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Physicochemical properties analysis of experimental retrograde filling materials

Análise das propriedades físico-químicas de cimentos retrobturadores experimentais

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ABSTRACT

Objetive: To evaluate radiopacity, setting time, flowability, pH, ions release and volumetric change of four experimental endodontic repair cements, MTA white and MTA Repair HP Angelus. The experimental tricalcium cement groups were composed of zirconia oxide or calcium tungstate as a radiopacifier associated to calcium phosphate, the vehicle tested composed by 80% distilled water and 20% arnica extract. Also, the other two experimental consisted of an association of polydimethylsiloxane to tricalcium silicate and same radiopacifiers. **Material and Methods**: Radiopacity, flow, and setting time tests were done according to ISO 6876 and ASTM C266/2008 specifications. pH was determined with a calibrated pH meter. The ions calcium release was carried out by an atomic absorption spectrophotometer. Volumetric change was assessed by micro-computed tomographic imaging before and after 28 days of immersion in ultrapure water. One-way ANOVA followed by Tukey's test (α=0.05) was performed for pH, setting time and flow rate. Kruskal-Wallis test, followed by Dunn's test (α=0.05), were performed for radiopacity, ions release and volumetric change. **Results**: All experimental cements presented radiopacity above 3 mm/Al ($p < 0.05$). Polydimethylsiloxane experimentals showed a higher flow rate ($p < 0.05$) and better dimensional stability ($p < 0.05$). Calcium silicate cements resulted in more favorable properties such as alkalinization, longer working time and higher ions release ($p < 0.05$), though more significant volumetric loss. **Conclusion**: polydimethylsiloxane experimental cements presented greater flow and dimensional stability, the addition of tricalcium silicate was not able to enhance calcium release nor perform a favorable pH.

KEYWORDS

Dental cements; Endodontics; Root repair; Tricalcium silicate; X-ray microtomography.

RESUMO

Objetivo: Avaliar características de quatro cimentos retrobturadores experimentais, MTA branco e MTA Repair HP Angelus, incluindo radiopacidade, tempo de presa, escoamento, pH, liberação de íons e alteração volumétrica. Os cimentos tricálcio experimentais foram compostos por óxido de zircônia ou tungstato de cálcio como radiopacificador, associados a fosfato de cálcio, com veículo contendo 80% de água destilada e 20% de extrato de arnica. Os outros experimentais envolveram polidimetilsiloxano com silicato tricálcio e os mesmos radiopacificadores. **Material e Métodos**: Os testes de radiopacidade, escoamento e tempo de presa seguiram especificações ISO 6876 e ASTM C266/2008. O pH foi medido com pHmetro. Liberação de íons cálcio foi analisada com espectrofotômetro de absorção atômica. Alteração volumétrica foi avaliada por microtomografia computadorizada antes e após 28 dias de imersão em água ultrapura. ANOVA e teste de Tukey (α=0,05) foram usados para pH, tempo de presa e escoamento. O teste de Kruskal-Wallis e teste de Dunn (α=0,05) foram aplicados para radiopacidade, liberação de íons e alteração volumétrica. **Resultados**: Todos os cimentos experimentais

mostraram radiopacidade acima de 3 mm/Al ($p < 0,05$). Experimentais de polidimetilsiloxano exibiram maior escoamento ($p < 0,05$) e estabilidade dimensional ($p < 0,05$). Cimentos de silicato de tricálcio demonstraram propriedades vantajosas como alcalinização, tempo de trabalho prolongado e maior liberação de íons ($p < 0,05$), apesar da perda volumétrica. **Conclusão**: Cimentos de polidimetilsiloxano apresentaram melhor escoamento e estabilidade dimensional, no entanto, a adição de silicato tricálcio não melhorou a liberação de cálcio nem favoreceu o pH.

PALAVRAS-CHAVE

Cimentos dentários; Endodontia; Materiais de reparo; Silicato tricálcico; Microtomografia de raios X.

INTRODUCTION

Clinicians in the field of endodontics require reliable retrograde filling materials that ensure proper handling, exhibit stable dimensional properties, are biocompatible, and possess adequate radiopacity to enable effective treatment. These materials are frequently employed to address procedural complications, such as perforations during pulp chamber access, and as filling material for the root-end cavities, with their physicochemical and biological properties playing a crucial role in the healing of periapical tissues [1].

A wide range of materials has been developed for root apex sealing [2], including mineral trioxide aggregate (MTA), intermediate restorative material (IRM), super ethoxy benzoic acid (Super-EBA), glass ionomer cement, amalgam, resin, calcium hydroxide, calcium silicate, and silicone-based materials. However, no single root-end filling material encompasses all desirable attributes. Consequently, the search for the ideal root-end filling material remains ongoing [3].

Mineral trioxide aggregate (MTA) and Portland cement share similar compositions, including tricalcium silicate, dicalcium silicate, tricalcium aluminate, tretacalcium aluminoferrite, and dihydrated calcium sulfate [4]. The low radiopacity of Portland cement can be addressed by incorporating alternative radiopacifying agents, such as zirconium oxide (ZrO_2) and calcium tungstate ($CaWO_4$) [5].

These alternative radiopacifiers have been investigated as substitutes for bismuth oxide (Bi_2O_3). Although less radiopaque than Bi_2O_3, they are less likely to stain tooth structure and do not interfere with MTA hydration [6]. Notably, the inclusion of ZrO_2 and $CaWO_4$ into Portland cement yields materials with radiopacity levels exceeding those recommended by ANSI/ADA Specification 57 [5,7].

MTA has emerged as a dynamic root repair material. This cement interacts with dentin, providing superior sealing, bioactivity and setting capabilities even in the presence of blood. Its chemical bond to dentin and regenerative potential occurs through a hydration reaction that forms calcium hydroxide [3]. However, its handling limitations, extended setting time, and susceptibility to washout can impact its clinical use [8]. Furthermore, bismuth oxide (Bi_2O_3), the radiopacifier in its composition, can cause discoloration of dental structures [9].

MTA Repair HP (Angelus; Londrina, PR, Brazil) is a derivative of the traditional MTA composition, incorporating calcium tungstate for radiopacity and a mixing liquid containing a plasticizing agent. Its intended applications include root-end filling, pulp capping, pulpotomy, apexogenesis, apexification, and repairing root canal perforations. According to the manufacturer guidelines, this novel formulation retains the chemical characteristics of the traditional MTA while enhancing its handling and manipulation properties [10].

The incorporation of propylene glycol to improve flow characteristics has been proposed as a means of enhancing the overall properties of MTA. Furthermore, enhancing the antimicrobial properties of MTA is particularly advantageous in the critical apical regions. Plant extracts with inherent antimicrobial properties, when combined with MTA, offer potential alternatives. The augmentation or reinforcement of MTA's antibacterial efficacy through the substitution of distilled water or its combination with antiseptic solutions is already demonstrated [11].

Previous research has shown that the ethanolic extract of *Lychnophora trichocarpha*

possesses anti-inflammatory, antinociceptive, and xanthine oxidase inhibitory properties. Regarding the control of cellular response and the creation of inflammatory mediators, the mechanism underlying the anti-inflammatory effect of the ethanol extract and its active components has not yet been established [12, 13]. These properties justify the incorporation of this extract into experimental cements intended for direct application to areas of critical inflammation.

Silicon-based cements, such as Roeko Seal (Roeko, Langenau, Germany) have demonstrated great dimensional stability and seal capabilities, in addition to low cytotoxicity [14]. Polydimethylsiloxane, a biocompatible material, has shown promising results in previous studies involving silicon-based cements. However, while these materials are suitable for clinical applications, they lack components that actively stimulate tissue repair [15].

Based on the foregoing, the objective of this study was to evaluate the physic chemical properties of experimental sealers containing varying proportions of calcium silicate, arnica glycolic extract and alternative radiopacifiers; as well as experimental sealers containing silicone, calcium silicate and alternative radiopacifiers agents. The goal for calcium silicate-based cements was to enhance their properties, such as flowability and handling, by adding arnica glycolic extract and evaluating its interaction with zirconium oxide and calcium tungstate in terms of radiopacity. For the silicone-based cements, it was hypothesized that the addition of tricalcium silicate would promote alkalinization and calcium ions release, and improved dimensional stability.

MATERIALS AND METHODS

Sample preparation

The cements evaluated are shown in Table I.

Two commercially available MTA based cements MTA white (G1) and MTA HP (G2) (Angelus; Londrina, PR, Brazil) were handled as suggested by manufacturers. An electronic analytical balance (Gehaka AND-GR-202, Tokyo, Japan) was employed to prepare the experimental cements, following the 1 gram of powder ratio to 0.3 mL of liquid for the experimental cements G3 (CSZO) and G4 (CSCT). For experimental G5 (CSSilZO) and G6 (CSSilCT), powder portions were placed in the base paste, the exact length of base and catalyst paste were employed in the handling.

Radiopacity

Metallic rings with an internal diameter of 10 mm and a thickness of 1 mm were used according to ISO 6876 [16], with three cement-filled specimens per group. Freshly mixed cements were inserted into the rings, supported by a glass plate, and kept in an oven at 37 °C until fully setting. The thickness of the samples was measured using a digital caliper (Mitutoyo Corp, Tokyo, Japan).

Cement specimens and an aluminum step wedge (graduated from 2 to 16 mm of Al) were placed on occlusal film (Kodak Comp, Rochester, New York, USA). Radiographs were taken using a radiographic unit (Gnatus XR 6010; Gnatus, Ribeirão Preto, SP, Brazil) set at 60 kV and 10 mA, with an exposure time of 0.3 seconds. The focus-

Table I - Composition of each cement used in the study

Cements	Composition
G1 – MTA White (MTAW) (Angelus)	Powder: silicon dioxide, potassium oxide, aluminium oxide, sodium oxide, ferric oxide, sulfur trioxide, calcium oxide, calcium tungstate, magnesium oxide. (Batch number: 42605) Liquid: distilled water;
G2 - MTA HP (MTAHP) (Angelus)	Powder: tricalcium silicate, calcium silicate, tricalcium aluminate, calcium oxide, calcium tungstate (Batch number: 41296) Liquid: water and plasticizer;
G3 - Experimental 1 (CSZO)	Powder: 60% calcium silicate, 10% calcium phosphate, 30% zirconium oxide. Liquid: 80% water and 20% arnica glycolic extract;
G4 - Experimental 2 (CSCT)	Powder: 60% calcium silicate, 10% calcium phosphate, 30% calcium tungstate Liquid: 80% water and 20% arnica glycolic extract;
G5 - Experimental 3 (CSSilZO)	50% polydimethylsiloxane + silicone oil + paraffin + 20% (by weight) tricalcium silicate + 30% (by weight) zirconium oxide;
G6 - Experimental 4 (CSSilCT)	50% polydimethylsiloxane + silicone oil + paraffin + 20% (by weight) tricalcium silicate + 30% (by weight) calcium tungstate.

film distance was 30 cm. After processing, the radiographs were digitized using a digital scanner and imported into the Adobe Photoshop CS6 13.0.

The area corresponding to each specimen was selected in the radiographic image to determine the thickness of the aluminum step wedge that corresponded to the radiographic density of the specimen. This assessment quantified the radiopacity of the specimen in millimeters of aluminum using a conversion equation, as proposed in previous studies [5].

Setting time

ISO 6876 [16] normative was also followed to obtain the samples, and the ASTM C266/08 [17] to determine the setting time of the cements. Freshly mixed cements were immediately poured into metal rings with internal diameter of 10 mm and a thickness if 2 mm. Three specimens per cement group were prepared and stored in an oven at 37 °C with 95% throughout the test.

After 180 seconds from the start of the spatulation, the specimens were subjected to vertical pressure using Gilmore needles (113.4 g and 453.6 g). The setting time, measured in minutes, was recorded as the time elapsed from the beginning of the spatulation until no visible indentation was observed on the surface of the samples, representing the initial and final setting time of the cements.

Flow rate

A total volume of 0.5 ± 0.05 mL of cement was mixed and placed at the center of a 40 mm x 40 mm glass plate with a thickness of 5 mm using a graduated disposable 1 mL syringe. After 3 minutes from the start of mixing, a second glass plate weighing 20 ± 2 g was carefully positioned centrally on top of the cement, followed by an additional weight of approximately 100 g, resulting in a total applied load of 120 g.

Ten minutes after mixing, the weight was removed. The values of maximum and minimum diameters of the compressed discs cements were measured using a digital caliper (Mitutoyo MTI Corporation, Tokyo, Japan). The mean of the two diameters was recorded as the cement flow. Three measurements were taken for each cement group (n = 3), and the results were expressed in millimeters. This test also was conducted following ISO 6876 [16].

Volumetric change

Volumetric change was assessed using computerized microtomography (micro-CT), based on a previous study [18,19]. Sixty acrylic teeth (n = 10) with standardized root-end cavities created using a #1012 diamond burr (KG Sorensen, São Paulo, SP, Brazil) were filled with the tested cements using an MTA carried device. The specimens were then individually scanned using a micro-CT (SkyScan 1174v2; SkyScan, Kontich, Belgium) at 50 kV and 800 μA.

The images were captured with a voxel size of 14.1 μm, using 360º rotation scan. Each scan produced images with a resolution of 1024 x 1304 pixels. For volumetric analysis, the data were reconstructed using NReconv software (version 1.6.4.8, SkyScan) and CTan software (version 1.11.10.0, SkyScan). In CTan software, each sample was analyzed individually, and the region of interest (ROI) was delineated for subsequent scans.

A quantitative analysis of the material volume was performed using three-dimensional reconstruction, and the total volume (mm^3) was automatically calculated. After the initial scan, the samples were immersed in individual flasks containing 15 mL of deionized water and stored in an oven at 37ºC for 28 days. At the end of this period, the samples were removed, dried on filter paper, and re-scanned using the same parameters as the initial scan. The solubility of the cements was determined by calculating the volume lost during immersion, and the results were expressed as percentages [18,19].

pH and calcium release

Sixty acrylic teeth (n = 10) with standardized root-end cavities created using a #1012 diamond burr (KG Sorensen) were filled with the tested cements using an MTA carried device. The specimens were then individually immersed in flasks containing 10 mL of ultrapure water (Purelab Option Q, Elga, Brazil) with an initial pH of 6.61.

The flasks were sealed and placed in an oven at 37 °C for the duration of the experimental period. Evaluations were conducted after 3, 7, and 15 days of immersion, as described in previous

studies [18,20]. At each time point, the specimens were transferred to new flasks containing 10 mL of ultrapure water. pH measurements were performed using a calibrated pH meter (Orion Star Plus pH meter; Thermo Scientific Electron Corporation, San Jose, CA) with control solutions at known pH values of 4, 7, and 14.

After specimen removal, the liquid in each container was agitated in a shaker (Farmen, São Paulo, SP, Brazil) for 5 seconds, poured into a Becker, and measured using the pH meter electrode. The calibration was conducted at a controlled temperature of 25 °C.

Calcium ion release was assessed in the same periods using an atomic absorption spectrophotometer (Thermo Fisher, São Paulo, SP, Brazil) equipped with a calcium-specific hollow cathode lamp. To prevent possible alkali metal interferences, a lanthanum solution was used.

A standard calcium solution was prepared at concentrations of 20 mg/L, 10 mg/L, 5 mg/L, 2.5 mg/L, and 1.25 mg/L. A blank sample was prepared by mixing 6 mL of ultrapure water with 2 mL of lanthanum chloride solution. The standards, blank, and the samples solutions were analyzed using an atomic absorption spectrophotometer [18,20].

Statistical analysis

Data distribution was assessed using the Kolmogorov-Smirnov normality test. After normality evaluation, pH, setting time and flow rate data followed a parametric distribution, while radiopacity, ions release, and volumetric change data followed a non-parametric distribution.

One-way ANOVA followed by Tukey's test was performed for pH, setting time and flow rate. The Kruskal-Walli's test, followed by Dunn's test, was used for radiopacity, ions release and volumetric change. A significance level of 5% ($\alpha = 0.05$) was adopted for all statistical tests.

RESULTS

Table II presents the data of radiopacity, setting time, volumetric change and flowability of the cements tested.

All experimental cements exhibited radiopacity values above 3 mm/Al, the minimum recommended by ISO 6876. Statistically significant differences were observed when compared to MTA (2.12 mm/Al) ($p < 0.05$). The highest radiopacity value was recorded in Group 3 (6.14 mm/Al), which contained zirconium oxide as a radiopacifier.

Regarding the initial setting time, statistically significant differences were found among all groups ($p < 0.05$), except between MTA white and Group 4 - Experimental cement 2 (CSCT), as well as between the silicon-based experimental groups (G5 and G6) ($p > 0.05$). MTA White exhibited the longest final setting time (129 minutes) while the silicon-based experimental cements had the shortest setting times (44 – 47 minutes), with statistically significant differences among the studied groups ($p < 0.05$).

Despite the addition of tricalcium silicate, the silicone-based experimental groups demonstrated similar flow rates (14.27 mm – 14.84 mm) and significantly higher values ($p < 0.05$) when compared to the other cements.

Volumetric change analysis showed that G6 – Experimental cement 4 (CSSilCT) (Figure 1) exhibited a statistically lower volumetric loss rate compared to the other groups ($p < 0.05$), except for CSSilZO ($p > 0.05$). Meanwhile, the experimental groups CSZO (Figure 2) and CSCT

Table II - Mean (X) and standard deviation (SD) values of radiopacity, setting time, and flowability of both commercial MTA cements and experimental cements. The median (med) and the range of minimum and maximum (min–max) values are provided for volumetric change after 28 days of immersion in ultrapure water.

	Radiopacity (mm Al) X ± SD	Setting Time (min) X ± SD		Volumetric change (%) Med (Min-Max)	Flow rate (mm) X ± SD
		Initial	Final		
G1 – MTA	2.39 ± 0.23 ^{A,C}	41.00 ± 5.5 ^{A}	129.7 ± 4.5 ^{A}	14.36 (7.6 – 17.62) ^{A,C}	7.39 ± 0.48 ^{A}
G2 – MTA HP	2.12 ± 0.44 ^{A}	14.67 ± 2.5 ^{B}	110.0 ± 8.0 ^{B}	15.94 (7.99 – 21.84) ^{A,C}	7.92 ± 0.15 ^{A}
G3 –Experimental cement 1 (CSZO)	5.98 ± 0.41 ^{B,C}	59.33 ± 3.0 ^{C}	99.33 ± 3.05 ^{B}	15.44 (6.2 – 30.44) ^{A,C}	8.66 ± 0.33 ^{A}
G4 – Experimental cement 2 (CSCT)	5.81 ± 0.54 ^{B,C}	45.00 ± 2.0 ^{D,A}	84.33 ± 6.02 ^{C}	16.59 (10.19 – 37.49) ^{A}	8.51 ± 0.41 ^{A}
G5 –Experimental cement 3 (CSSilZO)	6.14 ± 2.12 ^{B,C}	25.00 ± 3.6 ^{E}	44.33 ± 3.51 ^{D}	9.62 (4.81 – 13.61) ^{B,C}	14.27 ± 1.52 ^{B}
G6 – Experimental cement 4 (CSSilCT)	5.33 ± 2.53 ^{C}	29.00 ± 3.6 ^{E}	47.67 ± 2.51 ^{D}	5.49 (3.0 – 10.75) ^{B}	14.84 ± 0.12 ^{B}

Different Capital letters represent statistically significant differences among groups ($p<0.05$).

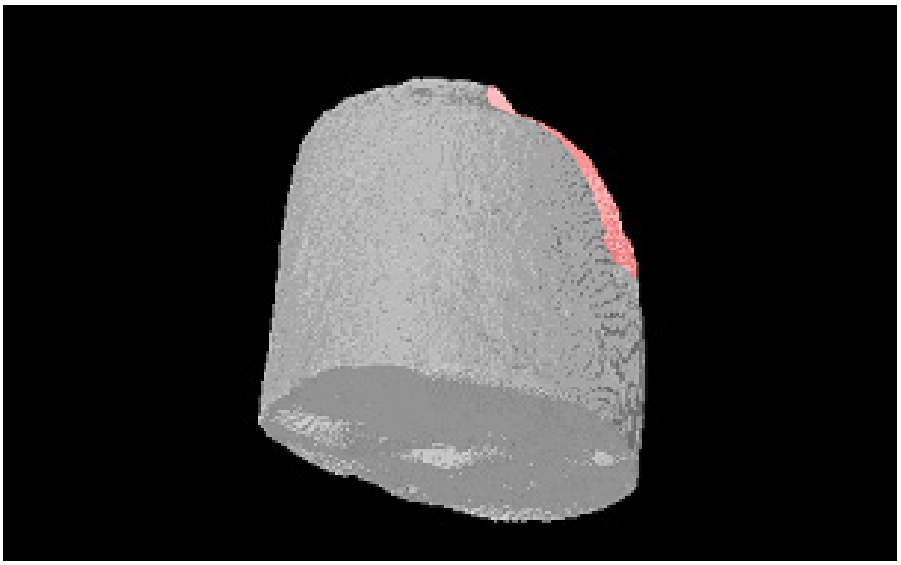

Figure 1 - Representative micro-computed tomography (micro-CT) 3D image showing the volumetric change of the silicon-based experimental cement. The initial volume (gray) is superimposed with the final volume (red) after immersion in ultrapure water.

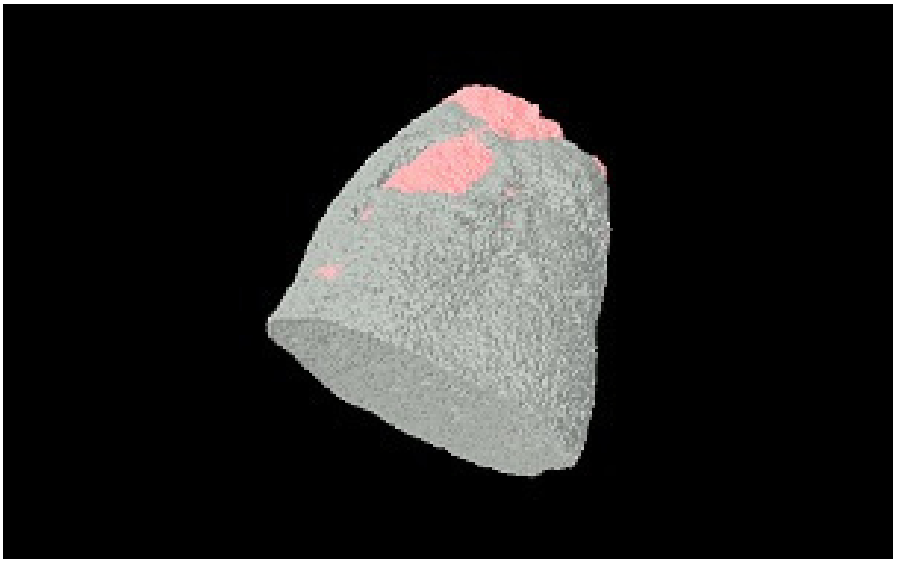

Figure 2 - Representative micro-computed tomography (micro-CT) 3D image showing the volumetric change of the silicate-based experimental cement. The initial volume (gray) is superimposed with the final volume (red) after immersion in ultrapure water.

presented higher solubility (15.44% and 16.59%, respectively), although these values were not significantly different from those of MTA white and MTA HP ($p > 0.05$).

Table III presents the averages and standard deviations of the pH and calcium release of the analyzed materials in the analyzed periods.

After 3 days, the silicon-based experimental groups showed a slight decrease in pH compared to the initial value. On day 7, MTA white and MTA HP differed statistically from all experimental groups, with a slight increase in alkalinity. After 15 days, only MTA HP remained statistically different from all experimental groups, maintaining a stable pH of 7.64. When analyzed within the same group, MTA HP, G3 – Experimental 1 (CSZO) and G6 – Experimental 4 (CSSilCT) showed stable pH values ($p > 0.05$).

Regarding calcium ion release, after 3 days, MTA White stood out with the highest release values, with a statistically significant difference compared to the others ($p < 0.05$). Group 4 (CSSilCT) showed the lowest calcium ion release and differed significantly from MTA White and MTA HP at both the 3-day and 7-day time points ($p < 0.05$). After 15 days,

Table III - Mean (X) and standard deviation (SD) values for pH (A) and calcium ions release (B) of the cements in different studied periods.

		3 days X ± SD	7 days X ± SD	15 days X ± SD
(A) pH of soaking water	G1 – MTA	7.45 ± 0.93 ^{A,a,b}	8.11 ± 1.03 ^{A,a}	6.70 ± 0.22 ^{A,b}
	G2 – MTA HP Angelus	7.73 ± 0.86 ^{A,a}	7.66 ± 0.84 ^{A,a}	7.64 ± 1.0 ^{B,a}
	G3 – Experimental 1 (CSZO)	7.01 ± 0.70 ^{A,C,a}	6.53 ± 0.80 ^{B,a}	6.42 ± 0.48 ^{A,a}
	G4 –Experimental 2 (CSCT)	7.03 ± 0.61 ^{A,a}	6.49 ± 1.20 ^{B,a,b}	5.93 ± 0.78 ^{A,b}
	G5 –Experimental 3 (CSSilZO)	6.20 ± 0.36 ^{B,C,a}	5.47 ± 0.29 ^{B,b}	5.84 ± 0.68 ^{A,a,b}
	G6 – Experimental 4 (CSSilCT)	6.20 ± 0.45 ^{B,C,a}	5.88 ± 0.61$^{B,\ a}$	6.28 ± 0.69 ^{A,a}
(B) Calcium release	G1 – MTA	238.6 (215.8 – 270.6) ^{A,a}	213.8 (204.7 – 224.2) ^{A,b}	206.5 (199.1 – 215.4) ^{A,b}
	G2 – MTA HP Angelus	5.4 (1.54 – 14.18) ^{B,a}	7.01 (3.16 – 14.7) ^{A,B,a}	6.82 (0.60 – 9.37) ^{A,B,a}
	G3 – Experimental 1 (CSZO)	3.37 (0.28 – 37.82) ^{B,a}	1.43 (0.10 – 12.14) ^{B,C,a}	2.22 (0.67 – 30.2) ^{B,a}
	G4 –Experimental 2 (CSCT)	2.9 (0.14 – 6.61) ^{B,a}	2.48 (1.49 – 6.4) ^{B,C,a}	4.28 (0.12 – 10.69) ^{B,a}
	G5 –Experimental 3 (CSSilZO)	2.8 (2.13 – 4.76) ^{B,a}	1.97 (1.32 – 3.02) ^{B,C,a,b}	0.63 (0.06 – 5.24) ^{B,b}
	G6 – Experimental 4 (CSSilCT)	0.35 (0.02 – 7.91) ^{C,a}	0.7 (0.22 – 5.71) ^{C,a}	0.7 (0.11 – 8.78) ^{B,a}

Different capital letters represent statistically significance differences ($p < 0.05$) in the same line, whilst different small letters represent differences in the same colum

MTA White continued to exhibit the highest calcium release, while G5 –Experimental 3 (CSSilZO) and G6 – Experimental 4 (CSSilCT) with the lowest values ($p < 0.05$). Within-group comparisons revealed that only MTA White and G5 –Experimental 3 (CSSilZO) exhibited a slight decrease in calcium release over time, with statistically significant differences between the 3-day and 7-day periods ($p < 0.05$).

DISCUSSION

Radiopacity plays a crucial role in the radiographic visualization of the materials used for root-end fillings or perforation repair. This study reported that the MTA and MTA HP presented radiopacity below the ISO standard, suggesting that both material presents the similar and same quantities radiopacifier agent. The experimental cements demonstrated higher radiopacity compared to the commercial MTA cements tested, with values ranging from 5.33 to 6.14 mm Al. These differences may be attributed to the higher proportion of radiopacifiers in the experimental cements (30% by weighted) compared to the commercial materials, which contain approximately 15%. Increased radiopacity facilitates the distinction between dentin and adjacent anatomical structures [5].

In cases of root resorptions, perforations, apexification and retrograde fillings, cements with prolonged setting times may be more susceptible to dissolution, potentially compromising clinical success [10]. The silicon-based experimental cements exhibited the shortest setting times compared to the calcium silicate-based group, which may be associated with the hydration time [18] and the composition of polydimethylsiloxane itself [21].

The initial setting time of MTA HP in this study (14 minutes) was similar to the manufacturer's reported value of 15 minutes. The final setting time was 25 minutes, which was longer than reported in previous study [22]. This difference may be related to variations in the powder-to-liquid ratio during mixing. MTA White demonstrated an initial setting time of 41 minutes and a final setting time of 129 minutes, in accordance with other study [23].

Concerning the experimental cements containing calcium silicate and Arnica's propylene glycol, their initial setting times were longer than those of MTA and MTA HP. This could be attributed to the presence of 20% propylene glycol extract, in agreement with previous studies that incorporated pure propylene glycol or other extracts [11]. A shorter setting time may contribute to reduced material solubility, which is beneficial for clinical application.

Flowability is a critical property that enables cements to fill retro-end cavities and penetrate dentinal tubules, improving their sealing capacity [8]. In this study, the silicone-based experimental groups exhibited greater flowability, likely due to the intrinsic plasticity of the material [21]. The experimental cements containing propylene glycol extracts also demonstrated higher flow rates than MTA and MTA HP. This is attributed to propylene glycol's ability to improve material wettability, allowing

better adaptation to irregularities in the tooth structure or cavity. Additionally, propylene glycol lowers surface tension compared to water, leading to smoother and more homogeneous flow [10,11].

Volumetric change is another relevant physical property considering that root repair cements remain in direct contact with adjacent tissues for extended periods [1]. Materials with high solubility tend to create voids, compromising the sealing ability and increasing the risk of bacterial infiltration, which can lead to treatment failure [18]. Micro-CT analysis has been widely used to assess volumetric loss in previous studies [18,19]. In the present study, the lowest solubility values were observed in the silicone-based groups (9.62% and 5.49%). The calcium silicate-based cements exhibited greater mass loss (15.44%–16.59%), indicating that silicon contributes to lower volumetric loss, even when calcium silicate powder and radiopacifiers are present. MTA White and MTA HP showed no significant discrepancies, with volumetric losses of 14.36% and 15.94%, respectively. Lower solubility prevents the formation of voids that may allow fluid infiltration and bacterial colonization [18,22].

The pH of calcium silicate cements has been widely investigated [18,21-23], as mineralized tissue repair is thought to depend on alkalinity and calcium ions release [24]. Previous studies have reported pH values for MTA ranging from 8 to 12 [23,25,26]. In the present study, MTA White, MTA HP, and the calcium silicate-based experimental cements exhibited slight alkalinization in the initial period, whereas the silicone-based cements maintained a lower pH, likely due to their reduced solubility.

MTA White showed an increase in pH over the first 7 days, followed by a decrease at 15 days. In contrast, MTA HP maintained a stable pH throughout the experimental periods. The experimental cements containing *Arnica* extract had the highest alkalinity only at the 3-day mark, with no significant alkalinization at 7 or 15 days. This may be explained by the fact that these materials contain only calcium silicate and not Portland cement. Consequently, the hydration reaction and Portlandite formation occur entirely within the first 3 days, with no further pH increase thereafter.

A recent study [26] reported an alkaline pH of 8.5 in the 2 days, followed by a decrease to 8.1 at 7 days and 7.8 at 28 days for MTA White. These differences may be attributed to variations in methodology or the initial pH of the immersion water. Although the present study reported lower pH values, it aligned with the previous study at the 7-day mark. Notably, pH levels above 7.8 may inhibit fibroblast migration and interfere with the repair process [27].

Regarding calcium ion release, MTA White exhibited the highest release levels in the present study, likely due to increased Portlandite formation and the presence of calcium tungstate. Among the experimental cements, the calcium silicate-based groups demonstrated the highest release levels at 3 days, suggesting that the setting reaction facilitates ion diffusion.

Conversely, the silicone-based experimental groups exhibited the lowest calcium ion release across all time points, which can be attributed to their lower calcium silicate content. While MTA White and MTA HP contain approximately 85% Portland cement, the experimental cements contain only 60% calcium silicate. The bioactivity of calcium silicate materials is largely dependent on the release of calcium and hydroxyl (OH^-) ions [28].

Despite the limitations of this in vitro study, the experimental cements demonstrated higher radiopacity than the commercial materials, regardless of the radiopacifier used. This property may assist clinicians in differentiating dentin from other structures. The addition of 30% by weight of zirconium oxide or calcium tungstate was found to improve the radiopacity of the experimental cements.

An alkaline pH and calcium ion release are desirable properties in repair cements. The calcium silicate and calcium phosphate-based experimental cements exhibited these characteristics, whereas the silicone-based materials demonstrated lower solubility and greater flowability. These properties may facilitate their handling and placement in perforations within the root canal while providing dimensional stability, thereby reducing the risk of void formation and bacterial infiltration. The longer setting time observed in calcium silicate-based cements may also enhance handling properties, making them suitable for endodontic applications.

CONCLUSION

Although the polydimethylsiloxane-based experimental cements exhibited greater flowability and dimensional stability, the addition of tricalcium silicate did not enhance calcium ion release or achieve a favorable pH. Further studies are necessary to evaluate the long-term behavior and biocompatibility of these new experimental materials.

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Author's Contributions

PCGT: Writing – Original Draft Preparation, Review & Editing, Visualization, Supervision, Conceptualization, Methodology, Validation, Formal Analysis, Investigation, Data Curation. HGSC: Writing – Review & Editing, Formal Analysis, Investigation, Data Curation. BCV: Writing – Review & Editing, Formal Analysis, Investigation, Data Curation.

MPA: Writing – Review & Editing, Visualization, Supervision, Project Administration, Conceptualization, Methodology, Validation.

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Conflict of Interest

The authors declare no conflict of interest.

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Regulatory Statement

Not applicable.

REFERENCES

1. Li H, Guo Z, Li C, Ma X, Wang Y, Zhou X, et al. Materials for retrograde filling in root canal therapy. Cochrane Database Syst Rev. 2021;10(10):CD005517. http://doi.org/10.1002/14651858.CD005517.pub3. PMid:34647617.
2. Nassar MAM, Abdelgawad LM, Khallaf ME, El Rouby DH, Sabry D, Radwan MM. Experimental nano calcium aluminate/tri calcium silicate root repair: Synthesis, physical and mechanical properties compared to mineral trioxide aggregate and Biodentine. Braz Dent Sci. 2022;25(4):e3368. http://doi.org/10.4322/bds.2022.e3368.
3. Torabinejad M, Parirokh M, Dummer PMH. Mineral trioxide aggregate and other bioactive endodontic cements: an updated overview - part II: other clinical applications and complications. Int Endod J. 2018;51(3):284-317. http://doi.org/10.1111/iej.12843. PMid:28846134.
4. Oliveira MG, Xavier CB, Demarco FF, Pinheiro ALB, Costa AT, Pozza DH. Comparative chemical study of MTA and portland cements. Braz Dent J. 2007;18(1):3-7. http://doi.org/10.1590/S0103-64402007000100002. PMid:17639192.
5. Duarte MAH, Oliveira El Kadre GD, Vivan RR, Guerreiro Tanomaru JM, Tanomaru Filho M, Moraes IG. Radiopacity of portland cement associated with different radiopacifying agents. J Endod. 2009;35(5):737-40. http://doi.org/10.1016/j.joen.2009.02.006. PMid:19410095.
6. 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(3):231-40. http://doi.org/10.1111/j.1365-2591.2009.01670.x. PMid:20158535.
7. American National Standards Institute. American Dental Association. Specification (ANSI/ADA). Endodontic sealing materials. Chicago: American National Standards Institute; 2000.
8. Dawood AE, Parashos P, Wong RHK, Reynolds EC, Manton DJ. Calcium silicate-based cements: composition, properties, and clinical applications. J Investig Clin Dent. 2017;8(2):e12195. http://doi.org/10.1111/jicd.12195. PMid:26434562.
9. Marciano MA, Costa RM, Camilleri J, Mondelli RF, Guimarães BM, Duarte MA. Assessment of color stability of white mineral trioxide aggregate angelus and bismuth oxide in contact with tooth structure. J Endod. 2014;40(8):1235-40. http://doi.org/10.1016/j.joen.2014.01.044. PMid:25069940.
10. Guimarães BM, Prati C, Duarte MAH, Bramante CM, Gandolfi MG. Physicochemical properties of calcium silicate-based formulations MTA Repair HP and MTA Vitalcem. J Appl Oral Sci. 2018;26(0):e2017115. http://doi.org/10.1590/1678-7757-2017-0115. PMid:29641748.
11. Cavenago BC, Del Carpio-Perochena AE, Ordinola-Zapata R, Estrela C, Garlet GP, Tanomaru-Filho M, et al. Effect of using different vehicles on the physicochemical, antimicrobial, and biological properties of white mineral trioxide aggregate. J Endod. 2017;43(5):779-86. http://doi.org/10.1016/j.joen.2016.12.023. PMid:28320540.
12. Ferrari FC, Ferreira LC, Souza MR, Grabe-Guimarães A, Paula CA, Rezende SA, et al. Anti-inflammatory sesquiterpene lactones from Lychnophora trichocarpha Spreng. (Brazilian Arnica). Phytother Res. 2013;27(3):384-9. http://doi.org/10.1002/ptr.4736. PMid:22619042.
13. Guzzo LS, Saúde-Guimarães DA, Silva AC, Lombardi JA, Guimarães HN, Grabe-Guimarães A. Antinociceptive and anti-inflammatory activities of ethanolic extracts of Lychnophora species. J Ethnopharmacol. 2008;116(1):120-4. http://doi.org/10.1016/j.jep.2007.11.006. PMid:18155374.
14. Tanomaru-Filho M, Tanomaru JM, Leonardo MR, da Silva LA. Periapical repair after root canal filling with different root

canal sealers. Braz Dent J. 2009;20(5):389-95. http://doi.org/10.1590/S0103-64402009000500006. PMid:20126907.

15. Lodiene G, Morisbak E, Bruzell E, Ørstavik D. Toxicity evaluation of root canal sealers in vitro. Int Endod J. 2008;41(1):72-7. http://doi.org/10.1111/j.1365-2591.2007.01321.x. PMid:17931390.

16. International Organization for Standardization. ISO 6876. Dentistry - Root canal sealing materials. London, UK: British Standards Institution; 2012.

17. American Society for Testing and Materials. ASTM C 266-08. Standard test method for time of setting of hydraulic-cement paste by gilmore needles. West Conshohocken, PA: ASTM; 2008.

18. Cavenago BC, Pereira TC, Duarte MAH, Ordinola-Zapata R, Marciano MA, Bramante CM, et al. Influence of powder-to-water ratio on radiopacity, setting time, pH, calcium ion release and a micro-CT volumetric solubility of white mineral trioxide aggregate. Int Endod J. 2014;47(2):120-6. http://doi.org/10.1111/iej.12120. PMid:23647286.

19. Sousa A, Leão DA, Guimarães FM, Gonçalves MO, Pinheiro RF, Cunha TC, et al. Influence of the calcium hydroxide paste vehicle on penetration into lateral canals. Braz Dent Sci. 2018;21(3):282-7. http://doi.org/10.14295/bds.2018.v21i3.1574.

20. Costa Neto PF, Gelio MB, Zaniboni JF, Monteiro JCC, Jorge Júnior AJ, Kuga MC. Light-curing of calcium hydroxide-based liners: pH analysis and calcium ion release. Braz Dent Sci. 2023;26(4):e3368. http://doi.org/10.4322/bds.2023.e3945.

21. Flores DS, Rached FJ Jr, Versiani MA, Guedes DF, Sousa-Neto MD, Pécora JD. Evaluation of physicochemical properties of four root canal sealers. Int Endod J. 2011;44(2):126-35. http://doi.org/10.1111/j.1365-2591.2010.01815.x. PMid:21091494.

22. Vivan RR, Zapata RO, Zeferino MA, Bramante CM, Bernardineli N, Garcia RB, et al. Evaluation of the physical and chemical properties of two commercial and three experimental root-end filling materials. Oral Surg Oral Med Oral Pathol Oral Radiol Endod. 2010;110(2):250-6. http://doi.org/10.1016/j.tripleo.2010.04.021. PMid:20659702.

23. de Vasconcelos BC, Bernardes RA, Cruz SM, Duarte MA, Padilha Pde M, Bernardineli N, et al. Evaluation of pH and calcium ion release of new root-end filling materials. Oral Surg Oral Med Oral Pathol Oral Radiol Endod. 2009;108(1):135-9. http://doi.org/10.1016/j.tripleo.2009.02.026. PMid:19451009.

24. Okabe T, Sakamoto M, Takeuchi H, Matsushima K. Effects of pH on mineralization ability of human dental pulp cells. J Endod. 2006;32(3):198-201. http://doi.org/10.1016/j.joen.2005.10.041. PMid:16500225.

25. Duarte MA, Demarchi AC, Yamashita JC, Kuga MC, Fraga Sde C. pH and calcium ion release of 2 root-end filling materials. Oral Surg Oral Med Oral Pathol Oral Radiol Endod. 2003;95(3):345-7. http://doi.org/10.1067/moe.2003.12. PMid:12627108.

26. Tanomaru-Filho M, Chaves Faleiros FB, Saçaki JN, Hungaro Duarte MA, Guerreiro-Tanomaru JM. Evaluation of pH and calcium ion release of root-end filling materials containing calcium hydroxide or mineral trioxide aggregate. J Endod. 2009;35(10):1418-21. http://doi.org/10.1016/j.joen.2009.07.009. PMid:19801243.

27. Lengheden A, Jansson L. pH effects on experimental wound healing of human fibroblasts in vitro. Eur J Oral Sci. 1995;103(3):148-55. http://doi.org/10.1111/j.1600-0722.1995.tb00016.x. PMid:7634130.

28. Estrela C, Cintra LTA, Duarte MAH, Rossi-Fedele G, Gavini G, Sousa-Neto MD. Mechanism of action of Bioactive Endodontic Materials. Braz Dent J. 2023;34(1):1-1. http://doi.org/10.1590/0103-6440202305278. PMid:36888836.

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