Bioactivity of Calcium Aluminate Endodontic Cement

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Abstract

Introduction: Calcium aluminate endodontic cement (CAEC) developed for use in root canal therapy has been produced with additives that improve handling properties and provide higher mechanical strength than mineral trioxide aggregate (MTA) according to prior studies. The aim of this study was to evaluate the bioactivity of CAEC containing accelerating additives (A-CAEC) in comparison with MTA, both in contact with simulated body fluid (SBF) solutions. **Methods:** pH measurements were taken for set cement samples immersed in water or SBF solutions prepared according to the Kokubo and Rigo techniques. The surface of these materials kept in contact with SBF solutions were also evaluated by means of scanning electron microscopy, energy-dispersive X-ray analysis, and X-ray diffraction. **Results:** Because of the calcium hydroxide dissociation, MTA cement is able to release more Ca^{2+} ions and results in a higher pH increase compared with A-CAEC. This behavior enhances the supersaturation of Kokubo solution, resulting in the precipitation of calcium phosphate phases on the MTA surface. On the other hand, for MTA in Rigo SBF solution, the pH value attained was higher than for the Kokubo SBF solution as a result of the Mg^{2+} ion precipitation, which inhibited the calcium phosphate phase formation. For A-CAEC, the optimal precipitation conditions of calcium phosphate phases are achieved in Rigo SBF solution. **Conclusions:** MTA and A-CAEC present bioactivity in contact with SBF solution although the composition of this solution defines the type of phase precipitated. *(J Endod 2013;39:774–778)*

Key Words

Bioactivity, calcium aluminate cement, chemical and physical properties, hydroxyapatite, mineral trioxide aggregate, pH, setting time

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Ideally, filling materials used in root canal therapy should have a good sealing ability between root canal and periradicular tissues and they should be nontoxic, noncarcinogenic, nongenotoxic, biocompatible, insoluble in tissue fluids, and dimensionally stable (1). Mineral trioxide aggregate (MTA) was developed as a root-end filling material, but because of its clinical features regarding biocompatibility, sealing ability, and bioactivity, its application has been extended to several other applications in endodontics (2, 3). However, the following drawbacks of MTA cement make its use difficult for such an application: low mechanical strength, sandy consistency (poor handling characteristics), long setting time, tooth and gum darkening, and high cost (4).

MTA is mainly composed of Portland cement (tricalcium silicate [$3CaO \cdot SiO_2$] and dicalcium silicate [$2CaO \cdot SiO_2$]), calcium sulfate, and bismuth oxide. The tissue repairing process with MTA begins during hydration of the material when calcium disilicate and trisilicate react with water forming calcium hydroxide and hydrated calcium silicate gel, leading to an alkaline pH. Calcium ions are then released and diffused through dentinal tubules, increasing the Ca^{2+} concentration as the setting time of the material progresses (5).

Calcium aluminate cement has been studied for usage in dentistry (4–11). In water, calcium aluminate cement's main phases, calcium aluminate ($CaO \cdot Al_2O_3$) and calcium dialuminate ($CaO \cdot 2Al_2O_3$), are decomposed, releasing Ca^{2+}, $Al(OH)_4^-$, and OH^- ions (12). When the solubility products for hydrate phases are reached, calcium aluminate hydrate and aluminum hydroxide precipitate.

Calcium aluminate endodontic cement (CAEC) was designed to overcome some drawbacks of the currently available aggregate mineral including its long setting time and its negative implications for clinical needs (8, 11). Extended workability can be attained by adding additives that speed up the precipitation process and, consequently, induce faster hardening.

This material presented suitable physical and mechanical properties (11), biocompatibility (9, 10), and a chemical mechanical barrier against bacterial microleakage (4). Additionally, other characteristics of endodontic cements must be biocompatibility and radiopacity. Subcutaneous implants in rats have frequently been used to evaluate the biological compatibility of various dental materials because they are capable of determining with precision the type and extension of the local reaction caused by these materials (5). Calcium aluminate–based cement showed an absence of an inflammatory reaction, presented less tissue reaction than MTA, and was biocompatible when tested in rat subcutaneous tissue (5). Endodontic cements also must be more radiopaque than dentin or bone to allow the quality of the root canal filling to be radiographically visualized and for the cement to be distinguished from the adjacent anatomic structures (13). Calcium aluminate–based cement in the presence of a radiopacifier (bismuth oxide) showed adequate radiopacity in all studied thicknesses, as recommended by ISO 6876; this is similar to MTA (13). These results may attest the possibility for its multipurpose use in endodontics.

Another important desired property of a root-end filling material is the bioactivity of endodontic materials, which is associated with its capacity to develop a stable bond with the living tissue via hydroxyapatite deposition (14). The bioactivity benefit can be evaluated by *in vitro* tests in which a substrate is kept in contact with simulated body fluid (SBF) solutions (15). Therefore, the aim of this study was to evaluate the setting time and bioactivity for MTA and CAEC when combined with accelerating additives.

Materials and Methods

White MTA (Angelus, Londrina, Paraná, Brazil) and calcium aluminate cement (Secar 71; Kerneos, Neuilly sur Seine, France) were the materials used in this study. The chemical analysis of the cements tested showed that the nature and content of heavy metals present were acceptable for endodontic purposes. Standard ISO 9917-1 stipulates that the arsenic and lead contents in dental water-based cements should be less than 2 and 100 ppm, respectively (16).

The preparation of CAEC was performed by adding selected additives to the commercial cement via dry ball milling homogenization for 1 hour. The additives used were as follows:

1. 0.6 wt% of a polyglycol-based dispersant (Bayer, Trostberg, Germany)
2. 2.8 wt% of $CaCl_2 \cdot 2H_2O$ (Labsynth, Diadema, SP, Brazil), which is an additive to induce plasticity to the cement
3. 25 wt% of zinc oxide (JT Baker, Phillipsburg, NJ) to provide radiopacity to the cement

The additive content (wt%) was based on the cement amount.

Aqueous suspensions of MTA (65 wt% solids) and CAEC (75 wt% solids) were prepared using a standard laboratory mixer (Marconi, Piracicaba, Brazil) under 2000 rpm. CAEC suspension was evaluated in the presence of 0.4 wt% of a mixture comprising high-purity lithium carbonate (Synth, Diadema, Brazil) and calcium oxide (Vetec, Duque de Caxias, Brazil) for a 1:1 mass ratio. This resulting material, CAEC containing accelerating additives, is called A-CAEC. MTA was evaluated only as received. After mixing for 1 minute, the suspensions were poured into a container (180 mL) where the setting time was measured with the help of an automatic recording Vicat apparatus (Vicatronic E044-Solotest; Matest, Treviolo, Italy). In this method, 1 needle is inserted in the suspension with a fixed time interval. The penetration distance of the indentation needle in the samples was measured every 2 and 5 minutes for A-CAEC and MTA, respectively. The time in which the penetration distance is equal to 0 indicated the setting time of the sample.

The suspensions of A-CAEC were also used to prepare cylindric samples (10-mm diameter × 5-mm height). After shaping, the samples were kept at 37°C in a climatic chamber under a saturated environment (100% relative humidity [RH]) for 24 hours. After that, the samples were withdrawn out of the molds and kept for 7 days at 37°C under the same environmental conditions described earlier. Later, they were placed into containers with 50 mL water or SBF solutions and kept at 37°C (100% RH). The pH was measured for these solutions at certain time intervals using a sensor connected to an automatic data recorder system (MA 522/E; Marconi, Piracicaba, SP, Brazil).

The SBF solutions (ie, Kokubo [KSBF] and Rigo [RSBF]) were prepared according to the procedure described in the literature (17, 18). The 7-day-set samples were also placed into containers with 47 mL SBF solutions in order to maintain a surface area-to-volume ratio of 0.1/cm and were kept under stirring at 37°C with the help of a shaker (MA420, Marconi). Afterwards, the samples were gently rinsed with deionized water, followed by drying at room temperature according to the literature (19). The surface of the samples was analyzed by scanning electron microscopy (EVO MA10; Zeiss, Oberkochen, Germany) and energy-dispersive X-ray analysis (EDX) before and after treatment in the SBF solutions. The samples before and after immersion in SBF were also studied by X-ray diffraction (XRD) (XRD-6000; Shimadzu, Kyoto, Japan) using CuKα radiation (1.54439 Å) in order to identify the phases formed on the sample surface.

Results

Measurements of the setting time using the Vicat apparatus were taken for suspensions of MTA and A-CAEC. This latter material presented a setting time of 25 minutes, whereas MTA did not set until 180 minutes.

pH measurements as a function of time for water and SBF solutions in contact with previously set samples of MTA and A-CAEC showed pH values close to 11 in the presence of MTA as soon as the sample was placed in water, whereas a pH level of approximately 10 was attained for A-CAEC until day 5. MTA presented a slower pH increase in KSBF than in RSBF, reaching values close to 9.5 only after 9 days in the former, whereas in RSBF these values were detected in the first day after immersion. A-CAEC did not result in a pH increase in KSBF-containing samples, and higher pH values were only attained in RSBF.

The EDX spectra of the surface of the MTA and A-CAEC samples before immersion in SBF confirmed the presence of the main chemical constituents of MTA (ie, calcium, silicon, oxygen, and bismuth) and those for A-CAEC (ie, aluminum, oxygen, calcium, and zinc). (Supplemental Table S1 is available online at www.jendodon.com.)

Scanning electron microscopic analysis and EDX spectra of set samples after immersion for 7 days in KSBF or RSBF are shown in Figures 1*A* and *B* and 2*A* and *B*. These analyses confirmed the presence of calcium and phosphorus for MTA and A-CAEC after immersion in KSBF and RSBF solutions, respectively. The association of these elements indicates the formation of a calcium phosphate phase on the sample surface. (Supplemental Table S2 is available online at www.jendodon.com.)

XRD analysis of set samples before and after immersion for 7 days in KSBF or RSBF solutions are shown in Figure 3. Carbonated apatite ($Ca_{10}[(PO_4)_3(CO_2)_3(OH)_2]$) was identified on the MTA surface after immersion in KSBF solution. On the other hand, hydroxyapatite ($Ca_5[PO_4]_3OH$) was detected on the surface of A-CAEC after immersion in RSBF solution.

Discussion

CAEC composition has overcome some negative properties of the currently available materials based on aggregate minerals. The results have shown that CAEC has improved handling properties, higher mechanical strength, and reduced porosity with a lower pore size and is also a nonstaining material when compared with MTA (8, 12). However, for a suitable setting time, the addition of accelerating additives is required. CAEC plus accelerators ($1Li_2CO_3$:1CaO) (ie, A-CAEC) showed a suitable setting time (close to 20 minutes) when compared with MTA, hence matching the clinical requirements. (Supplemental Table S3 is available online at www.jendodon.com.)

A marked decrease in the setting time is observed in the presence of lithium carbonate (Li_2CO_3) because the Li^+ ions favor the formation of insoluble compounds such as $LiAl(OH)_4$, withdrawing $Al(OH)_4^-$ from the solution. Therefore, during cement hydration, the lithium salt increases the calcium ion concentration in the medium, inhibiting the formation of soluble hydrate and speeding up the precipitation stage. Moreover, $LiAl(OH)_4$ presents a crystalline structure that acts as nuclei for the calcium aluminate hydrates at any measured temperature (20, 21).

The addition of CaO and Li_2CO_3 also increases the calcium ion concentration in the suspension, inducing the formation of a less soluble hydrate (richer in Ca^{2+} ions), which speeds up the precipitation stage. In the presence of water, CaO generates $Ca(OH)_2$, which dissociates in Ca^{2+} and OH^- ions.

Because A-CAEC has a reduced setting time, this should decrease the need of constant professional procedures during the treatment. When used as a root-end or root-canal filling material, the fast set should also reduce the risk of contamination and dislodgement after placement (22, 23).