Influence of different processing phases on the physicochemical properties of two calcium silicate-based cements

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ABSTRACT

Objective: The purpose of this study is to evaluate if the physicochemical properties are influenced by the processing steps of cement production. The chemical composition, setting time, solubility, pH value and calcium ion released by Portland cement were measured through all stages of the manufacturing process (G1), as well as the cement that was obtained through the step of calcination (G2). **Methods:** The chemical composition was examined by energy dispersive x-ray spectroscopy (EDS). Setting time and solubility tests were performed in accordance with regulation #57 of the ADA. Calcium ion release was analyzed using an atomic absorption spectrophotometer. The change in pH was determined using a pH meter. **Results:** The chemical composition of both cements contained high levels of calcium and silicon, but the Portland cement showed traces of sulfur. The setting times of G2 were significantly lower than those of G1 ($p < 0.05$). Both cements presented values within those recommended by the ADA for solubility, which is at most 3%; however, the solubility of G2 was higher when compared with G1. The analysis of pH and calcium ions release exhibited alkalinized pH and calcium ion release in both groups, independent of the time of analysis. **Conclusion:** The results suggest that the physicochemical properties are influenced by the processing steps of cement production.

Keywords: Endodontics. Solubility. Physical and chemical properties.

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Introduction

The aim of the endodontic procedure is to clean and shape the root canal system.[1] After the biomechanical preparation, a satisfactory root obturation should be performed in order to obtain a satisfactory sealing, avoiding the percolation of fluids to the periapical tissues and consequently maintain or reestablish its integrity.[1,2] Although endodontic treatment is generally considered to have a high success rate, failures can occur after treatment.[2,3] In these cases, paraendodontic surgery presents itself as an alternative for the resolution of failure, showing success rates above 80%.[4,5]

Many materials have been used as retrofillings, such as amalgam and zinc oxide and eugenol based cements. However, these materials have presented clinical failures due to some inappropriate properties.[6] Besides possessing good biological behavior, retrofilling cements need to present certain physicochemical properties according to the criteria of the International Standards Organization.[7] Among the physicochemical properties, the setting time of an endodontic sealer cement must allow for adequate working time, solubility should not exceed 3% according to the standards of ADA[8] # 57, radiopacity must be greater than dentine and it must have the ability to release calcium ions, promoting alkalinization in the adjacent tissues, inducing the formation of mineralized tissue.

Mineral trioxide aggregate (MTA) is currently the most widely used material for this finality,[9,10] which presents good physicochemical properties and biocompatibility.[11] The main chemical component of MTA is Portland cement, which has the same chemical elements, physical, chemical and biological properties and is low cost.[12,13,14]

According to Camilleri,[15] the main components of Portland cement are: calcium oxide (CaO) 60-66%, silicon dioxide (SiO_2) 19-25%, aluminum oxide (Al_2O_3) 3-8% and ferric oxide III ($F_{e2}O_3$) 1-5%. The manufacture of Portland cements involve the mixing and milling of raw materials, clinker formation in industrial rotary kilns by calcination, followed by rapid cooling, grinding of clinker and subsequent addition of some substances.

However, during the heating phase at high temperatures, fine cement particles are attached on the walls of furnaces and from time to time are removed. These are characterized as not participating in the manufacturing steps and submit thin and homogenous particles. Nevertheless, the physicochemical behavior of this material is unknown, which justifies the study design. The aim of this study is to evaluate if the physicochemical properties are influenced by the processing steps of cement production.

Material and Methods

For analysis of the different material properties, the following groups were established: G1: Portland cement going through all stages of the manufacturing process, G2: Portland cement obtained in the stage of calcination. Both groups were manipulated with distilled water in the proportion of 3/1.

SEM-EDX analysis

The cements were prepared and fixed on a metal ring (10x2mm) and stored in a stove at 37°C with 95% relative humidity. The samples were then fixed with carbon tape on aluminum stubs and analyzed in a scanning electron microscope (SEM) (Aspex Express, Fei Europe, Eindhoven, Netherlands) at accelerating voltages of 15-20 kV. Photomicrographs of the cement surfaces were obtained at 500x magnification. Energy-dispersive X-ray spectroscopy analysis, which is fully integrated to the SEM Aspex Express (Fei Europe, Eindhoven, Netherlands), was used to determine the elemental composition of the samples.

Setting Time

The determination of the setting time was carried out according to the American Society for Testing and Materials specifications (ASTM-C266-08),[16] and the samples were made following standard #57 of the American Dental Association (ADA).[8] The test was conducted under controlled temperature and humidity, 37 °C and 95%, respectively. Each cement was mixed and inserted in three metallic rings having an internal diameter of 10 mm and a thickness of 2 mm. After 180 s from the onset of mixing, a Gilmore-type needle with a mass of 113.5 g was carefully lowered vertically onto the horizontal surface of the testing sample until it was no longer possible to observe the mark in the cement surface, thereby determining the initial setting time. In the same manner, but using a heavy Gilmore needle (453.5 g), the final setting time was determined. In both analyses, the setting times were recorded at the moment in which the needle failed to leave a complete circular indentation on the surface of the specimen. Statistical analysis was performed using the paired t-test with a 5% significance level.

Solubility

The determination of the solubility of the cements were determined according to ADA Specification #57 (American National Standards Institute, 1984).[8] Three 1.5-mm-thick Teflon cylindrical rings measuring 20 mm in inner diameter were filled with the material. An impermeable nylon thread was placed inside the material with the aim of keeping the specimens suspended and immersed in distilled water during the trial period. To correct the filling, the rings were placed on a glass plate covered with cellophane film, and after filling, another glass plate also covered with cellophane film was placed on the rings and the assembly was placed in a stove at 37°C, where they were left to stand for a period corresponding to three times the setting time. Next, the samples were removed from the mold and residues and loose particles were removed with the use of a brush tool. The samples were weighed on an analytical balance and placed inside containers containing 50 ml of distilled water with care taken so that the samples were entirely immersed in water, not permitting any contact between the sample and the walls of the container. After this period, the samples were removed, thoroughly dried with filter paper, placed in a dehumidifier for 24 hours and weighed again. The solubility values were determined by the difference between the weight before and after the water immersion. Statistical analysis was performed using the paired t-test with a 5% significance level.

Calcium ion release and pH evaluation

For the pH and calcium ion release evaluations, the cements were manipulated and inserted in single open-ended polyethylene tubes with 1.0 mm internal diameter and 10.0 mm length, using a type Paiva condenser for the condensation until the complete filling. Ten specimens of each cement were used for both tests. After the tubes were filled, the specimens were immersed in flasks containing 10 mL of deionized water, which were sealed and incubated at 37°C, and kept as such throughout the study. Before the immersion, the pH of the deionized water was verified, attesting not to have calcium and hydroxyl ions. To avoid any interference in the results, all glassware was previously treated with nitric acid. The evaluations were performed at intervals of 3, 24, 72 and 168 hours. After each period, the specimens were carefully removed from the tubes and immersed in new ones containing the same volume of deionized water.

pH

The pH measurements were performed with a pH meter previously calibrated using standard solutions (4, 7 and 14). A shake for 5 seconds was performed in the tubes after the removal of the specimen. Next, the liquid was placed into a beaker and put in contact with the electrode pH meter. Statistical analysis was performed using the Mann-Whitney test with a 5% significance level.

Calcium ion release

The release of calcium ions was measured using an atomic absorption spectrophotometer equipped with a cathode specific lamp for calcium ions. The spectrophotometer was used following the manufacturer's instructions: wavelength of 422.70 nm, gap of 0.5 nm, lamp current of 10 mA, and slightly reduced stoichiometry, and were maintained by an air-supported acetylene flow of 2.0 L per minute. The samples and standards were diluted in 10% EDTA to eliminate the interference of phosphates and alkali metal. A standard stock solution of 10 mg % was diluted in 10% EDTA to obtain the following concentrations: 0.025mg%, 0.05 mg%, 0.1 mg%, 0.2 mg%, and 0.5 mg%. A 10% EDTA solution was used like white for calibration. The calculation of calcium ions release was made according to a standard curve, established on the basis of solutions with predefined pH concentrations. Statistical analysis was performed using the Mann-Whitney test with a 5% significance level.

Results

SEM/EDX

The micrographs and their respective EDX spectra of the elements obtained by two cement surface analyses in different processing steps are demonstrated in Figure 1. Superficial analyses of conventional cements and their respective EDX spectra are illustrated in Figure 1A. The conventional cement`s EDX spectra revealed the presence of high amounts of calcium, oxygen and silicon, suggesting the presence of calcium silicate particles, with traces of carbon, magnesium, iron, aluminum and sulfur. Figure 1B represents surface analysis and EDX spectra of cements taken directly from the furnace. The EDX analysis revealed peaks similar to those of the conventional cement revealing the presence of calcium, oxygen, silicon and carbon, as well as some traces of magnesium and aluminum. However, this cement showed no peaks of sulfur, which is suggested as a dopant element.

Setting time

Table 1 shows the mean and standard deviation of the initial and final setting times in minutes of the cements evaluated. The cement group taken directly from the furnace had lower initial and final setting time values compared to the conventional cement ($p < 0.05$).

Solubility

Table 1 shows the mean and standard deviation of solubility percentage of the cements evaluated. All materials exhibited lower solubility than 3%, which is the maximum recommended by the standards of ADA #57.[8] A statistically significant difference ($p < 0.05$) was observed between the evaluated cements, observing more solubility for the cement that was removed from the furnace.

pH

Figure 2 shows the plot of the median, minimum and maximum pH values of the materials studied in different periods. All materials provided alkalization of water in which they were immersed. In a statistical comparison between the materials, at 3, 24 and 168 hours, no significant differences were found. In the analysis of 72 hours, the conventional cement had pH values higher than the cement withdrawn directly from the furnace ($p < 0.05$).

Calcium ion release

Figure 3 shows the graphical representation of the median, minimum and maximum release of calcium ions values in mg / L of the studied materials. Zero is the amount of calcium in water that was used for the measurement, indicating release of calcium ions for all materials. In a statistical comparison between groups at 3, 24 and 72 hours, no significant differences were found. In the period of 168 hours, the cement group taken directly from the furnace show higher values than those found in the conventional cement ($p < 0.05$).

Table 1. Means and standard deviations of initial setting time (in minutes), final setting time (in minutes) and solubility percentage of the studied materials.

Cements	Initial setting time	Final setting time	Solubility
Conventional	30.05 ± 0.009^a	65.12 ± 0.009^a	-1.750 ± 0.026^a
Furnace	21.20 ± 0.009^b	40.22 ± 0.01^b	0.573 ± 0.098^b

Negative values show an increase of the cement weight. Different letters indicate statistically significant difference ($p < 0,05$).

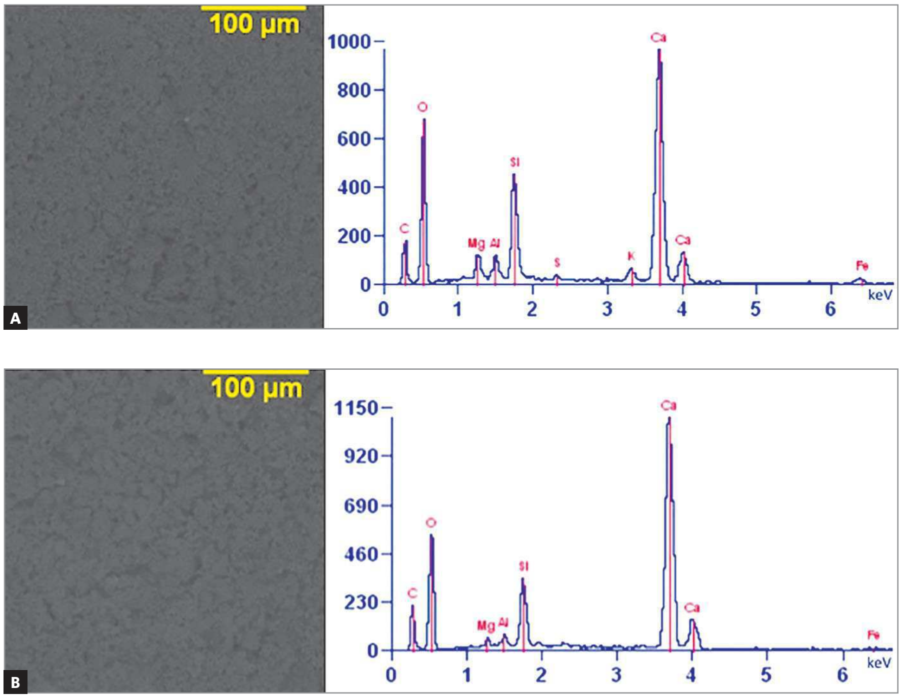

Figure 1. Representative image of the EDS analysis (**A**) Conventional material; **B**) Furnace material).

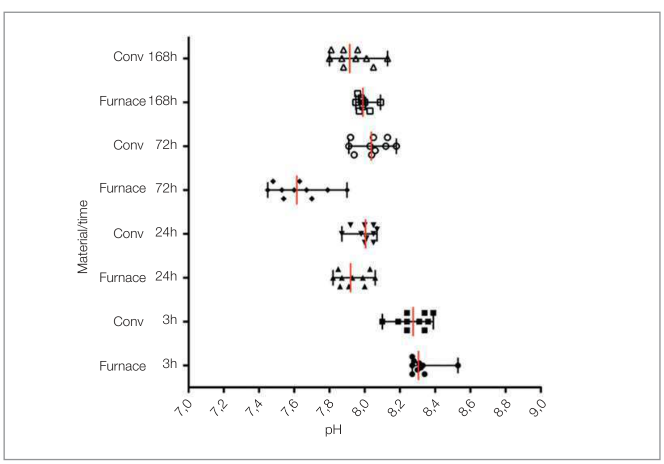

Figure 2. Graphical representation of the pH provided by the studied materials.

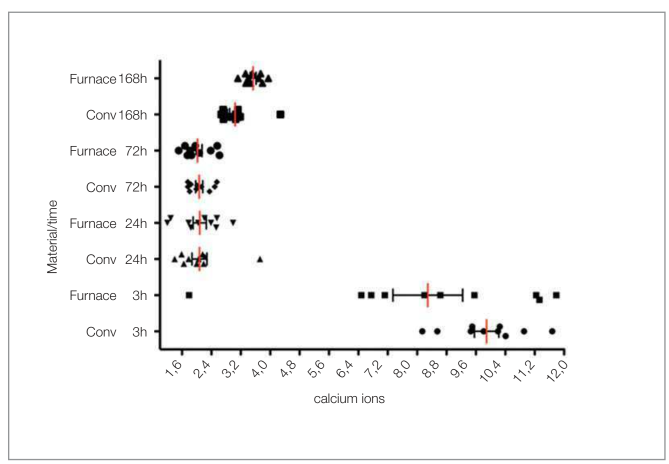

Figure 3. Graphical representation of the calcium release (in mg/dL) provides by the studied materials.

Discussion

The production of Portland cement occurs through a basic raw material that is limestone which undergoes a grinding process, performing the required homogeneity. Next, the flour obtained is calcined in a rotary furnace and a clinker is obtained. Few additions are performed with gypsum, pozzolana and slag obtained as the final Portland cement product. In the calcination step, during the processing, several fine particles are adhered to the walls of the rotary kiln and are not used in the subsequent steps of the manufacturing process. From time to time, these particles are removed and characterized by not presenting the substances that are added in the final stage.

The chemical composition, setting time, solubility, pH value and calcium ion released of Portland cement were measured, passing through all stages of the manufacturing process, and a cement was obtained in the calcination step.

The SEM/EDX are extensively used in the chemical analysis of cements and characterization of materials used in endodontics.[17,18,19] In the present study, the analysis revealed that the conventional cement consists mainly of calcium silicate particles due to the silicon, oxygen and calcium peaks, and lower concentrations of carbon, sulfur, aluminum and magnesium, as shown in other studies.[20,21] The cement taken directly from the furnace mostly presented calcium and oxygen in its constitution and a lower concentration of carbon and silicon with magnesium and aluminum traces. The fact that there isn´t the presence of sulfur in the cement taken directly from the furnace may be beneficial, seeing it is a dopant element, which can arise when other components are included in it, such as gypsum or slag. In view of this, a better biological response of the material was expected.

When the setting time of both cements was analyzed, the best statistical results were obtained from the cement removed from the furnace, having a lower setting time, however, with enough time to work properly. This was because of a lack of gypsum (plaster), which is added at the manufacturing process in the final stage. Its main function involves the working time and cure of the material delay. This increased time makes the cement more prone to dissolution during endodontic surgery, which could increase the leakage or even promote the displacement of cement in the cavity.[6]

Both cements presented values inside that recommended by the ADA[8] for solubility which is at most 3%. The cement taken from the furnace had solubility average values of 0.5% while the conventional cement, for being a hydrophilic material, obtained a negative average (-1.750%). However, water absorption can offset the dissolution of cement, so with these results, it cannot be said that the conventional cement is insoluble.[22] Furthermore, because of the methodology, the samples that were only immersed may present false results. What occurs in clinical conditions is not the same, where the material comes immediately into contact with the oral fluids.[23]

All the cements showed alkaline pH, especially in the early periods. No statistical differences were found in the periods of 3, 24 and 168 hours. At 72 hours, the conventional cement showed significantly higher pH values than the cement taken from the furnace. This can be explained by the fact that the conventional cement presented a higher setting time, which contributes to greater hydroxyl ions release. In the period of 168 hours, the cements showed higher pH values than in 72 hours, and this was probably due to the dissolution that occurs in these cements, releasing hydroxyl ions and thus raising the pH.[10]

When the calcium ions release was analyzed, the highest values were observed in the earlier periods for both tested cements, with no statistical difference between them. At 168 hours, an increase in the amount of ions released in relation to 24 and 72 hours was observed. In addition, these values were statistically higher in the cement taken from the furnace. This was probably due to the greater porosity and cracks of this cement compared to the conventional cement or due to the cement passing through all stages of the manufacturing process which may have sulfate and calcium in its composition which can react with the calcium, reducing the ion release.[24]

The results suggest that the physicochemical properties are influenced by the processing steps of the cement production. The cement that is taken directly from the furnace is characterized by presenting a chemical composition similar to conventional cement, but without observing the presence of sulfur, having a lower setting time and increased calcium ions release. Meanwhile, the conventional cement that passed through all stages of the manufacturing process was characterized by having lower solubility and higher pH values. Because of the lower setting time, the cement removed from the furnace would have advantages over those that suffer complete processing in cases of paraendodontic surgery, which aims for more rapid setting of the cements.

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The authors deny any conflicts of interest related to this study.

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