

Understanding mineral trioxide aggregate/Portland-cement: A review of literature and background factors

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Abstract

AIM: This was to carry out a review of the literature concerning mineral trioxide aggregate (MTA) and Portland cement with regards to clinical, biological and mechanical findings and a possible substitution of MTA through Portland cement for endodontic use. **STUDY DESIGN:** Electronic literature search of scientific papers from January 1993 to January 2009 was carried out on the MEDLINE and Scopus databases using specific key words. In total, 57 papers were identified that dealt with MTA and Portland cement in a relevant way. **RESULTS:** The review of 50 papers conforming to the applied criteria showed that MTA and Portland cements have the same clinical, biological and mechanical properties. In animal experiments and technical characterisations both materials seemed to have very similar properties. The only difference is bismuth oxide in MTA added for better radio opacity. It seems likely that MTA materials are based on industrial Portland cements mixed with bismuth oxide. More studies, especially some long-term studies comparing MTA and Portland cement, are necessary. **CONCLUSION:** The existing literature gives a solid base for clinical studies with Portland cement in order to replace MTA as an endodontic material. Portland cement could be a substitute for most endodontic materials used in primary teeth.

Background – Development of MTA

Portland cement. Portland cement (PC) is a fine powder produced by grinding cement clinker. It is classified as a hydraulic cement, which normally is, composed of 65% lime, 20% silica, 10% alumina and ferric oxide and 5% other compounds. Lime is composed of calcium and magnesium oxides. PC is produced by grinding clay and lime-bearing minerals in the correct proportions and then heating the mixture to 1,400°C. This process called calcination produces physical and chemical changes in the raw materials. The resulting "clinker" is ground to a fine powder and a small amount of gypsum is added to retard the setting process.

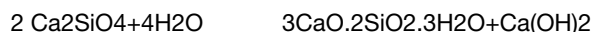
Two principle constituents are tricalcium silicate ($3\text{CaO}\cdot\text{SiO}_2$) and dicalcium silicate ($2\text{CaO}\cdot\text{SiO}_2$). Adding water to set PC results in a complicated hydration reaction as PC sets in a series of stages. First there is dispersion of clinker grain in water. Secondly hydration products eat into and grow out from surface of each grain. Thirdly setting occurs when the different clinker grains join together. Finally, hardening

occurs with further development of the gel and crystalline particles are disseminated throughout [Harrington, 2005]. Chemical expression is called alite and belite phase reaction. The simplified reaction of alite with water may be expressed as:



It is a fast reaction and causes setting and strength development in the first few weeks.

The simplified reaction of belite is:



This is a relatively slowly reaction responsible for gaining strength after one week [Taylor, 1997].

About one third of the volume of these end products is $\text{Ca}(\text{OH})_2$ (CH phases) and it is enclosed in the form of complex gels or crystalline substances. There exist also a C-S-H (calcium-silicate-hydrate) phase and an Aft (sulphatic hydrates) phases. The forces that bind the colloidal particles together in the gel are thought to be hydrogen bonds, Vander Waals forces, ionic attractions and covalent bonds such as Si-O-Si bonds. Part of the water will be consumed by the reaction but other parts of the water will be trapped in the pores. Evaporation may occur during or even after setting. This water that is lost will refill in an "osmotic-effect". During setting the continuity of the capillary system is broken. The hydration of the powder produces tricalcium silicate, tricalcium phosphate, tricalcium oxide and others [Harrington, 2005].

Dental mineral trioxide aggregate. In 1993 so called Mineral trioxide aggregate (MTA) was described for the first time in dental literature [Lee et al., 1993]. Commercial MTA materials such as ProRoot MTA (Tulsa Dental Products, Tulsa, OK, USA) or MTA Angulus (Industria de Produtos Odontologicos Ltda, Londrina, Brazil) are a mixture of Portland cement (PC), gypsum and bismuth oxide (BO). These materials contain fine hydrophilic particles of tricalcium silicate, tricalcium aluminate, tricalcium oxide, silicate oxide and bismuth oxide. Hydration of MTA material forms a colloidal silicate hydrate gel that sets in about 3-4 hours. All setting processes of MTA are very similar to the setting mechanism of PC as described above [Taylor, 1997; Camilleri et al., 2005a]. The resulting MTA gel contains CH that is mainly responsible for its biocompatibility.

Key words: MTA, Portland cement, mineral trioxide aggregate, discoloration, biocompatible.

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MTA materials have excellent potential as pulp-capping and pulpotomy medicaments, as an apical and furcation restorative material as well as preparation for apexogenesis and apexification treatments [Roberts et al., 2008]. Biocompatibility of MTA materials has been proven in in-vitro and in-vivo studies [Roberts et al., 2008]. Since 1999 MTA has been in use in paediatric dentistry, and has been used for pulp-tomies in primary teeth [Rocha et al., 1999]. Recent studies have shown that MTA materials show a significantly higher clinical and radiographic success in primary teeth pulp-tomies than any other materials [Ng and Messer, 2008].

Clinical use of MTA materials is limited by the extended setting time and by the fact that it can only be used in low stress-bearing areas [Camilleri et al., 2008b]. According to the manufacturer, and proved by clinical experience, a colour change of MTA is to be expected [Bortoluzzi et al., 2007]. Also according to manufacturer's instructions MTA materials should not be used in visible areas (above the crestal bone level). Trying to avoid discolouration grey MTA materials have been replaced by using white MTA materials [Asgary et al., 2005, Bortoluzzi et al., 2007]. Commencing in 1995 and to date, studies of physical and chemical properties of MTA materials have shown their origin to be with PC. [Torabinejad et al., 1995, Roberts et al., 2008]. PC is the primary component of MTA [Bye, 1999]. Knowing the classifications and methods of production of PC means understanding the primary structure and chemistry of MTA.

Portland cement versus mineral trioxide aggregate. The European Union (EU) standard for PC, EN 197-1 regulates the industrial production of cement in Europe (this substitutes the old British standard BS12, similar to American standard ASTM Type I). EN 197-1 makes a distinction of the material into five groups of cement (CEM I – V). Only CEM I is pure PC. The cement's hardness is expressed by numbers (from 32.5 - 52.5), showing minimal resistance to pressure (N/mm²) after 28 days. Hardness differences of cement are dependant, for example, on different particle size, meaning different grinding and sieving processes. Letters R or N stand for rapid or normal primary setting time [Bye, 1999].

The amount of gypsum (<5%) in MTA materials is brought in with the PC. Content of heavy metal ions in grey PC and is mainly caused of selected clinker and characteristics of the burning processes (pollution through coal or oil-products). White PC is manufactured from purest raw materials (kaolinite with very low iron content) and requires a burning temperature of about 1,600°C. As this temperature normally cannot be achieved by burning coal, gas is mostly used here as an energy source. This is why white PC contains very few heavy metal ions and soluble Chrom IV. Once set, PC is a very inert system and heavy metal ions can only be washed out with difficulty. As mentioned above, hydration products of PC contain CH (portlandite, CH) and almost amorphous calcium silicate hydrate (C-S-H). PC is an outstanding controlled, well investigated and very designed product [VDZ, 2008, Taylor, 1997].

The first study which used ordinary PC as a reference material to MTA has been published in 2000 [Estrela et al., 2000]. Since then numbers of studies used PC as material of reference. These studies showed that the only difference between PC and MTA materials is the bismuth oxide [Funteas et al., 2003, Camilleri et al., 2005b, Islam et al., 2006].

Aim of the review

The aim of this review is to evaluate the dental literature concerning MTA materials and Portland cement. Specific interests are:

- to compare clinical, biological and mechanical findings about MTA and PC,
- to develop recommendations for further investigations,
- to develop recommendations for the use of MTA / PC in pediatric dentistry,
- to assess if it is possible to replace the expensive commercial MTA materials through PC especially for pulp-tomies in pediatric dentistry.

Materials and methods

Literature search criteria. A literature review was performed for articles published between January 1993 and January 2009. The internet database PubMed (www.ncbi.nlm.nih.gov/entrez) and Scopus (www.scopus.com) were used to search for the keywords:

- MTA,
- mineral AND trioxide AND aggregate,
- Portland cement.

No language exclusion was been made. All articles identified (57) received a full text examination for relevance. Two articles had to be excluded as they had nothing to do with dentistry. Five selected articles used Portland cement as a reference to new experimental cements and were accordingly excluded in this review. No formal evaluation was made of the publications, and this review has a narrative approach. The review therefore considered the 50 articles for analysis.

Results

Relevant articles. There has been an increasing number of published articles on MTA / Portland cement since the appearance of the first paper in 2000. Thus there was 1 in the year 2000, 2 in 2001, 1 in 2002, 2 each in 2003 and 2004, but 9 in 2005, 10 in 2006, 9 again in 2007 and rising to 13 in 2008.

Chemical, physical and mechanical studies. The microleakage and sealing ability has been evaluated using bacterial penetration [Tselnik et al., 2004, De Deus et al., 2006,], and all sorts of capillary flow porometry [Islam et al., 2005, Hong et al., 2008, Costa et al., 2008] and airbubble leakage models have been used [De Deus et al., 2007]. In all of these stud-

ies there was no statistically significant difference between MTA and PC. Compressive strength, dimensional change, setting time, pH and radiopacity have been compared [Islam et al., 2006, Bidar et al., 2007; Storm et al., 2008]. MTA and PC have similar properties. The only significant difference is a lower radiopacity of PC. The difference between white and grey MTA is more significant than that between white MTA and white PC. X-ray diffraction analysis of crystalline phases of grey and white MTA and PC showed absence of bismuth ions and presence of potassium ions in grey PC. Grey MTA contained a significant higher amount of iron when compared with white MTA [Song et al., 2006]. MTA and PC showed both no [Estrela et al., 2000; Miyagak et al., 2006.] or little [Sipert et al., 2005] antimicrobial activity. White MTA and white PC showed significant lower arsenic levels than grey MTA and grey PC [Duarte et al., 2006, Monteiro et al., 2008].

Biocompatibility and toxicity studies. Biocompatibility evaluation of MTA and PC has been reported in 12 articles. In vitro tests showed comparable tissue reactions with both grey MTA and PC [Saidon et al., 2003]. No genotoxic effects with white MTA and Portland cements have been reported when using alkaline single cell gel [Ribeiro et al., 2005], human ECV 305 endothelial cells [De Deus et al., 2005], cell proliferation [Camilleri et al., 2005b] and growth of hamster ovary cells [Ribeiro et al., 2006]. Cytomorphology of in vitro osteosarcoma cells and quantification for cytokine by ELISA showed very similar results for MTA and PC, as well as PC accelerated by calcium chloride (CaCl₂) [Abdullah et al., 2002].

In vivo test were made with rat implanted dentine tubes, either filled with MTA, PC or CH. The results were similar for all tested materials [Holland et al., 2001a].

Pulpotomized dog teeth were capped with MTA or with PC. Both materials showed similar comparative results in histomorphological analysis. Effects such as forming a complete hard tissue bridge, maintaining pulp vitality and absence of inflammatory signs were found [Holland et al., 2001b, Menezes et al., 2004]. A pulpotomy study evaluated and compared white MTA (wMTA), white PC (wPC), beta-tricalcium phosphate (BCP), ferric sulphate (FS) and formocresol (FC) when used in primary pig teeth. It showed equally good results in wMTA, wPC and BCP with normal pulp tissue preservation. FC and FS showed irritated pulp tissue and more inflammatory pulp response [Shayegan et al., 2008]. Genotoxic effects of MTA and PC were evaluated in peripheral lymphocytes from 10 human volunteers by alkaline single cell gel assay. Exposure to MTA or PC does probably not increase the level of DNA lesions in human peripheral lymphocytes [Braz et al., 2006].

Characterization of MTA / PZ. The different MTA materials (white ProRoot, grey ProRoot, white MTA-Angulus, grey MTA-Angulus and PC) showed different numbers of small particles and different range of size distribution [Komabayashi and Spangberg, 2008a]. PC has a cumulative percentage

of particles diameter between 0.5 and 3 µm, which may be able to penetrate dentine tubuli [Komabayashi and Spangberg, 2008b]. Comparative analysis of MTA materials and PC using plasma emissions spectrometry [Funteas et al., 2003], Energy Dispersive Analysis by X-ray [Camilleri et al., 2005a] and X-ray diffractometry [Islam et al., 2006] showed similar constitution and no significant difference between MTA and PC. Using Energy Dispersive Analysis by X-ray as well, differences have been found between MTA materials and PC. Less gypsum, heavy metals (Cu, Mn, Sr) and chromophores (Fe³⁺) in MTA than in PC. These results correspond exactly with the procentual reduction of the amount of PC in MTA through the addition of Bismuth oxide. Looking to the comparative results for materials (Cem II: mixed cement = Portland cement / limestone, CEM I: pur grey PC and white MTA) it was obvious that such results would have been obtained. Grey and white MTA and especially CEM II PC are, as materials, not comparable with regard to iron or heavy metal ions [Dammachke et al., 2005].

The role of bismuth oxide (BO). Testing PC and a linear increasing amount of BO, mechanical strength, porosity and flaw size have been compared [Coomaraswamy et al., 2007]. Strong linear correlations were found between relative porosity, dry and strut densities and BO content. The amount of gypsum in PC is relatively smaller when BO is added to MTA materials. This has probably had an influence on hardness and solubility of MTA [Danesh et al., 2006].

Detailed analysis of white MTA compared with white PC showed some differences: unhydrated MTA showed no aluminate phase. This and the presence of BO affected the precipitation of CH in the hydrated past (Large aeras of CH were present in the PC and absent in the MTA sample). MTA has also a weaker microstructure [Camilleri et al., 2007]. BO has an influence on the release of bismuth- and calcium ions. MTA releases, over several weeks, more calcium ions than white PC while white PC releases nearly no bismuth ions [Camilleri et al., 2008a]. MTA materials show a linear correlation between radioopacity and amount of BO. No difference has been found in the amount of BO and cytotoxicity [Kim et al., 2008]. MTA, pure PC and a mixture of PC and BO have been compared in subcutaneous connecting tissue reactions. A positive correlation between BO concentration and radioopacity was observed. Histological evaluation suggested all materials were biocompatible [Coutinho-Filho et al., 2008].

Previous reviews. Two reviews have been made contrasting both, MTA and PC.

One, a review of the constituents and biological properties of MTA materials [Camilleri and Pitt Ford, 2006] found 53 articles on biocompatibility and 13 articles on constituents of MTA. No specific distinction was made between MTA and PC articles. Reviewing every MTA article from 1990 to August 2006 gave 156 articles.

The second review, gave an overview concerning most sci-

entific work published but in English (only) [Roberts et al., 2008]. Their conclusion was, that MTA materials could not be substituted by PC. Basing this statement as they did on only two articles [Abdullah et al. 2002, Islam et al. 2006], can be questioned, as these authors emphasize exactly the opposite.

Important for pediatric dentistry is the latest review giving an overview on use of MTA, not PC, in paediatric dentistry [Sirinivasan et al., 2009]. The review of 100 relevant papers has shown that paediatric dentists have successfully employed MTA in a variety of endodontic and restorative applications. But these authors claim there is a paucity of studies designed to conform with CONSORT guidelines in terms of power, blinding, control groups and recall times.

Accelerated MTA and PZ. MTA materials and PC have been mixed with calcium chloride (CaCl₂) [Bortoluzzi et al., 2006a, Bortoluzzi et al., 2006b, Wiltbank et al., 2007], with Jodoform [deMorais et al., 2006] and with methylcellulose [Ber et al., 2007]. All of these modifications brought advantages in setting time, but also disadvantages, for example in calcium ion release and in hardness.

Specification of PC. Only in 5 of the 57 articles reviewed an exact description of the tested PC has been made. In 18 of the articles a commercial name or the name of the manufacturer have been given to describe the tested PC. The rest of the articles only mentioned the use of ordinary or pure PC.

Summary

MTA materials have an excellent potential for endodontic use. Their good radioopacity keeps them indispensable for certain clinical applications. PCs seem to have a biocompatible nature and similar technical characteristics like commercial MTA materials. A disadvantage of Portland cement is that it has lower radioopacity and its main advantage is its very low cost. The use of very expensive commercial dental MTA materials for primary teeth endodontics in an attempt to substitute less efficient or toxic materials is economically not possible and therefore an ethical problem. Different published articles analysing the constitution and properties of commercial MTA, found very few differences in its chemical constitutions compared with PC. It is interesting that no information has been published regarding details that led to the precise delineation of the present MTA materials. Claiming that white MTA is the result of a new investigation is not tenable. Changing usage from grey to white MTA was simply changing from grey to white PC as base material to mix with bismuth oxide. Precise information about production processes are not available. PC contains the same principle chemical elements as MTA, with similar mechanisms of action and physical properties and biocompatibility. Accordingly several articles recommended starting substituting MTA materials by PC for clinical use. Only very few articles enable an exact identification of the actual type of PC used in those studies. The hydration characterizations as

described of MTA materials are very close to the hydration characterizations of portland cement that have been well investigated. Further investigations concerning the role of BO in chemical reaction and biocompatibility have started and are very necessary.

As yet unsolved is the occurrence of clinical discolouration after the use of MTA materials. Clinical studies testing PC on discolouration are desirable. It should be mentioned that to date PC has undergone more tests to show its suitability for clinical use, then MTA materials in 1995. PC intended for clinical use should be tested for any pollution effects by heavy metal ions, should be sieved to unique particle size and sterilized, all to fulfil practices of good manufacturing.

PC has a great potential to be used as a root-filling material. However, a serious selection of the material for clinical use and subsequent tests shall ensure that as used PC meets the medical device requirements set out by appropriate medical regulation authorities.

Conclusions and Recommendations:

- Investigations are necessary in the role of bismuth oxide being responsible for discolourations of MTA treated teeth, and it's role in hydration.
- It would seem that it should be possible to start with well designed, clinical studies using pure Portland cement.
- Studies using Portland cement should precisely describe the type of tested cements.
- Studies to compare MTA and Portland cement as endodontic medicament in paediatric dentistry are necessary.
- A debate should be encouraged to determine the level of substitution needed for formocresol by Portland cement.

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