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Hydration characteristics of zirconium oxide replaced Portland cement for use as a root-end filling material

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ABSTRACT

Objective. Zirconium oxide can be added to dental materials rendering them sufficiently radiopaque. It can thus be used to replace the bismuth oxide in mineral trioxide aggregate (MTA). Replacement of Portland cement with 30% zirconium oxide mixed at a water/cement ratio of 0.3 resulted in a material with adequate physical properties. This study aimed at investigating the microstructure, pH and leaching in physiological solution of Portland cement replaced zirconium oxide at either water–powder or water–cement ratios of 0.3 for use as a root-end filling material. The hydration characteristics of the materials which exhibited optimal behavior were evaluated.

Methods. Portland cement replaced by zirconium oxide in varying amounts ranging from 0 to 50% in increments of 10 was prepared and divided into two sets. One set was prepared at a constant water/cement ratio while the other set at a constant water/powder ratio of 0.3. Portland cement and MTA were used as controls. The materials were analyzed under the scanning electron microscope (SEM) and the hydration products were determined. X-ray energy dispersive analysis (EDX) was used to analyze the elemental composition of the hydration products. The pH and the amount of leachate in Hank's balanced salt solution (HBSS) were evaluated. A material that had optimal properties that satisfied set criteria and could replace MTA was selected. The microstructure of the prototype material and Portland cement used as a control was assessed after 30 days using SEM and atomic ratio diagrams of Al/Ca versus Si/Ca and S/Ca versus Al/Ca were plotted.

Results. The hydration products of Portland cement replaced with 30% zirconium oxide mixed at water/cement ratio of 0.3 were calcium silicate hydrate, calcium hydroxide and minimal amounts of ettringite and monosulphate. The calcium hydroxide leached in HBSS solution resulted in an increase in the pH value. The zirconium oxide acted as inert filler and exhibited no reaction with the hydration by-products of Portland cement.

Significance. A prototype dental material composed of Portland cement replaced with 30% zirconium oxide as radiopacifier leached calcium ions on hydration which reacted with phosphates present in simulated tissue fluids. This resulted in bioactive cement that could prospectively be used as a root-end filling material. The zirconium oxide acted as inert filler and did not participate in the hydration reaction of the Portland cement.

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1. Introduction

Mineral trioxide aggregate (MTA) was introduced as a root-end filling material due to its hydraulic characteristics. MTA is composed of a mixture of Portland cement and radiopacifier namely bismuth oxide [1]. The bismuth oxide is added as Portland cement has a radiopacity lower than the recommended 3 mm thickness of aluminum [2–4] as suggested by ISO 6876; 2002 [5]. The addition of 20% bismuth oxide to Portland cement increases the radiopacity value to 6–8 mm Al [2,3,6–9].

The addition of bismuth oxide to Portland cement resulted in the bismuth taking silicon lattice sites in the calcium silicate hydrate structure [10]. After 28 days of hydration only 8% of the original bismuth oxide added to the cement remained in the oxide form. The rest was either incorporated in the cement matrix or leached out in solution [11]. Other radiopacifying materials have been suggested in the literature. These include gold powder, silver/tin alloy [6], barium sulfate [6,12,13], iodofom, zirconium oxide [12,13], zinc oxide [6,13], lead oxide, bismuth subnitrate, bismuth carbonate and calcium tungstate [13]. A number of these alternative radiopacifiers have been investigated and it was demonstrated that the replacement of 20–25% of Portland cement resulted in a material which was sufficiently radiopaque without any deleterious effects on the physical properties [14]. Addition of silver/tin alloy although resulting in a cement of adequate physical properties leached high levels of tin as the tin was not stable in alkaline solution [15]. Barium sulfate replacement and was more inert. However it exhibited a lower radiopacity value than MTA. Gold was stable and no leaching of gold was reported. Despite its good chemical behavior, gold is relatively expensive and imparts a yellowish color to the material [15].

The addition of various percentage replacements of Portland cement with zirconium oxide mixed at either water/cement or water/powder ratio of 0.3 was also investigated. All percentage replacements resulted in radiopacity values higher than 3 mm Al. The addition of zirconium oxide did not affect the physical properties of the material [16]. Using the digital logic method it was concluded that 30% replacement of Portland cement with zirconium oxide mixed at a water/cement ratio of 0.3 exhibited optimal properties [16].

This study aimed at investigating the microstructure, pH and leaching in physiological solution of Portland cement replaced zirconium oxide at either water–powder or water–cement ratios of 0.3 for use as a root-end filling material. The hydration characteristics of the materials which exhibited optimal behavior were evaluated.

2. Methods

The materials used in this study included white Portland cement (PC; CEM 1, 52.5N; LaFarge Cement, Birmingham, UK) and zirconium oxide (ZrO_2 ; Sigma–Aldrich, Buchs, Switzerland). ProRoot MTA (Dentsply Tulsa Dental, Johnson City, TN, USA) lot number: 08003394 was used as control. The Portland cement was replaced by zirconium oxide in varying amounts ranging from 0 to 50% in increments of 10. The Portland cement/zirconium oxide mixtures were mixed with

water either at a water/powder (WP) ratio or at a water/cement (WC) ratio of 0.3 (Table 1). ProRoot MTA was mixed at a water/cement ratio of 0.3 as recommended by the manufacturer.

2.1. Microstructural examination

The morphology of both un-reacted powders and hydrated cements was evaluated using a scanning electron microscope (SEM Leo 1430 Oxford, Cambridge, UK) with both secondary electron and backscattering modes. Elemental analysis was also performed using X-ray energy dispersive analysis (EDX). The Portland cement, zirconium oxide and ProRoot MTA powders were sprinkled on the top side of carbon double-sided tape attached to an aluminum stub.

Cubes measuring 7 mm × 7 mm × 7 mm ± 1 mm were prepared for each cement mixture and were allowed to cure for 28 days in distilled water at 37 ± 1 °C. Longitudinal cross sections of the cube specimens were prepared using a circular micro-cutter. The cut surface of the cross-sections was left unpolished. The specimens were attached to aluminum stubs using carbon double-sided tape and carbon coated. SEM/EDX analysis was carried out to analyze the microstructure and the elemental composition of selected regions within each specimen. Particle size determination was performed from the micrographs of the powders.

2.2. Evaluation of pH

Six disks 15 ± 1 mm diameter with a thickness of 1 ± 0.1 mm of each cement type were prepared. These were stored in an incubator at 37 ± 1 °C for 24 h and then were removed from the molds, and immersed upright in 10 mL Hanks balanced salt solution (HBSS; H6648, Sigma–Aldrich, St. Louis, MO, USA). The composition of the HBSS was (g/L) 0.4 KCl, 0.06 KH_2PO_4 anhydrous, 0.35 $NaHCO_3$, 8.0 NaCl, 0.05 Na_2HPO_4 anhydrous and 1.0 D-glucose. The pH readings of the storage solution were taken using a pH meter (Hanna HI 9811, Hanna Instruments, Woonsocket, RI, USA) prior to immersion and after 1, 7, 14 and 28 days.

2.3. Evaluation of leaching

Determination of leaching of cements in physiological solution was performed using inductively coupled plasma atomic emission spectroscopy (ICP–AES). Specimens 10 ± 1 mm in diameter with a thickness of 1 ± 0.1 mm were prepared. These were allowed to cure for 24 h in an incubator at 37 ± 1 °C and a relative humidity of not less than 95%. The cements were weighed and placed in sealed plastic containers filled with 5 mL HBSS. A blank HBSS in a plastic container was also prepared. The specimens were placed in an incubator at 37 ± 1 °C for 28 days. Following this period, the HBSS solutions were analyzed using ICP–AES. Leaching in solution was calculated in µg/g using the following formula:

Amount of leachate per weight of cement

$$= \frac{\text{Amount of leachate per litre} \times 0.005}{\text{Weight of cement specimen}} \times 1000$$

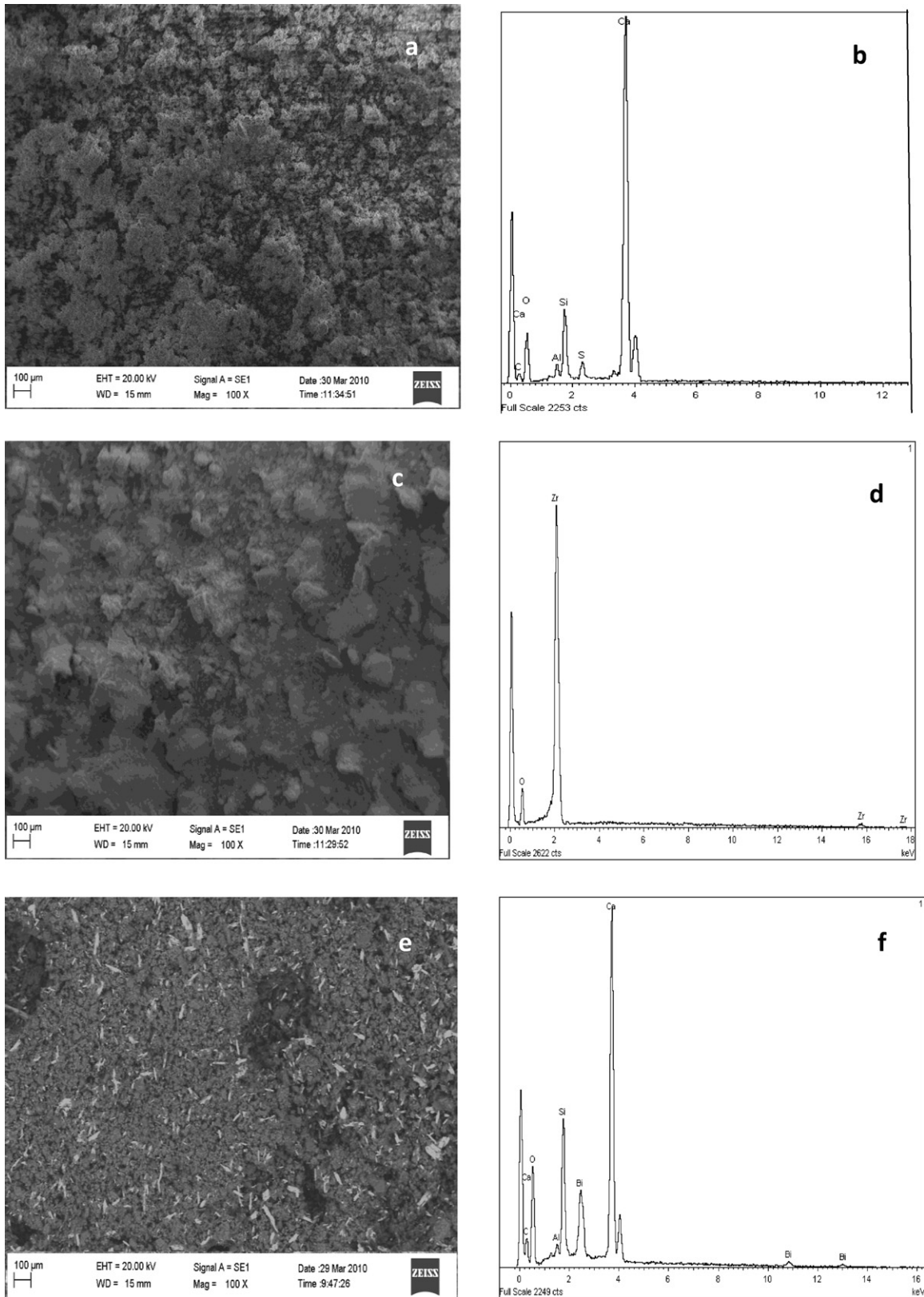


Fig. 1 – Secondary electron images of (a) Portland cement powder, (c) zirconium oxide powder, (e) ProRoot MTA powder (100× magnification); and X-ray energy dispersive spectrum of (b) Portland cement powder, (d) zirconium oxide powder, (f) ProRoot MTA powder.

Table 1 – Mix proportions of different specimens mixed at either water/cement or water/powder ratios of 0.3.

Sample name	PC (wt.%)	ZrO ₂ (wt.%)	Water/powder ratio	Water/cement ratio
WP/WC 0	100	0	0.3	0.3
WP 10	90	10	0.3	0.333
WP 20	80	20	0.3	0.375
WP 30	70	30	0.3	0.429
WP 40	60	40	0.3	0.5
WP 50	50	50	0.3	0.6
WC 10	90	10	0.27	0.3
WC 20	80	20	0.24	0.3
WC 30	70	30	0.21	0.3
WC 40	60	40	0.18	0.3
WC 50	50	50	0.15	0.3

2.4. Assessment of hydration characteristics

Portland cement replaced with 30% zirconium oxide was mixed with water at a water/cement ratio of 0.3. Portland cement mixed at the same water/cement ratio was used as control. The pastes were compacted in a cylindrical mold (30mm in diameter) using a stainless steel plugger. The specimens were cured in sealed plastic (polythene) containers at 37 °C for 30 days using a thermostatically controlled water bath (MGW Lauda M 20, Leica Microsystems SA, Rueil-Malmaison, France). They were immersed in acetone for four days to remove any remaining water, and then dried in a vacuum desiccator for 8 h. The dried specimens were mounted in epoxy resin using vacuum impregnation. The hardened resin block was sawn (Labcut 1010, Agar scientific, Stansted, UK) and ground under copious water irrigation using progressively finer grits of abrasive paper to produce a flat surface. A thin conductive carbon coating was applied to the sections prior to examination in the SEM (ISI SS40; ISI, Tokyo, Japan). Elemental analysis was performed using energy-dispersive X-ray analysis (SAMx Numerix, Levens, France). Quantitative chemical analyzes (verb)/analyses (noun) were carried out using X-ray standards obtained from minerals for each element. Oxygen was calculated by stoichiometry [17]. The examination procedure consisted of collecting backscattered electron images to show the general microstructure, and a series of X-ray spectra. For each specimen, between 50 and 60 spectra were collected. The X-ray spectra were quantified using suitable mineral standards and the data plotted in a standard format showing atomic ratios of Si/Ca versus Al/Ca and Al/Ca versus S/Ca. These atomic ratio plots are used in SEM/EDX studies of cementitious materials and enable the principal hydration products to be differentiated.

3. Results

3.1. Microstructural examination

The scanning electron micrographs and X-ray energy dispersive analysis of the Portland cement, zirconium oxide and ProRoot MTA powders are shown in Fig. 1. The particle size and shape of the powders were evaluated from the micrographs. Portland cement powder was composed of spherical and angular particles of varying size (Fig. 1a) with particle size ranging between 7 and 16 μm. Calcium, silicon, aluminum and

sulfur peaks could be detected (Fig. 1b). Zirconium oxide powder was in the form of spherical particles ranging from 0.5 to 4.5 μm (Fig. 1c). EDX spectrum displayed peaks from Zr and O only (Fig. 1d). Analyzes (verb)/analyses (noun) on ProRoot MTA demonstrated bismuth oxide particles that were evenly distributed throughout the cement. These particles appeared shiny and elongated (Fig. 1e) with a particle size ranging from 5 to 100 μm. The ProRoot MTA was composed of calcium, silicon, aluminum and bismuth (Fig. 1f).

ProRoot MTA, Portland cement and zirconium oxide replaced cements exhibited similar features when hydrated specimens were examined after 28 days of curing. The hydration products for all the materials tested included un-hydrated cement particles (Fig. 2a), featureless calcium silicate hydrate (Fig. 2a), hexagonal crystals of calcium hydroxide (Fig. 2b and c), and ettringite needles (Fig. 2d). Capillary cracks and capillary voids were also identified (Fig. 2e). The bismuth oxide particles in ProRoot MTA (Fig. 2a) and zirconium oxide particles (Fig. 2f) were evenly distributed in all the specimens analyzed.

3.2. Evaluation of pH

The results for the pH of the cements are shown in Fig. 3. The pH of the Hanks balanced salt solution (HBSS) ranged from 7.6 to 8. The storage solution of the various cement compositions was alkaline and the pH varied from 11.7 to 12.4. The pH of storage solutions of all the experimental cements was similar to that of ProRoot MTA ($P > 0.05$). The pH remained stable over a period of 28 days.

3.3. Evaluation of leaching

The results for the leaching of ions in HBSS are shown in Table 2a. The amount of leachate of zirconium in the prototype cements was an order of magnitude lower than the leaching of bismuth from ProRoot MTA. All the cements released a high proportion of calcium ions. The HBSS was composed of 2617 parts per million (ppm) of sodium and 25.88 ppm phosphorus. The sodium and phosphorus ions present in the solution in ppm after cement immersion are shown in Table 2b. There was no phosphorus present in solution indicating that the cements took up all the phosphorus reacting with it. The levels of sodium also decreased when the cements were placed in solution.

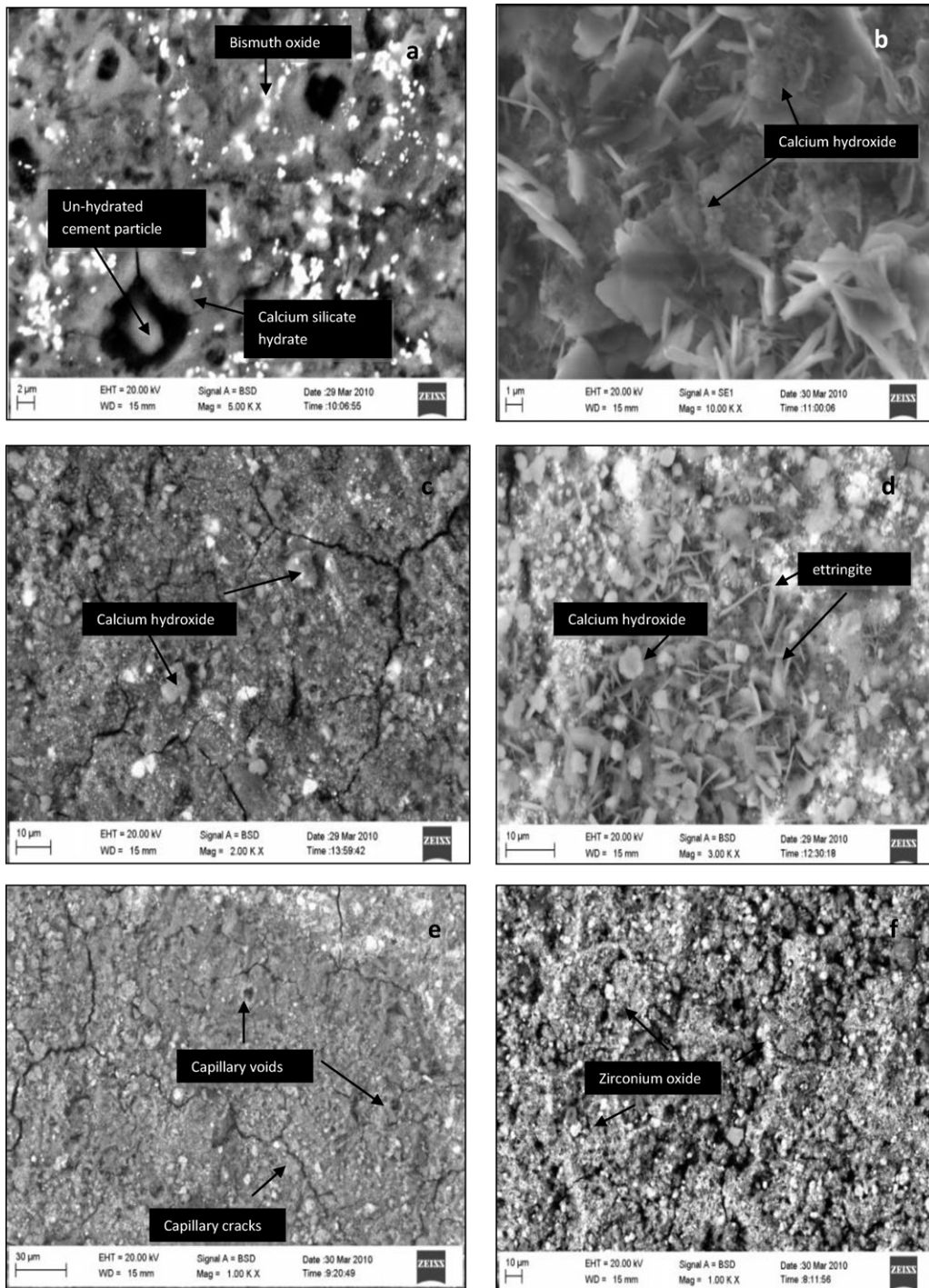


Fig. 2 – Scanning electron microscopy of (a) hydrated MTA showing un-hydrated cement particles, bismuth oxide and calcium silicate hydrate, (b and c) calcium hydroxide in ZrO₂ replaced cement (d) ettringite, (e) capillary pores and cracks, (f) zirconium oxide radiopacifier.

3.4. Assessment of hydration characteristics

The backscattered SEM images of the hydrated Portland cement and Portland cement replaced with 30% zirconium oxide are shown in Fig. 4. Both hydrated cements exhibited un-reacted cement grains with a rim of hydration product which was composed mostly of pure calcium silicate

hydrate. Ettringite, monosulphate and calcium hydroxide were present interspersed within the cement matrix. Analyzes (verb)/analyses (noun) of hydration product at the rim of the un-reacted cement grains gave EDX spectra that were free of ZrO₂. The zirconium oxide particles appeared bright in the backscattered electron images and were evenly distributed throughout the cement.

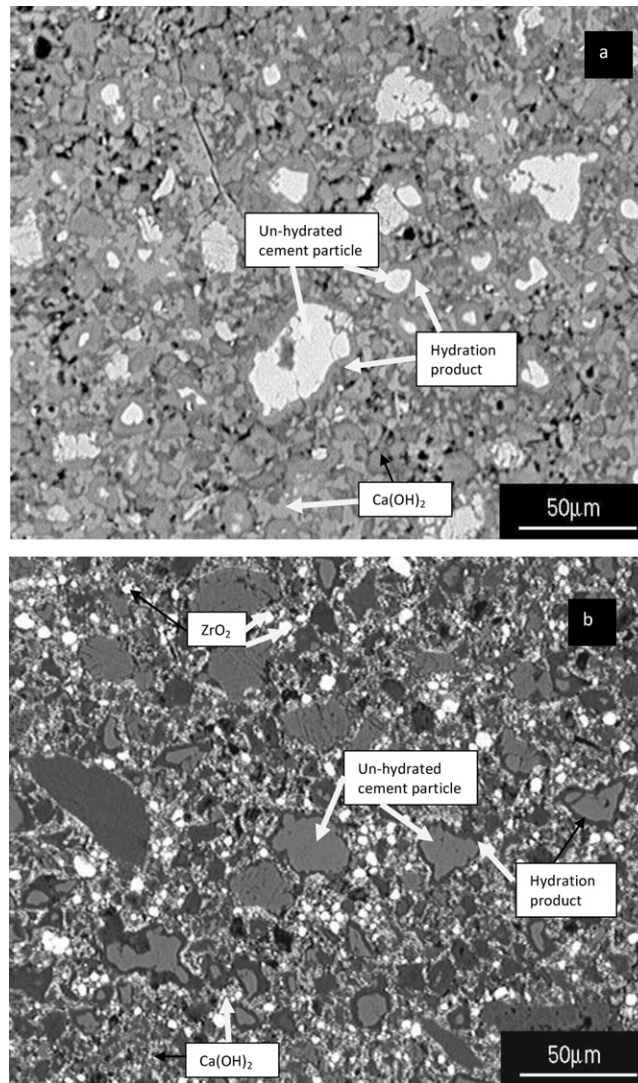


Fig. 4 – Back-scattered electron micrographs of (a) Portland cement; (b) zirconium oxide replaced cement showing hydrated microstructure.

between the zirconium and aluminum and silicon in the Portland cement.

4. Discussion

The microstructure, topography and chemical activity of Portland cement, ProRoot MTA and zirconium oxide replaced cements mixed at either a water/power ratio or a water/cement ratio of 0.3 was assessed. In addition the hydration characteristics of Portland cement replaced with 30% zirconium oxide mixed at water to cement ratio of 0.3 were investigated. The 30% zirconium oxide replacement was the optimal filler loading necessary to render the radiopacity of the material comparable to ProRoot MTA [16]. This filler loading and the use of a water/cement ratio of 0.3 resulted in adequate physical properties for a cement intended for use as a root-end filling material [16]. The use of SEM in conjunction with EDX analysis and atomic ratio plots have previously been used to assess the hydration characteristics of Portland

cement and ProRoot MTA [10,11], Portland cement loaded with different radiopacifying materials [15] and MTA sealer cement [18]. The semi-quantitative analysis of the hydrated phases was carried out using X-ray energy dispersive analysis (EDX). Atomic ratios plots were then drawn based on the EDX analysis. This is an established technique used to express X-ray microanalyses data. Depending on the atom ratios used, different hydrate phases can be differentiated. Common ratios are Si/Ca versus Al/Ca and Al/Ca versus S/Ca.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used to determine the amount of leachate due to its high sensitivity and fast data pick-up [19,20]. Other methods of analysis include atomic absorption spectroscopy (AAS) and flame atomic absorption spectroscopy (FAAS). ICP-AES uses a portion of the aqueous storage solution of the corresponding cement sample and is aspirated in the form of fog in an argon plasma torch to temperatures ranging from 6000 to 10,000 K. During this process, most of the elements present in the solution would emit light at a particular wavelength following excitation. These characteristic wavelengths

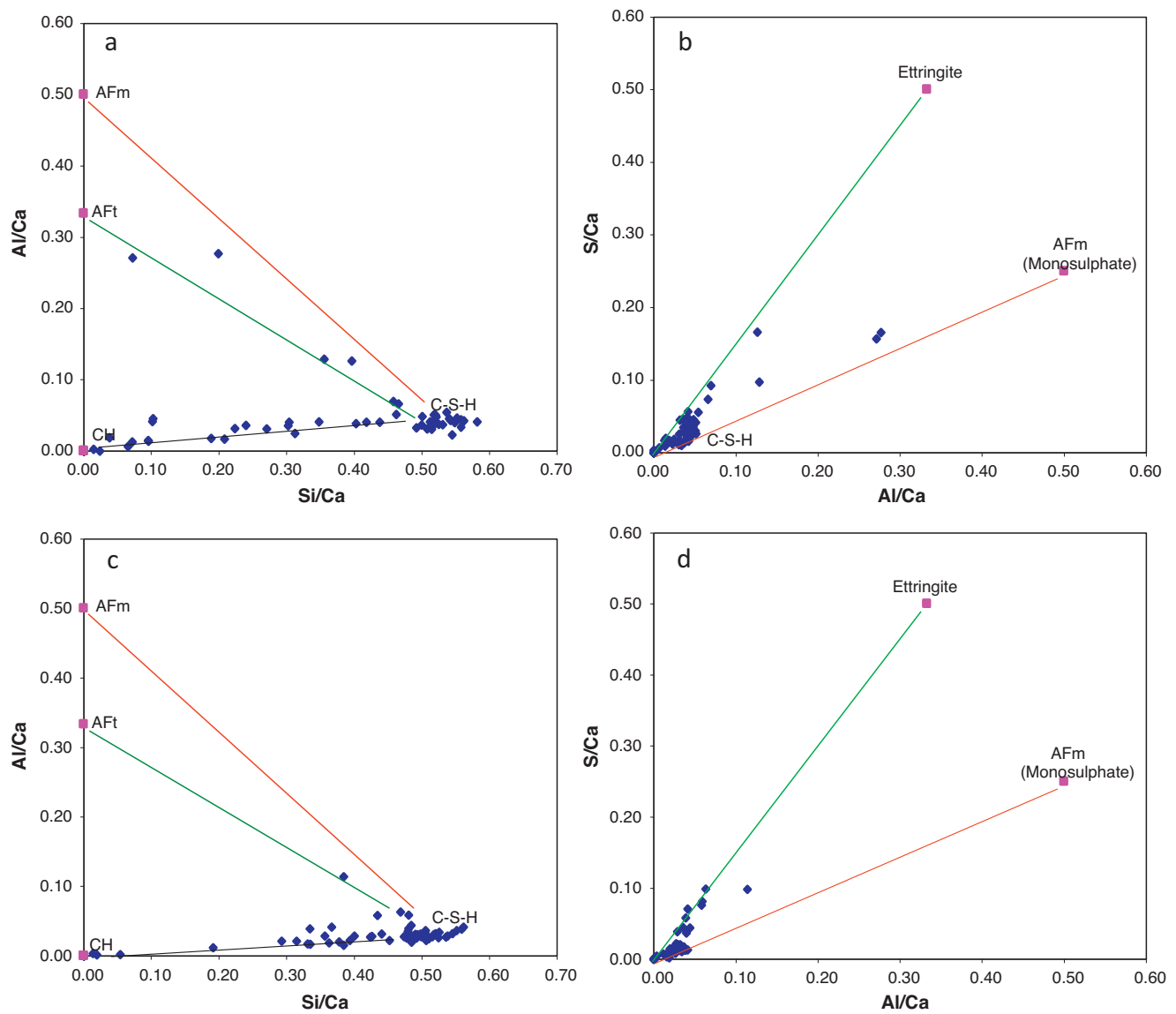


Fig. 5 – Atomic ratio plots of (a and b) Portland cement and (c and d) zirconium oxide replaced Portland cement.

are used to determine elements present in solution [20]. This technique allows both qualitative and quantitative analyses (verb)/analyses (noun) to be carried out simultaneously on various elements with very good detection limits ranging from parts per billion (ppb) to parts per million (ppm). The disadvantages of this technique includes the presence of spectral interferences [21] and the limitation of sample presentation as samples have to be able to vaporize to be tested using this technique [20].

The cements exhibited an alkaline pH which was stable over time. This was similar to the pH of ProRoot MTA reported in this study and by other researchers [14,22–24]. The release of calcium hydroxide from the hydrated cement resulted in the alkalinity of the storage solution. The leaching of high levels of calcium was also demonstrated by ICP. This is in accordance to previous studies reporting high levels of calcium leached out from Portland cement and ProRoot MTA [11,15]. A much lower concentration of zirconium was released in solution compared

to bismuth in ProRoot MTA. This showed that zirconium oxide was more stable than bismuth oxide in the cement matrix when immersed in HBSS.

The levels of sodium and phosphorus were reduced when the HBSS was in contact with the cement due to reaction with the hydration products of the cement. This is in accordance to other studies where HBSS was placed in contact with a sealer based on MTA. The ICP analysis also resulted in a reduction in levels of phosphorus and sodium [25]. The exposure of the surface of Portland cement to physiological solutions induces the formation of hydroxyapatite [26,27].

The reaction by-products of the zirconium oxide replaced cements did not differ from that Portland cement. SEM showed the formation of silicate hydrate gel around the un-hydrated cement grains with the precipitation of calcium hydroxide. Ettringite was also formed by the reaction of tricalcium aluminate and calcium sulfate with water. These hydration products are characteristic of Portland cement hydration [28]. The addi-

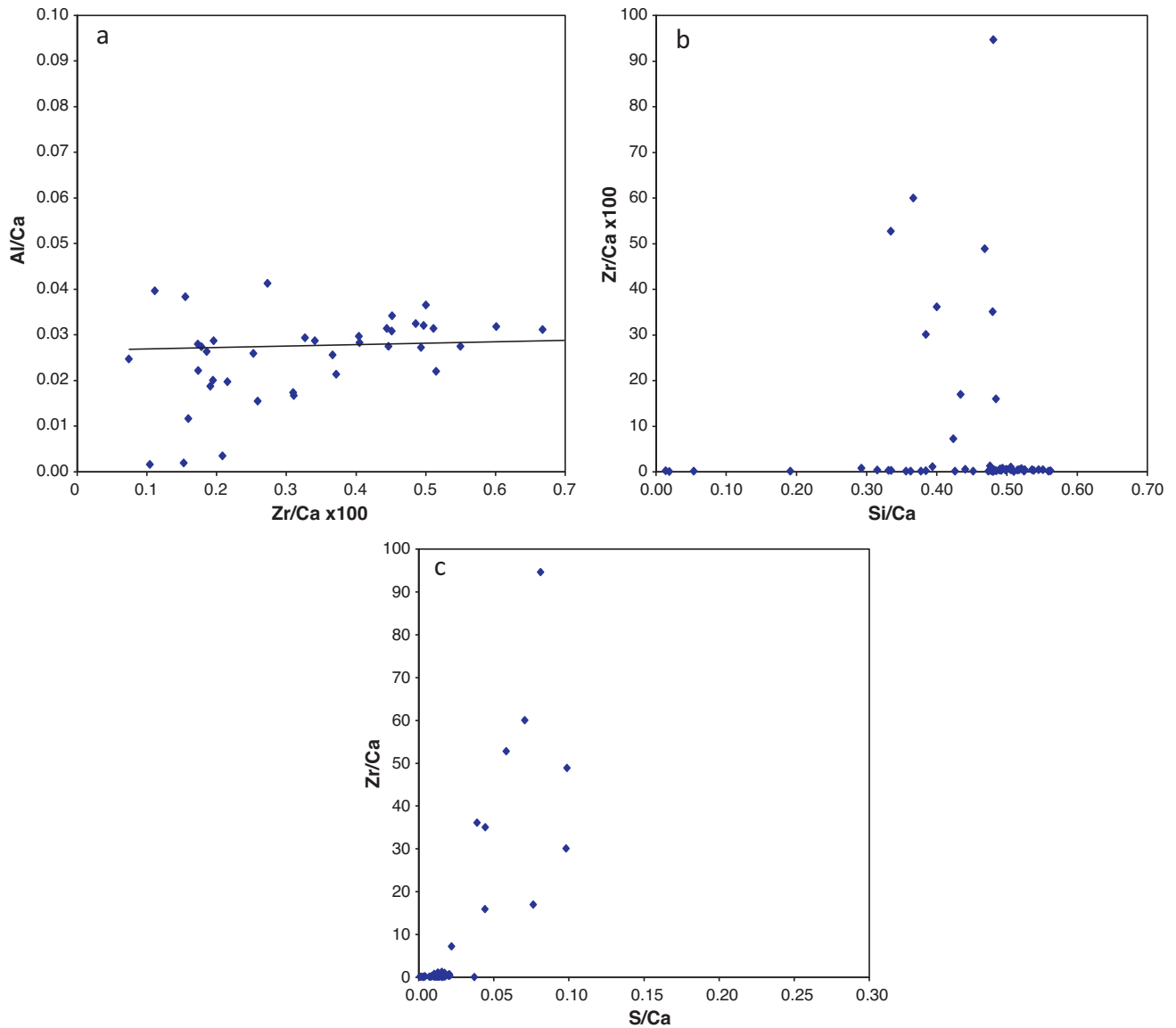


Fig. 6 – Atomic ratio plots of (a) Al/Ca versus Zr/Ca, (b) Zr/Ca versus Si/Ca and (c) Zr/Ca versus S/Ca showing the relationship of zirconium to aluminum, calcium and silicon of the parent cement.

tion of zirconium oxide did not affect the hydration of the cement. The zirconium oxide acted as inert filler. There was no relationship between the zirconium and the calcium, silicon and aluminum which are the constituent elements of Portland cement. In MTA the bismuth replaced the silicon in the cement forming a complex microstructure with the calcium silicate hydrate [10,11].

5. Conclusions

A prototype dental material composed of Portland cement replaced with 30% zirconium oxide as radiopacifier leached calcium ions on hydration which reacted with phosphates present in simulated tissue fluids to form calcium phosphate thus resulting in bioactive cement that could prospectively be used as a root-end filling material. The zirconium oxide acted

as inert filler and did not participate in the hydration reaction of the Portland cement.

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REFERENCES

- [1] Torabinejad M, White DJ. Tooth filling material and use. US patent number 5,769,638; 1995.
- [2] Islam I, Chng HK, Yap AU. Comparison of the physical and mechanical properties of MTA and Portland cement. *J Endod* 2006;32:193–7.

- [3] Kim EC, Lee BC, Chang HS, Lee W, Hong CU, Min KS. Evaluation of the radiopacity and cytotoxicity of Portland cements containing bismuth oxide. *Oral Surg Oral Med Oral Pathol Oral Radiol Endod* 2008;105:54–7.
- [4] Saliba E, Abassi-Ghadi S, Vowles R, Camilleri J, Hooper SM, Camilleri J. Evaluation of the strength and radio-opacity of Portland cement with varying additions of bismuth oxide. *Int Endod J* 2009;42:322–8.
- [5] International Standards Organization. Dental root canal sealing materials. ISO 6876-7.8; 2002.
- [6] Camilleri J, Gandolfi MG. Evaluation of the radiopacity of calcium silicate cements containing different radiopacifiers. *Int Endod J* 2010;43:21–30.
- [7] Laghios CD, Benson BW, Gutmann JL, Cutler CW. Comparative radiopacity of tetracalcium phosphate and other root-end filling materials. *Int Endod J* 2000;33:311–5.
- [8] Chng HK, Islam I, Yap AUJ, Tong YW, Koh ET. Properties of a new root-end filling material. *J Endod* 2005;31:665–8.
- [9] Danesh G, Dammaschke T, Gerth HU, Zandbiglari T, Schafer E. A comparative study of selected properties of ProRoot mineral trioxide aggregate and two Portland cements. *Int Endod J* 2006;39:213–9.
- [10] Camilleri J. Hydration mechanisms of mineral trioxide aggregate. *Int Endod J* 2007;40:462–70.
- [11] Camilleri J. Characterization of hydration products of mineral trioxide aggregate. *Int Endod J* 2008;41:408–17.
- [12] Bortoluzzi EA, Guerreiro-Tanomaru JM, Tanomaru-Filho M, Duarte MA. Radiographic effect of different radiopacifiers on a potential retrograde filling material. *Oral Surg Oral Med Oral Pathol Oral Radiol Endod* 2009;108:628–32.
- [13] Húngaro Duarte MA, de Oliveira El Kadre GD, Vivan RR, Guerreiro Tanomaru JM, Tanomaru Filho M, de Moraes IG. Radiopacity of Portland cement associated with different radiopacifying agents. *J Endod* 2009;35:737–40.
- [14] Camilleri J. Evaluation of the physical properties of an endodontic Portland cement incorporating alternative radiopacifiers used as root-end filling material. *Int Endod J* 2010;43:231–40.
- [15] Camilleri J. The hydration mechanisms of calcium silicate cements with alternative radiopacifiers used as root-end filling materials. *J Endod* 2010;36:502–8.
- [16] Cutajar A, Mallia B, Abela S, Camilleri J. Replacement of radiopacifier in mineral trioxide aggregate; characterization and determination of physical properties. *Dent Mater*; submitted for publication.
- [17] Scrivener KL, Taylor HFW. Delayed ettringite formation: a microstructural and microanalytical study. *Adv Cem Res* 1993;20:139–46.
- [18] Camilleri J. Evaluation of selected properties of MTA sealer cement. *J Endod* 2009;35:1412–7.
- [19] Mauras Y, Allain P. Determination of barium in water and biological fluids by emission spectrometry with inductively-coupled plasma. *Anal Chim Acta* 1979;110:271–7.
- [20] Montaser A. Inductively coupled plasma mass spectrometry. New York: Wiley VCH; 1998.
- [21] Oppenheimer JA, Eaton AD, Leong LYC. Multi-elemental analytical techniques for hazardous waste analysis: the state of art. Las Vegas, NV: US Environmental Protection Agency, Office of Research and Development Environmental Monitoring Systems Laboratory; 1984. EPA600/484028.
- [22] Antunes Bortoluzzi E, Juarez Broon N, Antonio Hungaro Duarte M, De Oliveira Demarchi AC, Monteiro Bramante C. The use of a setting accelerator and its effect on pH and calcium ion release of mineral trioxide aggregate and white Portland cement. *J Endod* 2006;32:1194–7.
- [23] Fridland M, Rosado R. MTA solubility: a long term study. *J Endod* 2005;31:376–9.
- [24] Fridland M, Rosado R. Mineral trioxide aggregate solubility and porosity with different water-to-powder ratios. *J Endod* 2003;29:814–7.
- [25] Camilleri J, Gandolfi MG, Sibboni F, Prati C. Dynamic sealing ability of MTA root canal sealer. *Int Endod J* 2011;44:9–20.
- [26] Sarkar NK, Caicedo R, Ritwik P, Moiseyeva R, Kawashima I. Physicochemical basis of the biologic properties of mineral trioxide aggregate. *J Endod* 2005;31:97–100.
- [27] Bozeman TB, Lemon RR, Eleazer PD. Elemental analysis of crystal precipitate from gray and white MTA. *J Endod* 2006;32:425–8.
- [28] Taylor HFW. Cement chemistry. London: Thomas Telford; 1997.