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Characterization and chemical activity of Portland cement and two experimental cements with potential for use in dentistry

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Abstract

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Aim To evaluate the chemical activity of Portland cement and two other cement types with similar chemical composition to mineral trioxide aggregate with the aim of developing these cements for further applications in dentistry.

Methodology The chemical composition of the three cement types namely Portland cement, calcium sulpho-aluminate cement and calcium fluoro-aluminate cement was evaluated by elemental analysis using energy dispersive analysis with X-ray under the scanning electron microscope and by X-ray diffraction analysis (XRD) to determine the phases. The constituents of the hydration reaction by-products were evaluated by XRD analysis of the set cements at 1, 7, 28 and 56 days and by analysis of the leachate by ion chromatography. The pH of both cements and leachate was determined at different time intervals. Cements admixed with micro-silica were also tested to determine the effect of micro-silica on the reaction by-products.

Results All three cement types were composed of tricalcium silicate as the main constituent phase. The hydration reaction of Portland cement produced calcium hydroxide. However, this was not present in the other cements tested at all ages. Admixed micro-silica had little or no effect on the cements with regard to reaction by-products. The pH of all cements tested was alkaline.

Conclusions Both the experimental calcium sulpho-aluminate cement and calcium flouro-aluminate cement had different hydration reactions to that of Portland cement even though calcium silicate was the major constituent element of both cement types. No calcium hydroxide was produced as a by-product to cement hydration. Micro-silica addition to the cement had no effect on the hydration reaction.

Keywords: accelerated cements, chemical analysis, Portland cement.

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Introduction

Mineral trioxide aggregate (MTA) is used mostly in endodontics as a root-end filling material. The material has been shown to be biocompatible when tested by a variety of techniques including cell culture with established human osteo-sarcoma cells (Koh *et al.* 1997, 1998, Mitchell *et al.* 1999, Abdullah *et al.* 2002, Camilleri *et al.* 2004), radiochromium release and agar overlay (Torabinejad *et al.* 1995b), subcutaneous and intra-osseous implantation (Torabinejad *et al.* 1995d, 1998, Moretton *et al.* 2000, Holland *et al.* 1999, 2001a, 2002) and periradicular tissue assessment (Torabinejad *et al.* 1995c, 1998). MTA induces apical hard tissue formation with cementum being a frequent finding when root-ends were filled with the material (Torabinejad *et al.* 1997). In addition, MTA used for pulp capping or partial pulpotomy, stimulated reparative dentine formation with reports showing that MTA-capped pulps resulted in complete

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dentine bridge formation with no signs of inflammation (Pitt Ford *et al.* 1996, Tziafas *et al.* 2002, Andelin *et al.* 2003, Faraco & Holland 2004, Nair *et al.* 2008). The same results were obtained when MTA was placed over pulp stumps following pulpotomy (Holland *et al.* 2001b). These properties would be ideal for dressings over vital pulps as it would preserve their integrity.

Unfortunately all commercial forms of MTA have an extended setting time (Torabinejad *et al.* 1995a), which makes their use in the oral cavity limited. The compressive strength of MTA was shown to be comparable with that of other root-end filling materials (Torabinejad *et al.* 1995a). However, improvements in setting time and compressive strength of MTA are necessary to improve the material and facilitate its use in other situations.

Mineral trioxide aggregate is composed of Portland cement with bismuth oxide added for radio-opacity (Torabinejad & White 1995). Portland cement is composed of tricalcium and dicalcium silicate, tricalcium aluminate and tetracalcium aluminoferrite with the white Portland cement (WPC) lacking the ferrite phase. Calcium sulphate (gypsum) is added to control the rate of reaction (Taylor 1997). The hydration mechanisms of Portland cement are well documented (Taylor 1997). The calcium silicates react with water to produce calcium silicate hydrate gel and calcium hydroxide. In addition, the tricalcium aluminate in the presence of calcium sulphate reacts to produce a high-sulphate calcium sulpho-aluminate (ettringite). The reactions take place simultaneously resulting in a final set after approximately 4 h (Taylor 1997). The hydration mechanisms of MTA are similar to those of Portland cement. The main constituent phases of MTA are tricalcium and dicalcium silicate, which on hydration produce calcium silicate hydrate gel and calcium hydroxide (Camilleri *et al.* 2005a). However, it has been shown that MTA has low levels of tricalcium aluminate thus affecting the production of ettringite usually formed on hydration of Portland cement (Camilleri 2007). The bismuth oxide added as a radiopacifier also affects the hydration mechanism of the MTA as it forms part of the structure of C–S–H and also affects the precipitation of calcium hydroxide in the hydrated paste (Camilleri 2008). The calcium hydroxide produced as a result of the hydration mechanism accounts for the biocompatibility of the cement. Whilst osteosarcoma cells grew and formed a monolayer over both grey and white MTA (Camilleri *et al.* 2004), cell growth was observed mostly on the elusion produced by the cement at different stages of curing, rather than over the cement itself (Camilleri *et al.* 2005b). Fast-setting proprietary brand Portland cements with a similar chemical composition but where calcium hydroxide was not produced as a by-product of hydration did not encourage cell growth (Camilleri *et al.* 2008). This indicated that it is the calcium hydroxide produced rather than the cement itself that produces the biocompatible effect.

The aim of this study was to investigate the chemical composition and mechanism of hydration of two cement types with potential for use in dentistry compared with that of Portland cement.

Materials and methods

Two cement types were used in this study.

1. CSA: calcium sulpho-aluminate cement mixed in the following proportions:
   - 3 parts calcium aluminate (Lafarge Special Cements, Nottingham, UK)
   - 8 parts WPC (Lafarge Asland, Valencia, Spain)
   - 1 part synthetic anhydrite (Lafarge Special Cements, Nottingham, UK)
2. CFA: calcium flouro-aluminate cement, (Italcementi SPA, Bergamo, Italy).

A superplasticizing admixture (Degussa Construction Chemicals, Manchester, UK) was added to the mixing water to increase the workability of the mix and also to reduce the amount of mixing water required by the cement. The cement was replaced by micro-silica (Elkem Materials, High Wycombe, UK) by weight to improve the mechanical properties of the material. In addition, the effect of micro-silica on these cements was also investigated. WPC (Lafarge Asland, Valencia, Spain) was used as the control.

Chemical analysis of unset cements

The chemical composition of the two cement types was determined using energy dispersive analysis by X-rays (EDAX) in the scanning electron microscope (SEM) (Hitachi S3500, Hitachi, Wokingham, UK). A thin layer of powder was dispersed over a Perspex® slab mounted on an aluminium stub (Agar Scientific, Stansted, UK). The stubs were carbon coated (Emitech K250, Ashford, UK) for electrical conductivity. The specimens were then viewed under the SEM and EDAX was carried out to determine the constituent elements of the powders. Two stubs were made for each material and the analysis was performed twice for each sample.

In addition, phase analysis was carried out on the calcium aluminate and synthetic anyhdrite, CFA and WPC using X-ray diffraction (Ital Structures Compact 3K5, Riva del Garda, Italy). The diffractometer used Cu Kα radiation at 30 mA and 40 kV. Samples were presented in powder form on a sample holder. The crystalline structure of the test cement was determined by passing a beam of X-rays of known wavelength into the specimen whilst rotating it through an angle θ. The intensity of X-rays from the sample was measured by a detector. The detector was rotated between 5–60° at 0.02°θ per 0.1 s.

Phase identification was accomplished by use of search-match software utilizing ICDD database (International Centre for Diffraction Data, Newtown Square, PA, USA).

Chemical analysis of set cements

The phase analysis of the set cements was performed after 1, 7, 28 and 56 days of curing using X-ray diffraction analysis. Twenty grams of powder was mixed on a glass slab with water at a water/cement ratio of 0.37 and superplasticizer was added to the CSA and CFA and the micro-silica replaced versions. The mix was cast in circular moulds 20 mm in diameter and 20 mm high. The samples were removed from the moulds after 24 h and allowed to cure at 37 °C and 100% humidity. At each time-point, the cement samples were crushed to a fine powder using a mortar and pestle and X-ray diffraction analysis was performed using the same conditions used for phase analysis of unset cements.

Chemical analysis of leachate

Chemical analysis of cement products in solution was performed using ion chromatography. One gram of cement was mixed with water and superplasticizer. Micro-silica was used to replace 10% of the cement in micro-silica replaced versions. WPC was mixed with water only. The cement was compacted in circular moulds 10 mm in diameter, cured at room temperature and removed from the moulds after 24 h. The samples were weighed and placed in closed plastic sterile containers (Labplex, Birmingham, UK). Five millilitres of deionized water were added to each container. Containers filled with deionized water were used as controls. The samples were placed in a refrigerator at 4 °C and allowed to cure for 1, 7, 28 and 56 days. At each time-point, the cement sample was discarded and the solution filtered using 0.45 μm filter paper (Whatman, Maidstone, UK). The soluble calcium ions released by the cement samples were measured by ion chromatography (DX120 Ion Chromatograph; Dionex, Sunny Vale, CA, USA). The retention time of the cation was measured against a standard and plotted against the amount of cation in micro-siemens. Ten per cent dilution was necessary for some of the samples after 56 days of curing.

Determination of pH of cements

The pH of the cements was determined during setting and for a period of 56 days. Five grams of prototype cement were mixed on a glass slab at a water/cement ratio of 0.37. The pH was measured using a pH meter (Jenway Scientific, Felsted, UK). The first reading was taken during mixing. After mixing, the materials were compacted into metal moulds 10 mm in diameter. The materials were allowed to cure in the moulds for 24 h at 37 °C and 100% humidity. The disks were removed from the moulds and placed in sealed containers filled with 6 ml distilled water. The containers were kept in an incubator at 37 °C. Three discs were made for each material. The pH determinations were made of the disks and solutions separately at 1, 7, 28 and 56 days. The pH of the discs was measured by grinding the disc surface with a fine grit sandpaper under water and measuring the pH of the slurry produced.

Results

Chemical analysis of unset cements

Elemental analysis of the calcium aluminate cement and synthetic anhydrite showed the cement to be composed primarily of calcium and aluminium with small sulphur and silica peaks (Fig. 1a). The calcium fluoro-aluminate cement had a predominant calcium peak with intermediate aluminium and silicon peaks and a smaller sulphur peak (Fig. 1b). The calcium and silicon peaks for the fluoro-aluminate cement were more pronounced than for the calcium aluminate cement. The fluorine peak for CSA was visible when the material was excited at 5 kV.

Phase analysis of WPC (Fig. 2a) revealed that it was composed primarily of tricalcium silicate (ICDD: 31-0301) with the strongest peaks at 29.6, 32.2, 32.7 and 51.8 2θ and dicalcium silicate (ICDD: 31-0299) with the major peaks at 2θ: 32. The CSA cement was used in combination with WPC, thus the two powder peaks

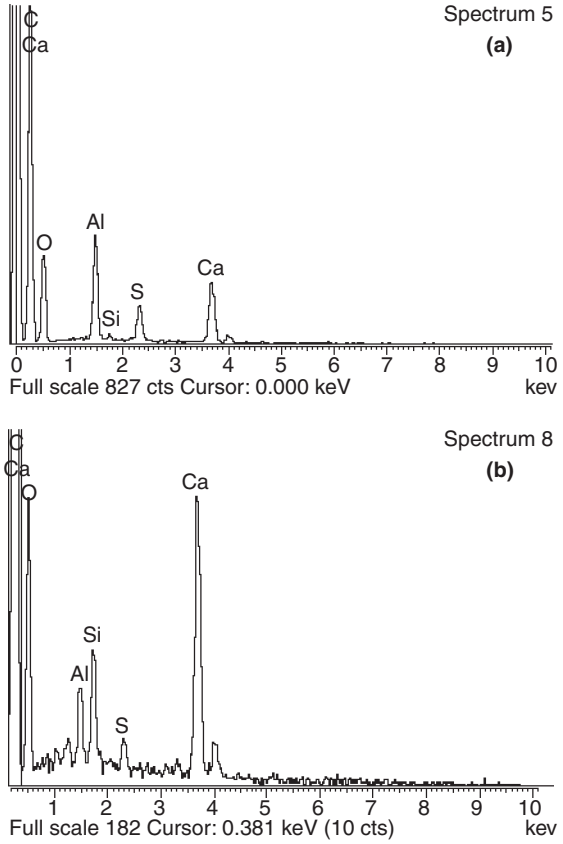

Figure 1 EDAX of powders (a) calcium sulpho-aluminate cement, (b) calcium fluoro-aluminate cement.

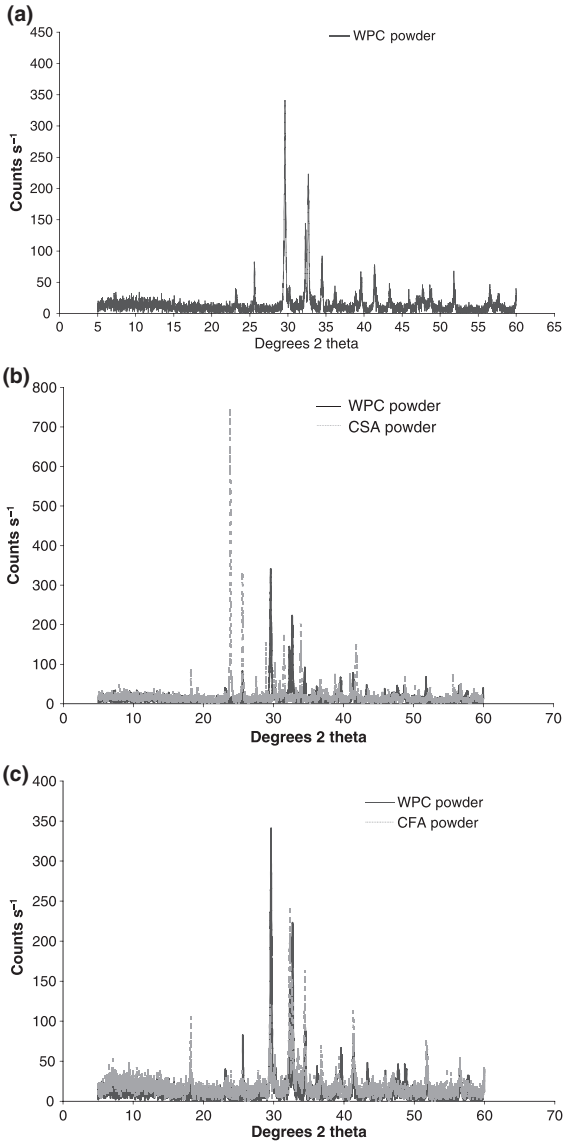

Figure 2 X-ray diffraction analysis of powders (a) white Portland cement (WPC), (b) calcium sulpho-aluminate (CSA) and WPC, (c) calcium fluoro-aluminate (CFA) and WPC.

were superimposed (Fig. 2b). The calcium sulpho-aluminate cement powder was composed primarily of calcium aluminate (2θ: 23.8, 33.9) and calcium sulphate (2θ: 25.5). The CFA cement (Fig. 2c) had lower levels of tricalcium silicate and no calcium aluminate peak. The calcium fluoro-aluminate peak was present at 2θ: 33.

Chemical analysis of set cements

X-ray diffraction (XRD) analysis of the powders and the set cements after 1, 7, 28 and 56 days of curing was performed. The main aim of the test was to account for the presence of calcium hydroxide. Analysis of Portland cement over a period of 56 days revealed a stable amount of calcium hydroxide produced. The presence of calcium hydroxide was monitored qualitatively by measuring portlandite peaks (ICDD: 44–1481) at 2θ: 18 (Fig. 3). The portlandite peaks were slightly displaced. This could have been due to mechanical strain of the cement during sample preparation. The CSA cement did not show any detectable levels of calcium hydroxide (Fig. 4a–d) at all ages. CFA cement showed an initial portlandite peak at 1 day (Fig. 5a) and a higher portlandite peak at 28 days (Fig. 5c). No portlandite was evident at the other time periods (Fig. 5b,c). Addition of micro-silica to both CSA and CFA cements did not cause any changes in the production of calcium hydroxide.

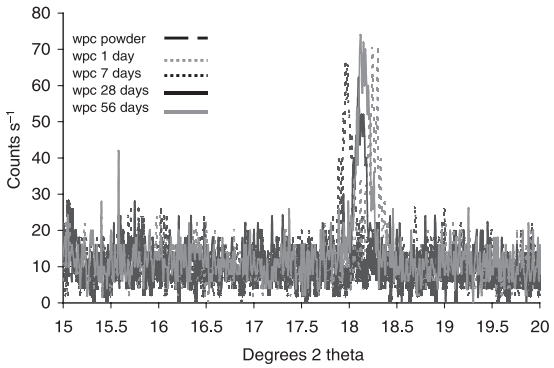

Figure 3 X-ray diffraction analysis of white Portland cement (WPC) cured for 56 days showing presence of calcium hydroxide.

Chemical analysis of leachate

Ion chromatography demonstrated the release of soluble calcium ions over a period of 56 days (Fig. 6). The CSA cement had very low release of calcium ions at all time intervals and addition of micro-silica suppressed calcium ion release further. Production of soluble calcium ions was low for the CFA cement at all time intervals except at 28 days where there was increase in calcium ion release. Addition of micro-silica increased the calcium ion output in CFA cement at all time intervals. Production of soluble calcium ions was suppressed at 56 days in all cement types except the WPC. The WPC had a high calcium ion output with the highest levels registered at 28 days.

Determination of pH of cements

The pH of the cements (Fig. 7a) was high during mixing ranging between 11 and 12. The pH reduced slightly on curing in water ranging from 10 to 11.4 for all cement types at all time-points. The WPC had the lowest pH after 1 day of curing (8.86) compared with the other cement types. The pH of the CFA was higher than that of CSA at all ages. The addition of micro-silica did not affect the pH levels except for the CSA at 28 days where addition of micro-silica caused a drop in pH.

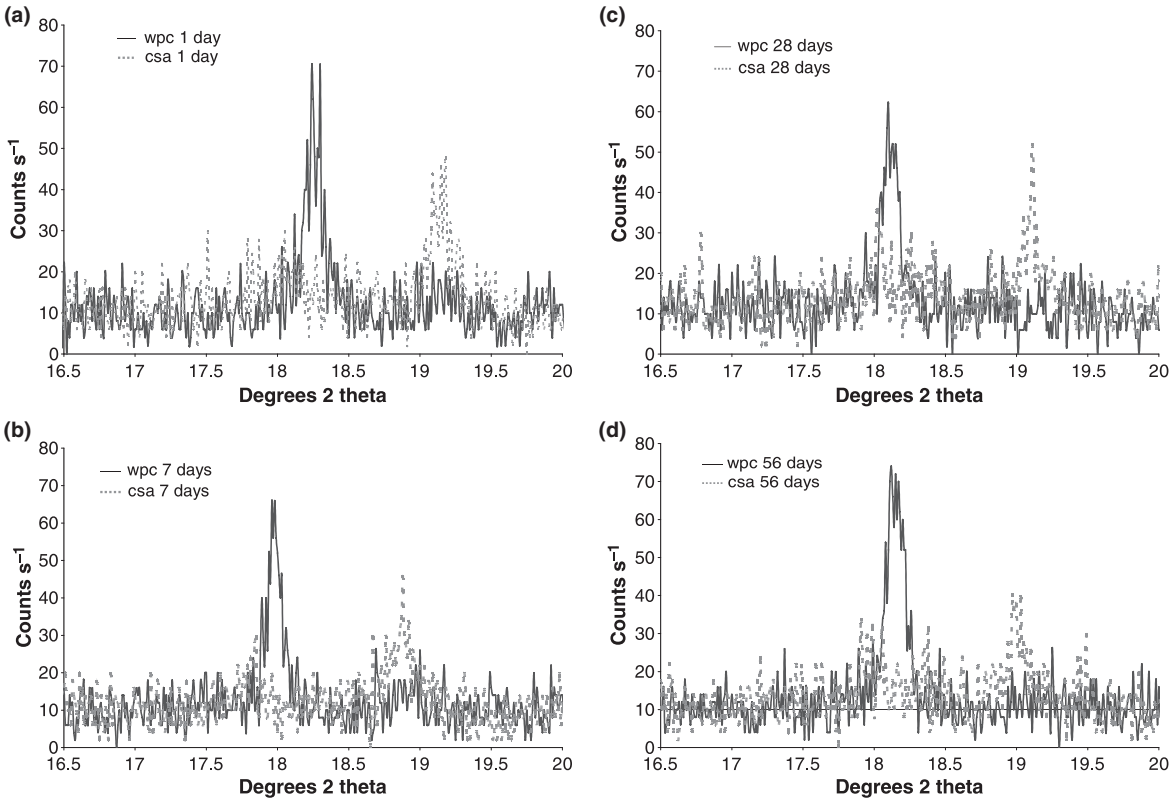

Figure 4 X-ray diffraction analysis of set calcium sulpho-aluminate cement (CSA) and white Portland cement (WPC) over a period of 56 days; (a) 1 day, (b) 7 days, (c) 28 days, (d) 56 days.

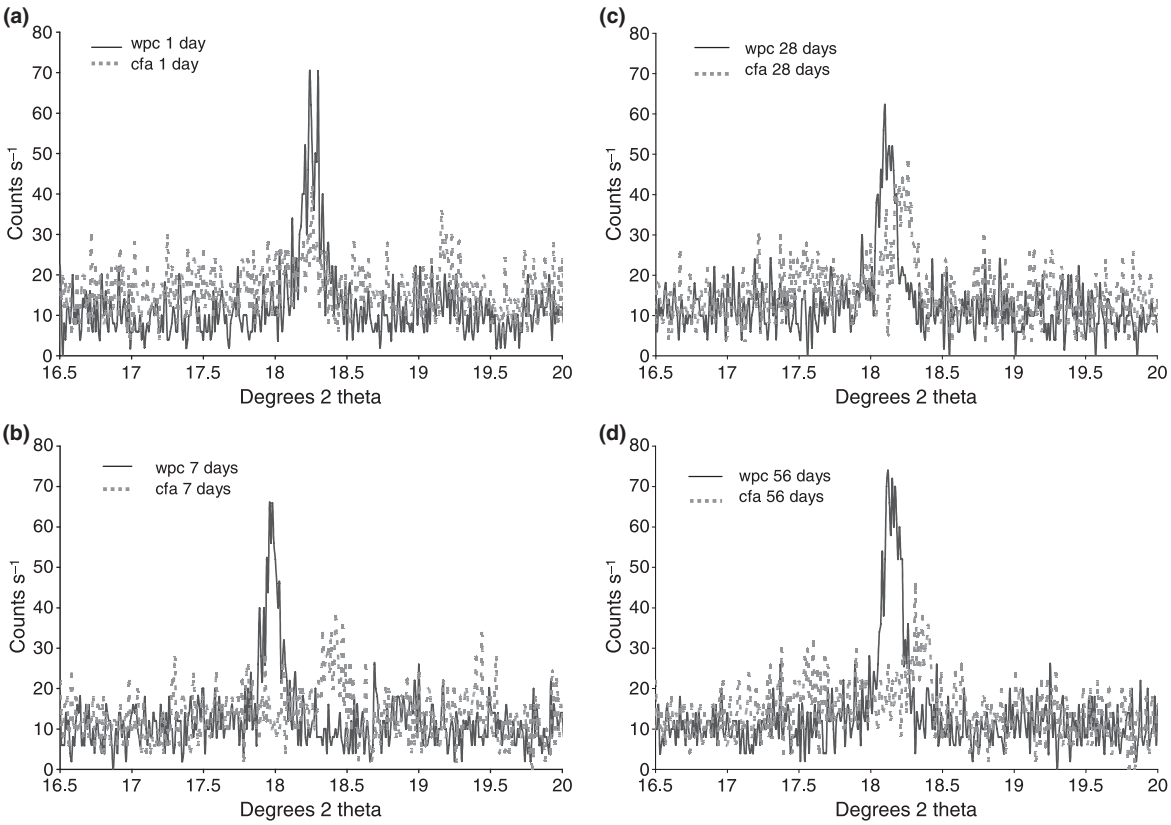

Figure 5 X-ray diffraction analysis of set calcium fluoro-aluminate cement (CFA) and white Portland cement (WPC) over a period of 56 days; (a) 1 day, (b) 7 days, (c) 28 days, (d) 56 days.

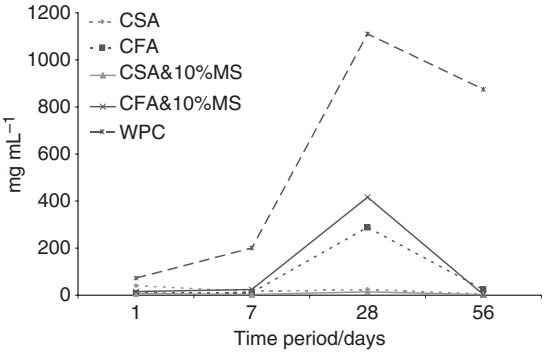

Figure 6 Calcium ion release by calcium sulpho-aluminate (CSA) and calcium fluoro-aluminate (CFA) cement, with and without additions of micro-silica (MS) and white Portland cement (WPC) over a period of 56 days.

The pH registered for the storage solution (Fig. 7b) revealed that the CSA cement had the lowest pH, which was kept constant over the time interval of study. The CFA cement had a higher pH which also remained constant throughout. Addition of micro-silica did not affect the pH values of the storage solution. The WPC had a high pH at 1 day which reduced to normal levels by 28 days of curing. At 28 and 56 days, the pH was the same for all cement types.

Discussion

In this study, two fast setting cements with a similar chemical composition as Portland cement were tested. The CFA was used on its own as instructed by the manufacturer. The CSA was used in combination with white Portland and synthetic anhydrite again as instructed by the manufacturer. A liquid superplasticizing admixture was used to improve the handling properties and reduce the water required by the mix as it is known that a reduction in the water/cement ratio improves the mechanical properties of the material. Addition of these admixtures does not affect the biocompatibility of the material (Camilleri *et al.* 2005b). When micro-silica is added to Portland cement, it reacts with

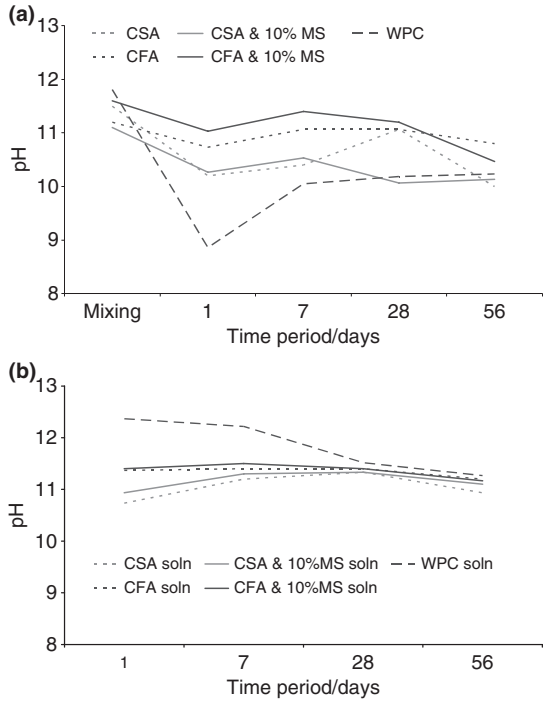

Figure 7 pH at different time intervals of (a) calcium sulpho-aluminate (CSA) and calcium fluoro-aluminate (CFA) cement with and without additions of micro-silica (MS) and white Portland cement (WPC), (b) storage solution (soln).

the calcium hydroxide produced converting it to calcium silicate. This enhances the mechanical properties of the material. However, it depletes the calcium hydroxide produced by the cement and may cause reduction in biocompatibility (Camilleri *et al.* 2008).

Ion chromatography measures the calcium ions released from the material. Addition of micro-silica to Portland cement results in the formation of more calcium silicate hydrate. In addition, micro-silica also causes pore blockage in the hydrating cement which densifies the hydrating gel structure and acts as a nucleation site for cement hydration, accelerating the process (Mitchell *et al.* 1998). The calcium ions leached out of the material may belong to the calcium silicate hydrate rather than to the calcium hydroxide. It has been demonstrated previously that calcium silicate hydrate decalcifies with leaching (Camilleri 2008). Thus, more research is necessary to determine the origin of calcium ions released from MTA and Portland cement. The addition of micro-silica enhances the strength of Portland cement (Wang *et al.* 2001) and may enhance the compressive strength of both cement types under investigation.

Chemical analysis performed showed that the CFA cement was composed primarily of calcium, silicon, aluminium and some sulphur. These are the same elements present in Portland cement. XRD analysis of the powder showed the main phase of CFA cement to be tricalcium silicate which is also the main phase found in Portland cement. The main constituent elements of CFA cement are tricalcium silicate and calcium fluoro-aluminate (Uchikawa & Tsukiyama 1973), which accounts for the higher aluminium peak present in the EDAX analysis. The initial reaction with water is the hydration of the tricalcium silicate forming silicate hydrate gel and calcium hydroxide. However, the calcium hydroxide produced in the reaction readily reacts with the calcium fluoro-aluminate to produce ettringite, which in the presence of excess calcium sulphate will be converted into monosulphate. Thus, even though the main tricalcium silicate reaction occurs with the production of calcium hydroxide, at the early stages the calcium hydroxide produced is depleted by a further reaction. The absence of calcium hydroxide was shown by both XRD analysis and by ion chromatography. Ion chromatography measured the levels of calcium ions available in solution which originate from the calcium hydroxide produced because the calcium silicate hydrate gel is insoluble in water. At 28 days of curing, the CFA showed an increase in the calcium hydroxide levels. The formation of ettringite in calcium fluoro-aluminate cements is slow. Thus, at 28 days excess calcium hydroxide was still present as it would not have been taken up to form ettringite (Odler & Colán-Subauste 1999). The levels of tri- and di-calcium silicate are high enough to allow the hydration of these phases and the calcium hydroxide is produced regardless of the early formation of ettringite (Uchikawa & Tsukiyama 1973). The production of ettringite at such an early stage in the setting reaction is responsible for the high early strength exhibited by CFA cements (Costa & Cucitore 2000).

The calcium sulpho-aluminate cement is formed by incorporation of calcium sulphate into the cement raw materials and firing at low temperatures. The resultant cement has different setting and hardening properties (Ali *et al.* 1994). Addition of calcium aluminate cement to Portland cement and calcium sulphate results in a cement which is rapid setting, has high early strength and shrinkage compensation (Evju & Hansen 2001). In such a system on addition of water, the hemihydrate is converted to gypsum which in turn is converted to

ettringite in the first few hours of hydration. Formation of ettringite from calcium aluminate and calcium sulphate requires additional calcium ions which are taken up from the calcium hydroxide produced during the hydration of the Portland cement present in the system (Evju & Hansen 2001). Systems utilizing aluminium ions from calcium sulpho-aluminate exhibit a rapid production of ettringite within the first few hours of hydration (Odler & Colán-Subauste 1999). This was verified in this study by both the XRD analysis and ion chromatography which demonstrated the absence of calcium hydroxide even though the major constituent element was Portland cement.

In contrast, in the Portland cement hydration the ettringite is produced by reaction of the tricalcium aluminate and calcium sulphate. Precipitation of ettringite crystals around the tricalcium aluminate particles is responsible for the dormant period of the Portland cement hydration reaction (Bye 1999). When the aluminium ion originates from tricalcium aluminate deposition of ettringite is slower (Odler & Colán-Subauste 1999). The tricalcium silicate hydration reaction continues undisturbed with the production of increasing levels of calcium hydroxide in contrast to the CSA and CFA cements where the soluble calcium ions are used up for further reaction and production of high levels of ettringite in the early stages of the hydration reaction. Production of calcium hydroxide seemed to be high at 28 days of curing for the WPC. This is unlike what was speculated in a previous publication (Camilleri *et al.* 2004) where the osteosarcoma cells seemed not to proliferate at 28 days. From this study, it was shown that release of soluble calcium ions is high at 28 days. In the previous study, the samples were allowed to cure for 28 days at 100% humidity. This could have caused surface carbonation thus prohibiting cell proliferation over the cement surface.

The pH studies of the storage solution showed similar results to the ion chromatography. Addition of microsilica had a marginal effect on the amount of calcium ion released. The production of soluble calcium ions was low for the CSA cement which even registered the lowest pH values of the storage solution. The drop in pH at 1 day for the WPC could be due to surface carbonation during curing until the specimens were removed from the moulds. This could have hampered the release of calcium hydroxide from the cement. The pH and calcium ion released by MTA has already been reported (Hungaro Duarte *et al.* 2003). However, the reason for the calcium ion release was cited as dissolution of the calcium oxide which is the main constituent phase in MTA and Portland cement.

Conclusions

Both experimental cement types tested had a hydration reaction different from that of Portland cement even though calcium silicate was the major constituent element of both of them. No calcium hydroxide was produced as a by-product of cement hydration. Microsilica addition to the cement had no effect on the hydration reaction.

Acknowledgements

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