REVIEW ARTICLE

THE SETTING MECHANISM OF MINERAL TRIOXIDE AGGREGATE

Mineral Trioksit Aggregatın Sertleşme Mekanizması

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ABSTRACT

Mineral trioxide aggregate (MTA) is a powder containing calcium silicate composed of hydrophilic particles which harden at the presence of moisture. MTA was initially introduced as a root end filling material. Due its practical advantages that include superior biocompatility, effective sealing capability, and the ability to improve regeneration of the pulp and peripheral root tissues, it is used in different clinical applications such as pulp capping, apexification, pulpotomy and perforation. Despite being a promising material in endodontic treatment, MTA is not commonly used. Long setting time is the main clinical disadvantage of MTA. The aim of this review is to provide an overview of the current literature concerning the setting mechanism of MTA, accelerators and devices used to evaluate various steps of the hardening process.

ÖZ

Mineral trioksit agregat (MTA) nem varlığında sertleşen hidrofilik parçacıklardan oluşan kalsiyum silikat içerikli bir tozdur. MTA ilk olarak kök ucu dolgu materyali olarak kullanıma sunulmuş, ancak MTA'nın üstün biyouyumluluğu, iyi kapama yeteneği, pulpa ve kök çevresi dokuların rejenerasyonunu arttırma kapasitesi gibi özelliklerinden dolayı çeşitli klinik uygulamalarda kullanım alanı bulmuştur. MTA endodontik tedavi yaklaşımlarında hekimlere yeni ufuklar açan bir materyal olmasına rağmen yaygın olarak kullanılmamaktadır. Bu durumun başlıca sebebi sertleşme süresinin uzun olmasından kaynaklanmaktadır. Bu makalenin amacı, güncel kaynaklara dayanarak MTA'ın sertleşme mekanizmasını, hızlandırıcıları ve sertleşme sürecinin farklı aşamalarını değerlendirmekte kullanılan cihazları incelemektir.

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Introduction

MTA is a powder that contains calcium silicate and consists of hydrophilic particles which causes setting under humidity conditions (1). MTA is classified in type-1 Portland cement (PS) category combined with 4:1 ratio of bismuth oxide to provide radiopacity according to the American Standards for Testing Materials (ASTM) (1-4). The main component of Portland cement material consists of mainly tricalcium silicate (3CaO·SiO2), dicalcium silicate (2CaO·SiO2), tricalcium aluminate (3CaO·Al2O3), tricalcium oxide (Ca2O3), silicate oxide (SiO2), aluminoferrite (4CaO·Al2O3·Fe2O3), and gypsum (CaSO4·4H2O) (2, 5-7). MTA was initially introduced as a root end filling material and it is used in a variety of clinical applications (such as pulp capping, apexification, pulpotomy perforation and root perforation) due its practical advantages that include superior biocompatility, effective sealing capability, and the ability to improve regeneration of the pulp and peripheral root tissues (8-15). Even though MTA sets slowly approximately in 3 to 4 hours in mouth and this might also be interpreted in favour of the material to prevent microleakage, long setting time is considered as the most important disadvantage of the material (14, 16, 17). Setting mechanism of MTA should be evaluated in order to eliminate this disadvantage (18).

Setting mechanism of MTA

Setting reaction starts with the contact of MTA powder comprising fine hydrophilic particles and water (18-20).

Hydration of MTA

Chemical reaction that leads to the setting of hydrophilic cement is called "hydration" (20-22). Components of MTA cement are partially soluble in water. Soluble components react at different speeds and rates, heat occurs during the reaction, and new products form. The resulting new products cause the setting of MTA cement and provide bonding to each other in the content of the components (19-22).

Hydration reaction is divided into different steps including mixing process, sleep process, setting process, cooling process, and condensation process (Figure 1) (20-23). The characteristics of the components in the process must be known to better understand the hydration reaction. Calcium silicates (C3S,C2S), calcium aluminates (C3A, C4AF) and calcium sulphate (CS2H) in the MTA's structure directly affects the hydration reaction (20-22).

Silicates

Silicates consist of combination of silicon dioxide (SiO2) and calcium oxide (CaO) (20-22, 24).

Tricalcium silicate - Alita (C3S)

It comprises approximately 55% of the volume of MTA cement. It provides rapid hydration and setting of the cement. It is largely held responsible for initial setting and early strength (21).

Dicalcium silicate - Axiom (C2S)

It comprises approximately 20% of the volume of MTA cement. It provides slow hydration and setting of the cement. It is largely held responsible for late strength (21).

Aluminates

Tetracalcium aluminate - Aluminite (C3A)

Alumina is the combination of calcium oxides with tricalcium aluminate (C3A) and combination of iron oxides with tetracalcium aluminoferrite (C4AF). Aluminites comprise approximately 20% of cement. During hydration, C3A reacts too fast and resists to sulphate (CS2H) (21).

Tetracalcium aluminoferrite - Ferrite (C4AF)

It balances and decreases the heat that occurs during the setting of cement. Moreover, due to the iron component, it causes coloration (21).

Calcium sulphate

It controls the effect of C3A which starts the setting reaction quickly and reduces the reaction rate. When there is no sulphate in cement (CS2H), the setting occurs very early. In addition, initial setting of CS2H controls the rise in early strength (21).

Processes encountered during cement setting
Mixing Process

In this process, aluminate and gypsum (CaSO4·4H2O) dissolve in water and react within a few minutes. As a result of rapid dissolution of gypsum added to cement, aluminates dissociated from cement forms a gel-like layer around the powder particles by reacting with water. This gel-like layer prevents the quick reaction of aluminates and, therefore, rapid setting of cement (20, 21, 24).
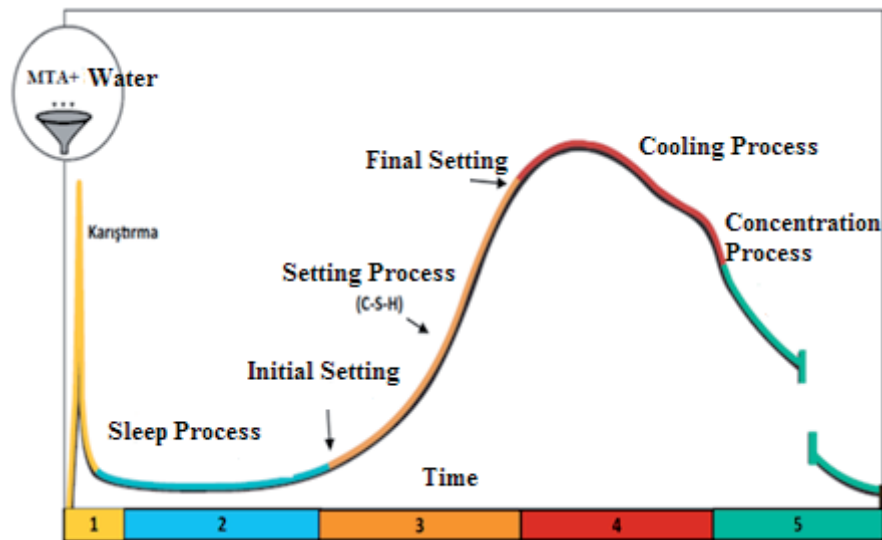

Figure 1. *Hydration reaction is divided into different steps including mixing process, sleep process, setting process, cooling process, and condensation process.*

Sleep Process

During this process, cement can be transported, placed or processed. The duration might vary with chemical additives. Rate of heat generation remains almost constant. However, reaction still continues. Cement components dissolve and saturate with water calcium in the cement (Ca2+) and hydroxyl (OH-) ions (20, 21, 24).

Setting Process

When the water of cement is oversaturated with soluble calcium ions, new hydration products begin to form. As a result of this reaction, temperature increases. It is called the beginning of setting. Once the setting starts on the surface of cement, neither the vibrator usage nor applications such as surface finishing, cannot be performed. Such interventions lead to permanent separation (20, 21). The amount of new products formed in the setting period increases constantly. The resulting product is collected around the hydrophilic particles that connect each other and surrounds the particles. Through this process the cement starts to set and solidify (20, 21). Initial setting time is the duration between the mixing of MTA powder with water and the moment when the cement start precipitation by showing physical changes (20, 21). Final setting time is the duration between the mixing of MTA powder with water and the moment when the cement solidifies (20, 21, 24).

Cooling Process

During this process, a reaction called "topochemical" occurs. Cement has become saturated in terms of components. Hydration starts at the surface of cement particles (C3S), and hydration products (C-S-H and CH) are formed at the surface. The process of cement gaining strength also begins in this period (21, 24).
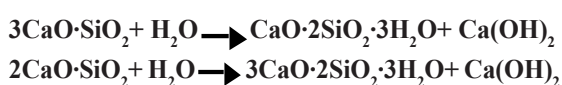
Concentration Process

In this period, the reaction slows down and the heat output is reduced significantly. Hydration

products continue to generate and develop slowly. Cement reaches the most rigid and robust structural properties that can be gained (5, 21, 24).

The chemical reactions that occur in the hydration step of MTA cement that we have described above are as follows:

As a result of the hydrolysis of calcium silicate, calcium hydroxide in the aqueous cement (CaOH) and some calcium silicate hydrate ($3CaO \cdot SiO2$, $2CaO \cdot SiO2$) are formed (5, 7, 24). The reaction of dicalcium silicate and tricalcium silicate is as follows:

$$3CaO \cdot SiO_2 + H_2O \longrightarrow CaO \cdot 2SiO_2 \cdot 3H_2O + Ca(OH)_2$$
$$2CaO \cdot SiO_2 + H_2O \longrightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + Ca(OH)_2$$

As a result of this reaction, crystal structure of hydrate is weak which forms a porous solid. This structure is called "silica gel". Ca ions in silica gel combine with the OH ion and convert into Ca(OH)2 (24).

Once tricalcium aluminate ($3CaAl2O4$) is hydrated in the presence of calcium sulphate (CaSO4), it forms etringite (or sulphoaluminat calcium) with high sulphate concentration ($6CaO \bullet Al2O3 \bullet 3SO3 \bullet 32H2O$). Etringite formation continues until all sulphate ions are used. Ettringite is converted to monosulphate once sulphate (SO2) ions are depleted.

$$3CaO \bullet Al_2O_3 \bullet 6\ H_2O + H_2O + CaSO4 \bullet 2H_2O$$
$$\longrightarrow$$
$$6CaO \bullet Al2O3 \bullet 3SO3 \bullet 32H2O$$
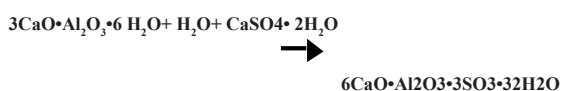
The resulting ettringite is disintegrated on the surface of cement particle and silicate hydrate coating is formed. After the destruction of the silicate hydrate coating, hydration can take years (20). It has been reported that MTA sets slowly approximately 3-4 hours in clinical conditions (3, 25). Long setting time of MTA can cause clinical problems. Researchers have added various chemicals to MTA in order to shorten the long curing time of MTA and to strengthen the structure of gritty texture and low density (26-29).

The accelerators added to MTA

Substances which are used to improve mechanical and chemical properties of cement are called "additives" (1, 30, 31). There are numerous additives with various compositions that can be used selectively (14). Because of the difficulty of indentification of each additives, additives are divided into groups and thus, their common features can be better understood (32). Chemical additives can be summarized in four groups according to their main function (29, 31, 33, 34):

- setting time accelerators
- setting time abbreviators
- those that alleviative normal or high the amount of water
- air-dragging

Accelerator/abbreviator additives are used to reduce the setting time of MTA (18, 26). MTA has similar structure to Portland cement (6, 7, 35, 36). Portland cement was first produced in 1824 to be used in the construction industry. Therefore, adding of Portland cement to make the concrete and the use of additives in this concrete had begun after that date (7, 22, 36). Considering studies with cement, the first used accelerator material is calcium chloride (CaCI2). Patents were assigned in Germany in 1873 and in England in 1885 concerning the CaCI2 cement production (6, 30, 37). Chemicals such as sodium silicate ($SiO2 \bullet Na2O \bullet H2O$), potassium silicate ($SiO2 \bullet K2O \bullet H2O$), sodium carbonate (Na2CO3), potassium carbonate (K2CO3), sodium nitrite (NaNO2), sodium aluminate (Na2Al2O4), oxalate (NaC2O4), hydrated lime, sodium gluconate (C6H11NaO7) or urea (C5H4N4O3) were used as accelerators to reduce the setting time of Portland cement (17, 21, 26). After the construction industry, Portland cement has been introduced in dentistry following a variety of heat treatments (22, 35, 38). Because of its low radiopacity, new products have developed, and finally MTA was produced (2, 4, 39). Setting time of MTA is similar to Portland cement as well as its other properties (7, 40). Therefore, chemicals which are used to shorten the setting time of Portland cement were also used to shorten the setting time of MTA (1, 17, 26, 29, 31, 36). These are calcium chloride, calcium nitrite/nitrate, calcium lactate gluconate, sodium chloride, disodium hydrogen phosphate (1, 11, 29, 31, 34, 41-44). Besides, the effects of dental materials such as sodium hypochlorite (NaOCl), saline, lidocaine and chlorhexidine gluconate on the setting time of MTA have been examined (1, 26, 27, 29, 45).

Measurement of setting time of MTA

Because of silica particles in MTA/Portland cement, setting reaction is initiated by contact with

water and described as "hydraulic cement" (1, 19, 22, 46). Initial and final setting times of cement are determined by the setting time test (penetration test) using various instruments and according to different standards (29, 31, 47).

Gillmore Apparatus (Gillmore Needle)

Gillmore apparatus is used to test the initial and final setting time of hydraulic cement (35). The apparatus consists of two horizontal arms with different weights and two stainless steel needles with cylindrical flat-end needles (Figure 2). Cylindrical flat-end needles are called "Gillmore needles". ASTM C266-04 standard is used for test of setting time performed by Gillmore needle (48). One of Gillmore needles, with which the initial setting time is measured, is 2.12 mm in diameter, weighing 113.4 g. The second needle is 1.06 mm in diameter, weighing 453.6 g and it is used to measure final setting time. Gillmore apparatus' base diameter is 76 mm, top diameter is 50 mm and thickness is 13 mm height (1, 48).

According to the ASTM C191-04 standard, it has been reported that 650 g cement has to be used during the test. Initial and final setting times are defined as the time points when there are no detectable traces of the needle on the cement surface (1, 48).
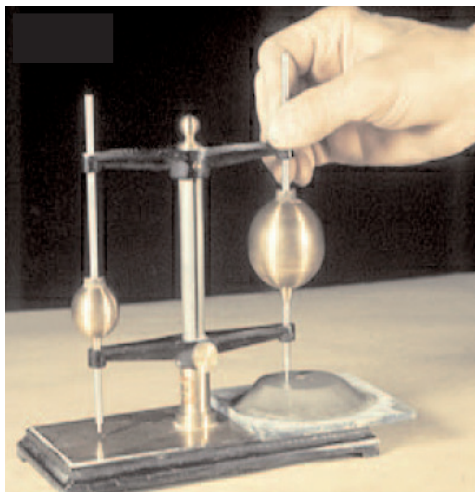

Figure 2. *Gillmore Apparatus.*

Vicat Apparatus (Vicat needle)

Vicat apparatus is one of the tools used to test the initial and final setting time of hydraulic cements (47). ASTM C191-04 standard is used for testing procedures (Figure 3) (49, 50). There are two types Vicat apparatus defined as "standard" and "automatic". Standard Vicat apparatus is set on a flat plate, and it is a tool that has a cylindrical shaft which is perpendicular to the axis of the plate. There are indicators on the cylinder. The Vicat needle is mounted on the lower end of the shaft, the shaft has a weight of 300g. Vicat needle is a cylinder with 1 mm in diameter (Figure 3 and 4).

Hydraulic cement is placed in a conical mold in Vicat apparatus with 40 mm depth, 70 mm top inner diameter and 80 mm base inner diameter. According to the ASTM C191-04 standard, it has been reported that 500 g cement has to be used during the test. After the mixed cement is inserted in the mold, measurement starts by releasing Vicat needle right after the contact with the cement surface (49).

Initial setting time measured with Vicat apparatus is the time between the contact of powder with water and when penetration is measured as 25 mm. Final setting time is considered as the time between the contact of powder with water to the moment when no circular trace of needle on cement surface is detectable (49, 50).

Automatic Vicat apparatus (Vicatronic) was designed to eliminate user-related errors, to obtain precise measurements data and to easily collect data (Figure 3) (51). Automatic Vicat apparatus has an electronic memory in which and the various standards used in the setting of cements are already stored. In addition, the test data can be archived by users (51). Standard Vicat needle has a free end operated by the user which may cause overflowing of test material beyond the mold and the deterioration of the prepared cement surface.

In automatic Vicat apparatus, a mode called "driven drop", has been designed to adjust the dropping of Vicat needle on the cement surface to eliminate such disadvantages. After selecting the appropriate mode, the test procedure can be automatized and be resumed if necessary. The measurement values are displayed on the screen and can be printed instantly using the integral printer (51).
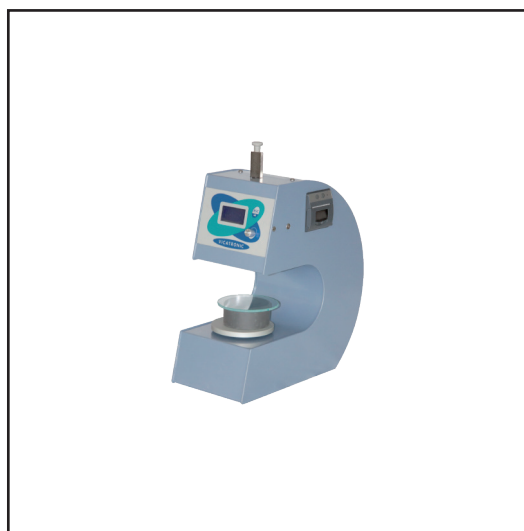
Figure 3. *Original Vicat Apparatus.*

Figure 4. *Automatic Vicat Apparatus.*

Conclusion

Hydration reaction of MTA is categorized into mixing process, sleep process, setting process, cooling process and condensation process. The physical and biochemical characteristics of the components which participate in the setting process should be well understood in order to control the long setting time which is usually measured by using traditional Vicat or Gillmore apparatus. Automatic Vicat device is a viable alternative to minimize the dependency on user skills and data loss.

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None declared

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