

# In Vitro Evaluation of a Ceramicrete-based Root-end Filling Material

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## Abstract

Ceramicrete is an impervious inorganic binder widely used for encapsulating radioactive and hazardous wastes. This study evaluated the feasibility of using a radiopaque Ceramicrete-based material for root-end fillings. Apical seals of root-end preparations filled with Super EBA (Harry J. Bosworth Co, Skokie, IL), White ProRoot MTA (Dentsply Tulsa Dental Specialties, Tulsa, OK), or Ceramicrete-D were evaluated using a computerized fluid filtration approach after the fillings were immersed in phosphate-containing fluid (PCF). The Ceramicrete-D fillings exhibited significantly ( $P < 0.05$ ) better seals than the other two commercially available, frequently advocated root-end-filling materials. Scanning electron microscopy and x-ray diffraction of Ceramicrete-D after setting revealed a relatively nonporous  $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$  matrix that binds other incompletely reacted and new reaction phases such as  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ . Polished dentin slabs filled with Ceramicrete-D and immersed in PCF for 72 hours revealed depositions of acicular-shaped, apatite-like crystallite clusters on the material surface as the pH of the PCF increased with immersion time. The experimental Ceramicrete-based material is potentially bioactive in the presence of PCF. (*J Endod* 2007;33:1438–1443)

## Key Words

Ceramicrete, Flodec, fluid filtration, mineral trioxide aggregate, root-end filling, Super EBA

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Periapical surgery is an alternative treatment when nonsurgical root canal treatment or retreatment fails or when nonsurgical retreatment is impossible (1, 2). During the surgical procedure, a root-end filling is placed to provide an apical seal that prevents the penetration of bacteria or diffusion of bacterial products from the leaking root canal system into the periapical tissues (3–7). Super EBA (Harry J. Bosworth Co, Skokie, IL), a reinforced zinc oxide-eugenol cement, has a good clinical track record as a root-end-filling material (8); however, its long-term solubility renders the material potentially undesirable for a lifelong seal (9). Mineral trioxide aggregate (ProRoot MTA; Dentsply Tulsa Dental Specialties, Tulsa, OK) has also shown promising results as a root-end-filling material because of its sealing properties (10–12), bioactivity (13, 14), and cementogenesis potential (15–18). Despite these advantages, MTA is fairly difficult to manipulate in the absence of a rheologic modifier (19) and exhibits low washout resistance during its initial slow setting phase when it is mixed without a setting accelerator (20).

Ceramicrete is a self-setting phosphate ceramic developed at the Argonne National Laboratory that sets at ambient temperature by acid-base reaction between an acid phosphate ( $\text{KH}_2\text{PO}_4$ ) and a sparingly soluble, basic divalent metal oxide (calcined MgO) (21). Because of the impervious characteristics of its potassium magnesium phosphate hexahydrate ( $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$ ) ceramic matrix phase, Ceramicrete has been used as a binder for encapsulation of radioactive and hazardous wastes (22–24). Improvement in mechanical properties was achieved when calcium silicate whiskers were included in the Ceramicrete binder, producing a phosphosilicate ceramic material that contains an additional dicalcium phosphate dihydrate ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  or brushite) phase (25). More recently, a biocompatible, radiopaque Ceramicrete-based dental or bone material has been created by incorporating hydroxyapatite powder and cerium oxide radiopaque fillers into the phosphosilicate ceramic (26). The Ceramicrete-based material has an initial setting time of 6 minutes and a final setting time of 12 minutes (Gilmore needle method at 37°C), can be rolled into a sausage-like formation for easier manipulation with dental instruments, and sets under water with minimal washout. Because the material is nonporous and generates calcium and phosphate ions during the setting reactions (25, 26), it has potential applications as a root-end-filling material. Thus, the objectives of this study were to investigate the apical seal of Ceramicrete-based root-end fillings and to examine the morphologic characteristics of the set material after immersion in a phosphate-containing fluid (PCF).

## Materials and Methods

### Ceramicrete-Based Cement

A Ceramicrete-based powder (26) was prepared by combining calcined MgO with  $\text{KH}_2\text{PO}_4$ ,  $\text{CaSiO}_3$  whiskers, hydroxyapatite powder, and cerium oxide (Sigma-Aldrich, St Louis, MO). A modified version of the material (designated as Ceramicrete-D) was used in the present study by mixing the Ceramicrete-based powder with deionized water in a powder/liquid ratio of 0.65/0.35 (1.85:1). In addition, a 50 wt%  $\text{MgH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  aqueous solution (pH 3.0) was applied as a conditioner on smear layer-covered dentin for 30 seconds without additional rinsing.

## Teeth

Thirty-six human single-rooted teeth and three third molars were stored until use in 0.9% NaCl solution containing 0.02% sodium azide to prevent bacterial growth. Each single-rooted tooth was cleaned and shaped under an operating microscope. Instrumentation was performed with a crown-down technique using ProTaper nickel-titanium rotary instruments (Dentsply Tulsa) until 1 mm of a F3 file tip extruded beyond the apical foramen. The canals were rinsed with 10 mL of 6.15% sodium hypochlorite in between instrumentation and 5 mL of 17% ethylenediamine tetraacetic acid as the final rinse.

## Root-End Preparation

The apical 3 mm of each instrumented root was resected 90° to the longitudinal axis of the root. A single ProTaper F3 gutta-percha cone (Dentsply Tulsa) was inserted into the canal and with the protruding apical portion cut off. A provisional restoration (Tempit; Centrix, Shelton, CT) was placed in the coronal access cavity to stabilize the gutta-percha cone. Root-end preparations were made to a depth of 3 mm using ultrasonic tips (ProUltra Surgical Endodontic Tips; Dentsply Tulsa) powered by an ultrasonic unit (Satelec P5; Dentsply Tulsa) with copious water spray.

The teeth were divided into three groups ( $n = 10$ ) and two control groups ( $n = 3$ ). The three groups were as follows: group 1: Super EBA, group 2: White ProRoot MTA, and group 3: Ceramicrete-D. For groups 1 and 2, the materials were mixed according to the manufacturers' instructions. The materials were compacted into the root-end preparations using microsurgical pluggers (KiS Microsurgical Instruments; Obtura/Spartan, Fenton, MO). The filled teeth were placed inside a humidifier at 37°C and 100% relative humidity for 24 hours to ensure setting of the materials. Each tooth was subsequently stored in 15 mL of PCF containing 0.8 wt% NaCl, 0.02 wt% KCl, 0.118 wt%  $\text{Na}_2\text{HPO}_4$ , and 0.017 wt%  $\text{KH}_2\text{PO}_4$  in deionized water (pH 7.31) (13) for 3 days before leakage evaluation.

Three roots with unfilled root-end preparations were used as the positive control. Three roots were used as the negative control. Each negative control root contained a Super EBA root-end filling and an empty canal and was dipped in molten sticky wax.

## Leakage Evaluation

Leakage was evaluated using a fluid filtration technique developed by Derkson et al (27). In this study, the technique was further refined with the use of a computerized Flodec measuring device (De Marco Engineering, Geneva, Switzerland) that permits digital data collection every 1.04 second (28) (Fig. 1A). Each tooth was sectioned along its cemento-enamel junction using a slow-speed Isomet saw (Buehler Ltd, Lake Bluff, IL) under water cooling. The gutta-percha cone was removed, leaving an empty canal with the root-end filling. The root segment was attached via its coronal orifice to an 18-G needle-perforated plastic platform and sealed with cyanoacrylate glue. The external root surface was also covered with cyanoacrylate to 3 mm beneath the resected root end. Nitrogen gas pressure was applied at 10 psi (69 kPa) via polyethylene tubings through the apical end of the roots. Fluid flow was recorded by monitoring the displacement of a water bubble inside the glass capillary tube of the Flodec device.

Data were plotted as fluid flow ( $\mu\text{L}/\text{min}^{-1}$ ) versus time and expressed as mean fluid flow. Because the normality (Kolmogorov-Smirnoff test) and homoscedasticity (Levene test) assumptions of the data were violated, they were analyzed using one-way analysis of variance on ranks and Dunn's multiple comparison test at  $\alpha = 0.05$ .

## Morphologic and Composition Analyses

Ceramicrete-D was mixed and allowed to set in flexible bullet-shaped molds. The material bullets were fractured and sputtered coated with gold/palladium for examination with a field emission-scanning electron microscope (Model XL-30 FEG; Philips, Eindhoven, The Netherlands) at 5 KeV.

Additional specimens were milled to produce a fine powder. X-ray diffraction (XRD) patterns were recorded with a D/max B Geigerflex XRD unit (Rigaku America, Woodlands, TX) using Ni-filtered  $\text{Cu K}\alpha$  radiation (30 KeV, 10 mA), in the  $2\theta$  range of 10° to 80°, with a step size of 0.05° and a normalized count time of 4 s/step. Results were analyzed with the Jade5 software (Materials Data, Inc, Livermore CA) using JCPDS files.

## Interfacial Examination of Material-Dentin Interfaces After PCF Immersion

Flat smear layer-covered dentin surfaces were prepared from third molars by removing the occlusal enamel and polishing the dentin with 320-grit silicon carbide paper. These surfaces were conditioned with the  $\text{MgH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  solution for 30 seconds without rinsing before placement of Ceramicrete-D. After setting, 3-mm thick cement-dentin slabs were prepared with the Isomet saw under water cooling and polishing with 1,200-grit silicon carbide paper. These slabs were immersed in PCF for 12 or 72 hours. They were thoroughly rinsed in deionized water, air dried, and sputter coated for scanning electron microscope examination.

## pH Evaluation

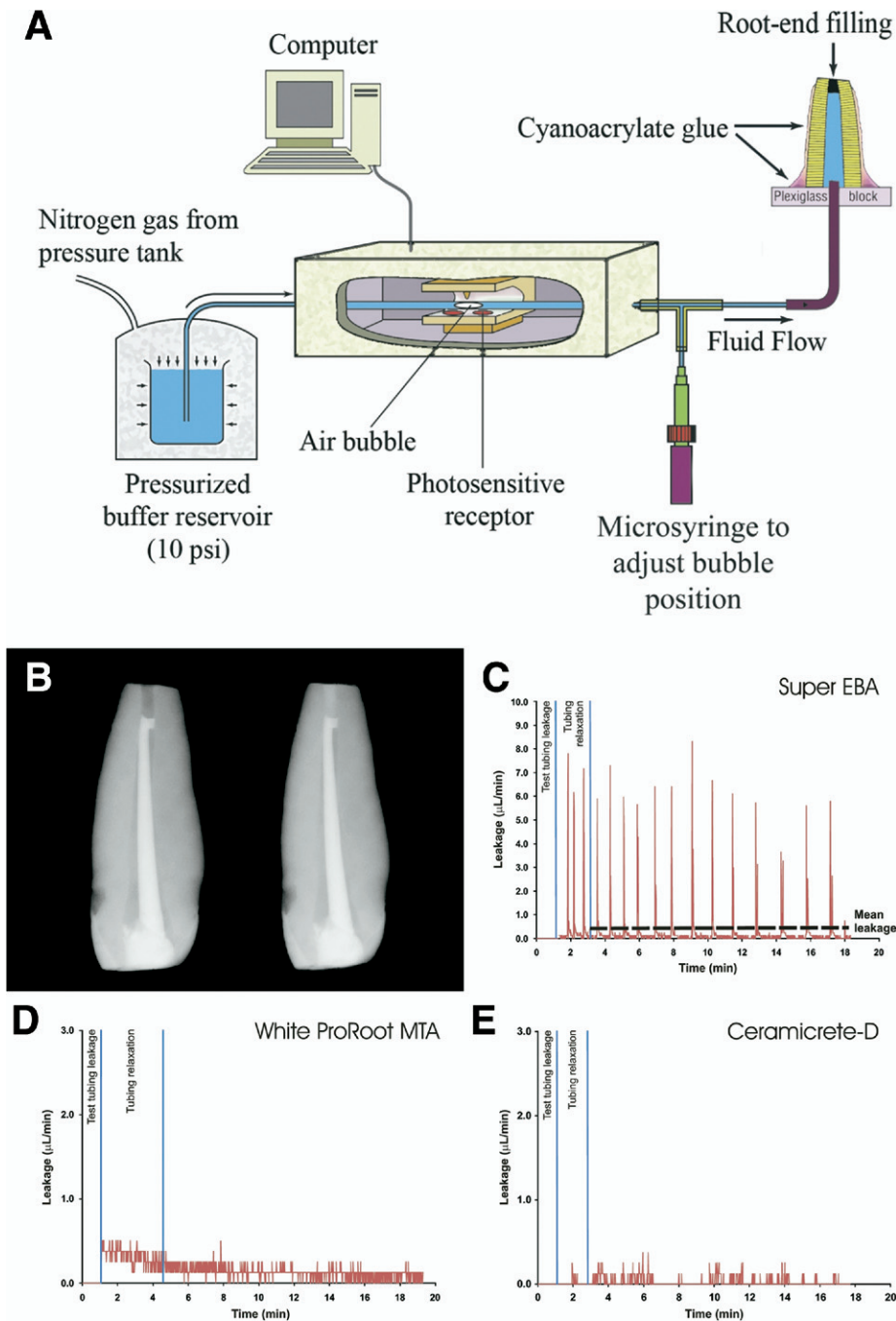
Set Ceramicrete-D specimens (1 g) were immersed in either 15 mL of deionized water (pH 6.75) or PCF. The pH changes over a 72-hour period were recorded with a pH meter (AR10; Fisher Scientific, Fair Lawn, NJ) at 25°C.

## Results

The Ceramicrete-D root-end fillings had a radiopacity that is similar to that of root dentin (Fig. 1B). Representative fluid flow versus time plots for the three root-end-filling groups are shown in Figures 1C-1E. The mean (standard deviation) fluid flow for the Super EBA, White ProRoot MTA, and Ceramicrete-D root-end fillings were  $0.271 \pm 0.113$ ,  $0.109 \pm 0.022$ , and  $0.025 \pm 0.004 \mu\text{L}/\text{min}$ , respectively. Leakage in the Super EBA group was significantly higher than the White ProRoot MTA group, which, in turn, was significantly higher than the Ceramicrete-D group ( $P < 0.05$ ). There was no leakage in the negative control. The positive control specimens exhibited leakage values of  $105.6 \pm 23.2 \text{ mL}/\text{min}$ , which were 5 to 6 orders of magnitude higher than the fluid flow in the root-end filling groups.

Fractured Ceramicrete-D exhibited a nonporous surface except for the occasional observation of air voids, with the Ceramicrete matrix binding large incompletely reacted fillers (Fig. 2A). The Ceramicrete matrix appeared glassy and encapsulated additional mineralogical phases within its matrix (Fig. 2B). XRD of the set cement revealed the formation of  $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  reaction phases together with incompletely reacted inorganic filler component phases (Fig. 2C).

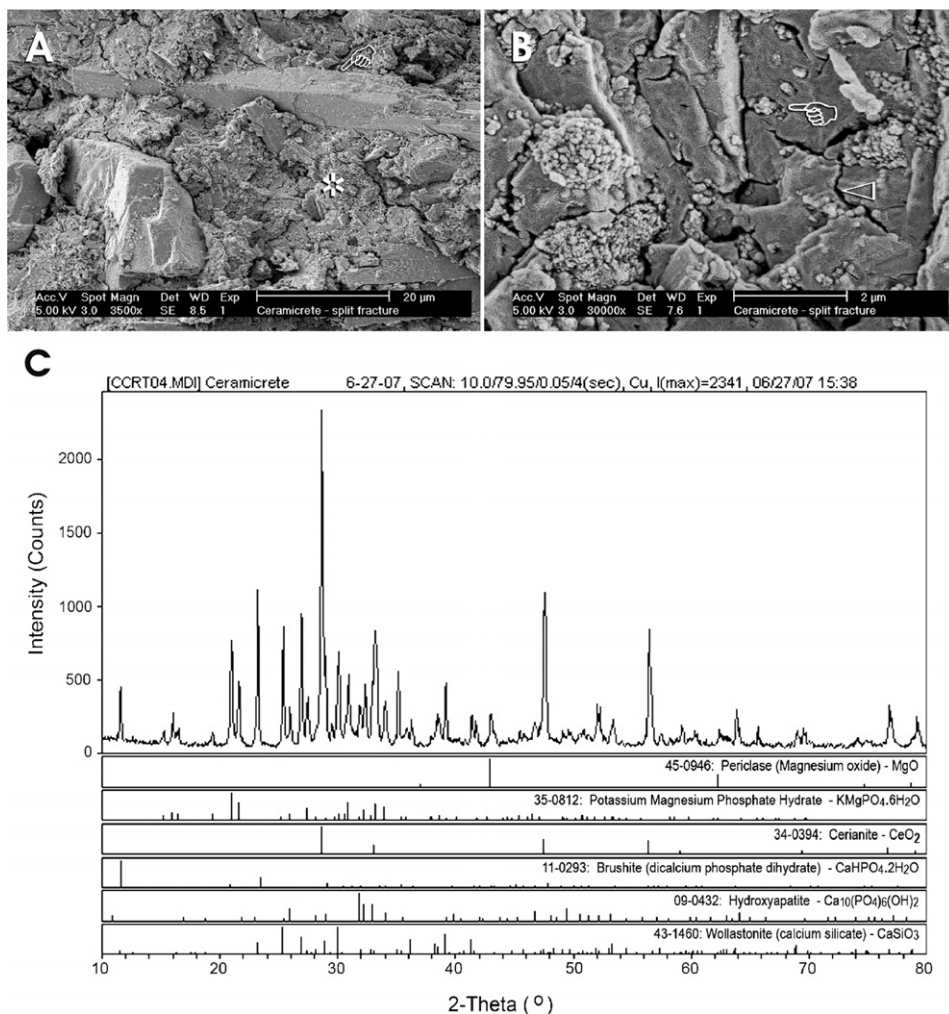
Polished Ceramicrete-D exhibited rod-shaped crystalline outgrowths from the material surface after immersion in PCF for 12 hours (Fig. 3A). Despite the taxing conditions of dehydration and high vacuum SEM examination, remnant material was retained along the smear layer-covered dentin (Fig. 3B). The rod-shaped outgrowths that were formed on the Ceramicrete-D surfaces at 12 hours were replaced by heavy deposits consisting of finer acicular-shaped crystalline clusters (Fig. 3C, D). Large (50–150  $\mu\text{m}$  wide) hexagonal crystalline plates not



**Figure 1.** (A) A schematic of the computerized fluid filtration setup for leakage evaluation of the root-end-filling materials. (B) Digital radiographs showing the preparation of root-end cavities and placement of root-end-filling materials in cleaned and shaped canals that were fitted with single gutta-percha cones without the use of sealers to simulate incompletely filled root canals. (C) A representative plot of fluid leakage over time in the Super EBA group. For each specimen, leakage of the tubing connections was first tested by clamping the polyethylene tubing from the specimen end followed by the application of 10-psi pressure for approximately 1 minute (first blue line). This was followed by releasing the hemostat and allowing the system to run for 2 to 3 minutes to enable relaxation of the clamped tubing before the actual fluid filtration measurement (second blue line). The latter was conducted for 15 minutes. Because there is nonuniform flow in the plot, the mean leakage over the testing period is represented by the dotted black line. (D) A representative plot of fluid leakage over time in the White ProRoot MTA group. (E) A representative plot of fluid leakage over time in the Ceramicrete-D group.

present in the original material were also identified (Fig. 3C). At high magnifications, the surfaces of the acicular crystallites were covered with amorphous droplets. In addition, partially coalesced amorphous (ie, noncrystalline) globular phases were occasionally observed among the acicular crystallites (Fig. 3E).

When Ceramicrete-D was immersed in deionized water, the pH of the solution rose to 10.85 after 12 hours and 11.31 after 72 hours. When Ceramicrete-D was immersed in PCF, the pH of the solution rose to 8.82 after 12 hours and 9.46 after 24 hours (Fig. 3F). In both cases, the solutions remained clear with minimal crystalline or turbid precipitation.



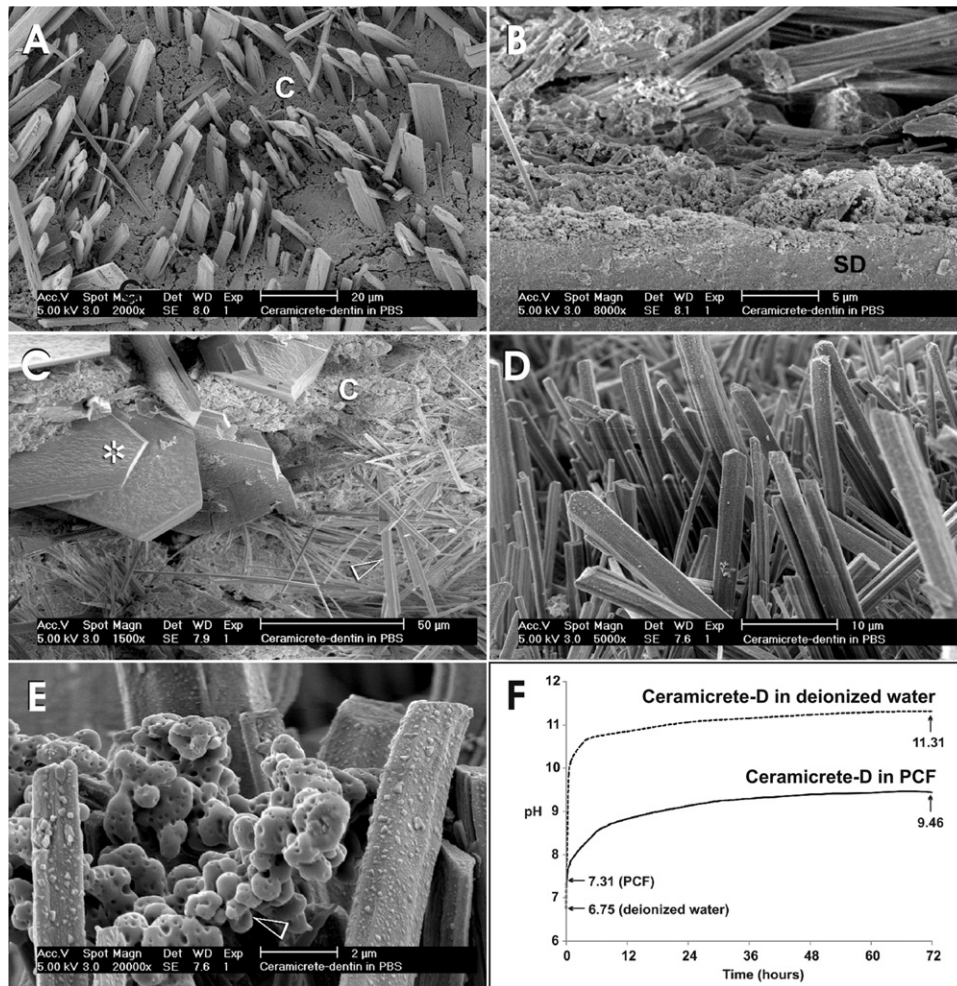
**Figure 2.** (A) Before immersion in water, a fractured surface of the set Ceramicrote-D appeared nonporous when examined by scanning electron microscopy. The Ceramicrote phase (ie,  $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$ , reaction product of  $\text{MgO}$  and  $\text{KH}_2\text{PO}_4$ ) served as a binder (asterisk) for large, incompletely reacted fillers such as calcium silicate whiskers (pointer) and hydroxyapatite powder that were incorporated in the Ceramicrote-based cement. (B) A high-magnification view of the region depicted by the asterisk in the previous micrograph, showing the glassy nature of the Ceramicrote binder. Additional fine particulate phases (pointer) were encapsulated by the Ceramicrote binder. Dehydration of the material during scanning electron microscopic examination resulted in the formation of artifactual cracks within the Ceramicrote binder (open arrowhead). (C) XRD of powdered set Ceramicrote-D, showing the presence of the cerium oxide ( $\text{CeO}$ ) radiopaque fillers, incompletely reacted magnesium oxide ( $\text{MgO}$ ), calcium silicate ( $\text{CaSiO}_3$ ), hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ), potassium magnesium phosphate hexahydrate ( $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$ ) as the primary Ceramicrote binder phase, and dicalcium phosphate dihydrate ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ) that is formed between the calcium ions released from the calcium silicate and the hydrogen phosphate ions available in the material (25).

## Discussion

The high-quality apical seal created by Ceramicrote-D is probably attributed to the nonporous nature of the set material and the use of the acidic  $\text{MgH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  conditioner to loosen or partially dissolve the smear layer, thereby allowing better adaptation of the material to intact dentin. In the original material formulation (26), acidic  $\text{MgH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  solution (pH 3) was used as the cement liquid, resulting in gas release and a macroporous set material with large interconnecting pores (KYC Tay, unpublished results, June 2007). Although this has potential use as an osteoconductive bone grafting material that facilitates bone ingrowth (29), such a biomaterial design defeats the purpose of taking advantage of the excellent encapsulating properties of the Ceramicrote binder to achieve impervious root-end seals. This problem was solved by formulating a nonporous Ceramicrote-D version in which deionized water was used as the cement liquid.

Calcium phosphate crystal formation appears to be a common characteristic for calcium silicate-containing biomaterials (30). How-

ever, unlike the immersion of set Portland cement in PCF (31), the solution remained clear instead of becoming turbid after immersion of set Ceramicrote-D specimens, with the crystalline precipitations forming predominantly on the material surface. This may be because of the reduced reactivity of calcium silicate (wollastonite) in the Ceramicrote-D as compared with the more reactive dicalcium silicate and tricalcium silicate that are present in Portland cements. Composition analyses of the crystalline precipitations on the material surface have not been performed because the results would have been inaccurate because of interferences from the underlying material. Nevertheless, based on the pH changes of the PCF and morphologic characteristics of the crystalline precipitates, we speculate that the initial rod-shaped outgrowths from the material surface after 12 hours of PCF immersion represent continuous dicalcium phosphate dihydrate (DCPD) formation in the presence of supplemental phosphate ions from the PCF and magnesium ions from the material. Usually, at pH values below 9.25 (32), the formation of octacalcium phosphate is kinetically more favor-



**Figure 3.** (A) A scanning electron micrograph taken from a polished section of smear layer–covered dentin that was covered with Ceramicrete-D and immersed in a phosphate-containing fluid (PCF) for 12 hours. Rod-shaped crystalline outgrowths were identified from the polished surface of the Ceramicrete-D (C). (B) The material-dentin interface taken from a specimen after immersion in PCF for 72 hours. The bulk of the Ceramicrete-D had separated from the dentin due to dehydration shrinkage, resulting in an artifactual gap (not shown). Nevertheless, remnants of the material could still be observed along the surface of the smear layer-covered dentin (SD). (C) At 72 hours, the originally polished Ceramicrete-D surface (C) was heavily covered by acicular-shaped crystalline clusters (open arrowhead). Large hexagonal crystalline plates (asterisk) were also observed from the material surface, intermingling with the acicular-shaped crystallites. (D) A higher-magnification view of the acicular-shaped crystalline clusters that were identified from the material surface after 72 hours. (E) A very high-magnification view of the acicular-shaped crystallites, showing partially coalesced amorphous globular structures (open arrowhead) that were occasionally seen around these crystallites. (F) pH changes when Ceramicrete-D bullets were immersed in either deionized water (initial pH 6.75) or PCF (initial pH 7.31) for up to 72 hours.

able than DCPD or hydroxyapatite (33). However, the formation of DCPD is favored in the presence of magnesium ions, with the latter stabilizing the DCPD (34) and modifying their conventional plate-shaped morphology to rod-shaped crystals (35). Because the pH of the PCF solution exceeded 9.25, apatite is more likely to be the predominant calcium phosphate phase produced (32, 35). Formation of these apatite phases may be preceded by amorphous calcium phosphate precursors (Fig. 3E) that subsequently hydrolyze to carbonated apatites (32, 35). The large hexagonal plates may represent calcium hydroxide crystals that were also seen when Portland cement was immersed in PCF (31).

Although the Ceramicrete-D tested in the present study exhibits excellent apical seal when used as a root-end–filling material and appears to show some forms of in vitro bioactivity after immersing in PCF, it is prudent to emphasize that this work represents only a feasibility study of a novel class of material for endodontic use. Because the material was initially formulated for use as bone cement, augmentation of its radiopacity has to be achieved by increasing the amount of cerium oxide or bismuth oxide. The reactivity of the material may further be

improved by replacing the wollastonite calcium silicate component with dicalcium or tricalcium silicate. The optimized material will also require biocompatibility evaluations before it may be recommended for clinical testing.

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