ABSTRACT:
Calcium silicate cements are widely used in contemporary dentistry. Their properties, such as biocompatibility, osteoinductive potential, and stimulation of pulp regeneration, are valuable for the treatment of perforations, pulp capping procedures, retrograde fillings, etc. This article aims to present the new calcium silicate cements available on the market, review the recent modifications in their composition, describe the evolution of each generation of these materials, and reveal how these changes impact their different properties and improve their characteristics. At the same time, this paper makes a brief retrospection of the first calcium silicate-based cements, which started the era of contemporary mineral trioxide aggregate materials. This article also points out some future tendencies in the development of calcium silicate cements and attempts to differentiate their generations mentioned in the literature.

Keywords: Calcium silicate cements, Mineral trioxide aggregate, New dental materials,

BACKGROUND:
The era of bioactive materials in dental practice was initiated by Mahmoud Torabinejad at Loma Linda University and Dean White. They make a patent of an endodontic material that is based on Portland cement. Its name is Mineral Trioxide Aggregate (MTA). [1] During the setting process, calcium hydroxide is produced, which leads to the release of Ca ions, which are important for the biocompatibility and bioactivity of MTA. [2]
The original MTA, ProRoot MTA Gray (GMTA) (Dentsply Tulsa Dental Specialties, Johnson City, TN, USA), has been on the market since 1998. ProRoot MTA is the first commercially available product in the form of grey-colored powder. The reason is the presence of iron (ferrous oxide). [3]
MTA has been used for conservative treatment of root fractures, pulp capping, sealing of perforations, in apexifications, retrograde filling material in apical surgeries, and as a coronal barrier in revascularization. [4] Unfortunately, the gray colour of the material affects the aesthetics. That is why later, the ferrous oxide was replaced with magnesium oxide. The modified composition of this cement is well known as white ProRoot MTA. [5]

REVIEW RESULTS:
The particle size of contemporary MTA cements is large, and this creates the disadvantage of slow setting time. MTA, being a hydrophilic cement, requires moisture to set. The presence of moisture during the setting also improves flexural strength. The setting time of gray ProRoot MTA was reported by Torabinejad et al. as 2 h and 45 min (± 5 min). Other authors reported final setting times of 140 min (2 h and 20 min) for white MTA and 175 min (2 h and 55 min) for gray MTA. [6]
All introduced commercial forms of MTA represent the first generation of bioactive materials. [7] A classification of calcium silicate-based materials based on chemistry has been mentioned in the literature. The long setting time is not the only disadvantage of calcium silicate cements. Other problems are high crystallinity, irregular shapes of the MTA particles as well as the cost. [6]
The main drawbacks of MTA are its long setting time, discoloration potential, manipulation that makes its usage difficult, and sometimes multiple visits are indicated for treatment completion. Scientists are trying to find and investigate new and different formulations to avoid the disadvantages of ProRoot MTA. The main changes refer to the modification of cement, including alternative radiopacifiers, additives, and the achievement of smaller particle sizes mentioned above. [8]
To avoid these limitations and enhance the clinical application, the composition of MTA was modified. Such changes are applied in MTA Angelus (MTA-Angelus, Angelus, Londrina, PR, Brazil), which was released in 2001, where calcium sulfate is excluded from the cement’s composition to decrease the setting time. [9]
For avoiding negative features, there is a new attempt published in the literature – changing the size of the particles. Scientists claim that a new MTA material – called MTA HP Repair is better because its particle size is nanometric. The nanometric size automatically increases the active surface for hydration, optimizes the setting time (12 min initial setting time), and favors the formation of nanoporous calcium aluminate silicate hydrate microstructure. [10] The radiopacifier incorporated in this material is calcium tungstate.

The difference between Angelus MTA and MTA Repair HP is in the replacement of distilled water with a liquid...
that contains water and another organic plasticizer that gives the product high plasticity.

Nowadays, the improved handling of MTA is due to the use of hydrogel instead of water. This is represented by Angelus MTA Repair HP (Angelus, Londrina, BR), MTA Flow (Ultradent, Utah, US), MTA Plus, and Neo MTA Plus (Avalon Biomed Inc, Bradenton, FL). The replacement of the radiopacifier (from Bismuth Oxide to Calcium Tungstate) ensures the absence of dental discoloration. Later the same company introduced two new modifications of MTA: MTA Bio in 2013 and Bio-C Pulpo in 2019.

MTA Bio is an experimental water-based cement. MTA Bio’s initial and final setting time was reported to be 11 min and 23.33 min, respectively. The material’s solubility is similar to that of MTA Angelus. [11-14]

Another modification of MTA-like cements is MTA Bio-C Pulpo, mainly indicated for pulpotomy. According to the manufacturer -Angelus, Londrina, Brazil, MTA Bio-C Pulpo contains powder and liquid. According to the manufacturer, the plasticizing material increases the plasticity of the material, which improves handling properties.[15] Another important ingredient is silicon oxide which increases viscosity. The combination of these two agents facilitates the insertion of the material into the cavity. According to some authors, the higher plasticity enables better adaptation of the MTA material to the hard dental tissues and increases the bond strength.[16] Calcium chloride in Bio-C Pulpo is the accelerator that lessens the setting time. Zirconium oxide is the radiopacifier in this material.

All modifications of MTA belong to the second generation of calcium silicate cements. Other MTA-like materials were marketed after 2006. An ideal dental repair material should possess certain additional properties such as adequate adhesive ability, insolubility, dimensional stability, biocompatibility, bioactivity, etc. New materials claiming better performance are continuously being introduced in the market to optimize the care of dental patients.

The main changes in the new MTA modifications refer to the particle size (its reduction), improvement of handling properties, and overcoming tooth discoloration after treatment with these cements. These modifications mainly include: changing the particle size distribution of the reactant powder; altering the radiopacifier; presence of a chemical accelerator. Altering the particle size distribution influences handling properties and the setting time. The smaller the particles are, the greater the surface area, and thus the faster the rate of reaction is.

The choice of radiopacifier has other implications, including whether the cement darkens over time or causes discoloration of adjacent tooth structure, e.g. when bismuth oxide is used. Different radiopacifiers provide different levels of radiopacity, and therefore radiopacity is expected to vary between products. [17] Plasticizers, also known as water-reducing agents, work by bonding to the cement particles and applying their negative charge to the cement particles.

<table>
<thead>
<tr>
<th>Modifications</th>
<th>Method</th>
<th>Commercial product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Improving setting time</td>
<td>Removal of gypsum</td>
<td>MTA angelus, MTA Bio and MTA HP</td>
</tr>
<tr>
<td></td>
<td>Reduction of particles size</td>
<td>MTA plus, Endo Sequency, Bioaggregate, Biodentine, MTA Flow TM, Ortho MTA, Retro MTA/ Bio MTA</td>
</tr>
<tr>
<td></td>
<td>Addition of accelerators</td>
<td>Biodentine, MM MTA</td>
</tr>
<tr>
<td></td>
<td>Incorporation of resin</td>
<td>Theracal</td>
</tr>
<tr>
<td>Improving discoloration: removal of bismuth oxide</td>
<td>Replacement by zirconium oxide</td>
<td>Biodentine, Endo Sequency, MTA Bio-C Pulpo, MTA Vitalclem, Medcem MTA, TMR MTA, EndocemZr, Rootdent</td>
</tr>
<tr>
<td></td>
<td>Replacement by tantalum oxide</td>
<td>Neo MTA, Bioaggregate, Endo Sequency</td>
</tr>
<tr>
<td></td>
<td>Replacement by calcium tungstate</td>
<td>MTA HP, PD MTA White, MTA BioRep</td>
</tr>
<tr>
<td>Improving handling properties</td>
<td>Addition of propylene glycol</td>
<td>MTA Angelus</td>
</tr>
<tr>
<td></td>
<td>Addition of water-soluble polymer</td>
<td>MTA Plus, Neo MTA, Biodentine</td>
</tr>
<tr>
<td></td>
<td>Addition of hydrosoluble proprietary gel</td>
<td>Theracal, BIOfactor</td>
</tr>
<tr>
<td></td>
<td>Addition of an organic plasticizer</td>
<td>MTA HP, MTA BioRep</td>
</tr>
</tbody>
</table>
CERKAMED, a Polish company, introduced BIO MTA+ in 2012. According to the manufacturer, the MTA+ particle is three times smaller than the smallest particles of material produced by other manufacturers.

The composition of MTA plus is almost similar to MTA and MTA-Angelus, and X-ray diffraction showed similar mineral phases. Its setting time is approximately 3 h (165 min), and its pH is 10.2 immediately after mixing, which increases to 12.5 after 3 h.

A new type of MTA, called BIOfactor MTA (Imicryl Dental, Konya, Turkey, 2019), has recently been introduced for pulp capping, pulpotomies, apexification, root perforation repairs, root-end filling, and apical plug procedures. The BIOfactor MTA powder is composed of tricalcium and dicalcium silicate, tricalcium aluminate, and ytterbium oxide as a radiopacifier agent. The liquid consists of 0.5%–3% hydrosoluble carboxylated polymer and demineralized water. The manufacturer claims that BIOfactor MTA has a finer powder for faster hydration, easier handling properties, stronger sealing, and shorter setting time and that it does not cause tooth discoloration. Additionally, BIOfactor MTA seems to be a lower-costing product.

MTA Flow is another calcium silicate-based material with a smaller particle size and a more purified composition than conventional MTA. MTA Flow (Ultradent Products, Inc., South Jordan UT, USA 2016) is a bioactive powder and liquid-gel system consisting of an extremely fine, radiopaque, inorganic powder of tricalcium and dicalcium silicate that sets with a water-based gel. This material, when set, forms a layer of hydroxyapatite, which induces a healing reaction. According to the manufacturer, MTA Flow may be manipulated in different powder/gel ratios, resulting in a smooth consistency and, therefore, easy compared to the other available cements. MTA Flow has an alkaline pH, low solubility, satisfactory radiopacity, biocompatibility, and induces biomineralization. [18]

The powder’s particle size is less than 10µm. The other physical characteristics of MTA FlowTM are the same as the conventional MTA. MTA Flow has a short setting time of up to 15 minutes. [18-20]

NeoMTA Plus is a new finer powder tricalcium silicate material and has tantalum oxide (Ta2O5) as a radiopacifying agent that is mixed with a water-based gel that imparts good handling properties (Avlon Biomed 2017). NeoMTA Plus (Avlon Biomed Inc, Bradenton, FL) is a material with a composition similar to Pro-Root™ MTA but with a shorter setting time, higher ion release, and nonstaining radiopacifiers. [21] The powder-to-gel mixing ratio can be varied, and a thin consistency can be used as an orthograde sealer or a thick mixture for root-end filling.

PD MTA White repair material is an ultrafine mineral trioxide aggregate repair cement formulated with calcium tungstate. The powder mixed with distilled water forms a gel, which sets in a humid environment. The material starts setting after approximately 10 minutes, and the final setting time is 15 minutes. According to manufacturer, PD MTA White is free of Bismuth oxide to avoid staining and discoloration. The second generation also includes Medcem MTA. [22]

The third generation calcium silicate cements include all modifications of Portland cement. This generation includes BioAggregate, Biodentine, Ortho MTA, MTA plus and others. [7] BioAggregate (Innovative Bioceramix, Vancouver, BC, Canada) was introduced in 2006. It was the first nanoparticle-based cement introduced commercially.

In 2008 MM MTA (Micro Mega, France) was introduced in dental practice. MMMTA, like ProRoot MTA, is mainly composed of Portland cement with a variation in the amount of gypsum in the radiopaque component (for purposes of dental diagnostics) and the addition of calcium carbonate (CaCO3) for enhanced viscosity and putty consistency. According to the manufacturers, MM-MTA presents three main advantages over MTA: MM-MTA accelerated setting time allows completion of the final restoration within a single appointment time frame (20 minutes) instead of postponing it. MM-MTA is available in a capsule form to be used in a high-frequency capsule mixer, thus assuring mixing of the correct powder: liquid ratio and ensuring the homogeneity of the material. [23]

Biodentine (BD) (Septodont, Saint Maur de Fosses; France) was developed in 2009 and was introduced by Septodont in 2011 as a novel tricalcium silicate-based cement- a bioactive dentine substitute. [24] This new biologically active material improves its penetration through opened dentinal tubules, which produces a superior bond with dentin. [25] The material is claimed to possess better physical and biological properties compared to other tricalcium silicate cements such as MTA. The presence of an accelerator reduces the setting time of Biodentine and improves its handling properties. The initial setting time, according to the manufacturer of Biodentine, is about 12 min. [26]

With the introduction of Biodentine in practice, numerous studies have been done with it. Unfortunately, there are many conflicting results regarding its physicochemical properties, such as hermetic sealing ability, solubility, dimension stability, and biological properties. [27-29]

Since 2010 there is a new direction in the development and improvement of calcium silicate-based cements. The need for a better MTA material has been led to the introduction of Ortho MTA and Retro MTA/Bio MTA Korea/ in 2010. The elimination of Portland cement and its replacement with a new generation of nanomaterials resulted in the elimination of toxic compounds and heavy metals from the composition of MTA. Also, iron content, which was mainly responsible for tooth discoloration, was minimized. These modifications significantly decreased the setting time of MTA as Retro MTA sets in 180 seconds and Ortho MTA sets in 150 minutes. RetroMTA has greater washout resistance. [30] These products are available in the form of powder comprised of hydrophilic particles that set in the presence of water and form an impermeable barrier with a primary pH of 12.5.
OrthoMTA and RetroMTA products are fine powders, presented to have an average particle size of 2.6 µm. But independent testing has shown that the powders have a median particle size of about 10 µm. [31]

Endocem Zr (Maruchi, Wonju, Korea, 2013) is another newly developed MTA-based material, the composition is similar to Pro Root, but it differs with more content of Ferrous oxide (Fe₂O₃) and the presence of Zirconium oxide (ZrO₂). The last component is not presented in ProRoot. Endocem MTA contains a fine size of pozzolan. Pozzolan is a material that contains silica or silicate (sometimes with aluminum), which in the presence of water, reacts chemically with calcium hydroxide to form calcium silicate, with good cementing properties. According to previous research, tooth discoloration can be reduced by the replacement of the radiopacifier, so the radiopacifier in Endocem Zr has been changed from bisphenol A-diphenyl glycol dimethacrylate (BisGMA) to barium zirconate (BZO₂). The last component is not presented to have an average particle size of 2.6 µm. [31]

The fourth generation of MTA cements is represented by the so-called Hyform 2.3 minutes with EndoCem. The advertised setting times of commercial MTA cements range respectively shorter final setting time (4±0.5 min). [32] The admixture of anhydrous calcium silicate (sometimes with aluminum), which in the presence of water, reacts chemically with calcium hydroxide to form calcium silicate, with good cementing properties. According to previous research, tooth discoloration can be reduced by the replacement of the radiopacifier, so the radiopacifier in Endocem Zr has been changed from bis-muth oxide to zirconium oxide. Endocem Zr has a relatively shorter final setting time (4±0.5 min). [32] The advertised setting times of commercial MTA cements range from 2.3 minutes with EndoCem. The fourth generation of bioactive materials is represented by the so-called Hybrid cements.

Another approach in calcium silicate-based cements for improvement of their manual and physical characteristics, mechanical properties, biocompatibility, and bonding is the transformation of the setting reaction to a dual-cure setting of the cement. As was mentioned above, the limitations for placing MTA are related to the long setting time and its difficult handling. For this purpose, some scientists try to develop resin-based MTA, which means they add monomers as ingredients of this pulp capping material. Light cured based MTA was also introduced to control the setting reaction. Further, 2-hydroxyethyl methacrylate (HEMA) and triethylene glycol dimethacrylate (TEGDMA) were added to the liquid component to initiate the setting reaction.

TheraCal LC has been classified as a 4th generation calcium silicate material. [3] According to the manufacturer, TheraCal LC is a light-cured, resin-modified calcium silicate filled liner designed for use in direct and indirect pulp capping and as a protective liner under composites, amalgams and other base materials. TheraCal LC performs as a barrier that protects the dental pulpal complex. Safety data sheets since 2012 reveal that the material does not contain HEMA and is composed of Portland cement (30–50%), polyethylene glycol dimethacrylate (10–30%), and barium zirconate (1–10%) (Bisco, Inc., Schaumburg, IL, USA). The material is supplied as a single component, which is applied onto the tooth in the same manner as a flowable resin. The setting reaction is based on light-initiated cross-linking of the polyethylene glycol dimethacrylate, which is a slightly water-soluble methacrylic monomer. [33] Thus, the setting reaction depends upon the polymerization of the resin component rather than a reaction with water. [34] TheraCal can also be applied to permanent teeth. In studies comparing it to Biodentine, TheraCal LC displayed in a study lower calcium ion release and a slower reaction rate. [24, 25] Bio-C Repair is a new silicate-based material which is introduced to Biodentine and ProRoot MTA, Bio-C Repair contains more carbon and oxygen than the other two materials, less calcium, but its biocompatibility is similar. [35]

MTA is also well known as a hydraulic calcium silicate cement. The presence of many MTA-based materials on the market which are applied in the field of endodontics leads to the need for a new classification. Camilleri offers two new classifications of hydraulic cements based on their clinical use and chemical composition. According to the clinical use, the cements are categorized as intracoronal, intraradicular and extraradicular. The chemical classification is important because it also means different setting reaction. [36]

The modifications of new brand materials include: changing the particle size distribution of the reactant powder; altering the radiopacifier; the presence of chemical accelerators; including of rheological modifiers; and the absence of mixing water. The distribution of particle size may be an effective method to improve the mechanical properties of the different materials. [37]

CONCLUSIONS

The range of so many new products associated with the term MTA can be confusing to the contemporary dental practitioner. There is limited published data in the literature regarding the physicochemical properties of the new commercial brand MTA-like material. Many practitioners are unsure of how the various products differ from one another. Perhaps to some extent, closely specialized dentists in the field of endodontics have more knowledge regarding these materials. Most of the data available for these new materials is from the manufacturers. Which is the best MTA cement for clinical use in dentistry available on the market?
REFERENCES:
28. Aksoy S, Ünal M. Shear bond strength of universal adhesives systems to a bioactive dentin substitute (Bio-
Please cite this article as: Tsanova-Tosheva D, Dimitrova I. Major Changes in The Development of Calcium Silicate-based Cements in Dentistry. J of IMAB. 2022 Oct-Dec;28(4):4612-4617. DOI: https://doi.org/10.5272/jimab.2022284.4612

Received: 07/02/2022; Published online: 12/10/2022

Address for correspondence:
Assist. Prof. Dr Desislava Milcheva Tsanova-Tosheva,
Department of Conservative Dentistry, Faculty of Dental Medicine, Medical University- Sofia,
1, St. G. Sofiisky Blvd., 1431, Sofia, Bulgaria,
E-mail: desitadental@abv.bg,

J of IMAB. 2022 Oct-Dec;28(4)
https://www.journal-imab-bg.org