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Calcium hydroxide pastes: pH values and release of calcium ions

ABSTRACT

Aim: to evaluate the release of calcium ions and the pH of three calcium hydroxide pastes: UltraCal XS, Calcicur and an aqueous calcium hydroxide paste.
Methodology: the analysis of calcium in the pastes under study was conducted by atomic absorption spectrophotometry. A pH-meter was used for pH readings. Measurements of pH and release of calcium ions were made at 1 hour and at 1, 3, 7, 15, 30, 45, 60 days.
Results: the analysis of baseline values, minimum and maximum values, and the difference between final and baseline values revealed significant differences in pH and calcium release between the three pastes. The greatest pH and calcium release values were found for the control paste, followed by Calcicur (1-way ANOVA). Release of hydroxyl and calcium ions in the control and Calcicur pastes was faster up to 45 days. pH values for the UltraCal, Calcicur and control pastes were always above 12. The release of hydroxyl and calcium ions occurred more slowly and gradually in the UltraCal paste.
Discussion: based on this study's results and methodology, the following conclusions were reached:

1. the pH values for the UltraCal, Calcicur and control pastes were above 12 at all time points.
2. the release of hydroxyl and calcium ions occurred more slowly and gradually in the UltraCal paste.
3. the release of hydroxyl and calcium ions in the control and Calcicur pastes was faster up to 45 days.

Key words:
Endodontics, chemical compounds, hydroxyl and calcium ion concentration.

INTRODUCTION

Endodontics, a science and specialization in Dentistry, is based not only on technical developments, but also, and fundamentally, on biological principles that determine that respect to apical and periapical tissues is the guiding rule of root canal treatment. These principles should be followed in the different phases of endodontic treatment, which are all interrelated and equally important: overlooking any of them will lead to endodontic treatment failure.
In teeth with pulp necrosis or chronic periapical lesion identified by radiography not only the lumen of the main canal is infected, but also the dentinal tubules and the ramifications that compose the complex system of root canals (Byström & Sundqvist, 1981; Peters et al., 2001). The viability of microorganisms within this system and the impossibility to remove them by means of adequate chemomechanical preparation (Nair et al., 1990; Nair et al., 2005) are factors that decisively contribute to endodontic treatment failure and reduce chances of tissue repair.
Therefore, additional disinfection with intracanal dressings has been proposed to reduce the number of microorganisms found in dentin and in the root canal system. Calcium hydroxide pastes have been recommended as intracanal dressings because of their ability to fight infection in the root canal system (Sjögren et al., 1991; Leonardo et al., 1995).
Since studies by Hermann (1920) was published, calcium hydroxide has been proposed as an intracanal dressing in cases of pulp necrosis and chronic periapical lesion. The mechanism of action of calcium hydroxide has been attributed to its release of calcium ions and hydroxide ions. Its pattern of ionic dissociation is responsible for the biological properties of calcium hydroxide, such as its antibacterial activity (Safavi & Nichols, 1993; Safavi & Nichols, 1990), and its repair potential by inducing hard tissue formation (Holland et al., 1979; Leonardo et al., 1995).
Three basic types of vehicles are available for calcium hydroxide pastes: aqueous, viscous and oily. Aqueous vehicles (distilled water, saline solution) promote faster ionic dissociation, and thus a longer contact of ions with tissues and microorganisms. Viscous vehicles (propylene glycol 400, polyethylene glycol 400) release hydroxyl and calcium ions slowly and progressively, and also promote the type of contact described for aqueous vehicles. Oily vehicles (olive oil), however, are nonpolar substances that have low solubility in water, and thus slow down solubility and dissociation of calcium hydroxide pastes in tissues (Fava & Saunders, 1999).
Therefore, it is important to study the vehicles chosen for calcium hydroxide paste in different clinical situations because they may affect the form and the intensity of ion dissociation.
The physicochemical properties of calcium hydroxide pastes, specifically pH and calcium ion production, have been the focus of several studies because of the importance these properties have in its mechanism of action (Tronstad et al., 1981 Leonardo et al., 1992; Esberard et al., 1996; Beltes et al., 1997; Duarte et al., 2004).
The purpose of this study was to evaluate the physicochemical properties of calcium ion release and the pH of three calcium hydroxide

pastes: UltraCal XS, Calcicur and an aqueous paste.

MATERIALS AND METHODS

Two commercial calcium hydroxide pastes were used in this study: UltraCal XS (Ultradent Product, Inc. South Jordan, USA) and an aqueous paste Calcicur (VOCO, Cuxhaven, Germany). A third calcium hydroxide paste was prepared with 1.2 g calcium hydroxide (Riedel De Haën AG, Seelze, Hannover, Germany) and 1.0 ml distilled water (Farmácia Escola, ULBRA, Canoas, RS, Brazil) to serve as the control paste. The manufacturer of UltraCal XS did not provide information about the formulation.

An analytical balance (Adventurer, Ohaus Corp., USA) was used to weigh 0.206 g of each paste; the samples were placed in 120 ml plastic flasks with a lid. Three samples were prepared for each paste, that is, there were three flasks for each paste. Ultra pure water (100.0 ml; Milli-Q, Milipore, São Paulo, Brazil) was added to each sample. After about 30 min of water and paste contact, the mixture was stirred with a glass rod, and 2 minutes were allowed for sedimentation of the particles in solution.

Calcium ion analysis

The analysis of calcium in the pastes under study was conducted by atomic absorption spectrophotometry with a model 4000 spectrophotometer (Perkin-Elmer Corporation, Connecticut, USA).

Calcium concentrations were calculated by comparison with a calibration curve using 0.5, 1.0, 2.0, 4.0, 5.0, 10.0 and 20 ppm standard solutions (Calcium Standard Solution, Merck, Darmstadt, Germany) in ultra pure water.

For each reading, 100.0 ml was taken from the sample with an automatic pipet and diluted in 2 ml 0.15 % potassium chlorate (Reagen, Rio de Janeiro, Brazil). To promote better calcium atomization, 250 ml nitric acid (Merck, Darmstadt, Germany) was added to the mixture. Calcium in the form of aerosol, obtained by the aspiration of 2 ml of the solution, was processed (drying, burning, atomization) at about 2900°C on a nitrous oxide-acetylene burner. Ground state calcium, when excited, absorbs radiation emitted by a Ca-Mg hollow cathode lamp (wavelength = 422.7 nm; current = 20 mA; slit width = 0.7 nm; length = 5.0 nm). The amounts of calcium released at 1 hour and at 1, 3, 7, 15, 30, 45 and 60 days were measured, and software in the computer coupled to the spectrophotometer was used to print the values.

Analysis of hydroxyl ions (pH)

After a 2-minute resting period, pH was measured directly inside the flasks by dipping a glass electrode into the solutions. This glass electrode was coupled to a pH-meter (CG 840, Schott, Germany) previously calibrated with pH 7.0 and 4.0 buffer solutions (Synth Ltda, Diadema, Brazil). Between readings, the electrode was abundantly rinsed with distilled water and dried with absorbent paper. The electrode remained in contact with the buffer solution while not being used.

A standardized form was used to record pH readings at 1 hour and at 1, 3, 7, 15, 30, 45, 60 days.

After each reading, a cannula attached to a nitrogen gas cylinder was inserted in each flask without contacting the solution surface, and a low but continuous flow was applied for 20 seconds. The flasks were then covered with a lid and kept in an incubator at 36.5°C until the next reading time.

Descriptive statistical analyses were calculated based in the mean and standard deviation of pH and calcium release. The data were then analyzed through 1 way ANOVA related to the initial, minimum, maximum and delta values. Tukey's Post Hoc test was used in time follow-up situations significant at $\alpha = 0.05$.

RESULTS

Statistical analysis with 1 way ANOVA of initial (baseline), minimum and maximum pH values, and difference between final and baseline values revealed significant differences in the pH of the pastes under study (Table 1).

The analysis Table 1 reveals a linear pattern of mean pH values, except on the 15th day, when a slight decrease was observed. Moreover, higher mean pH values were found for the control paste up to the 45th day, followed by Calcicur and UltraCal XS, in this order. At 60 days, these values were slightly greater for UltraCal XS.

Table 2 shows the mean values (mg/l) of release of calcium ions for the three pastes under study at all time points according to the absorbance values obtained by atomic absorption spectrophotometry .

Statistical analysis with 1 way ANOVA of baseline values, minimum and maximum values, and the difference between final and baseline values revealed significant differ-

	Calcicur N=3	UltraCal XS N=3	Control N=3	p
1 hour	12.49 ±0.06^{a}	12.14 ±0.05^{b}	12.62 ±0.01^{c}	< 0.001
1 day	12.32 ±0.05	12.17 ±0.02	12.48 ± 0.01	-
2 days	12.47 ±0.01	12.42 ±0.03	12.54 ±0.06	-
3 days	12.26 ±0.03	12.18 ±0.01	12.37 ±0.01	-
7 days	12.29 ±0.03	12.25 ±0.01	12.42 ±0.02	-
15 days	12.08 ±0.02	12.02 ±0.03	12.20 ±0.02	-
30 days	12.35 ±0.03	12.30 ±0.03	12.46 ±0.02	-
45 days	12.54 ±0.06	12.52 ±0.03	12.57 ±0.06	-
60 days	12.35 ±0.10	12.41 ±0.03	12.36 ±0.08	-
Minimum	12.08 ±0.06^{a}	12.02 ±0.05^{a}	12.20 ±0.02^{b}	= 0.001
Maximum	12.54 ±0.06^{ac}	12.52 ±0.03^{ab}	12.62 ±0.01^{c}	= 0.035
Difference	-0.14 ±0.06^{a}	0.27 ±0.04b	-0.26 ±0.10^{a}	< 0.001

**Mean values followed by similar letters indicate no statistically significant differences. Significant at $\alpha = 0.05$*

Tab. 1 - *Mean pH values (± standard deviation) of calcium hydroxide pastes at different time points.*

	Calcicur	UltraCal XS	Control	P
1 hour	17.39±1.46[a]	8.43±1.18[b]	19.61±1.26[a]	< 0.001
2 days	20.42	15.86	23.43	-
3 days	20.97	15.84	21.95	-
7 days	21.44	16.75	24.04	-
15 days	22.81	17.79	25.57	-
30 days	22.05	17.84	26.05	-
45 days	24.01	17.56	25.00	-
60 days	16.96	16.77	16.25	-
Minimum	16.19 ±2.49[a]	8.43 ±1.18[b]	19.60 ±2.08[a]	= 0.005
Maximum	24.77 ± 2.90[a]	18.54 ±1.15[b]	26.85 ±1.11[a]	= 0.004
Difference	- 0.43 ±2.18[a]	8.33 ±1.03[b]	- 3.36 ±3.91[a]	= 0.004

**Mean values followed by similar letters indicate no statistically significant differences. Significant at α = 0.05*

Tab. 2 - *Mean calcium release values (mg/L± standard deviation) of calcium hydroxide pastes at different time points.*

ences in mean values of calcium ion release between the three calcium hydroxide pastes. The amount of ionized calcium in the three pastes increased in the first 30 days, and the greatest amounts were found for the control paste and the Calcicur paste. At 45 days, the Calcicur paste showed a progressive increase in the amount of calcium release, whereas the UltraCal and control pastes showed a slight decrease. At 60 days, a significant drop in the amount of ionized calcium was found for the Calcicur and control pastes, together with a slight decrease for the UltraCal paste, so that the three pastes had similar calcium release values at that time (Table 2).

DISCUSSION

Calcium hydroxide induction of hard tissue formation and its antibacterial activity could be explained by its ionic dissociation into calcium and hydroxyl ions. As the pH of calcium hydroxide is about 12.4, most bacteria strains isolated in infected root canals are sensitive to its effects, and are eliminated in a short period of time when in direct contact with this substance (Siqueira Jr & Uzeda 1998.).

The action of calcium ions obtained from calcium hydroxide has been observed in areas of hard tissue formation, in the hard tissue barriers found in pulp capping, pulpectomy, and in apical sealing (Holland, 1979; Leonardo et al., 1995). Tronstad et al., (1981) assumed that the activation of calcium-dependent ATPase in areas of hard tissue formation may be assigned to these ions.

The important physicochemical properties of calcium hydroxide are associated with its conditions of clinical use, which are more evident during the filling of root canal space. The vehicles used for the pastes should promote the ionic dissociation of calcium hydroxide because its biological effect is dependent on this dissociation and may be affected by the vehicle's viscosity and solubility in water.

Atomic absorption spectrophotometry has been used for the analysis of calcium in calcium hydroxide pastes and sealers because of its reliability, safety and speed, and has been adopted by several other authors (Gomes et al., 1996; Duarte et al., 2004). During our study, the pH values of the calcium hydroxide pastes were always above 12, which reveals their alkalinity. Up to 45 days, the pH of the control paste was higher than that of Calcicur and UltraCal. Similarly, the pH of Calcicur was higher than that of UltraCal during the same time. Such result may be associated with the type of vehicle used in each of the pastes. Both the control and Calcicur pastes have an aqueous vehicle, which promoted a faster ionic dissociation and, consequently, higher pH values observed since the beginning of the study. At the same time, the results found for UltraCal paste, which components were previously unknown, suggest that it had a viscous, and not an aqueous, vehicle. This greater viscosity led to a slower but gradual release of hydroxyl ions.

Within a narrow pH range (12.02 – 12.62), statistical analysis revealed a significant difference between the 3 pastes, with higher pH values for the control paste, followed by Calcicur and UltraCal, in this order. The inclusion of a neutral pH solution in the study (negative control) might have revealed a lack of significant difference between the three pastes under study.

When calcium hydroxide pastes are used as long-term intracanal dressings in cases of pulp necrosis or chronic periapical lesion, alkalinity is considered fundamental; the three pastes studied here proved to be capable of maintaining alkalinity.

Our results are in agreement with those reported by Beltes et al., (1997), who showed that pH was stable (above 12) in the aqueous calcium hydroxide pastes investigated in their studies.

The three calcium hydroxide pastes progressively released calcium during all time points in this study. However, the greatest values were found for the control paste, followed by Calcicur - both aqueous pastes - at 45 days. At 60 days, an important decrease in calcium release was observed in the aqueous pastes, and the mean values for the three pastes were very close for the first time. Perhaps the explanation for this may be the formation of calcium carbonate in the control paste e even though nitrogen was used to eliminate CO_2 from the flasks. This may also have occurred with the UltraCal paste, but not significantly.

The results of calcium release found in this study are in agreement with those reported by Leonardo et al., (1992), Beltes et al., (1997), who found a greater ion release in the first 30 days for aqueous calcium hydroxide pastes than for viscous pastes.

CONCLUSIONS

Based on this study's results and methodology, the following conclusions were reached:

1. the pH values for the UltraCal, Calcicur and control pastes were above 12 at all time points;
2. the release of hydroxide and calcium ions occurred more slowly and gradually in the UltraCal paste;
3. the release of hydroxide and calcium ions in the control and Calcicur pastes was faster up to 45 days.

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