Analysis of the color alteration and radiopacity promoted by bismuth oxide in calcium silicate cement

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Abstract: The aim of the study was to determine if the increase in radiopacity provided by bismuth oxide is related to the color alteration of calcium silicate-based cement. Calcium silicate cement (CSC) was mixed with 0%, 15%, 20%, 30% and 50% of bismuth oxide (BO), determined by weight. Mineral trioxide aggregate (MTA) was the control group. The radiopacity test was performed according to ISO 6876/2001. The color was evaluated using the CIE system. The assessments were performed after 24 hours, 7 and 30 days of setting time, using a spectrophotometer to obtain the ΔE, Δa, Δb and ΔL values. The statistical analyses were performed using the Kruskal-Wallis/Dunn and ANOVA/Tukey tests ($p < 0.05$). The cements in which bismuth oxide was added showed radiopacity corresponding to the ISO recommendations (> 3 mm equivalent of Al). The MTA group was statistically similar to the CSC/30%BO group ($p > 0.05$). In regard to color, the increase of bismuth oxide resulted in a decrease in the ΔE value of the calcium silicate cement. The CSC group presented statistically higher ΔE values than the CSC/50%BO group ($p < 0.05$). The comparison between 24 hours and 7 days showed higher ΔE for the MTA group, with statistical differences for the CSC/15%BO and CSC/50%BO groups ($p < 0.05$). After 30 days, CSC showed statistically higher ΔE values than CSC/30%BO and CSC/50%BO ($p < 0.05$). In conclusion, the increase in radiopacity provided by bismuth oxide has no relation to the color alteration of calcium silicate-based cements.

Descriptors: Endodontics; Bismuth; Color.

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Introduction

Mineral trioxide aggregate (MTA) has been used for several procedures including vital pulp therapies,[1] root fractures,[2] perforations[3] and apexifications,[4] with a high rate of success. It is well known that calcium silicate is the main component of MTA.[5] Previous studies have shown that calcium silicate and MTA present similar chemical, physical and biological properties,[6-8] with the exception of radiopacity.[8-10] Calcium silicate does not have the minimum radiopacity recommended (3 mm equivalent of Al) by ISO 6876/2001 specifications.[11] Thus, a radiopacifier agent should be added in order to distinguish it from anatomical structures, in clinical conditions.[9] Several radiopacity agents have been proposed for calcium silicate cement composition such as zirconium oxide, calcium tungstate, iodoform and bismuth oxide.[9,12]

Bismuth oxide (Bi_2O_3) is a yellow substance commonly added to various endodontic materials, e.g., MTA, AH 26 and Sealer 26, for the purpose of providing radiopacity.[13-15] The use of MTA as a pulp capping material in esthetic areas requires taking into account the changes in color of the dentin. Teeth discoloration is an undesirable consequence of some materials used in endodontic therapy.[16-18] Color alteration of calcium silicate-based cements has been reported.[17,19-21] It has been suggested that the radiopacifier bismuth oxide, present in the MTA composition, is the main cause of dental discoloration.[22] Furthermore, it has been previously demonstrated that AH 26 sealer, which also contains bismuth oxide, results in tooth discoloration.[18] Thus, it is possible that the presence of bismuth oxide in calcium silicate-based cements and in AH 26 sealer may induce discoloration over time. This hypothesis has been discussed in the literature, but there is no quantitative evidence in this regard.[16] The aim of the present study was to investigate if there is a relation between the increase in radiopacity provided by bismuth oxide and the color alteration of calcium silicate-based cement. The hypotheses tested were that the increase in the amount of bismuth oxide in the calcium silicate cement increases the radiopacity of this cement and interferes with the color of the material.

Methodology

A portion of calcium silicate cement (CSC; Irajazinho Votorantim, Cimento Rio Branco, Rio de Janeiro, Brazil) was mixed with 0%, 15%, 20%, 30% and 50% of bismuth oxide (BO; Merck, New Jersey, USA), proportioned in weight using an electronic analytic scale (Mettler Toledo PG5002-S, São Paulo, Brazil). MTA was used as the control group. The cements were divided into 6 groups:

- Group 1: MTA,
- Group 2: 100g of CSC and 0g of BO,
- Group 3: 85g of CSC and 15g of BO,
- Group 4: 80g of CSC and 20g of BO,
- Group 5: 70g of CSC and 30g of BO and
- Group 6: 50g of CSC and 50g of BO.

The manipulation of the cements was performed using a total of 1g of cement and 0.4 mL of distilled water.

Radiopacity

Three cylindrical samples were fabricated for each concentration by placing the manipulated cements into metallic rings with a 10 mm internal diameter and a 1 mm thickness (ISO 6876/2001).[11] Next, the filled rings were kept at 37°C, until the cements set completely. The thickness was confirmed with a digital caliper (Mitutoyo Corp., Tokyo, Japan) and the samples were radiographed on occlusal films (D-speed; Kodak Comp., New York, USA) with an aluminum step-wedge, graduated from 2 to 16 mm (in 2-mm increments). A radiographic unit (Gnatus XR 6010; Gnatus, São Paulo, Brazil) was used with the exposures set at 60 kV, 10 mA, 0.3 seconds and a focus-film distance of 30 cm. The radiographs were digitized and analyzed using the Digora 1.51 software (Soredex, Helsinki, Finland). The radiopacity was determined according to Duarte *et al.*[9]

Color assessment

Ten cylindrical stainless steel rings with an inner diameter of 10 mm and thickness of 2 mm were filled with the cements. They were stored in an incubator at 37°C, 100% humidity, for 24 hours to set completely. After the completion of the setting time, the cements were demolded and the baseline color of the specimens was measured with a spectrophotometer (Vita Easyshade, Vita Zahnfabrik H. Rauter, Bad Säckingen, Germany) against a white Teflon background to obtain the values of lightness (L*), red-green axis (a*) and yellow-blue axis (b*). Three measurements were performed for each sample. The samples were then stored at 37°C, 100% humidity, for 30 days, and the measurements were repeated. The color changes (ΔE) were calculated based on the ΔL^* $(L_2 - L_1)$, Δa^* $(a_2 - a_1)$ and Δb^* $(b_2 - b_1)$ values for each specimen, according to the following equation:[23]

$$\Delta E = [\ (L_2 - L_1)^2 + (a_2 - a_1)^2 + (b_2 - b_1)^2\ ]^{1/2}$$

In which L_1, a_1 and b_1 are the initial assessment color values and L_2, a_2 and b_2 are the final assessment color values.

Table 1 - Mean and standard deviation of ΔE, Δa, Δb and ΔL in initial 24 hours and after 7 days. Lowercase letters in columns indicate statistically significant difference among the groups ($p < 0.05$).

Group	ΔE	Δa	Δb	ΔL
MTA	16.96 ± 14.29^{a}	1.03 ± 1.01^{a}	3.99 ± 1.83^{a}	3.01 ± 2.08^{a}
CSC	13.00 ± 5.31^{a}	1.36 ± 0.39^{a}	2.63 ± 0.99^{b}	2.94 ± 2.90^{a}
CSC/15% BO	5.67 ± 5.69^{bc}	1.82 ± 0.69^{ab}	0.26 ± 0.94^{c}	2.13 ± 1.56^{ab}
CSC/20% BO	8.51 ± 8.49^{ac}	1.70 ± 0.80^{ab}	-1.66 ± 0.31^{d}	0.22 ± 3.44^{abc}
CSC/30% BO	7.25 ± 3.50^{ac}	2.32 ± 0.21^{b}	-1.77 ± 0.64^{d}	-1.42 ± 1.99^{bc}
CSC/50% BO	4.18 ± 1.71^{bc}	1.87 ± 0.14^{ab}	-1.48 ± 0.28^{d}	-1.52 ± 0.55^{c}

Table 2 - Mean and standard deviation of ΔE, Δa, Δb and ΔL in initial 24 hours and after 30 days. Lowercase letters in columns indicate statistically significant difference among the groups ($p < 0.05$).

Group	ΔE	Δa	Δb	ΔL
MTA	54.65 ± 33.26^{a}	3.93 ± 1.46^{a}	7.06 ± 2.69^{a}	4.84 ± 3.66^{ab}
CSC	66.87 ± 15.80^{a}	3.56 ± 0.51^{a}	7.39 ± 0.81^{a}	7.71 ± 2.61^{b}
CSC/15% BO	41.50 ± 18.54^{ab}	3.59 ± 0.67^{acd}	4.98 ± 1.05^{ab}	6.38 ± 1.88^{ab}
CSC/20% BO	24.30 ± 8.18^{abc}	3.20 ± 0.88^{acd}	2.68 ± 0.34^{bc}	4.38 ± 3.52^{ab}
CSC/30% BO	13.98 ± 6.64^{bc}	3.46 ± 0.25^{ac}	2.13 ± 0.66^{bc}	2.71 ± 2.01^{a}
CSC/50% BO	8.73 ± 0.63^{c}	2.75 ± 0.27^{bd}	1.79 ± 0.11^{c}	2.53 ± 0.50^{a}

The values of L* represent the value (lightness or darkness); a* is a measure of redness (positive a*) or greenness (negative a*); b* is a measure of yellowness (positive b*) or blueness (negative b*); and ΔE represents the color change. A color difference of $\Delta E < 4.0$ has been shown to represent clinically acceptable color matching.[24]

Statistical analysis

Statistical analysis was performed using the nonparametric Kruskal–Wallis and Dunn tests for color and radiopacity ($p < 0.05$). Insofar as the values for Δb showed normality after 7 days, the ANOVA/Tukey test was used ($p < 0.05$).

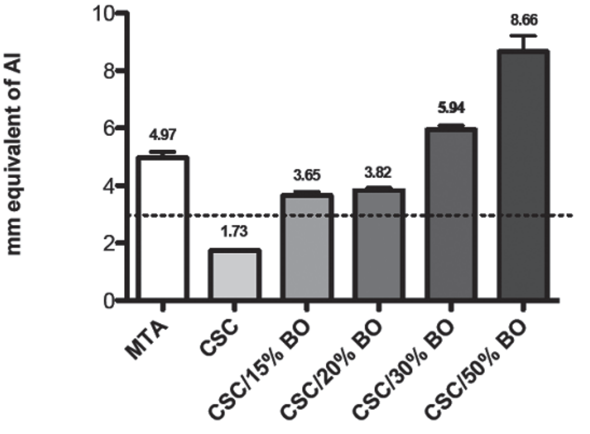

Figure 1 - Mean and standard deviation of radiopacity values in millimeters of aluminum equivalent.

Results

The values for radiopacity and the statistical differences are represented in Figure 1. All experimental groups in which BO was added presented radiopacity values higher than a 3 mm equivalent of Al. MTA was significantly more radiopaque than CSC, CSC/15%BO and CSC/20%BO ($p < 0.05$). MTA was statistically similar to CSC/30%BO ($p > 0.05$). The CSC/50%BO group was significantly more radiopaque than all the other groups evaluated ($p < 0.05$). The statistical differences in color of the cements after 7 and 30 days are shown in Table 1 and 2, respectively. The higher ΔE values were found for MTA at 7 days and for CSC after 30 days. All cements showed ΔE values higher than 4.0. Regarding the Δa values, all cements showed positive values at 7 and 30 days, indicating a tendency toward the redness axis. The evaluation of Δb values at 7 days showed positive values for MTA, CSC and CSC/15%BO, indicating yellowness, whereas the other cements showed negative values, indicating blueness. The analysis of color after 7 days showed higher values of ΔL for MTA and lower values for CSC/50%BO.

Discussion

The hypotheses tested in the present study were that an increase in the amount of bismuth oxide in calcium silicate-based cement could increase radiopacity, and additionally interfere with the color of the cement. In regard to radiopacity, the hypothesis was accepted. Higher amounts of bismuth have significantly increased the radiopacity of the cement. Radiopacity is an important physical property required for cements.[25] A minimal value of radiopacity is essential to identify the material in the root canal, and allow filling failures to be corrected prior to final restoration.[9] The analysis of the results showed that at least 15% of bismuth oxide must be added to provide the minimum radiopacity required by ISO 6876/2001 specifications (3 mm equivalent of Al).[11] Similar results were previously reported by Bueno *et al.* [26] The results reinforce the need to add a radiopacifier agent to calcium silicate-based cement. [9] The addition of 30% of BO to CSC provided a radiopacity statistically similar to that presented by MTA Angelus ($p > 0.05$). A previous analysis of MTA Angelus showed that the proportion of 20% of bismuth oxide provided a radiopacity corresponding to 5.93 mm equivalent of Al.[9] This difference in the results may be associated with the difficulty to obtain homogeneity of CSC and bismuth powders. It is possible that a portion of the cement contained higher or lower amounts of bismuth, and thus influenced the results.

The use of calcium silicate-based cements in vital pulp therapy causes concern regarding the color alteration of the cement and consequent dentin discoloration. The methods used to evaluate the color of materials include subjective[27] and quantitative analyses.[28] It has already been shown that sphere spectrophotometers, such as that used in this study, provide a more accurate assessment of the color change than subjective human evaluation.[29] This equipment measures the amount of visible radiant energy reflected or transmitted by an object, one wavelength at a time for each value, chroma, and hue present in the entire visible spectrum.

The change between the initial and the final color (ΔE) specify the color alteration of the material during a determined period of time. Previous laboratory and clinical studies have reported dental discoloration after using MTA.[17,19,21] Therefore, it is necessary to study if the agent responsible for the color alteration without the interference of other factors such as blood, dentin or saliva is actually the cement or its metallic components (bismuth). The ΔE observed for all the tested materials was higher than 3.3, which is not considered clinically acceptable.[24] Thus, the hypothesis tested was denied. Controversially, the increase of BO decreased the ΔE of the calcium silicate cement. The CSC group presented statistically higher ΔE values than the CSC / 50% BO ($p < 0.05$). These results could suggest that the main cause of discoloration of the cement was the calcium silicate and not the bismuth oxide. However, it is not possible to state that this change in color is clinically reproduced by the absence of components, such as dentin. It is possible that substances present in the dentin react with the components of CSC, including the bismuth oxide, to induce a chemical reaction of reduction resulting in darkness. Other factors may also be correlated with MTA darkness, such as the light curing performed when some restorative materials are used. Vallés *et al.*[30] suggest that an association between oxygen supply and light curing alter the color of MTA cement.

The radiopacifier bismuth oxide is yellow in color; however, contrary to what would be expected, the addition of a high proportion of bismuth oxide to calcium silicate cement did not result in an increase in yellowness (Δb). At 7 days of analysis, CSC with 20%, 30% and 50% of BO showed a tendency toward blueness (negative values), whereas CSC, CSC / 15% BO and MTA presented a tendency toward yellowness. After 30 days, all cements showed positive values of Δb, indicating a tendency to produce a yellow color. The findings indicated an inverse correlation between increase of bismuth oxide and color change in calcium silicate-based cements. However, further evaluations are required to clarify the chemical reactions involved in the color changes of these cements.

Conclusion

It may be concluded that the increase in radiopacity provided by bismuth oxide has no relation to the color change in calcium silicate-based cements. Other factors that may be associated with the reaction could cause the result in color change of calcium silicate-based cements.

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