

## Calcium Silicate Based Cements in Endodontics

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### Abstract

The introduction of Calcium Silicate Based Cements has been a great privilege in the field of Endodontics. From first introduced Portland Cement to currently available cements like Biodentine, NeoMTA Plus, the Calcium Silicate Based Cements have undergone various modification and improvisation in order to achieve better clinical outcomes. Improvement in the physical as well as biological properties has been noticed in the currently used Calcium Silicate Based Cements. They have wide applications - pulp capping procedures, apexification, perforation repair, retrograde filling material. Various cements available gives the clinician a wide range of option the get the desired outcomes. This paper gives a review of various Calcium Silicate Based Cements used in the field of endodontics.

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### Introduction

Calcium silicate-based cements for endodontic treatments have been on the market for several years. Indications for their use are mainly direct and indirect pulp capping, vital amputation, open apex and perforation filling, apexification, and retrograde canal filling<sup>1,2</sup>. These biomaterials provide a tight barrier against the migration of microorganisms, and they stimulate tissue healing without causing inflammation. Moreover, they are designed for biocompatibility and negligible neurotoxicity and cytotoxicity and often exhibit bactericidal and fungicidal properties.<sup>2,3,4</sup>

### PORTLAND CEMENT (PC)

In 1824, Joseph Aspdin patented a product called Portland cement (PC) obtained from the calcination of the mixture of limestones coming from Portland in England and silicon-argillaceous materials<sup>5</sup>. PC is an affordable

material and except for the absence of bismuth oxide and higher levels of calcium aluminate and calcium sulfate, PC and MTA have a similar main composition. PC like MTA is available as grey and white.<sup>6</sup>

Properties of Portland cement are as follows:

- Grey PC shows lower discolouration in comparison to Grey MTA. However there is no significant difference in the discolouration shown by White MTA and White PC<sup>7</sup>
- Vivaan et al in his study reported that PC shows better washout resistance compared to MTA, since MTA has greater solubility<sup>8,9</sup>
- Bioactivity is lower in PC when compared with MTA<sup>10</sup>
- PC shows antibacterial and antifungal properties similar to MTA<sup>11</sup>
- Sealing ability as a root end filling material is similar for PC (White and Grey) and MTA(White and Grey).<sup>12</sup> However sealing ability as a perforation repair material is better in White PC than in White and Grey MTA
- PC shows lower biomineralization when compared to MTA<sup>13</sup>

Limitations of Portland cement include higher release of arsenic and lead, high solubility which jeopardise seal in the long term, greater setting expansion, lower biomineralization when compared with MTA.<sup>11,13,14</sup>

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## MINERAL TRIOXIDE AGGREGATE (MTA)

MTA was introduced in 1990's since then it has been a revolutionary material in endodontics. MTA shows several desirable properties like biocompatibility, bioactivity, hydrophilicity, radiopacity, sealing ability and low solubility. The sealing ability of MTA is similar to that of Resin Epoxy Sealer.<sup>15</sup> It shows optimal healing responses due to high biocompatibility which has been observed histologically by the low inflammatory response with dentin bridge formation and also by the formation of new cementum in peri radicular tissues.<sup>16,17</sup> The flowability and porosity of MTA could be improved by using indirect ultrasonic placement technique in case of root end filling procedure.<sup>1</sup>

Studies have been concluded that an alkaline environment influences micro-hardness of MTA with setting times.<sup>19</sup> MTA products when compared to Portland cements possess smaller mean particle size and contain scarcely any toxic heavy metals.<sup>20</sup>

Types of MTA are as follows:

ProRoot MTA (Grey), ProRoot MTA (White), MTA Angelus, Micromega MTA, BioMTA – OrthoMTA, RetroMTA; MTA Plus (Grey), MTA Plus (White), NeoMTA Plus.

### ProRoot MTA

ProRoot MTA is a root canal repair material that is a one off improvement over other materials used for root canal repair. Made up of fine hydrophilic particles that set in the presence of water, ProRoot MTA notably reduces bacterial migration by sealing off all pathways between the root canal system and surrounding tissues. Its outstanding harmony with the dentinal wall allows for a predictable clinical healing response.

ProRoot MTA is predominantly composed of tricalcium silicate, Tricalcium aluminate, tricalcium oxide, and few oxides that can set in the presence of water.

Properties of ProRoot MTA:

- An in vivo study in monkeys propounded that MTA has many of the essential properties of root-end and perforation filling materials such as biocompatibility, sealing ability, and capacity of inducing regeneration of the dentoalveolar structure<sup>21</sup>.
- ProRoot MTA sets relatively slowly. Although this characteristic may allow less shrinkage, this material may wash out from the

preparation under hemorrhagic condition when it is used as a root-end filling material, which may cause treatment failure<sup>22</sup>.

- ProRoot MTA has a discoloration potential that can result in the discoloration of teeth and contains several toxic elements<sup>23,24</sup>.
- Ballal et al in a study exhibited that exposing a set mineral trioxide aggregate cement to maleic acid is more undesirable on its physical properties, when compared to exposing similar specimens to EDTA or QMix. In addition, EDTA more undesirable to the hydration of mineral trioxide aggregate cement than the other tested agents<sup>25</sup>.
- Shah et al's study shows that MTA is moderately less radiopaque than Kalzinol (reinforced zinc oxide-eugenol-based cement) and more radiopaque than IRM and Super-EBA<sup>26</sup>.
- MTA has lower initial compressive strength and its value increased with time and required presence of moisture<sup>27</sup>.

It is necessary to overpower the drawbacks of ProRoot MTA that are related to the health problems of patients. Moreover, because of its difficulty in manipulation and its high cost, many endodontists may hesitate to use it.

### MTA Angelus

MTA-Angelus is an endodontic reparative cement, incorporating mineral trioxide aggregate (MTA). It is desirable for the treatment of lateral and furcation perforations, apexification, internal resorption, pulpotomy, pulp capping, and apexogenesis. Calcium ions are released that stimulate the formation of a dentin bridge when used for pulp capping and promote biological healing.

MTA angelus is composed of Tricalcium silicate, Dicalcium silicate, Tricalcium aluminate, Bismuth oxide and Vehicle – distilled water.

Available in grey (AGMTA) and white (AWMTA), MTA-Angelus (Angelus Solucoes Odontologicas).

### Advantages

- Ions calcium release enhances formation of mineralised tissues, provide biological seal of perforations and total repair of damaged periradicular tissues.

- Capable of introducing neogenesis of periradicular cementum.
- Easy to use and properties is not affected by the surrounding moisture in oral tissues.
- High alkalinity: bactericidal.
- Low solubility and thereby does not disintegrate easily.
- Biocompatible to oral tissues as it exhibits low inflammatory response.
- Reasonable compressive strength.
- Increased radiopacity than dentin and bone.
- Faster setting time.

#### **MicroMega MTA**

Currently, clinically approved MTA products are available within the dental marketplace. However, MTA traditionally has a long setting time and an often-grainy consistency which makes placement more difficult. MICRO-MEGA® now offers the "State-of-the-Art" MM-MTA™, an endodontic repair cement that has excellent physiochemical characteristics delivered in innovative packaging. MM-MTA™ incorporates a faster set time with a pasty consistency for easy handling and placement.

Properties of MicroMega MTA:

- Biocompatible
- Formation of a protective waterproof layer, resistant to bacterial infiltration
- Excellent adhesion to the dentine
- Optimal results, even in humid conditions
- Radiopaque

#### **BioMTA**

BioMTA employs a uniquely modern production system, including filtration by Masteriser granulometer, which ensures the high quality of MTA powder (filtered by Masteriser granulometer). BioMTA offers systems for orthograde and retrograde grafting with MTA.

#### **Ortho MTA**

OrthoMTA has a fine granularity of only 2 microns. It penetrates into dental tubules and diffuses itself to the surface where it is applied. In addition it prevents micro-leakage by forming an interfacing layer of hydroxyapatite between the Ortho MTA and the canal wall. Furthermore, it exhibits a bioactive characteristic: it releases Calcium ions through the apical foramen and neutralizes the apical portion of the root. Thus forming an interfacial hydroxyapatite layer and releasing Calcium ions which induce

regeneration of the apical periodontium.

OrthoMTA is free from both shrinkage post-endodontic grafting operation and carcinogenic Cr<sup>6+</sup> ion, a heavy metal. The OrthoMTA grafting system means: reduced manual work, no micro-leakage or waste of material and last but not least, incredibly good prognosis.

#### **Retro MTA**

RetroMTA is a hydraulic bioceramic material for repair and vital pulp therapy. Portland cement is not used as a raw material. RetroMTA is a powder consisting of fine, hydrophilic particles that set in the presence of water and form a strong impermeable barrier. It contains hydraulic calcium zirconia complex as a contrast media. Setting time is 150 seconds. It has no discoloration even in case of blood contamination. Therefore, it is an ideal for aesthetic repair material. It contains no heavy metals. It has no toxicity to cells within 48 hours. This means it is a substance for vital pulp therapy. (pulp capping, pulpotomy and pulpectomy) In vivo condition, Initial Ph is up to 12.5 and down to 7.8-8.0 in 4 weeks. Ex vivo study shows it has the high potential for biomineralization. RetroMTA is composed of Calcium carbonate (60-80%), Silicon dioxide (5-15%) Aluminium oxide (5-10%), Calcium zirconia complex (20-30%).

Properties of RetroMTA includes:

- Rapid setting time: 150 seconds
- Excellent sealing ability
- Excellent bactericidal effect
- No discoloration
- No heavy metal like As, Ni, Bi, Cd
- Not toxic to cells
- Good radiopacity: Al 5mm above value

#### **MTA Plus**

MTA Plus (Prevest Denpro Limited, Jammu, India, for Avalon Biomed Inc) is a finer powder, lower-cost product that has a composition similar to tooth-colored Pro-Root MTA and is proposed for treating dental pulp (pulp capping, cavity lining, and pulpotomies) and root canals (root-end filling, perforation repair, root resorption, apexification, and obturation in pulpectomy). The MTA Plus kit includes 2 mixing liquids: a proprietary salt-free polymer gel and water. MTA Plus is indicated as a root canal sealer as well as a root-end filling material and a

pulp capping cement. By using the gel and varying the powder to gel ratio, different setting times and physical-rheologic properties can be obtained. The gel has been formulated to confer washout resistance, whereas its fine powder particle size improves handling and placement.<sup>28</sup> Although it has been suggested to avoid filling procedures using MTA-like cements to completely obturate the root canal because the collagen and flexural strength of the dentin can be negatively affected.<sup>29,30</sup>

MTA Plus is composed of Dicalcium silicate, Bismuth oxide, Calcium sulfate, Silica and vehicle- viscous polymer hydrogel/ distilled water.

Advantages of MTA Plus includes:

- Finer particle size
- Easier mixing, handling and placement
- Optional gel for stability and washout resistance
- Non-cytotoxic and anti-microbial

### Properties

	<b>MTA Plus</b>
Initial setting time (min)	45 ± 5
Final setting time (min)	55 ± 5
Radiopacity (mm Al)	6.94 ± 0.72

- The ESEM and micro-Raman analysis revealed that both MTA Plus contain a fine powder of tricalcium silicate (alite), dicalcium silicate (belite), calcium sulphate (as anhydrite). However, bismuth oxide is present in MTA Plus<sup>31</sup>.
- Ion release (Ca<sup>2+</sup> and OH<sup>-</sup>) were higher than conventional MTA<sup>31,32</sup>.

MTA Plus had a prolonged capability to release calcium and increase the local pH in comparison with ProRoot MTA. These ion-releasing properties are interlinked with its noticeable porosity, water sorption, and solubility and with the formation of a calcium phosphate layer. For clinicians, MTA Plus represents a lower-cost, bioactive tricalcium silicate material as a convenient alternative to the conventional calcium silicate MTA-like cements.

### NeoMTA Plus

Difficult manipulation and long setting time, however, limit the use of MTA. New calcium silicate-based, NeoMTA Plus, cement has been

recently introduced as fast-set root and periapical tissue repair material.

NeoMTA Plus is a new finer powder tricalcium silicate material and has tantalum oxide (Ta<sub>2</sub>O<sub>5</sub>) as a radiopacifying agent that is mixed with a water-based gel which imparts good handling properties. 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. The manufacturer states the indications include the application of this material for vital pulp therapy (pulp capping, pulpotomy or cavity liner/base), root apexification, root repair (resorption or perforation), root-end filling and sealing of root canals.

As reported in a previous study, bismuth oxide (Bi<sub>2</sub>O<sub>3</sub>), a radiopacifying agent contained in most MTA-based cements such as MTA Plus and Zirconium oxide in MTA Angelus, plays a crucial role in the hydration processes of calcium-silicates as well as in hypochlorite.<sup>33,34,35</sup> Bismuth oxide is replaced by tantalum oxide in Neo MTA Plus.

Due to fast setting, higher crystallinity, and better bioactivity of NeoMTA Plus™, it can be used as an alternative to MTA Angelus as pulp and root repair material.

### Biodentine

Biodentine has been acknowledged frequently as a promising material in the literature and serves as an important representative of tricalcium silicate-based cements used in dentistry. "Biodentine" became commercially available in 2009 and that was specifically designed as a "dentine replacement" material. It is formulated using the MTA-based cement technology and the improvement of some properties such as physical qualities and handling.<sup>36</sup> Biodentine has a wide range of applications including endodontic repair like root perforations, apexification, resorptive lesions, and retrograde filling material in endodontic surgery and as pulp capping agent in restorative dentistry.

Powder component of biodentine consists of tricalcium silicate, dicalcium silicate, calcium carbonate and oxide filler, iron oxide shade, and zirconium oxide. Tricalcium silicate is indicated as the main component and dicalcium silicate as the second core material. Zirconium oxide acts as a radiopacifier. On the other hand liquid contains calcium chloride as an accelerator and a



hydrosoluble polymer that acting as a water reducing agent.

Properties of Biodentine are as follows:

- The initial setting time of biodentine is 9 -12 minutes and final setting time to be 45minutes<sup>37</sup>.
- Compressive strength of biodentine is similar to that of natural dentine. Grech et al in his study reported that biodentine showed highest compressive strength compared to the other tested material due to the low liquid/powder ratio used in biodentine.
- Biodentine shows superior microhardness values compared to Bioaggregate and IRM<sup>37</sup>.
- Biodentine shows better push out strength when compared to MTA Plus, MTA and ProRoot MTA<sup>38</sup>.
- Zirconium oxide is the radiopacifier in biodentine, which demonstrates to have biocompatible attributes, bioinert material with great mechanical properties<sup>39</sup>.
- Biodentine with the capacity of calcium silicate materials to form hydroxyapatite crystals at the surface. These crystals can possibly increase the sealing ability, particularly when framed at the interface of the material with dentinal walls<sup>39</sup>.
- Laurent et al in his study reported that Biodentine was found to significantly increase TGF-B1 secretion from pulp cells. TGF is a growth factor whose role in angiogenesis, recruitment of progenitor cells, cell differentiation, and mineralization has been highlighted in recent research<sup>40</sup>.

### Bioaggregate

Bioaggregate is a modified version of MTA.<sup>41</sup> Bioaggregate is manufactured under controlled conditions to create a contamination and signalling-free ceramic biomaterial.<sup>42,43</sup> It has tantalum oxide as the radiopacifier instead of bismuth oxide seen in MTA.<sup>41,42</sup> Bioaggregate is a calcium silicate based material which is aluminate-free and with very levels of trace element contamination.<sup>41,42,43</sup> Initial setting time of bioaggregate is 2 to 5minutes whereas final setting time is noticed to be 4 hours, thereby permanent restoration is to be recommended to be placed after 4 hours and this serves as a clinical drawback when restoration to be done in a single visit.<sup>44</sup>

Properties of Bioaggregate are as follows:

- Compressive strength and surface microhardness of bioaggregate is lesser in comparison to other Calcium Silicate Based Cements.<sup>45,46,48</sup> Therefore limiting its applications in pulp capping and furcation repair where occlusal forces are high<sup>47</sup>
- Sealing ability of Bioaggregate is similar to MTA and is credited due to the setting expansion followed by hydration process and nano sized particles which achieve adhesion to root dentine<sup>48,49,50</sup>
- Bioaggregate manifest elevated porosity and scarcely any cracks at the cement-dentine interface compared to Biodentine<sup>51</sup>
- Incorporation of calcium and phosphate in Bioaggregate creates precipitates that resemble hydroxyapatite<sup>52-54</sup>
- Bioaggregate is biocompatible and non-cytotoxic. It has hardly any systemic and local inflammatory reaction in comparison with MTA<sup>45,55-59</sup>
- Bioaggregate has substantial antibacterial and antifungal properties against *Enterococcus faecalis* and *Candida albicans*. Moreover, also shows hard tissue-forming ability<sup>55,60,61</sup>

Inspite of the fact that Bioaggregate has comparable biocompatibility and sealing ability to MTA, accompanying hard tissue forming potential anticipated to be more significant than MTA due to the presence of phosphorus source in Bioaggregate, the prolonged setting time of Bioaggregate and deprived mechanical properties restrain conditions where it could replace MTA.

### Calcium-Enriched Mixture Cement

Calcium-enriched mixture cement is a tooth coloured water based endodontic repair cement. It has comparable applications to MTA with dissimilar chemical composition.<sup>62-64</sup> The powder of calcium-enriched mixture cement is composed of various calcium compounds.<sup>63</sup> The major chemical differences compared to MTA is the addition of phosphate.<sup>64</sup>

The particle size of calcium-enriched mixture cement powder is minute than MTA.<sup>62</sup> Properties of Calcium-Enriched Mixture Cement are as follows:

- Setting time is shorter than MTA, this could be due to the incorporation of 10% CaCl<sub>2</sub> to

#### Calcium-Enriched Mixture Cement<sup>62,65</sup>

- Compressive strength is similar to MTA Angelus but lower than ProRoot MTA and Biodentine<sup>66</sup>
- Sealing ability is similar to that of MTA. Unlike MTA it also has the potential to form hydroxyapatite-like precipitates<sup>67,68</sup>
- Cytotoxicity is similar to that of MTA<sup>69,70</sup>
- Calcium-Enriched Mixture Cement intensify the expression of mineralization-related genes, dentin bridge formation in vital pulp, encourage osteoblastic/ odontoblastic differentiation, and also induce cementum deposition when used as root-end filling materials<sup>71-74</sup>
- Biocompatibility and osteogenic potential is attributed to its ionic release<sup>75</sup>

#### TherCal

TherCal is a resin modified Calcium silicate Based Cement. It is indicated as a pulp-capping cement which induces dentin bridge and apatite-like precipitate formation.<sup>76-78</sup>

TherCal is available in the form of paste which consists of type III Portland cement, strontium glass, fumed silica, barium sulfate ( $\text{BaSO}_4$ ), barium zirconate ( $\text{BaZrO}_3$ ), and resin-containing Bis-GMA and PEGDMA.<sup>76</sup> The polymerization of TherCal is by low heat generation thereby reduce unfavourable pulpal effects when indicated for pulp-capping procedures.<sup>79</sup>

Properties of TherCal are as follows:

- Solubility is low when compared with ProRoot MTA, MTA Angelus and Biodentine<sup>76,77</sup>
- Water sorption and porosity of TherCal are lower when compared to MTA Angelus but is similar when compared to that of ProRoot MTA and Biodentine<sup>74</sup>
- It has good sealing ability<sup>76</sup>
- Push-out bond strength is higher than Biodentine and MTA in neutral and acidic conditions and lower than Glass ionomer cement, however in alkaline conditions it is higher than GIC and MTA but lower than Biodentine<sup>80</sup>
- TherCal chemically bond to dentine and induce the formation of hydroxyapatite-like crystals<sup>77,81</sup>
- TherCal being resin based cement depend primarily on micromechanical bonding

requiring acid etching and bonding, thereby contraindicated in pulp capping procedures<sup>82</sup>

The manufacturer suggests using TheraCal as a restorative liner and base and also in direct and indirect pulp capping procedures. Since TheraCal is off-white in color, its application under resin composite restoration as a liner or base is to avoid esthetic problems.<sup>83</sup> Another problem with the use of TherCal is the shrinkage and thereby causing bond failure.<sup>84</sup>

#### Endobinder

EndoBinder (Binderware, São Carlos, SP, Brazil) is a calcium alumino-silicate based endodontic cement. It has been manufactured in certain way as to incorporate the properties and clinical applications of MTA and eliminating its negative characteristics. Components like magnesium oxide (MgO), calcium oxide (CaO); and ferric oxide ( $\text{Fe}_2\text{O}_3$ ) responsible for the undesired expansion of the material and tooth darkening respectively has been eliminated from Endobinder. Among the currently available Calcium Silicate Based Cements Endobinder has shown adequate biocompatibility.<sup>85</sup>

#### Conclusions

Numerous Calcium Silicate Based Cements are available commercially as mentioned above. Various modifications have been done over the period to the latest available cements in order to overcome the limitations. Each Calcium Silicate Based Cements has its own advantages and disadvantages; thereby depending on the clinical preference the clinician should be able to decide based on the desired outcome.

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#### Declaration of Interest

The authors report no conflict of interest.

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