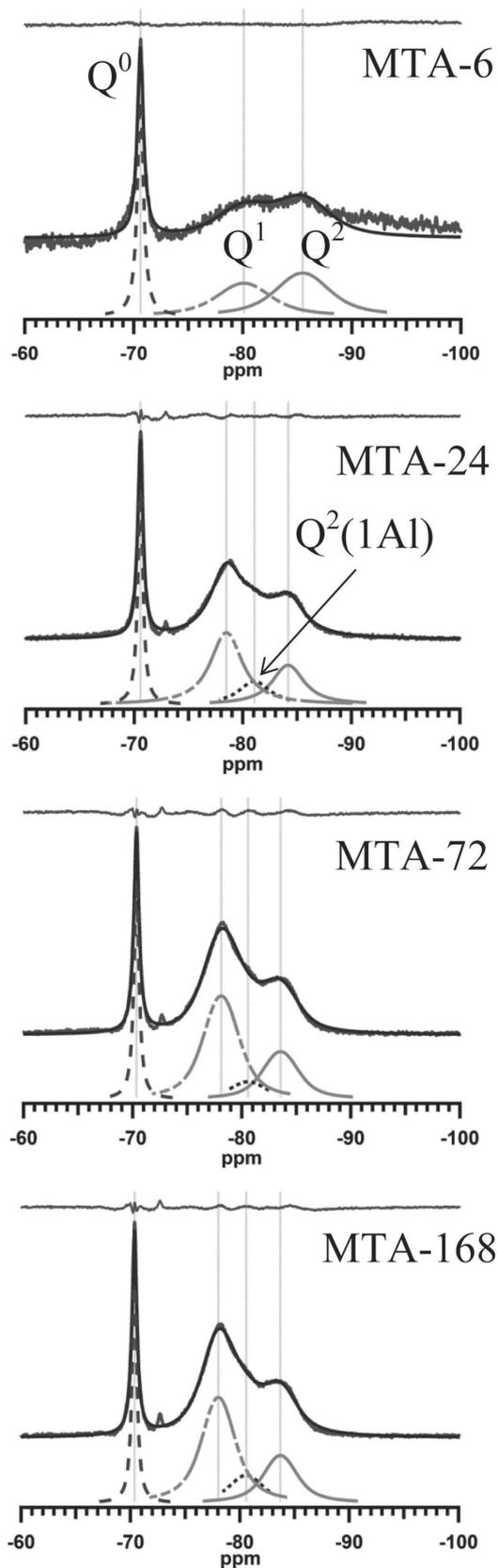
resonances at −80 and −85.5 ppm, respectively.

Fig. 6   Subtracted, fitted and deconvoluted ^{29}Si MAS NMR spectra of hydrating ProRoot MTA samples.

Table 1   Relative abundance of Q^n species and degree of hydration of MTA pastes

Sample	Q^0 (%)	Q^1 (%)	Q^2(Al) (%)	Q^2 (%)	Degree of hydration (%)
MTA-6	89.8	6.5	0	3.7	10
MTA-24	60.2	24.6	4.0	11.2	40
MTA-72	41.8	35.7	6.0	16.5	58
MTA-168	41.2	34.3	9.0	15.5	59

Tetrahedral aluminium resonates within the approximate chemical shift range of 100 to 50 ppm, five-co-ordinate aluminium resonates between 40 and 30 ppm, and octahedral aluminium environments give rise to signals in the 20 to −10 ppm region of the spectrum[19,20]. Despite its ability to discriminate between co-ordination environments, this technique is limited to providing semi-quantitative information as signal intensities arising from each aluminium species are not in direct proportion to their relative concentrations.

The ^{27}Al MAS NMR spectrum of anhydrous ProRoot MTA (Fig. 7) comprises a broad signal at *ca.* 81 ppm which arises from tetrahedrally co-ordinated aluminium species substituted into the alite and belite phases, and a less intense octahedral resonance at 9.5 ppm which is not common to anhydrous Portland cements[19,20]. On account of the presence of this octahedral signal, ^{27}Al MAS NMR spectra were collected for three anhydrous ProRoot MTA samples from separate sachets packaged in different boxes with the same lot number. The octahedral resonance appeared in all of the spectra and is tentatively assigned to the monosulphate AFm phase[20] which would indicate that the material has been exposed to moisture prior to packing and distribution. This may be a concern, as partial premature hydration can impact upon the ultimate strength and mechanical integrity of a Portland cement-based material. It should be noted that, resonances from aluminium in the aluminate and ferrite phases do not appear in the spectrum of Portland cements due to extensive line-broadening.

Within the first 6 h of hydration, the intensity of the aluminium resonance at 81 ppm is notably reduced and the signal is broadened. The development of a signal at 10 ppm with an unresolved downfield shoulder at ~14 ppm, are respectively indicative of the formation of monosulphate and ettringite. As hydration proceeds, the ettringite and monosulphate signals become better resolved and an upfield shoulder appears at ~4 ppm which is attributed to the presence of a third poorly crystalline calcium aluminate hydrate phase or aluminium hydroxide gel[12,17]. The upfield shift of the tetrahedral aluminium signal to 66.5 ppm during the first week of hydration is attributed to the progressive incorporation of aluminium into the silicate chain structure of the C-S-H gel phase[12].

Despite the existence of the unusual octahedral signal in the spectrum of ProRoot MTA, the ^{27}Al MAS NMR data collected for the hydrating samples closely
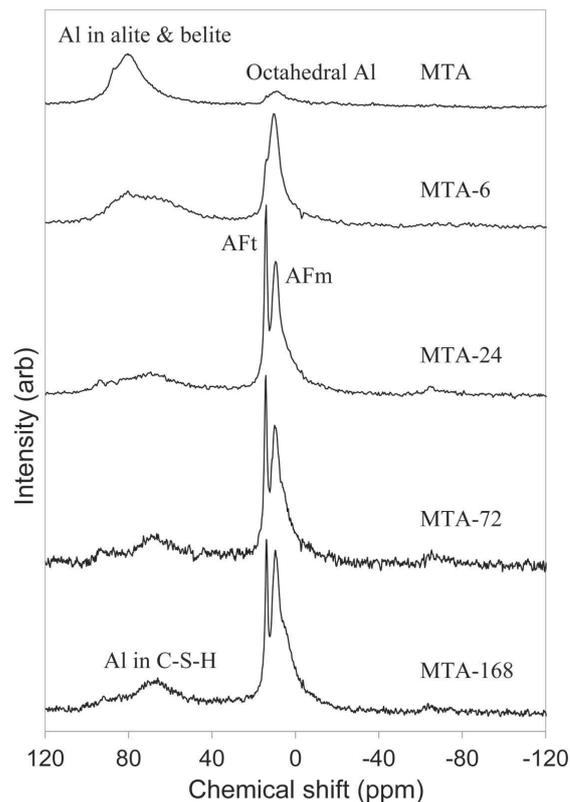

Fig. 7 ^{27}Al MAS NMR spectra anhydrous and hydrating ProRoot MTA samples.

resembles those reported for WPC cured under similar conditions[16]. From this technique, there is no evidence to suggest that the presence of bismuth oxide has influenced the calcium sulphoaluminate hydration chemistry of the WPC phases of ProRoot MTA.

Isothermal conduction calorimetry
The rate of heat evolution per kilogram of ProRoot MTA is plotted in Fig. 8. In this thermogram, the initial rapid heat evolution, arising principally from the wetting process, hydration of free lime and the precipitation of early hydrates, which takes place within the first few min of mixing is not calibrated, as the calorimeter requires 20 min to equilibrate[21,22].

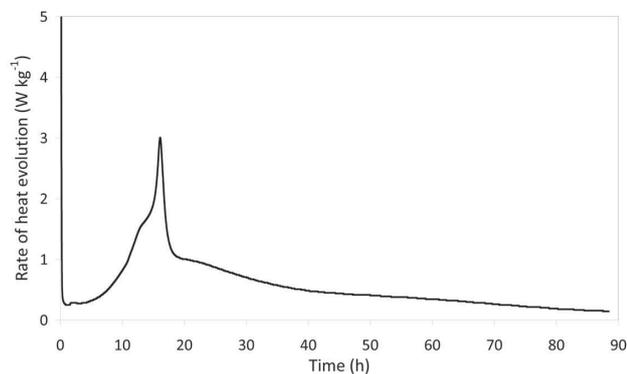The general thermal profile of ProRoot MTA during

Fig. 8   The rate of heat evolution of ProRoot MTA during hydration at 37.5°C.

the first 3 days of hydration compares well with those of Portland cements published in the literature[22,23]. After the initial exotherm, a dormant or 'induction' period ensues for approximately 4 h, during which time the hydration reactions are limited by the precipitation of a protective layer of early hydration products which coats the cement grains. The subsequent 'acceleratory period' is characterized by rapid hydration which is essentially determined by the rate of formation of the C-S-H gel product phase[21,22]. During this period, the distinct exothermic peak of maximum intensity 2.9 W kg^{-1} at 16 h is attributed to renewed ettringite formation[3], and the deceleratory stage marks a decline in hydration rate as the reactions become diffusion-controlled. The total heat of hydration of ProRoot MTA after 88 h is 176 kJ kg^{-1} (which is obtained from the area under the power curve) and the rate of heat evolution at this point is 0.141 W kg^{-1}.

The hydration chemistry of ProRoot MTA
Since its introduction in 1995, MTA has become widely accepted as a root-filling material owing to its sealing capacity, intrinsic antimicrobial properties and its ability to stimulate the regeneration of bone and dentin[2]. From a clinical point of view, the handing properties of MTA are not ideal. Clinicians report that the MTA paste is 'grainy', of 'poor consistency', and difficult to compact[24]. The reported setting times, of up to 3 h, are also relatively long and so it is suggested that improvements in these properties would be highly desirable. In order to modify and develop this generation of Portland cement-based dental materials, it is necessary to first understand their hydration chemistry.

The research carried out in this study confirms that bismuth oxide is an inert additive within the ProRoot MTA mixture which does not participate in the hydration reactions of the white Portland cement. ^{29}Si and ^{27}Al MAS NMR spectroscopy has shown that the initial hydration chemistry is characterized by the comparatively rapid reaction of alite to form C-S-H gel and the development of the AFt and AFm phases are as would be expected for the hydration of pure WPC cured

under similar conditions[16]. The thermal profile of the hydrating ProRoot MTA also confirms the anticipated stages of Portland cement hydration which include rapid initial reaction, induction, acceleratory and deceleratory periods, followed by continued diminishing diffusion-controlled reactions[22].

The reaction mechanisms that bring about the setting of MTA consist of a series of overlapping chemical reactions between the cement constituents and the added water. The various cement phases hydrate at differing rates, with alite and aluminate reacting considerably more rapidly than belite and ferrite.

During the first few minutes after the addition of the mix water to the MTA cement powder, a large exotherm accompanies the rapid dissolution of sulphate and aluminate phases and the initial formation of ettringite. After the first 40 min, the induction period commences and the rate of heat evolution decreases. During this stage, which continues for a further 4 h, the slow initial hydration of alite to form C-S-H gel and portlandite takes place.

At the onset of the acceleratory phase, ~5 h after mixing, the degree of cement hydration is approximately 10% and the C-S-H gel principally comprises very poorly crystalline dimeric and trimeric silicate species. The acceleratory phase is characterized by the further rapid formation of C-S-H gel, portlandite, ettringite and monosulphate. During this stage the degree of polymerization of the C-S-H gel increases and the cement sets to form a rigid matrix.

The deceleratory period, during which the hydration reactions become diffusion-controlled, begins 18 h after mixing, and corresponds with a marked decrease in the rate of heat evolution. Within the first 24 h, the hydration process is essentially 40% complete, and from this point onwards the kinetics of the hydration reactions will continue to decrease steadily as the initial cement phases are consumed and the porosity of the matrix decreases.

At 72 h after mixing, the cement is 58% hydrated and a proportion of the ettringite begins to convert to monosulphate. By this time, the hydration reactions have slowed to such an extent that hydration only increases by a further 1% within the week; during which time, ettringite conversion to monosulphate continues. A significant proportion of the belite phase persists at this point which will continue to react slowly for many months.

There is no evidence from MAS NMR and FTIR spectroscopies, XRD analysis or induction calorimetry to indicate that the bismuth oxide component of ProRoot MTA diverts the normal hydration processes of the WPC phases. This finding directly contradicts that of Camilleri[7], who reports that the hydration chemistry of WPC differs in the presence of bismuth oxide.

It has been suggested that the potential inertness of bismuth oxide is responsible for an undesirable decrease in the mechanical strength and durability of the resulting cement matrix[25]. Alternative radiopacifiers, various inorganic salts and gelatinous

vehicles have been proposed to improve durability, accelerate hydration kinetics, reduce setting times, and improve handling of MTA-like materials[5,16,26-28]. The phase evolution during the hydration of these modified cements is widely studied by powder XRD analysis; however, this technique is limited in its ability to provide information on the principal C-S-H gel product phase owing to its poor crystallinity. This study has indicted that ^{29}Si and ^{27}Al MAS NMR spectroscopy would be a powerful analytical tool to provide valuable structural information on new formulations of hydraulic calcium silicate cement-based dental restoratives, when used in tandem with the more commonly employed techniques of FTIR spectroscopy and powder XRD analysis.

CONCLUSIONS

ProRoot MTA is a popular proprietary root-end filling material comprising an 80:20 wt% mixture of Portland cement and bismuth oxide (a radiopacifier). The role of bismuth oxide within this system is currently disputed. This study monitors the early hydration chemistry of ProRoot MTA endodontic cement by powder XRD analysis, MAS NMR and FTIR spectroscopies, and isothermal conduction calorimetry. The findings of this research confirm that bismuth oxide is an inert additive in this cement system which does not participate in the hydration reactions. The study has also demonstrated that ^{29}Si, ^{1}H-^{29}Si CP and ^{27}Al MAS NMR spectroscopy is a valuable tool for the analysis of Portland cement-based biomaterials. It is particularly useful for the structural elucidation of the principal C-S-H gel phase which, owing to its poorly crystalline nature, is difficult to analyze by the more commonly employed powder XRD analysis.

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