2 Composition and Setting Reaction

Josette Camilleri

2.1 Introduction

Mineral trioxide aggregate (MTA) has been introduced as a root-end filling material due to its hydraulic properties. Most dental materials exhibit a deterioration in physical properties upon contact with moisture. Thus, a hydraulic material used in the construction industry was introduced in order to counteract this problem. The first US patent [79, 80] drawn for MTA explains this invention saying ‘Due to the presence of blood and moisture, the mouth is a less than ideal environment for many materials which could otherwise be useful as dental filling and sealing materials. For example, typical amalgams are sensitive to moisture and set less than adequately if care is not taken to minimize moisture. Not only is the cement of the present invention not adversely affected by moisture in the mouth, but such moisture actually plays an important role in the hydration reactions responsible for the hardening and sealing process’. The composition of MTA and the processes of hydration will be discussed in this chapter.

2.2 Composition of Un-hydrated Material

MTA is composed of a mixture of Portland cement and bismuth oxide. The bismuth oxide is added to the cement to enhance the radiopacity of the material. The original MTA patent registered in 1995 [79] stated that ‘MTA consists of 50–75 % (wt) calcium oxide and 15–25 % silicon dioxide. These two components together comprise 70–95 % of the cement. When these raw materials are blended, they produce tricalcium silicate, dicalcium silicate, tricalcium aluminate, and tetracalcium aluminoferrite’. The patent also stated that ‘MTA is Type 1 Portland cement (American Society for Testing Materials), with a fineness (Blaine number) in the range of 4,500–4,600 cm^2/g. A radiopacifier (bismuth oxide) is added to the cement for dental radiological diagnosis’.

Calcium oxide and silicon dioxide are the raw materials used for the manufacture of Portland cement. When these oxides are sintered together with other raw materials, tricalcium silicate, dicalcium silicate, tricalcium aluminate and tetracalcium aluminoferrite are produced. The aluminoferrite phase is only present in the grey cement [64]. White MTA was introduced later (circa 2001). The current US patent for white MTA is dated 2011. This supersedes all previous applications. The white MTA uses the same formulation of the grey version patented in 1995; however, the 2011 patent specifies the use of white Portland cement with low levels of iron [69].

J. Camilleri, BChD, MPhil, PhD, FIMMM, FADM
Department of Restorative Dentistry,
Faculty of Dental Surgery, Medical School,
Mater Dei Hospital, University of Malta,
Msida MSD 2090, Malta
e-mail: josette.camilleri@um.edu.mt

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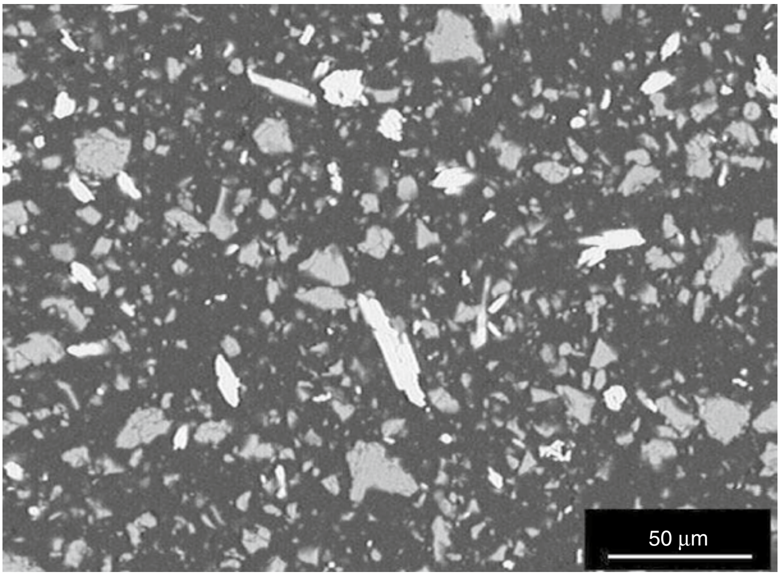


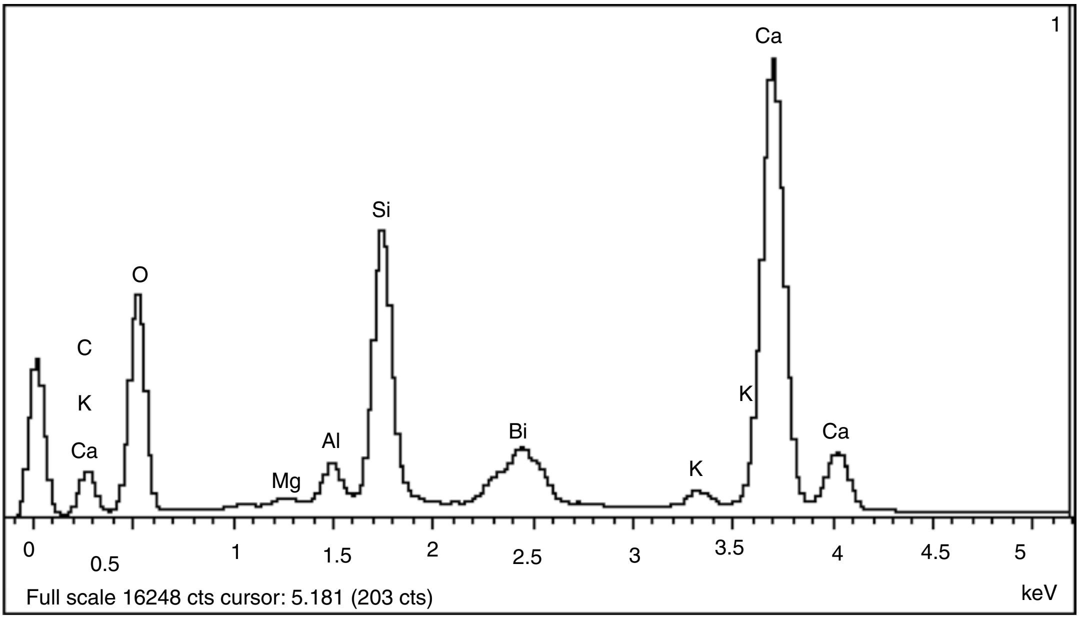
Fig. 2.1 Back-scatter scanning electron micrograph of polished surface of MTA powder (Reprinted with permission from Camilleri 2007 [21]. Copyright ©2007, John Wiley and Sons)

The US patent also states that the cement component is to be ASTM International Type 1 Portland cement with a specific Blaine fineness [2]. Portland cements used in industry are classified into different subcategories depending on their intended use. ASTM Type 1 Portland cements are common Portland cements that are intended for general purpose use, precluding contact with any chemical substances. The specified Blaine fineness is 4,500–4,600 cm^2/g indicating a very fine cement. In fact, the Colton Fast-Set brand was suggested for use.

The chemical composition and material microstructure of un-hydrated MTA have been investigated using various techniques. These techniques include scanning electron microscopy (SEM) [13, 17, 18, 21] and energy-dispersive spectroscopy (EDS) [5, 13, 17, 18, 21, 28, 30], X-ray fluorescence [17, 30] and X-ray diffraction (XRD) analysis [5, 7, 66] as well as XRD with Rietveld refinement [7, 17, 18]. The latter is valuable for quantitative analysis.

Scanning electron microscopy of polished sections of un-hydrated MTA embedded in resin shows distinctive cement grains and bismuth oxide particles, which are separated from one another. This feature indicates that the material is composed of a simple mixture of the two components (Fig. 2.1). The elemental composition of MTA as shown by EDS analysis indicates the presence of calcium, silicon and oxygen with minor peaks for aluminium, potassium, magnesium and bismuth. A semi-quantitative assessment of the elemental composition can be worked out using a cobalt standard assuming they are in the oxide form (Fig. 2.2). The oxide percentage composition depends on the mineralogy of the original cement. This can be quantitatively determined by X-ray fluorescence. The levels of silicon and calcium vary with the type of Portland cement used. Hence, these elemental levels are different for each brand of MTA.

The phases present in MTA are determined using X-ray diffraction analysis. Using this method of analysis, un-hydrated MTA exhibits peaks for tricalcium silicate, dicalcium silicate and bismuth oxide. Using a copper Kα tube, each phase has a particular pattern as shown in Fig. 2.3, which can then be searched and matched with data derived from the International Centre of Diffraction Data (ICDD) bank. Bismuth oxide (ICDD: 27-0053) exhibits typical peaks at 25.757, 26.906, 27.386, 28.010 and 33.229°2θ. Tricalcium silicate (ICDD: 86-0402) exhibits peaks at 29.414, 32.193, 32.504, 32.623, 34.355 and 41.298°2θ. Dicalcium silicate, usually exhibits a peak at 32.7°2θ,



Element	Weight%	Atomic%	Compd%	Formula%
Mg K	0.53	0.56	0.88	MgO
Al K	2.16	2.06	4.08	Al_2O_3
Si K	12.04	13.80	32.18	SiO_2
K K	1.13	0.74	1.36	K_2O
Ca K	38.08	24.47	53.28	CaO
Bi M	7.37	0.91	8.21	Bi_2O_3
O	35.69	57.46		
Totals	100.00			

Fig. 2.2 Energy-dispersive spectroscopy of a typical MTA powder and semi-quantitative elemental composition

however such a peak is difficult to discern, due to its superimposition with the peaks present in the tricalcium silicate phase. Tricalcium aluminate is also present in un-hydrated MTA but in minimal quantities. X-ray diffraction analysis of MTA thus eliminates the myth that MTA is composed mainly of oxides. Thus, the term ‘trioxide aggregate’ is essentially a misnomer.

Quantitative phase analysis can be performed by Rietveld refinement using an internal standard such as rutile (titanium dioxide) added to the unhydrated MTA. The principle of Rietveld analysis is to compare the experimental pattern with a pattern simulated based on the presumed amounts, crystal parameters and equipment parameters of a mixture of known phases. Rietveld refinement enables the amounts of different phases in anhydrous cementitious materials to be determined to a high degree of precision [71]. Quantitative assessment of ProRoot MTA (Dentsply Tulsa Dental, Johnson City, TN, USA) and MTA Angelus (Angelus, Londrina, Brazil) is shown in Table 2.1. Both cements exhibit different quantities of tricalcium silicate and dicalcium silicate when compared to Portland cement. The difference is due to variations in the manufacturing of Portland cement used as a raw material for preparing MTA. Phase analysis of ProRoot MTA has been published by Camilleri in 2008 [18] and has been validated by other researchers using Rietveld X-ray diffraction analysis [7] (Table 2.1). The main difference between the two

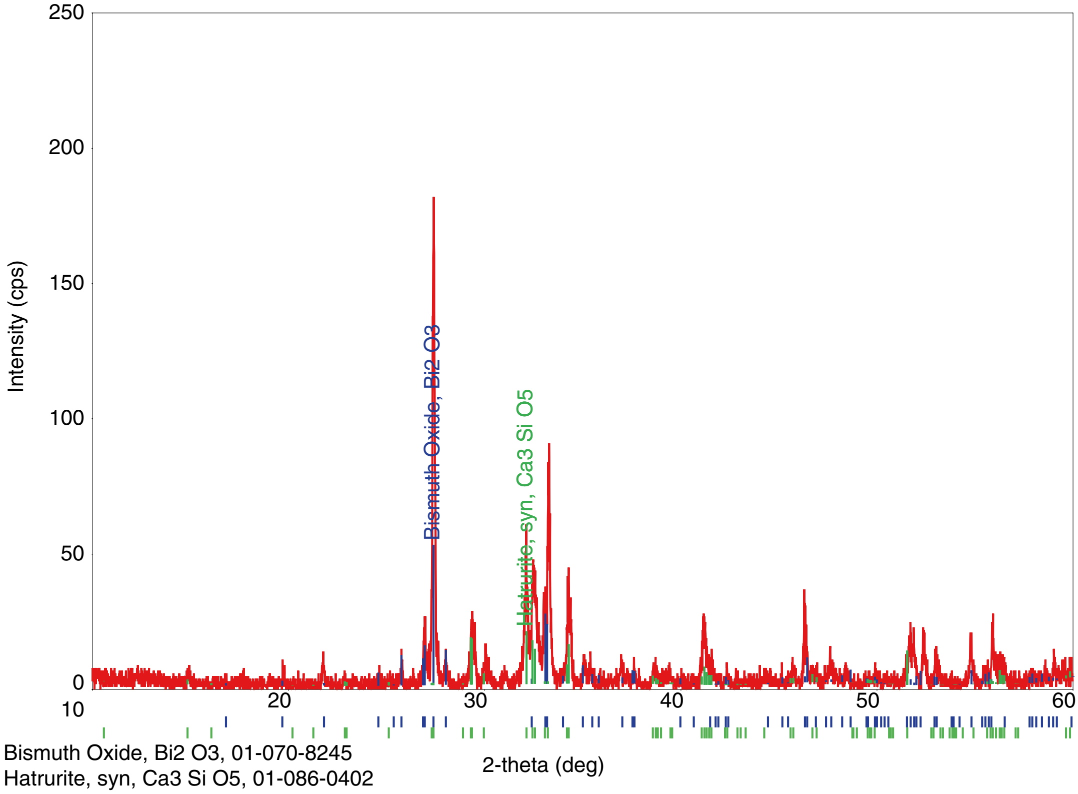


Fig. 2.3 X-ray diffractogram of un-hydrated MTA showing the main phases present

Table 2.1 Rietveld X-ray diffraction analysis of the phases present in un-hydrated Portland cement, ProRoot MTA and MTA Angelus

	Material type in mass %		
Phases identified	Portland cement	ProRoot MTA[a]	MTA Angelus[b]
Tricalcium silicate	74.7	53.1 (51.9)	66.1
Dicalcium silicate	7.4	22.5 (23.2)	8.4
Tricalcium aluminate	3.6	0.0 (3.8)	2.0
Gypsum	1.1	0.0	0.0
Hemihydrate	1.1	0.0	0.0
Anhydrite	2.7	1.5 (1.3)	0.0
Calcium carbonate	5.0	1.4	0.0
Calcium oxide	0.0	0.0	8.0
Bismuth oxide	0.0	21.6 (19.8)	14.0

Adapted from Camilleri [18], [a]Belío-Reyes et al. [7], [b]Camilleri et al. [17]

studies is the presence of tricalcium aluminate in ProRoot MTA in the latter study [7]. Lack of an aluminate phase was also evident in scanning electron microscopy of polished sections of ProRoot MTA powder [18]. The absence of tricalcium aluminate phase, low levels of anhydrite and absence of gypsum may infer that the cement component in ProRoot MTA may not be a commercial Portland cement manufactured in a kiln but a laboratory-made cement. The manufacturer of ProRoot MTA (Dentsply Tulsa Dental Specialties, Tulsa, OK, USA) in fact claims that ProRoot MTA does not utilise a commercial Portland cement but the raw materials are certified for purity by inductively coupled plasma (ICP) spectroscopy. In the same document, the manufacturer also disclaims the presence of phosphate, which was stated to be the main constituent of MTA in the original publication [78]. In that publication, MTA was purportedly reported to be composed of ‘calcium oxide and calcium phosphate. Further analysis demonstrated that the former appeared as discrete crystals and the latter as an amorphous structure with no apparent crystal growth but a granular appearance. The mean value of the prisms was 87 % calcium and 2.47 % silica, the remainder being oxygen. In areas of amorphous structure, there seemed to be 33 % calcium, 49 % phosphate, 2 % carbon, 3 % chloride, and 6 % silica'.

Another calcium silicate-based cement, MTA Angelus, was found to contain tricalcium aluminate but no sulphate-containing phase (Table 2.1). The absence of the gypsum is claimed by the manufacturer to reduce the setting time of the material. In fact, MTA Angelus has been shown to set in less than 50 min [59], as opposed to ProRoot MTA which was reported to have a setting time of over 2 h [9, 10, 20, 25, 30, 78]. Furthermore, 8 % calcium oxide is present in MTA Angelus [17]. This calcium oxide is a result of a raw mix with poor combustibility and with an unstable thermal profile. ProRoot MTA exhibits a higher level of bismuth oxide when compared to MTA Angelus (Table 2.1). This accounts for the higher radiopacity of ProRoot MTA [15, 20].

2.3 MTA Fineness

The MTA patent [79, 80] specifies the brand of Portland cement used in the original MTA formulation (Colton Fast-Set brand: Blaine number in the range of 4,500–4,600 cm^2/g). The Blaine number is a numerical value which is calculated using the Blaine fineness measuring equipment. This is the industrial standard for measuring cement fineness. The Blaine method is specified by both European (EN 196-6) [34] and American (ASTM C204) [3] standards. Both standards specify an air permeability method wherein a bed of cement of known density is prepared; the resistance to a flow of air passing through the cement is measured and the fineness of the cement is calculated. This method measures cement fineness compared to standard cement. A range of 4,500–4,600 cm^2/g is considered a fine cement.

Other industrial methods for measuring cement fineness include the Lea and Nurse apparatus. This method is an absolute method for determining the fineness of a cement and is adopted by most cement manufacturers. The particle size distribution of MTA has been calculated using laser particle size analysis [14], optical methods which involve measuring particle sizes of cement on polished sections of cement powder [5, 30], flow particle image analyser [54, 55] and by using the BET (Brunauer–Emmett–Teller) gas adsorption method [12] to calculate the specific surface area of MTA [13, 17]. The latter method is an extension of the Langmuir theory, which is a theory for monolayer molecular adsorption to multilayers. This theory hypothesises that gas molecules physically adsorb on a solid in layers infinitely; as there is no interaction between each adsorption layer, the Langmuir theory may be applied to each layer. The BET method is widely used in materials and surface science for the calculation of surface areas of solids by physical adsorption of gas molecules. By application of the BET theory, it is even possible to determine the inner surface area of hardened cement paste.

Optical assessment of MTA shows that the cement contains more uniform and finer-sized particles than Portland cement [5, 30]. However, other researchers using the same method reported coarser and more irregularly shaped crystalline particles in MTA [5]. Optical assessment shows that MTA consists of particles with diameters ranging from less than 1 μm to approximately 30 μm, and occasionally up to 50 μm. Particles of bismuth oxide (10–30 μm) are numerous [30]. Flow particle image analyses of various calcium silicate-based hydraulic cements indicate that the cumulative percentages of particles ranging from 6 to 10 μm for grey ProRoot MTA, white ProRoot MTA, grey MTA Angelus, white MTA Angelus and Portland cement are 65, 73, 48, 53 and 70 %, respectively. Thus, MTA Angelus contains a larger number of small particles with relatively low circularity and a wider range of size distribution and is less homogeneous than ProRoot MTA. Furthermore, white MTA contains smaller particles with a narrower range of size distribution than grey MTA [54]. The cumulative percentage of particles that are between 0.5 and 3 μm in size was reported to be 88 % [55]. Laser granulometry of MTA confirmed that this cement has a smaller particle size when compared to Portland cement

[28]. Moreover, bismuth oxide, which is not present in Portland cement, exhibits a large particle size when examined microscopically [13] and with the use of laser granulometry [15].

ProRoot MTA and MTA Angelus were found to have a similar fineness when tested using the BET gas adsorption method [13, 17]. Both materials exhibit a specific surface area of approximately 1 m^2/g. A novel MTA (MTA Plus compounded by Prevest Denpro, Jammu, India, for Avalon Biomed Inc. Bradenton, FL, USA) has a specific surface area of 1,537 m^2/g [13], which is higher than the values obtained for MTA Angelus [17]. The higher specific surface area results in more surface available for cement reaction, which, in turn, results in a more rapid reaction rate.

2.4 Manipulation

Mineral trioxide aggregate is a water-based dental cement. It is usually supplied in pre-dosed powder and liquid that are mixed together to obtain a homogeneous paste. The recommended water/powder ratio is about 0.33. Changing the water/powder ratio affects the properties of MTA. The degree of solubility and the porosity of the cement increases when the water/powder ratio is increased. Cement pastes with a water/powder ratio higher than 0.33 are not viscous enough for clinical application. A ratio of 0.26 was the minimum that allowed a mix of putty consistency that can be manipulated [39]. Most MTA manufacturers supply prepacked 1 g powders with ampoules containing 0.33 g of water. Since the amount of material in each package is large enough for several applications, clinicians commonly estimate the amount of water and powder at the chairside, which results in using an unknown water/powder ratio. Variations in the water/powder ratio do not seem to affect the clinical performance of the material, No significant difference in material expansion [48] and no influence on the histological outcome was observed for MTA mixed at different water/powder ratios when used as a direct pulp-capping material on human healthy pulps [74]. When taking into consideration water/powder ratios in MTA, a distinction from water/cement ratio should be made. MTA contains 20 % bismuth oxide, which does not react with water. Thus effectively the water/cement ratio for MTA mixed at a water/powder ratio of 0.33 would be 0.41. Thus, comparison of properties of MTA with those of other systems using a different quantity or no radiopacifier or mineral additives is not possible since the effective water/cement ratio will vary depending on the quantity of additive. Modification of the water/cement ratio affects the properties of the set cement [29].

There have been a large number of reports on addition of various chemicals to the mixing liquid or replacement of the water by other liquids. The most popular is calcium chloride [1, 4, 10, 53, 56, 85], calcium nitrite/nitrate and calcium formate [85]. These chemical additions are also used in the industry to accelerate the setting of Portland cement. Setting accelerators affect the setting reaction of both tricalcium silicate and tricalcium aluminate [65].

Addition of water-soluble polymers [11, 14, 16, 19] increases material flow. ProRoot Endo Sealer is a commercial formulation using cement particles dispersed in a water-soluble polymer [49, 84]. The water-soluble polymer creates charges on the cement particles, resulting in repulsion of these charged particles with reduced flocculation and increased material flow at low water/cement ratios [65]. Propylene glycol has also been used to improve MTA flow [33]. Other polymers have been included to reduce washout of the unset cement. Anti-washout liquid is included in the MTA Plus formulation (compounded by Prevest Denpro, Jammu, India for Avalon Biomed Inc. Bradenton, FL, USA).

Other clinically available liquids have been added to MTA to improve its handling characteristics. These include local anaesthetic solution [40, 50, 53, 81, 83], sodium hypochlorite, chlorhexidine gluconate, saline and physiological solution [42, 50, 53], calcium lactate gluconate [51, 56] and citric acid [56]. The use of un-hydrated MTA as a root-end filling material has been reported [67]. Un-hydrated MTA will hydrate using the physiological fluid available at the root-end cavity. Non-specific and contradicting effects have been reported with the use of these chemicals. Physiological and synthetic tissue fluids contain chloride ions and glucose. The former is a cement hydration accelerator [65] while glucose is a hydration retarder. The combination of these effects may adversely alter the cement paste microstructure. Local anaesthetic solution contains both chloride and sulphate ions which again have a conflicting effect on cement hydration. A higher content of sulphate in the cement may lead to sulphate attack, whereby excessive expansion and cracking will be observed over time due to delayed ettringite deposition [64]. MTA is known to have low levels of sulphate ions and, although these ionic levels would alter the relative proportions of ettringite and monosulphate phases for a given degree of cement hydration, they are unlikely to create sulphate attack of the set cement. The chloride present in both synthetic tissue fluids and anaesthetic solutions may also alter the relative proportions of ettringite and monosulphate phases due to the formation of Friedel's salt (calcium chloroaluminate, $3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$). The formation of Friedel's salt will change the lattice structure of hydrated cement monosulphate phases and can potentially lead to microcracking [64].

Other variations to the mixing liquid include replacement of the water by various resins. These modifications result in the development of light-activated MTA and resin-modified MTA for use as root canal sealer cement. Resin-modified MTA reduces the setting time and enhances the bonding to both dentine and overlying composite, thus purportedly reducing micro-leakage. The use of a number of resin systems has been reported, with the main ones being light-curing systems containing bisphenol A-glycidyl methacrylate (bis-GMA) and a biocompatible resin [45, 46] consisting of 2-hydroxyethyl methacrylate (HEMA), triethylene glycol dimethacrylate (TEGDMA), camphorquinone and ethyl-4-(dimethylamino)benzoate (EDMAB), with or without polyacrylic co-maleic acid [42, 43], bis-GMA and TEGDMA [36] and bis-GMA, pyromellitic acid diethylmethacrylate (PMDM) and HEMA [70]. Chemically cured resins have also been employed [26, 36]. Other resins were added with the aim of increasing material flow, thus making MTA suitable to be used as a sealer cement [45, 46]. One such formulation is marketed by Angelus (Angelus, Londrina, Brazil) as MTA Fillapex. The latter is composed of MTA, a salicylate resin (methyl salicylate, butylene glycol and colophony) and other additives. Other proprietary brands such as MTA Obtura and Endo CPM Sealer exist. These sealer cements contain other additives to the MTA formula, that enhance material flow. Other experimental epoxy resin-based systems that incorporate MTA as fillers have also been reported as sealer cements [57].

Classically, MTA is mixed by manipulating the powder and liquid components on a mixing pad. Alternative mixing techniques such as the use of an amalgamator have been investigated [6, 63, 73]. MM MTA™, manufactured by MICRO-MEGA (Besançon Cedex, France), is supplied as MTA capsules that enable the MTA to be mixed using an amalgamator. Ultrasonic agitation has also been employed for mixing MTA [6, 63, 73]. The effectiveness of mechanical mixing and ultrasonic agitation is not clear, although mechanical mixing was shown to enhance the compressive strength of the set material, while ultrasonic agitation was found to improve the compressive strength of the material regardless of the mixing technique [6]. In addition to enhanced material micro-hardness [63], other research has shown that the various mixing methods have no significant effects on the resultant MTA mixtures [73]. Application of a condensation pressure of 1.68 MPa results in enhanced compressive strength. Higher condensation pressures result in fewer voids and micro-channels, while specimens prepared with lower condensation pressures exhibit distinctive crystalline structures [62].

2.5 Washout

One of the drawbacks of MTA is washout after it is placed in situ. Washout refers to the tendency of a freshly prepared cement paste to 'disintegrate upon early contact with blood or other fluids' [82]. Washout can be measured using different methods. Most methods involve immersion of the unset cement in a liquid [24, 52, 58]. Agitation [82] or freeze drying [52] is then employed to disrupt the cement; alternatively the cement is sprayed with air from a specified distance [68]. The amount of material lost is then determined using photography [68] or quantified using a gravimetric method [52, 82]. One of the latest reported methods [37] includes a setup based on Specification CRD-C 661-06 [75] which was scaled down to allow testing of dental materials. When the results were compared to a metered water spray, they were found to yield quantitative, objective and reproducible results [37]. In the same study, MTA Plus and MTA Angelus exhibited washout when compared to Intermediate Restorative Material (IRM, Dentsply Caulk, Milford, Delaware, USA) and dental amalgam. The addition of anti-washout gel manufactured by Avalon Biomed Inc. reduced washout considerably [38].

2.6 Setting Reaction

Mineral trioxide aggregate hydrates when it comes in contact with water and undergoes two main reactions. The tricalcium silicate and dicalcium silicate react with water to form calcium silicate hydrate and calcium hydroxide. The tricalcium aluminate reacts with water and, in the presence of calcium sulphate, produces ettringite initially. When the sulphate-containing phases are depleted, a monosulphate phase is formed [21]:

$$\underset{\text{Tricalcium silicate + Water}}{2\left(3\text{CaO.SiO}_2\right) + 6\text{H}_2\text{O}} \rightarrow \underset{\text{calcium silicate hydrate + Calcium hydroxide}}{3\text{CaO.2SiO}_2\text{.3H}_2\text{O} + 3\text{Ca}\left(\text{OH}\right)_2} \tag{2.1}$$

$$\underset{\text{Dicalcium silicate + Water}}{2\left(2\text{CaO.SiO}_2\right) + 4\text{H}_2\text{O}} \rightarrow \underset{\text{calcium silicate hydrate + Calcium hydroxide}}{3\text{CaO.2SiO}_2\text{.3H}_2\text{O} + \text{Ca}\left(\text{OH}\right)_2} \tag{2.2}$$

$$\underset{\text{Tricalcium aluminate + Gypsum + Water}}{3\text{CaO.Al}_2\text{O}_3 + \text{CaSO}_4 + \text{H}_2\text{O}} \rightarrow \underset{\text{Ettringite}}{3\text{CaO.Al}_2\text{O}_3\text{.3CaSO}_4\text{.31H}_2\text{O}} \tag{2.3}$$

The reactions that occur in MTA after hydration are the same reactions that are seen in Portland cement. During the initial stages of reaction, calcium silicate hydrate is formed; coating the cement particles with calcium silicate hydrate prevents further reaction. Tricalcium aluminate dissolves and reacts with the calcium and sulphate ions present in the liquid phase to produce ettringite that also precipitates on the cement particle surface. The initial phase is followed by a dormant period wherein the hydrate coating on the cement grains prevents further hydration. The dormant period lasts for 1–2 h, and is a period of relative inactivity when the cement is plastic and workable. Following the completion of the dormant period, setting of the cement proceeds to the acceleration stage wherein the hydration process accelerates again. The rate of tricalcium silicate hydration increases and more calcium silicate hydrate gel is formed. Hydration of dicalcium silicate also increases at this stage. Sulphate ions are depleted and monosulphate forms from ettringite. Crystalline calcium hydroxide also precipitates from the liquid phase.

The hydration progress can be monitored using calorimetry. The heat flux released by the chemical reaction is monitored over time and enables estimation of the beginning of setting and the rate of increase of the mechanical performance of the cement paste. Both MTA Angelus and MTA Plus present an initial endothermic peak followed by an exothermic peak (Fig. 2.4). The first 2 h correspond to an induction period followed by initial setting and then hardening of the material. The initial endothermic peak is due

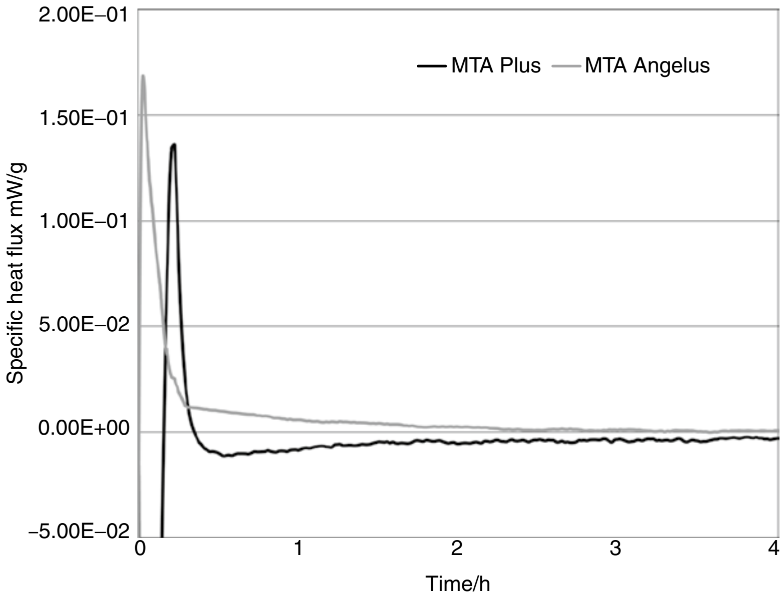


Fig. 2.4 Graphical representation of heat flux generated with time for MTA Plus and MTA Angelus

to the wetting of the surface. The first part of the exothermic peak is correlated with the very rapid and very exothermic hydration [13, 17]. It is interesting to note that MTA Angelus exhibits a higher exothermic peak, which occurs ahead of that of MTA Plus. This is caused by reaction of the calcium oxide present in MTA Angelus with water [17].

2.7 Characterisation of Set MTA

A combination of microscopy, elemental analysis and phase analysis has been used to characterise and evaluate the hydration mechanisms of MTA [13, 17, 18, 21]. The X-ray diffractograms are useful as MTA materials are mostly crystalline and individual mineral phases can be identified. Scanning electron microscopy allows observation of material microstructure and surface visualisation. Moreover, characterisation by X-ray energy dispersive analysis provides qualitative information of the elemental constitution of the test materials. Other useful methods have been employed for characterisation of MTA, including Fourier transform infrared spectroscopy (FT-IR) and Laser Raman spectroscopy. Laser Raman spectroscopy is largely complementary to infrared spectroscopy, but spectral interpretation is simpler [8]. The major components of Portland cement give distinctive Raman spectra [41, 44]. Both FT-IR and Raman spectroscopy have been used to investigate the interaction of calcium silicate cements with physiological solutions [27, 47, 76, 77]. These techniques are an adjunct to phase analysis by XRD and aid to verify the phases identified when peak overlap exists; which is the main disadvantage associated with the use of XRD to analyse Portland cement-based materials. This problem may be addressed by using the Rietveld method [71], which allows standardisation of powder diffraction analysis through the use of calculated reference diffraction patterns based upon crystal structure models.

Reaction by-products produced upon hydration of the cement are deposited around the periphery of the un-hydrated cement particles. As hydration proceeds, there is evidence of more reaction by-products. The hydration reaction takes several years to complete, although the cement mass would have achieved the final hardening and

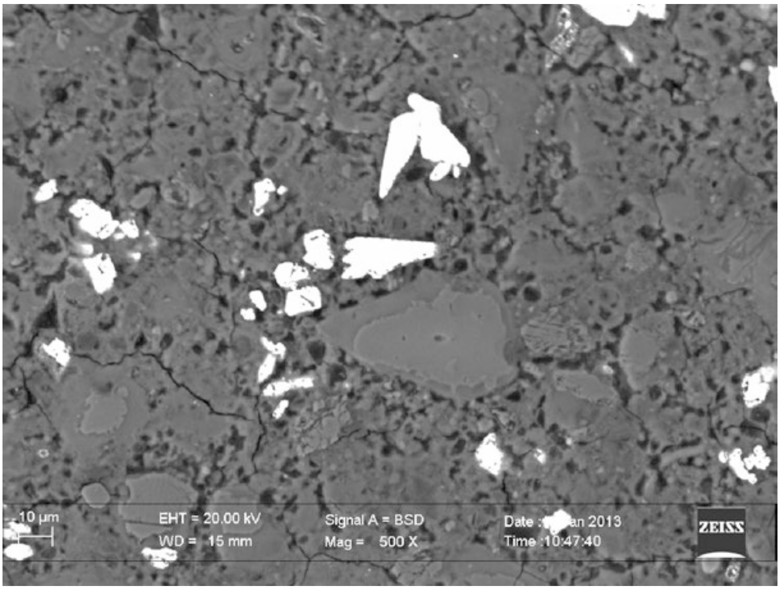


Fig. 2.5 Back scatter scanning electron micrograph of hydrated MTA after immersion in water for 28 days showing un-hydrated cement particle enclosed by a reaction rim. *Shiny particles* are bismuth oxide (×500 mag.)

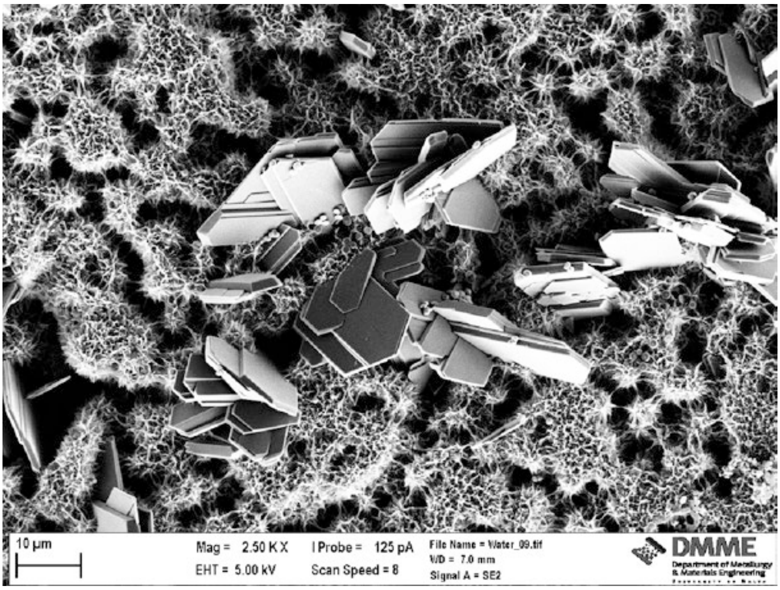


Fig. 2.6 Secondary electron scanning electron micrograph of MTA surface showing calcium silicate hydrate (*honeycomb appearance*) and calcium hydroxide (*hexagonal plates*) deposited on its surface (×2,500 mag.)

maximum physical and mechanical properties by 28 days. Hydrating MTA can be observed on back-scatter scanning electron micrographs of polished cement specimens (Fig. 2.5). The formation of cement by-products can be monitored by scanning electron microscopy in secondary electron mode. Calcium silicate hydrate exhibits a typical honeycomb appearance, while calcium hydroxide is deposited in the form of hexagonal plates (Fig. 2.6). The surface deposits are evident on the cement surface and may be measured by optical profilometry [35] (Fig. 2.7). The composition of the surface deposits in turn can be assessed using XRD analysis with the glancing angle modification. Phase analysis is usually performed by powder diffractometry using the Bragg–Brentano principle and thus moving both the X-ray source and the detector at a specified angle and speed.

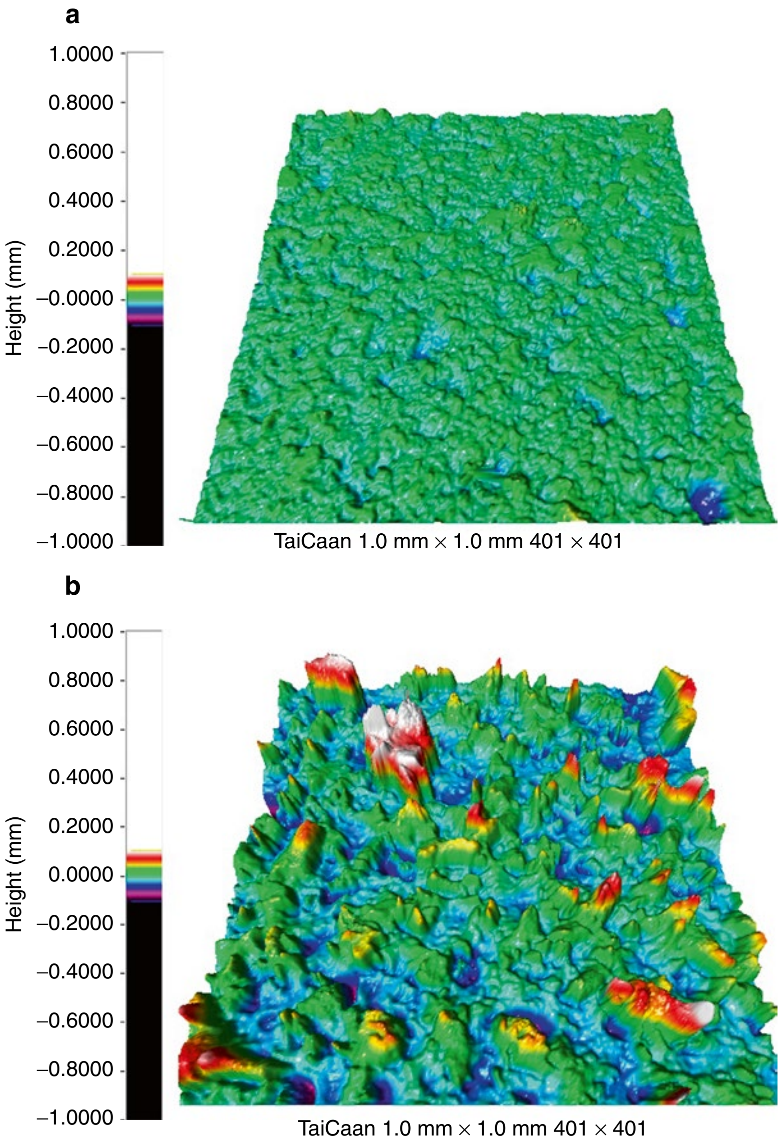


Fig. 2.7 Surface noncontact profilometry of MTA surface (**a**) before and (**b**) after immersion in Hank's balanced salt solution (Reprinted from Formosa et al. [35], copyright 2012, with permission from Elsevier)

With the glancing angle technique, the surface analysis is greatly enhanced by reducing the interference from the sample substrate and increasing the absorption path of the incident beam within the layer itself. An X-ray diffractogram of the MTA surface deposits exhibited a definite peak for beta-calcium phosphate when MTA was immersed in a physiological solution, whereas no peaks were visible when the material was immersed in water (Fig. 2.8).

Leaching of calcium hydroxide in solution may be monitored by inductive-coupled plasma mass spectroscopy (ICP-MS). High levels of calcium ions have been demonstrated in solution. If MTA is left exposed to the environment, the calcium hydroxide reacts with the atmospheric carbon dioxide resulting in deposition of calcium carbonate on the cement surface. These deposits are commonly mistaken to be an integral part of the cement microstructure.

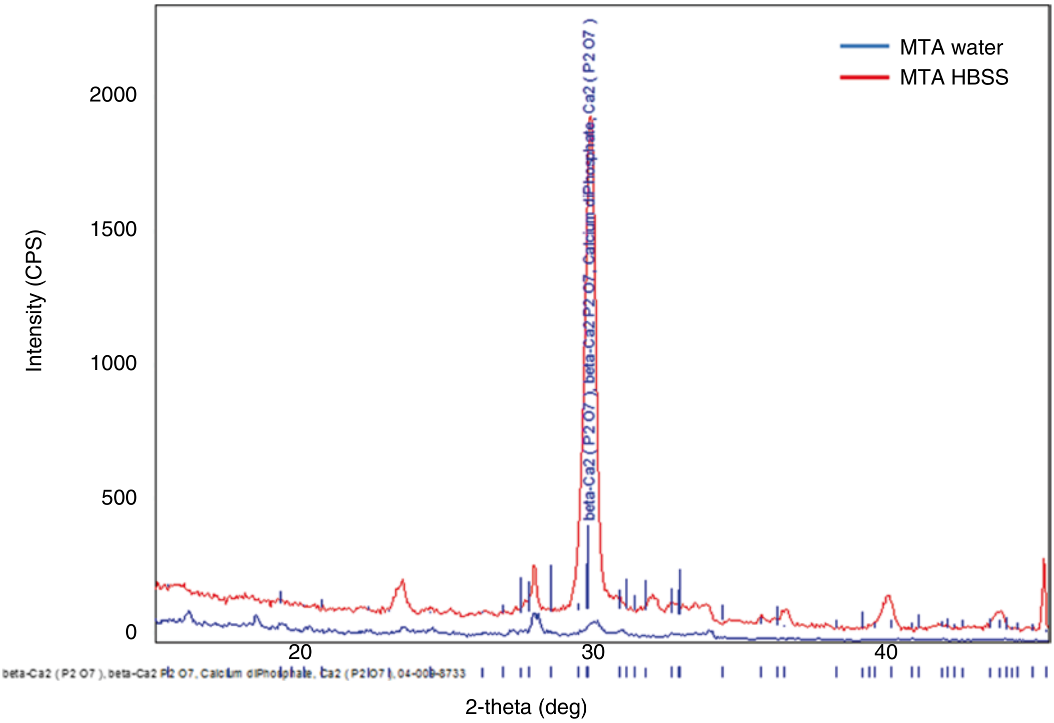


Fig. 2.8 Glancing angle X-ray diffractogram of MTA analysing surface deposits on MTA after immersion in water and Hank's balanced salt solution (HBSS) for 28 days

Table 2.2 Rietveld X-ray diffraction analysis of the phases present in un-hydrated and hydrated ProRoot MTA

	Material type in mass %	
Phases identified	Un-hydrated	Hydrated
Tricalcium silicate	53.1	10.6
Dicalcium silicate	22.5	14.9
Tricalcium aluminate	0.0	0.0
Gypsum	0.0	0.0
Hemihydrate	0.0	0.0
Anhydrite	1.5	0.0
Calcium hydroxide	0.0	14.4
Calcium silicate hydrate	0.0	49.5
Ettringite	0.0	2.1
Bismuth oxide	21.6	8.4

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Calcium silicate hydrate is amorphous and thus cannot be detected by X-ray diffraction analysis. However, the other cement components and bismuth oxide are crystalline. As hydration progresses, a rise in calcium hydroxide peak (ICDD: 44-1481) is seen at 18.008 and 34.102°2θ using a copper Kα X-ray radiation. The un-hydrated tricalcium silicate phase (ICDD: 86-0402) at 29.414, 32.193, 32.504, 32.623, 34.355 and 41.298°2θ usually decreases in intensity (Fig. 2.9). Quantitative measurements of the different phases of MTA may be performed using Rietveld refinement of X-ray diffraction plots (Table 2.2). This quantitative assessment verifies the reduction in tricalcium silicate and dicalcium silicate levels of the un-hydrated cement as hydration proceeds, with the formation of calcium silicate hydrate. Calcium hydroxide and low levels of ettringite are also produced.

Energy-dispersive spectroscopy gives the elemental distribution of particular elements in the hydrated MTA. A series of X-ray spectra are collected and quantified using suitable mineral standards. The data plotted in a standard format shows atomic ratios of silicon and calcium (Si/Ca) plotted against aluminium and calcium ratios (Al/Ca). These atomic ratio plots are used in

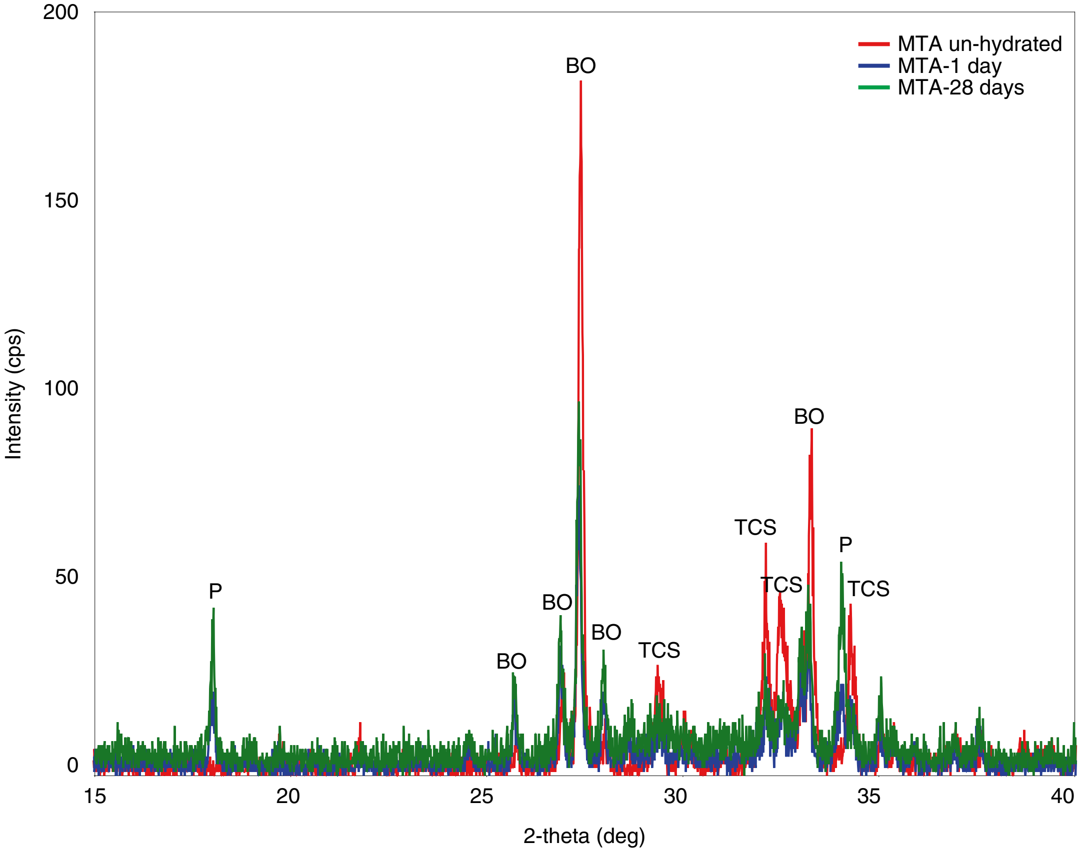

Fig. 2.9 X-ray diffractogram of un-hydrated and hydrated MTA after 1 and 28 days showing the main phases present. The tricalcium silicate peaks are more pronounced in the un-hydrated MTA compared to the hydrated forms. Portlandite is only present in the hydrated MTA. *BO* bismuth oxide, *P* portlandite or calcium hydroxide, *TCS* tricalcium silicate

scanning electron microscopy and X-ray energy-dispersive analyses (SEM/EDS) studies of cementitious materials and enable the principal hydration products to be differentiated. An atomic ratio plot for MTA's main constituents is shown in Fig. 2.10a. The atomic ratio plots of MTA show a mixture of calcium hydroxide and calcium silicate hydrate.

Infrared and Raman spectra also exhibit distinctive features for MTA [36, 44, 76]. Typical FT-IR plots for un-hydrated MTA and hydrated material before immersion and after immersion in solution for 28 days are shown in Fig. 2.11. The un-hydrated MTA displays a tricalcium silicate peak at ~875 cm^{-1}. Tricalcium silicate (peaking at ~875 cm^{-1}) is also identified in all the set cements with the peak reduced in intensity when compared to the un-hydrated material. The set MTA exhibits a characteristic set of bands at 973–981 cm^{-1} which are attributed to tricalcium silicate hydrate. These are the most intensive bands in all the spectra and can be assigned to Si–O stretching. In addition, very weak bands at 821–842 cm^{-1} also assigned to Si–O stretching vibrations are also present. The splitting of the band in the 1,000–850 cm^{-1} region results from the presence of silicate phases. The bands in the region of 1,640 cm^{-1} are due to H–O–H bending vibrations of H_2O molecules. Calcium hydroxide, which is a by-product of hydration of tricalcium silicate cement, also exhibits bands in the region of 1,600–1,400 cm^{-1}. The bands at 1,600–1,300 cm^{-1}

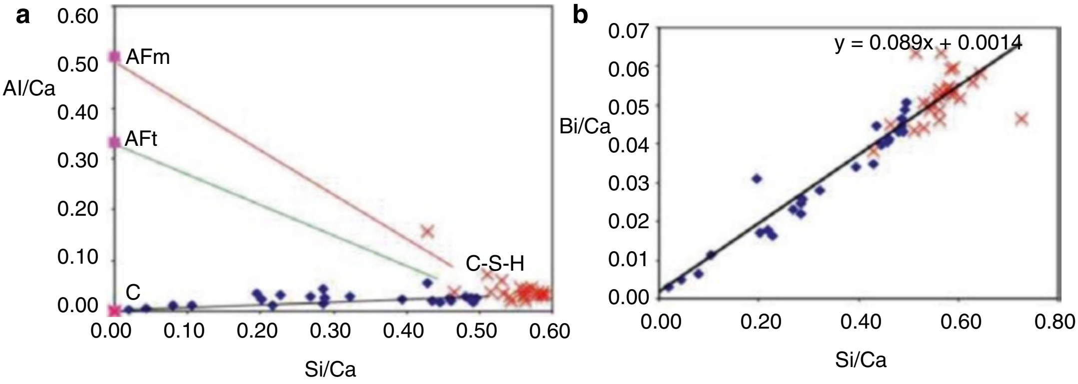

Fig. 2.10 (**a**, **b**) Atomic ratio plots of (**a**) Al/Ca versus Si/Ca indicating a mixture of calcium hydroxide and calcium silicate hydrate. *C* calcium hydroxide, *C–S–H* calcium silicate hydrate, *AFm* monosulphate, *AFt* ettringite and (**b**) Bi/Ca and Si/Ca demonstrating the relationship of bismuth and calcium silicate hydrate gel of MTA mixed with water and cured in different environmental conditions (*blue dots* are in the core region, while *red* crosses in the periphery) (Reprinted with permission from Camilleri [21]. Copyright ©2007, John Wiley and Sons)

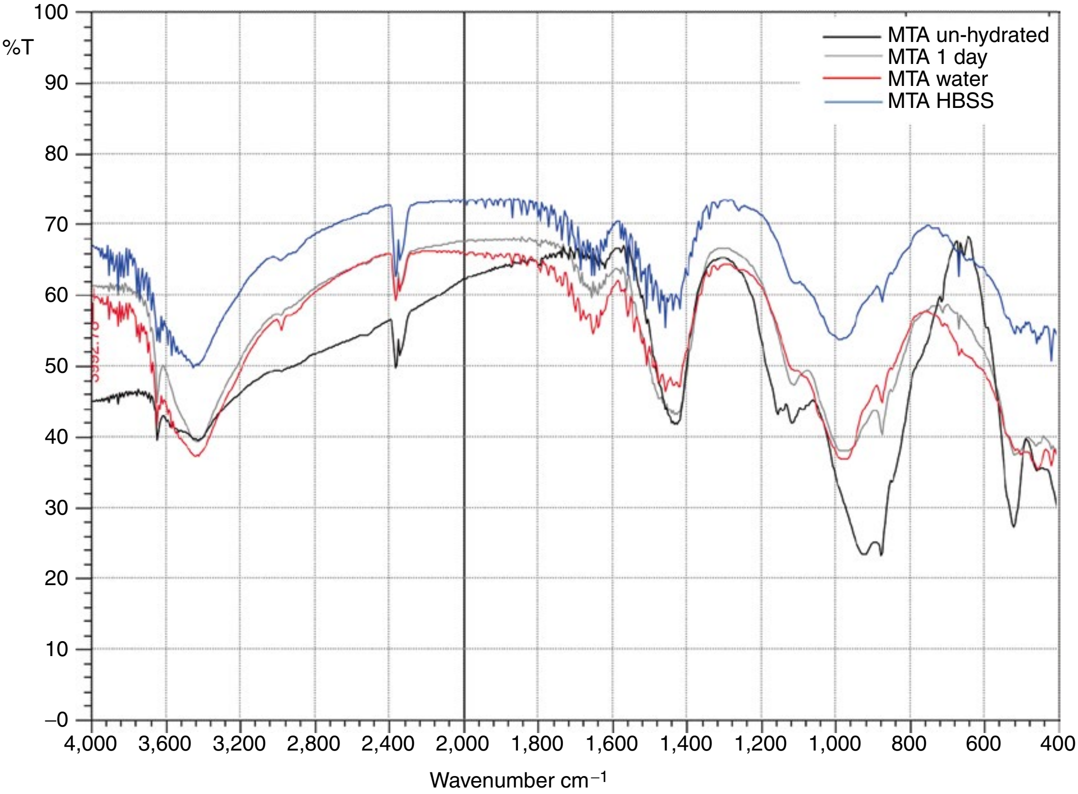

Fig. 2.11 Fourier transform infrared (FT-IR) spectroscopy of un-hydrated MTA, hydrated MTA and hydrated MTA stored in water and Hank's balanced salt solution (HBSS) for 28 days

correspond to the asymmetric stretching of CO_3^{2-}. Calcium carbonate is formed from the surface carbonation of cements by reaction of the calcium hydroxide with the atmospheric carbon dioxide.

Bismuth oxide is added to MTA to act as a radiopacifying agent since Portland cement is not sufficiently radiopaque. Quantitative X-ray diffraction analysis (Table 2.2) identifies a reduction of bismuth oxide after cement hydration, with 8.4 % present in the hydrated cement as opposed to the 21.6 % in the un-hydrated material [18]. Atomic ratio plots of Bi/Ca versus Si/Ca demonstrate a linear relationship between bismuth and silicon; the result infers that bismuth is replacing silicon in the calcium silicate hydrate structure (Fig. 2.10b).

2.8 Trace Elements

Since the main constituent of MTA is Portland cement, some concerns have been raised about the inclusion of trace elements in MTA. Portland cement is manufactured from naturally occurring raw materials in a kiln. Sometimes, waste materials are used as raw materials in the manufacturing of Portland cement for the construction industry. Additionally, waste materials are also used as replacement for primary fuels in order to keep the manufacturing costs low. This potentially leads to the inclusion of trace elements in the final product. Traces of arsenic, lead and chromium have been reported in both grey and white MTA [22, 23, 31, 32, 60, 61, 72]. Although the levels of acid-extractable trace elements are high, the amounts leached in solution are negligible. The inclusion of heavy metals in Portland cement has raised concerns regarding its use as a base material for MTA, since the latter is applied in contact with both hard and soft human tissues.

Conclusions

Mineral trioxide aggregate is composed of Portland cement and bismuth oxide radiopacifier. The cement component is in turn composed of tricalcium and dicalcium silicate and tricalcium aluminate which on reaction with water form calcium silicate hydrate and calcium hydroxide from the reaction of tri- and dicalcium silicate and ettringite and monosulphate from the reaction of tricalcium aluminate with water in the presence of gypsum. Addition of chemical and mineral oxides, cement fineness and incorporation of anti-washout gel can modify the setting time, workability, washout characteristics and reaction kinetics of the cement. Un-hydrated and set MTA can be characterised by a variety of techniques including SEM and EDS analysis, XRD with and without Rietveld correction, FT-IR and laser Raman techniques. A combination of techniques is always advisable.

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