

Mineral Trioxide Aggregate (MTA) Solubility and Porosity with Different Water-to-Powder Ratios

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This study tested mineral trioxide aggregate (MTA) solubility and porosity with different water-to-powder proportions. The study also determined the chemical composition of the salts dissolved by MTA. Four sets of specimens using the following water-to-powder proportions were prepared: 0.26, 0.28, 0.30, and 0.33 grams of water per gram of cement. The latter is the ratio recommended by the manufacturer. It was determined that the degree of solubility and porosity increased as the water-to-powder ratio increased. Significant differences were found among the sets of specimens. The chemical analyses of the salts dissolved by MTA in the water identified the presence of calcium as the main chemical compound. The pH level of the solution was highly alkaline, ranging between 11.94 and 11.99. It can be stated that the calcium found in the solution should be in its hydroxide state at this high pH level. This ability to release calcium hydroxide could be of clinical significance because it could be related to the proven capacity of MTA to induce mineralization.

Mineral trioxide aggregate (MTA) has been developed to seal off pathways of communication between the root canal system and the external surface of the tooth. MTA is a powder that consists of fine hydrophilic particles that harden when they come in contact with water. Hydration of the powder results in a colloidal gel that solidifies to a hard structure (1). Characteristics of hardened MTA depend on the size of the particles, the water-to-powder ratio, the temperature and humidity at the application site, and the amount of air trapped in the mixture (1).

According to its manufacturer, the chemical composition of Pro Root MTA (Tulsa Dental, OK, USA) is basically a mixture of oxides, quite similar to those of Portland cement. Bismuth oxide powder, which is practically insoluble in water and chemically inert, has been added to the Pro Root MTA formula to make the aggregate radiopaque and radiographically identifiable (2).

Portland cement has been thoroughly studied in engineering research; therefore, considering MTA's similarities, it is possible to study its properties from a well-established theoretical framework. In

engineering, the main property of this construction material is its compression resistance. In dentistry, resistance to solubility and disintegration in an aqueous environment such as the oral cavity is much more relevant (3). When Portland cement is mixed with water, it forms a special structure of micropores, capillary channels, and loosely trapped water. As water proportion increases, mixture porosity increases. A mixture of Portland cement is hygroscopic, and the water content is the key to this material's properties (4). Part of the water in the mix will be consumed by the chemical reactions involved in the setting process, while another part will be trapped in the pores and capillaries and can diffuse and evaporate during and even after the setting process is complete (5).

The water confined in hardened Portland cement finds itself within a structure saturated with calcium hydroxide. This calcium hydroxide is mainly the soluble fraction of set Portland cement. When the mix comes in contact with an aqueous environment of a different saline concentration, Portland cement absorbs water. The water trapped in the cement mix and saturated by calcium hydroxide is then released to the environment. The pores and capillaries of the structure, now empty, absorb fresh water. This water is again released along with the calcium hydroxide that has dissolved. In this way, water is continuously diffusing in and going out of the mass. As water is released to the environment, the mix loses weight. However, this is only a temporary loss because the empty pores and capillaries will quickly refill, and the newly captured water will then take part in the slow hydration process of cement, increasing its weight as water is being fixed in the structure. This osmotic effect goes on repeatedly and represents a peculiar idiosyncrasy and characteristic property of Portland cement (5). In Portland cement, the porosity and permeability are not necessarily related. The continuity of the capillaries is broken spontaneously during the setting process. Therefore, a well-prepared Portland cement could present a high volume of pores but very low permeability (5).

Considering the similarities between Portland cement and MTA, it is important to know how the water-to-powder ratio affects the properties of MTA. Therefore, the purpose of this study was to determine the solubility and porosity of MTA when mixed with different water-to-powder proportions and to establish the chemical composition of the salts dissolved from the mixture.

MATERIALS AND METHODS

The solubility of MTA (Pro Root) was determined in accordance with the ISO 6876 method (6) and with American Dental

Association (ADA) specification #30 (7, 2). Four different water-to-powder proportions were selected in a pilot study in which the consistency of the different ratios was evaluated. Ratios ranged from 0.26, the minimum water-to-powder ratio that allowed a mix of putty consistency to be manipulated, to 0.33, the ratio recommended by the manufacturer. Beyond 0.33, the resulting mix is too fluid to be manageable. Two intermediary water-to-powder ratios (0.28 and 0.30) were selected.

Six sets of specimens for each ratio were prepared in one operation. The materials were weighed in a Sartorius analytical balance to an accuracy of ± 0.1 mg. Powder and water for each ratio were weighed and mixed, and the specimens were prepared in less than 10 min. A single operator weighed and mixed the samples at $23 \pm 2^\circ\text{C}$ laboratory room temperature and a relative humidity of $60 \pm 5\%$. Each specimen was placed into a circular metal mold, following ISO standards (6). After the specimens were prepared, they were stored in a chamber for 21 h at $37 \pm 1^\circ\text{C}$ (98.6°F) and 100% relative humidity. Upon removal from the chamber, the specimens were dried for 24 h in an oven at 105°C (221°F) until they reached a constant weight.

During this test, it was necessary to dry the specimens at 105°C (221°F) to eliminate all free water trapped in the substance to establish a consistent net weight. In fact, in an earlier pilot study, it was determined that MTA specimens are humidity saturated after being cured and, when kept at normal laboratory room temperature, they slowly evaporate water. This is the reason why it was impossible to reach a constant weight. This situation forced the authors to deviate from the standards only in this aspect.

Before being weighed, the specimens were cooled in a desiccator with a controlled low humidity atmosphere (10%). The specimens were individually weighed in less than 20 s to minimize room humidity absorption. This weight was recorded as initial dry weight.

The specimens were then individually placed in tarred bottles, containing 50 cm^3 of distilled water, in balance with laboratory atmospheric conditions ($\text{pH} = 5.6$). The bottles were then transferred to an oven at 37°C (98.6°F), where they remained for 24 h. They were then removed from the oven and flushed with distilled water that was recollected in the same bottles. The water was clean and transparent, and no suspended or decanted material was observed. The pH values of this liquid were measured with a pH meter using a temperature-compensated glass electrode.

The water was then evaporated at a temperature slightly below boiling point. Bottles and residues were dried in an oven at 105°C (221°F), cooled down in the same desiccator, and weighed. The differences found between this weight and the original bottle weight were divided into the initial dry weight of the specimens and multiplied by 100. The result was recorded as solubility.

The following method was used to determine the volume of the pores of the specimens. They were removed from the bottles where they were immersed, superficially dried with absorbing paper, and weighed in their saturated water conditions. Any difference between this final wet weight and the initial dry weight represents the weight, expressed in grams, of the amount of water entrapped in the material's pores. Water density is defined as 1.0; therefore, this value also represents this water volume expressed in cm^3 .

The total volume of the specimens was established following Archimedes principle. This principle simply states that a body immersed in a fluid is buoyed up by a force equal to the weight of the displaced fluid. In this case, the buoyant force is measured by the difference, expressed in grams, between the weight of the submerged body in air (relative density of which is neglected) and

TABLE 1. Chemical analysis

Chemical Components	Concentration (mg/L)
Calcium (Ca^{2+})	482.00
Potassium (K^+)	45.20
Sodium (Na^+)	21.40
Iron (Fe^{3+})	4.96
Sulphate (SO_4^{2-})	5.20

The chemical components were identified in their ionized state by the atomic absorption spectrophotometer. The analyzed solution with a volume of 200 cm^3 was obtained after separating the insoluble silica.

the weight when submerged in water. This difference is also the volume, expressed in cm^3 , of the specimens.

The value reported as porosity is the relation between the volume of pores and the volume of specimens, multiplied by 100 and averaged for each set of a certain water-to-powder ratio. The specimens obtained with each water-to-powder ratio were observed with the scanning electronic microscope (SEM) to confirm the presence or absence of pores and capillaries.

The evaporated residues of the 0.26 and the 0.28 ratios, weighed and reported as solubility, were joined for the chemical analysis purposes. The residues were partially insoluble in water, due to the carbonation of the alkaline species by the atmospheric carbon dioxide.

By extracting the residues with hydrochloric acid, it was possible to separate the silica, which was assessed by the gravimetric method (8–10), from the rest of the chemical species now in solution. All the fixed carbon dioxide was eliminated by boiling. The resulting solution was analyzed with an atomic absorption spectrophotometer (Shimadzu, model AA6701F; Kyoto, Japan) by air-acetylene flame reading.

Results were analyzed by ANOVA test. Statistical difference level was set at $p < 0.01$. Normality assumption was verified with the one-sample Kolmogorov-Sminov test. Levene tests showed no variance heterogeneity among data taken from the two properties under study.

RESULTS

The presence of silica (silicon dioxide) assessed by the gravimetric method represents the 1.66% of the residues.

The chemical analyses of the salts dissolved by MTA in water tested by the atomic absorption spectrophotometer are listed in Table 1.

This study found that the water that had been in contact with the specimens had a highly alkaline pH that ranged between 11.94 and 11.99. It is worth mentioning that in high alkaline solution, the metals like calcium, sodium, potassium, and iron should be in their hydroxide state.

The results of solubility and porosity are listed in Tables 2 and 3. Table 2 shows that the degree of solubility increases with the amount of water used in preparing the mix. Statistical analyses showed that differences among the ratios are statistically significant (ANOVA $F = 37.795$; $p = 0.000$). This means that the amount of water used in preparing the mix has a direct effect on the solubility when the material is in contact with an aqueous environment. In Table 3, the statistical analyses of the values of porosity demonstrated that differences are statistically significant (ANOVA $F = 157.439$; $p = 0.000$). However, a larger dispersion in data corresponding to the 0.30 set of specimens was also

TABLE 2. Average of solubility recorded for each set of specimens

Ratio Water-to-Powder	Solubility
0.26	1.76
0.28	2.25
0.30	2.57
0.33	2.83

Solubility values were calculated from the weighed residues as a percentage of the initial dry weight of the specimens, following the ISO 6876 standard. All means are statistically different. Level of significance: 0.05.

TABLE 3. Average of porosity recorded for each set of specimens

Ratio Water-to-Powder	Porosity
0,26	30,25
0,28	35,72
0,30	35,19
0,33	38,39

Porosity values were calculated from the pore volume as a percentage of the specimen's volume. All means are statistically different. Level of significance: 0.05.

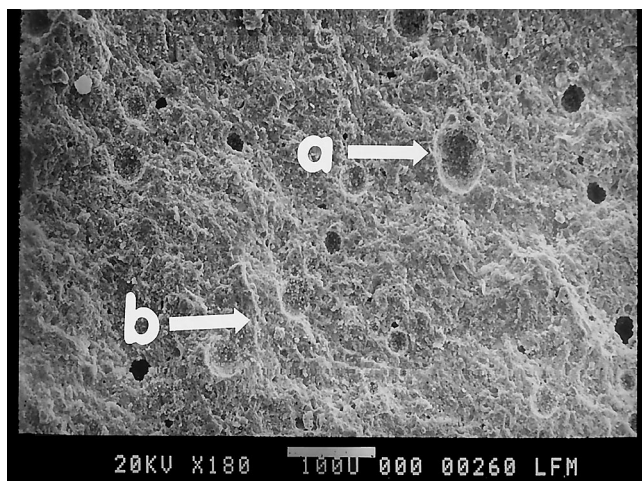


FIG 1. Scanning electronic microscope (SEM) image of a 0.26 water-to-powder ratio specimen. Presence of air bubbles (a) and a capillary structure (b) in the mass of mineral trioxide aggregate (MTA) (original magnification, $\times 180$).

detected and does not follow the upward trend found with the other ratios.

The views obtained from the SEM examination show specimens with different water-to-powder ratio with presence of air bubbles, pores, and capillary channels. This can be seen in Figs. 1–3.

DISCUSSION

This study demonstrates that the hardened material obtained when mixing MTA and water forms a porous matrix under these test conditions. This matrix retains a soluble fraction, able to be transferred to an aqueous environment. This study found that calcium hydroxide was the main compound released by MTA in water. It was also determined that within the water-to-powder ratios of this study, both solubility and porosity show a significantly increasing trend that follows the amount of water used when preparing the mix.

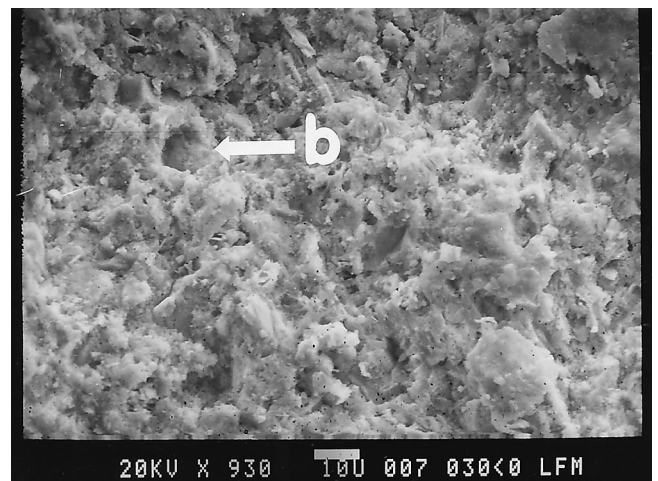


FIG 2. SEM image of a 0.30 water-to-powder ratio specimen. Irregular surface of MTA with porous capillaries (b) (original magnification, $\times 930$).

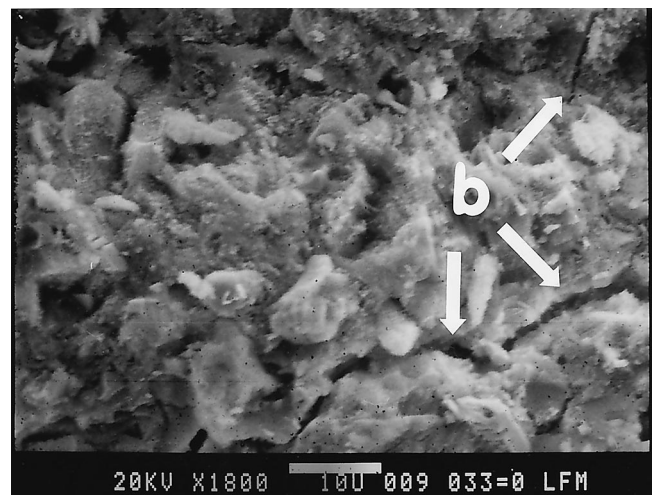


FIG 3. SEM image of a 0.33 water-to-powder ratio specimen. Capillary channels (b) across the mass of MTA (original magnification, $\times 1800$).

Some degree of porosity is characteristic of dental cements prepared by mixing powder and liquids. The porosity is due to the incorporation of microscopic air bubbles during the mixing operation (2, 3). However, with MTA, the presence of an amorphous porous and capillary structure, observed with SEM, could be another important cause of this material's porosity.

Hardened MTA mixture is influenced by several factors: quantity of water used during mixing, the mixing procedure itself, pressure used for compaction, environment humidity, and temperature (2). Some of these factors are not easy to control; it is therefore difficult to standardize methods used to determine the properties of MTA.

These results may at least be qualitatively transferable to a clinical situation, where MTA could become a releasing source of the calcium hydroxide it contains as it comes in contact with an aqueous environment. However, in any real clinical situation, only part of the MTA will be in contact with the aqueous environment (i.e. the periapical tissues). While under these test conditions, the osmotic effect would be more important because the whole spec-

imen is in contact with a large amount of distilled water. Following Standards requirements (6, 7), MTA was used after it was completely set; therefore, these test conditions differ from any clinical situation where MTA is used before its initial setting.

Calcium as hydroxide was the main chemical compound released by MTA in water. This hydroxide may be responsible for the advantageous properties that MTA (11, 12) has in contact with dental and periapical tissues. Torabinejad et al. (11, 12), reported the regeneration of new cementum over MTA as a unique phenomenon that might possibly be caused by MTA's sealing ability, biocompatibility, its high pH, or the release of substances that activate cementoblasts to lay down a matrix for cementogenesis. Holland et al. (13), who evaluated the reaction of rat connective tissue to implanted dentin tubes filled with MTA or calcium hydroxide, reported the same results for both materials and stated that it was possible that the mechanism of action of both materials might have some similarities. The present study determined that the substance released by MTA is basically calcium hydroxide, which could explain the similarities obtained in the Holland et al. study and the cementogenesis obtained in the Torabinejad et al. report (11, 12).

The release of calcium hydroxide may be advantageous (14); it is therefore logical to conclude that a high water-to-powder ratio might be beneficial. However, the amount of water incorporated in the mix is limited by its loss of consistency in the presence of excessive liquid. This limitation represents a serious management problem when transporting and compacting the material. Therefore, the 0.33 water-to-powder ratio, the one recommended by the manufacturer, would be the ideal proportion. When used in some applications, this ratio could result in a soupy mix. However, this inconvenience could be solved by waiting until the material has acquired an adequate consistency under a wet gauze (15).

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