The Use of a Setting Accelerator and Its Effect on pH and Calcium Ion Release of Mineral Trioxide Aggregate and White Portland Cement

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Abstract

The aim of this study was to evaluate the influence of adding 10% calcium chloride ($CaCl_2$) indicated as setting accelerator on pH and release of calcium ions of commercially available materials: ProRoot MTA (tooth-colored formula), MTA Branco, and White Portland cement. The products were mixed for 30 seconds in previously established ratios. To estimate the values of pH and release of calcium ion, polyethylene tubes were filled with the materials and immersed in containers with 10 ml of deionized water. The analyses were performed baseline, 30 minutes, 60 minutes, and 24 hours after the mixing process. A pHmeter (MicroNal B 371, Sao Paulo, SP, Brazil) and an atomic absorption spectrophotometer (Model GBC 904; CG Corp, Melbourne, Australia) equipped with a hollow cathode lamp were used to determine the data. According to the Student's *t*-test, the comparison between the pure and the $CaCl_2$-added products indicated that the presence of this substance increased immediately the pH, although the results were very similar when they were analyzed in the other intervals. In addition, products with $CaCl_2$ released more calcium ions than pure materials in the 24-hour period ($p < 0.05$). The results revealed that the addition of $CaCl_2$ to MTA enhanced the physicochemical properties of this product. Thus, materials mixed with $CaCl_2$ became easier to handle and needed lower amounts of water in the mixing process. *(J Endod 2006;32: 1194–1197)*

Key Words

Calcium chloride, calcium release, MTA, pH, Portland cement

Since its introduction as a root-end filling material in 1993, the use of Mineral Trioxide Aggregate (MTA) has expanded to many applications for root repair and bone healing (1–3). The gray MTA is commercially available as ProRoot MTA (GMTA) (Dentsply Tulsa Dental, Tulsa, OK). The major component, Portland cement, is a mixture of dicalcium silicate, tricalcium silicate, tricalcium aluminate, and tetra-calcium aluminoferrite. Recently, an alternative formulation to GMTA was developed by Dentsply, known as tooth-colored formula (white) ProRoot MTA (WMTA). Both products differ mainly in the constitution. GMTA contains tetra-calcium aluminoferrite (an iron-based chemical), whereas, the WMTA contains this element in a lower percentage (4). This reduction is intended to decrease the potential for tooth discoloration observed when GMTA is used in anterior teeth (5).

In 2001, the MTA-Angelus (Angelus, Londrina, PR, Brazil) was introduced into the Brazilian dental market. This material is composed by 80% of Portland cement and 20% of bismuth oxide. Calcium sulfate was removed from its composition to accelerate the setting time (6). Recently, the color of this product was also changed to white, receiving the commercial name of MTA Branco (MTAB).

Current studies have demonstrated that GMTA and WMTA presented similar physico-chemical (7) and biological properties (8–10). Furthermore, equivalent characteristics between MTA and Portland cement were described by other researchers (11–14).

However, the MTA has shown a setting time of 2 hours and 47 minutes (1). This relatively high setting time is considered a disadvantage, along with its difficult handling (7). Harrington (15) stated that adding 10 to 15% calcium chloride ($CaCl_2$) to the Portland cement decreases its setting time. The results have shown that in general, the addition of $CaCl_2$ decreased the setting time more than 50%. However, it is not known if adding $CaCl_2$ would not influence the physico-chemical properties of the material, i.e. pH and calcium release, which are essential for the suitable biological behavior of the material (16). Taking these things into consideration, the purpose of this study was to evaluate in vitro the influence of the addition of $CaCl_2$ in the pH and the calcium ion release of ProRoot MTA (tooth-colored formula), MTA Branco, and White Portland cement.

Materials and Methods

The analyzed materials were tooth-colored formula ProRoot MTA (WMTA) (Dentsply, Maillefer, OK), MTA Branco (MTAB) (Angelus, Londrina), and White Portland cement (WPC) (Irajazinho, Votorantim, SP, Brazil) with and without 10% $CaCl_2$. The materials were used in a ratio of 10% of $CaCl_2$ and 20% of bismuth oxide for WPC (AND, model GR-202, Tokyo, Japan, Biochemistry Laboratory, FOB-USP). To provide radiopacity, 20% bismuth oxide (Bi_2O_3) was added to WPC, resulting in a material with similar composition. The materials were mixed as shown in Table 1.

pH Analysis

Polyethylene tubes (10 mm length and 1 mm diameter) were used. The materials were mixed with distilled water for 30 seconds. After filling the tubes with the products, they were immersed individually in holders containing 10 ml of deionized water and the

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TABLE 1. Cements tested and respective admixtures.

Group	Cements	Admixtures
1	WMTA (1.0 g)	Mixed with 0.4 ml sterile distilled H_2O
2	WMTA with 10% $CaCl_2$	1.0 g WMTA with 0.1 g $CaCl_2$ mixed 0.3 ml sterile distilled H_2O
3	MTAB (1.0 g)	Mixed with 0.4 ml sterile distilled H_2O
4	MTAB with 10% $CaCl_2$	1.0 g MTAB with 0.1 g $CaCl_2$ mixed 0.3 ml sterile distilled H_2O
5	WPC (0.8 g) with Bi_2O_3 (0.2 g)	Mixed with 0.4 ml sterile distilled H_2O
6	WPC (0.8 g) with Bi_2O_3 (0.2 g) and 10% $CaCl_2$	1.0 g WPC with 0.1 g $CaCl_2$ mixed 0.3 ml sterile distilled H_2O

initial pH was immediately examined. Subsequent readings were made after 30 minutes, 60 minutes, and 24 hours. Before each reading, the filled tubes were put into new containers with deionized water to avoid liquid saturation. A pHmeter (B371, MicroNal S/A, Sao Paulo, SP, Brazil) was used to measure the pH of the specimens. The apparatus was previously calibrated with pH 7.0 and pH 4.0 solutions. Between each measurement the electrode was washed with ultrapure water and blot-dried. The initial pH of the deionized water was measured before the immersion of the materials.

Calcium Ions Release Analysis

Polyethylene tubes with 10 mm of length and 1 mm of internal diameter were used. The filled tubes with the test materials were immersed in 10 ml of deionized water. The evaluation periods were the same cited for pH analyses: baseline, 30 minutes, 60 minutes, and 24 hours, and all the tubes were moved to a new solution at the end of each interval. The calcium release was measured through the atomic absorption spectrophotometer (Model GBC 904; CG Corp, Melbourne, Australia), equipped with a hollow calcium cathode lamp, according to the operative conditions: lamp current: 3 mA; fuel: nitrous oxide; support: oxygen; stoichiometry: reducing; wavelength: 422.7 nm; slit: 0.2 nm.

To prevent interferences by phosphates and alkaline metals, all glassware was prewashed with 5% nitric acid (17). A pattern, stock solution of 10 mg% calcium (Ca) was diluted in deionized water to obtain 0.025 mg, 0.05 mg, 0.1 mg, 0.2 mg, and 0.3 mg % concentration readings, and the standard slope.

To calibrate the apparatus for zero absorbency, deionized water was used as calibration blank.

After the equipment adjustment, the water used to submerse the tubes containing the products was measured.

The samples were diluted in deionized water, when the calcium release was beyond the reading limits of the device, to the point it was judged required to perform the evaluation.

The results were estimated by using the equation of standard curve line, which was determined by the measurement of solutions with known concentrations (i.e. 0.025, 0.05, 0.1, 0.2, and 0.3 mg/dl).

pH and calcium release data were compared through ANOVA and Tukey's test for individual comparisons when differences were observed. Student's *t*-test was used for comparison between groups with and without calcium chloride, regardless of the materials.

Results

The presence of $CaCl_2$ increased significantly the pH, according with Student's *t*-test ($p < 0.05$) in the immediate period group. However, the pH for other periods was similar (Table 2).

Table 2 shows the individual comparisons for calcium release (average values, mg/dl). It could be noticed that the presence of $CaCl_2$ favored the release of calcium ions ($p < 0.05$) in the 24-hour period. The release of calcium ions was similar between all other groups.

Figure 1 shows the pH and release of calcium ions, regardless of the material.

Discussion

The addition of $CaCl_2$ aims to accelerate the setting time. However, it has been argued if this substance could influence the physico-chemical properties of this material.

Therefore, the results of this study have elucidated that the $CaCl_2$ have boosted the cements' pH immediately, and this condition was maintained during all analyzed periods. The explanation for this event remains in the additional calcium incorporated to the formula ($CaCl_2$). Consequently, the materials that have received this substance presented higher calcium ions release. These assumptions are relevant, considering that the biological properties of MTA are based on its alkaline pH and calcium release (1, 16, 18–21). Takita et al. (22) confirmed that the proliferation human dental pulp (HDP) cells in contact with MTA could be related to the continuous release of calcium ions. The exogenous $CaCl_2$ as a source of calcium ions was added to medium in the absence of MTA on the basis of the hypothesis that the effect of MTA on the increase of cell proliferation is related to the release of calcium ions from material. As a result, the $CaCl_2$ increased the proliferation of HDP cells compared with control levels. The amount of calcium ions re-

TABLE 2. Average and standard deviation of pH values and calcium ions release (mg/dl) for cements with or without $CaCl_2$, according with the periods

Material	Immediate	SD	60 Min	SD	24 h	SD
pH						
ProRoot MTA	9.6 (a)	0.14	11.0 (a)	0.14	11.5 (a)	0.20
ProRoot MTA + $CaCl_2$	10.0 (b)	0.07	10.6 (ab)	0.17	11.3 (a)	0.15
MTA Branco	9.6 (a)	0.18	10.9 (a)	0.18	11.5 (a)	0.14
MTA Branco + $CaCl_2$	10.0 (b)	0.14	10.8 (a)	0.28	11.7 (a)	0.20
CPB	8.8 (c)	0.07	10.2 (b)	0.14	11.4 (a)	0.10
CPB + $CaCl_2$	10.0 (b)	0.07	10.8 (a)	0.28	11.4 (a)	0.38
Calcium ions release (mg/dl)						
ProRoot MTA	0.04 (a)	0.01	0.10 (ab)	0.01	0.52 (a)	0.13
ProRoot MTA + $CaCl_2$	0.12 (a)	0.03	0.08 (a)	0.03	2.14 (b)	0.18
MTA Branco	0.12 (a)	0.005	0.03 (a)	0.01	0.8 (a)	0.05
MTA Branco + $CaCl_2$	0.14 (a)	0.10	0.15 (b)	0.01	1.59 (b)	0.66
CPB	0.10 (a)	0.05	0.13 (b)	0.05	2.18 (b)	0.13
CPB + $CaCl_2$	0.13 (a)	0.06	0.16 (b)	0.07	1.83 (b)	0.24

( ) Different letters indicate statistically significant differences (Tukey's test, $p < 0.05$).

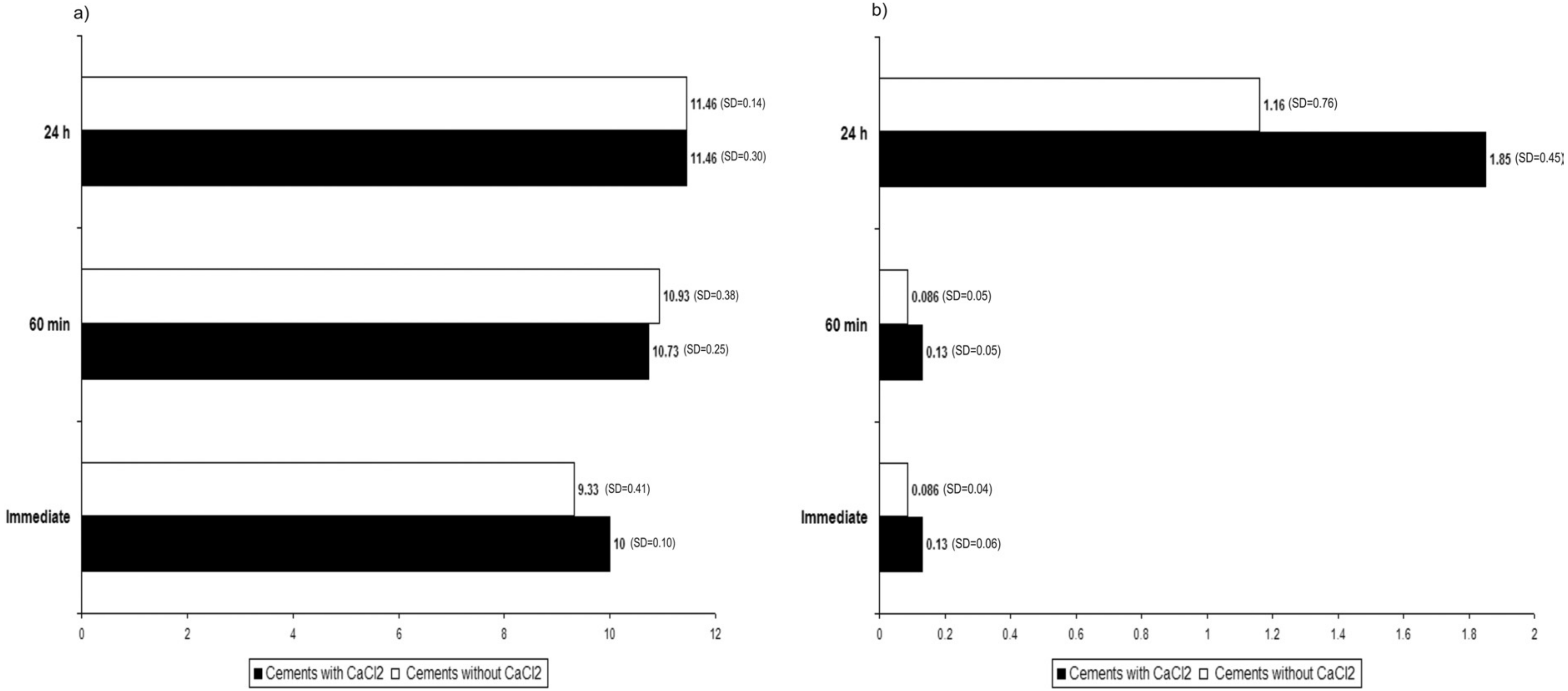

Figure 1. Average and SD of (*A*) pH values and (*B*) calcium ions released (mg/dl) for cements with or without $CaCl_2$, according to the periods.

leased from MTA was almost constant in each culture period, and the calcium ion concentration was approximately 0.3 mmol/L^{-1}, which is nearly the same as the concentration with the addition of 0.3 mmol/L^{-1} $CaCl_2$. They have shown similar patterns of cell proliferation. In our study, the addition of $CaCl_2$ increased the release of calcium ions, mainly in the 24-hour group.

$CaCl_2$ has a low pH (4.4), and has shown poor results when used alone for induction of calcified apical barriers in immature monkey teeth (23). However, when added to MTA and Portland cements, it has been shown that 10% $CaCl_2$ favored repair, formation of cementum, and re-establishment of the periodontal ligament in cases of root perforation in dogs' teeth (24). Despite its low pH, the addition of $CaCl_2$ did not change significantly the pH of the cement.

Abdullah et al. (25) investigated the biocompatibility of Portland cement with 10% and 15% $CaCl_2$, added to accelerate the hardening time. The authors concluded that the Portland cement with $CaCl_2$ in both concentrations, was potentially able to promote bone repair, presented biocompatibility and nontoxic qualities, and reduced hardening time.

It is interesting to accelerate the setting of MTA when it is used as a retrofilling material. An extended setting time facilitates the leakage and material dislodgement during the apical surgery. Bortoluzzi et al. (26) have shown that the addition of 10% $CaCl_2$ into the composition of ProRoot MTA, MTA-Angelus, and white Portland cement provided a significant decrease in dye leakage. The authors concluded that the cements' sealing ability was improved with the presence of $CaCl_2$.

The results obtained in this study corroborate those found by Duarte et al. (17), which found that ProRoot MTA and MTA-Angelus still released calcium and maintained an elevated pH, even after 126 hours.

In addition to the evidence described above, our experiments allowed to observe that these materials became easier to handle when mixed with $CaCl_2$, presented a higher luster, and needed lower amounts of water to complete the mixing procedures.

Conclusion

The results revealed that the addition of $CaCl_2$ improved the calcium release properties of all three MTA cements. Further studies of the influence of $CaCl_2$ on the biocompatibility of MTA should be performed.

References

1. Torabinejad M, Hong CU, McDonald F, Pitt Ford TR. Physical and chemical properties of a new root-end filling material. J Endod 1995;21:349–53.
2. Torabinejad M, Chivian N. Clinical applications of mineral trioxide aggregate. J Endod 1999;25:197–205.
3. Schwartz RS, Mauger M, Clement DJ, Walker WA 3rd. Mineral trioxide aggregate: a new material for endodontics. J Am Dent Assoc 1999;130:967–75.
4. Asgary S, Parirokh M, Eghbal MJ, Brink F. Chemical differences between white and gray mineral trioxide aggregate. J Endod 2005;31:101–3.
5. Moghaddame-Jafari S, Mantellini MG, Botero TM, McDonald NJ, Nör JE. Effect of ProRoot MTA on pulp cell apoptosis and proliferation in vitro. J Endod 2005;31:387–91.
6. Angelus. MTA-Angelus: cimento reparador. Londrina: Angelus.
7. Camilleri J, Montesin FE, Di Silvio L, Pitt Ford TR. The chemical constitution and biocompatibility of accelerated Portland cement for endodontic use. Int Endod J 2005;38:834–42.
8. Holland R, Souza V, Nery MJ, et al. Reaction of rat connective tissue to implanted dentin tubes filled with a white mineral trioxide aggregate. Braz Dent J 2002;13:23–6.
9. Parirokh M, Asgary S, Eghbal MJ, et al comparative study of white and grey mineral trioxide aggregate as pulp capping agents in dog's teeth. Dent Traumatol 2005;21:150–4.
10. Camilleri J, Montesin FE, Papaioannou S, McDonald F, Pitt Ford TR. Biocompatibility of two commercial forms of mineral trioxide aggregate. Int Endod J 2004;37:699–704.
11. Wucherpfennig AL, Green DB. Mineral trioxide vs Portland cement: two biocompatible filling materials [abstract]. J Endod 1999;25:308.
12. Estrela C, Bahmann LL, Estrela CRA, Silva RS, Pécora JD. Antimicrobial and chemical study of MTA, Portland cement, calcium hydroxide paste, Sealapex and Dycal. Braz Dent J 2000;11:19–27.
13. Menezes R, Bramante CM, Letra A, Carvalho VGG, Garcia RB. Histologic evaluation of pulpotomies in dog using two types of mineral trioxide aggregate and regular and White Portland cements as wound dressings. Oral Surg Oral Med Oral Pathol Oral Radiol Endod 2004;98:376–9.
14. Ribeiro DA, Duarte MAH, Matsumoto AM, Marques MEA, Salvadori DMF. Biocompatibility in vitro tests of mineral trioxide aggregate and regular and white Portland cements. J Endod 2005;31:605–7.
15. Harrington PP. Post retention with mineral trioxide aggregate and accelerated Portland cement. [dissertation]. Morgantown (WV): West Virginia University, 2005.
16. 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.
17. Duarte MAH, Demarchi ACCO, Yamashita JC, Kuga MC, Fraga SC. Ph and calcium ion release of 2 root-end filling materials. Oral Surg Oral Med Oral Pathol 2003;95: 345–7.
18. Yoshiba K, Yoshiba N, Nakamura H, Iwaku M, Ozawa H. Immunolocalization of fibronectin during reparative dentinogenesis in human teeth after pulp capping with calcium hydroxide. J Dent Res 1996;75:1590–7.
19. Estrela C, Sydney GB, Bammann LL, Felipe O Jr. Mechanism of action of calcium and hydroxyl ions of calcium hydroxide on tissue and bacteria. Braz Dent J 1995;6:85–90.
20. Holland R, Souza V, Nery MJ, Otoboni Filho JA, Bernabé PFE, Dezan E Jr. Reaction of rat connective tissue to implanted dentin tubes with mineral trioxide aggregate or calcium hydroxide. J Endod 1999;25:161–6.
21. Holland R, Souza V, Murata SS, et al. Healing process of dog dental pulp after pulpotomy and pulp covering with mineral trioxide aggregate or Portland cement. Braz Dent J 2001;12:109–13.
22. Takita T, Hayashi M, Takeichi O, et al. Effect of mineral trioxide aggregate on proliferation of cultured human dental pulp cells. Int Endod J 2006;39:415–22.
23. Javelet J, Torabinejad M, Bakland LK. Comparison of two pH levels for the induction of apical barriers in immature teeth of monkeys. J Endod 1985;11:375–8.
24. Broon NJ. Treatment of Root Perforations in Dogs' Teeth with Added Mineral Trioxide (MTA) and Portland Cement with and without Calcium Chloride [master's thesis, in Portuguese]. Sao Paulo, Brazil: Bauru Faculty of Odontology, University of Sao Paulo, 2004.
25. Abdullah R, Pitt Ford TR, Papaioannou S, Nicholson J, McDonald F. An evaluation of accelerated Portland cement as a restorative material. Biomaterials 2002;23: 4001–10.
26. Bortoluzzi EA, Broon NJ, Bramante CM. Avaliação da capacidade seladora do MTA e cimento Portland com ou sem cloreto de cálcio em obturações retrógradas [Abstract n. Pc082] Braz Oral Res 2004;18:213.