HHS Public Access

Author manuscript

Dent Mater J. Author manuscript; available in PMC 2018 January 31.

Published in final edited form as:

Dent Mater J. 2017 January 31; 36(1): 8–18. doi:10.4012/dmj.2015-425.

Calcium silicate-based cements and functional impacts of various constituents

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Abstract

Calcium silicate-based cements have superior sealing ability, bioactivity, and marginal adaptation, which make them suitable for different dental treatment applications. However, they exhibit some drawbacks such as long setting time and poor handling characteristics. To overcome these limitations calcium silicates are engineered with various constituents to improve specific characteristics of the base material, and are the focus of this review. An electronic search of the PubMed, MEDLINE, and EMBASE *via* OVID databases using appropriate terms and keywords related to the use, application, and properties of calcium silicate-based cements was conducted. Two independent reviewers obtained and analyzed the full texts of the selected articles. Although the effects of various constituents and additives to the base Portland cement-like materials have been investigated, there is no one particular ingredient that stands out as being most important. Applying nanotechnology and new synthesis methods for powders most positively affected the cement properties.

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CONFLICT OF INTEREST

Mohammad Ali Saghiri and Mehrdad Lotfi hold a US patent for Nano Cement.

Keywords

Calcium silicate-based cements; Dicalcium silicate; Mineral trioxide aggregate; Nanotechnology

INTRODUCTION

Recent advances have generated wide interest in the regenerative dentistry particularly Endodontics to restore or supplement the function of the maxillofacial system during disease. Among inorganic biomaterials, which recently have received great attention in regenerative medicine[1–3], calcium silicate-based cements (mineral trioxide aggregate (MTA); MTA like materials) are cements or root canal sealers that are prepared based on a composition of calcium and silicate. MTA is prepared by mechanical mixing of Portland cement, bismuth oxide, and gypsum powders[4]. Since Portland cement is the major constituent of MTA, there are also studies regarding differences between MTA and Portland cement[5–8]. There are four major components in Portland cement: tricalcium silicate [$(CaO)_3$•SiO_2; C3S], dicalcium silicate [$(CaO)_2$•SiO_2; C2S], tricalcium aluminate [$(CaO)_3$•Al_2O_3; C3A], and tetracalcium aluminoferrite [$(CaO)_4$•Al_2O_3•Fe_2O_3; C4AF]. According to a study by Dammaschke *et al.*[6], the gypsum content of MTA is approximately half that of Portland cement, which indicates that a prolonged maximum setting time is required for MTA. Moreover, there were also fewer aluminum species found, and this also results in longer setting times. In another study Portland cement was significantly more soluble, achieved lower microhardness values, and was less radiopaque than MTA[9].

MTA has some drawbacks such as long setting time[10], poor handling characteristics[11], and costs[12]. The promising results obtained from MTA research have encouraged further investigation of materials with similar favorable properties that are less expensive, as well as have fewer drawbacks when compared with the original MTA. These investigators claimed that their new materials had a similar composition to MTA with some modifications that may improve some of the clinical drawbacks of MTA. Some of the new formulations and their components are presented in Table 1[12–15]. In addition to formulation of the calcium silicate base materials, some other parameters also affect the final product properties including setting reaction and particle size. Thus, this review aimed to discuss the role of all the constituents in calcium silicate-based cement formulation, along with the parameters of their reactions and physical properties.

MTA cement has similar hydration mechanisms as Portland cement[16]. The surface of the particles is the first part that undergoes hydration. The hydration process continues by mixing more powder and liquid, followed by ion release from the calcium silicate surfaces. Camilleri believed that after mixing tricalcium silicate and dicalcium silicate with water they contribute to calcium hydrate's formation[17], whereas Dammaschke *et al.*[6] reported that tricalcium aluminates hydrogenation is the main cause for formation of calcium hydrate. However, characteristics of the mixture depends on the ratio of powder to liquid, environmental humidity and pH, compaction pressure, mixing technique, material's thickness, temperature, type of media, and the time interval between mixing and evaluation[6, 9, 18–37].

Calcium silicates based materials are engineered and additives are included to improve a specific characteristic of the base material. For example, if tricalcium silicate (C3S) and dicalcium silicate (C2S) mixtures employed as the main components instead of conventional mineral trioxide aggregate (MTA)[36], there would be some drawbacks including long setting time, intrinsic radiopacity, and alterations in handling characteristics. Thus, additives are included with the base material to give the desirable properties of the final product. However, a concern always remains that the additives may adversely affect biocompatibility, physical properties, and clinical applications of the base material.

Smaller particle size and increased surface area of white mineral trioxide aggregate (WMTA) compared with Portland cement[12,38–40] play important roles in its physical and chemical properties, partly because of better and more rapid hydration[38]. Initial and final setting time of WMTA were reported to be more than 40 min and 3 h, respectively[26,41], which is not desirable when WMTA is used as a root-end filling material[42]. A number of studies evaluated MTA's particle size and shape, which attribute to its handling ability demonstrating finer particles for WMTA compared to two types of Portland cement[6,28,43–53]. It is also reported that WMTA's good mechanical and biocompatibility properties are due to the uniform distribution of particles and their surface morphology[6]. The gray mineral trioxide aggregate (GMTA) particle size reported to range from 1–10 μm[28], whereas Camilleri[49] reported WMTA's particle size to be less than 1 to 30 μm. As particle size decreases the amount of surface contact that is ready to get mixed with the liquid increases contributing to faster setting time, greater early strength and improvement in handling. MTA particles as small as 1.5 μm have been reported and in comparison with some dentinal tubules diameter they are finer[51]. This might be a significant feature while the sealing ability of MTA are important in hydration action[51].

A nano modified version of MTA has been patented in the USA and claimed to set faster with acceptable resistance to acidic environments by adding a small amount of strontium and reducing particle size (US Patent Application No. 13/211.880). Saghiri *et al.*[40,54] analyzed the physicochemical properties of a Nano WMTA (NWMTA) and compared it with WMTA. In their study surface and biocompatibility area, setting time and microhardness were evaluated. These studies indicated significant differences in surface area, setting time and surface hardness for both cements. Despite the lack of significant differences in chemical composition of WMTA and NWMTA, the initial setting time of NWMTA was approximately 6 min. The difference in initial setting time might be attributed to the total surface area of NWMTA that was greater than WMTA specimens. Thus, NWMTA may react more rapidly with water and prevent washout of the cement plug before final setting. NWMTA had significantly greater microhardness and lower porosity than WMTA at different pH[54]. Moreover, a smaller particle size also leads to a smoother surface, which causes less irritation when in direct contact with living tissues[55]. This review was performed to determine the impact of various constituents of MTA, as a calcium silicate based cement. The main aspects perused in this review include: 1) Determining the exact role of each major component including tricalcium silicate and dicalcium silicate. 2) What physical and/or mechanical properties of MTA are attributed to these major components. 3) What are the common additive constituents to basic elements of MTA?

MATERIALS AND METHODS

The review purpose

The present review was conducted to evaluate the role of calcium silicate's constituents on its properties. Specifically, the potential effects of tricalcium silicate, dicalcium silicate, tricalcium aluminate, tertacalcium alumino ferrate, strontium salts, calcium sulfate, bismuth oxide, zirconium oxide, tantalum pentoxide, calcium chloride, methylcellulose, barium sulfate and their role in hydration of MTA were reviewed.

Inclusion and exclusion criteria

The inclusion criteria considered all articles including review studies, *in-vitro* and *in-vivo* studies, and case reports in peer reviewed journals published in English up to September 2015 that evaluated the role of tricalcium silicate, dicalcium silicate, tricalcium aluminate, tertacalcium alumino ferrate, strontium salts, calcium sulfate, bismuth oxide, zirconium oxide, tantalum pentoxide, calcium chloride, methylcellulose, barium sulfate in calcium silicate based materials. The properties of each component are briefly discussed.

Search methodology and strategy

An electronic search was conducted of the PubMed, MEDLINE, and EMBASE *via* OVID databases using appropriate terms and keywords related to the use, application, and properties of calcium silicate-based cements. A hand search also was conducted of issues cited by the reviewed articles. The following keywords were used to identify a list of potential papers: mineral trioxide aggregate composition, tricalcium silicate, dicalcium silicate, tricalcium aluminate, tertacalcium alumino ferrate, strontium salts, calcium sulfate, bismuth oxide, zirconium oxide, tantalum pentoxide, calcium chloride, methylcellulose, barium sulfate and their role in hydration of MTA. Two independent reviewers obtained and analyzed the full texts of the selected articles. The relevant full text articles and the reference lists of the related articles were evaluated to supplement the search as well. The assessment of the eligibility and finding related data were performed by two reviewers independently. A third reviewer was selected for further discussion and final agreement on any conflict met in the mentioned processes (Fig. 1). Of 1666 articles, 96 articles met the inclusion criteria and this review summarizes the role of calcium silicate-based cements constituents and outlines why each component was added to the mixture.

RESULTS AND DISCUSSION

Tricalcium silicate

Tricalcium silicate has been used on its own or with additives as bone cement[56–59], as a die material for the plastic-forming process by extrusion when admixed with cellulose based polymers[60], as a posterior restorative material[61], and as a root fi material[62]. The tricalcium silicate has been postulated to be able to replace the cement component in the MTA due to similar composition and bioactivity of the material[63,64], advantageously shortened setting time compared with MTA[64], and being more bioactive with respect to time[65].

Tricalcium silicate cement possesses good injectability, good bioactivity and moderate *in vitro* degradability, thus ultimately the body may be able to replace the implanted cement by natural tissue[56]. The addition of up to 30% calcium carbonate, calcium sulfate, and calcium chloride resulted in improvement in physical properties of tricalcium silicate cement[57,59,62], as well as enhancing the bioactivity and degradability of the resultant composite material[57]. Tricalcium silicate cement is presently used as the main constituent of a number of proprietary brands namely Biodentine (Active Biosilicate TechnologyTM, Septodont, Saint-Maur-des-Fossés Cedex, France) and Bioaggregate (Verio Dental, Vancouver, Canada). Its hydration greatly influences the setting and development of early strength. However, dicalcium silicate contributes to late strength, due to its lower reactivity (Fig. 2). The main product of the reaction of tricalcium silicate with water is calcium silicate hydrate, a nearly amorphous material, which primarily contributes to the strength and volume stability of cement-based materials[66,67]. Numerous studies have been conducted to understand various steps and mechanisms in the hydration of tricalcium silicate[67,68]. More detailed review on kinetic mechanisms of TRICALCIUM SILICATE could be find elsewhere[69]. Briefly, tricalcium silicate is more reactive because of its higher calcium content, and the presence of an oxide ion in the lattice. During clinker grinding, first step of partial dissolution of tricalcium silicate involves hydration of superficial oxide ions that leads to a hydroxylated tricalcium silicate surface.

$$3Ca^{2+}+\mathrm{SiO_4}^{4-}+\mathrm{O}^{2-}+\mathrm{H_2O}\rightarrow 3Ca^{2+}+\mathrm{SiO_4}^{4-}+2OH^{-}$$

The tricalcium silicate in Portland cement reacts with water through a dissolution-precipitation process to form calcium silicate hydrate gel and calcium hydrate[67]. This reaction is typical of calcium silicates and has been reported both for industrial Portland cement[67], and for MTA[49,50]. Both hydrated cements were composed of un-reacted cement particle surrounded by a rim of hydration product (Fig. 2). The calcium silicate hydrate of the hydrated tricalcium silicate cement had a ratio of Si/Ca of approximately 0.40 as opposed to the higher Si/Ca ratio of the Portland cement[63]. The lower Si/Ca ratio was due to a greater abundance of calcium in tricalcium silicate, which can result in a greater deposition of hydroxyapatite when the material is in contact with a physiological solution[63]. The ettringite and monosulphate phases were absent from the tricalcium silicate as the aluminate phase was not present in the un-reacted powder[63]. Tricalcium silicate reacts with water (roughly) according to the reaction:

$$2Ca_3\mathrm{SiO_5}+6\mathrm{H_2O}\rightarrow 3\mathrm{Ca\ \ O}\cdot 2\mathrm{SiO_2}\cdot 3\mathrm{H_2O}+3Ca\,(OH)_2$$

Tricalcium silicate can be manufactured by sol-gel[70], or spark plasma sintering methods using pure raw materials[71]. Calcium oxide and silicon oxide are used as raw materials to avoid aluminum which has been linked to Parkinson's and Alzheimer's disease[72]. Furthermore, tricalcium silicate ceramics sintered by spark plasma sintering have higher density and superior mechanical properties compared with those fabricated by pressureless sintering process[71].

Dicalcium silicate

There are five polymorphs of dicalcium silicate, designated α, α'H, α'L, β, and γ[73]. Dicalcium silicate hydrates much more slowly than tricalcium silicate and is responsible for the latter's strength. The impure form of dicalcium silicate is referred to as belite. Belite is stabilized by foreign ions in solid solution with respect to γ-dicalcium silicate. The γ-dicalcium silicate (fabricated by hydrothermal synthesis) is not hydrated in synthetic body fluid solution and exhibits a slower formation of carbonate-containing hydroxyapatite on the surface when compared with β-dicalcium silicate (fabricated by sol gel)[74]. Generally, there is a higher content of foreign ions taken into solid solution than with alite. Cations, such as Al^{3+}, Fe^{3+}, Mg^{2+} and K^{+}, and anions, such SiO_4^{2-} and PO_4^{3-}, stabilize dicalcium silicate at high temperatures. No link was found among the impurity content, dislocation density, and reactivity of different kinds of dicalcium silicate[75].

Calcium silicate hydrate is the principal phase that forms during the hydration process. The cement's pH values change from an initial pH 11 to a high pH 13[64]. It is hypothesized that the newly developed β-dicalcium silicate cement might possess the *in vitro* bioactivity and biocompatibility since its components are similar to that of MTA and SiO_2-CaO-based bioactive glass. The cement could quickly form bone-like apatite spherulites after immersion in a simulated body fluid at 1 h.

Dicalcium silicate releases silicon ions, which have important roles in skeletal development and repair[76]. Dicalcium silicate possesses excellent bioactivity when used as a coating material for titanium alloy substrates[77,78]. The *in vitro* and *in vivo* bioactivities and biocompatibilities of such implants increase when they are coated with α-tricalcium phosphate (αTCP) doped with dicalcium silicate[79].

Dicalcium silicate could be fabricated by hydrothermal synthesis[74], plasma spary (on titanum coatings), and sol-gel methods[64,74]. In sol gel method reagent grade tetraethyl orthosilicate and calcium nitrate are used as precursors for SiO_2 and CaO, respectively. Nitric acid is used as the catalyst and ethanol as the solvent. The molar ratio of calcium nitrate to tetraethyl orthosilicate was 3:2. Detailed description of the fabrication of the powder has been given in an earlier article[64]. Dicalcium silicate also can be fabricated by hydrothermal synthesis[74].

Dicalcium silicate cement exhibits high apatite-forming activity and low degradation in acidic environments when used as a root-end filling material[80]. Regarding its cytotoxicity, dicalcium silicate cement is significantly superior to the traditional root-end filler, MTA[81]. Dicalcium silicate cement is also a model system for drug release[74]. Dicalcium silicate cement has adequate biological properties and can be used as a root-end filling and pulp capping material, and exhibits good bioactivity and biocompatibility in *in vitro* studies[74,82–86].

Tricalcium aluminate

Tricalcium aluminate is known to have the fastest hydration rate amongst the main components of Portland cement (Portland cement). Thus, it accelerates the hydration process and improves the short-term compressive strength of tricalcium silicate/tricalcium

aluminates composites when compared with that of pure tricalcium silicate[67,87]. The reactivity of tricalcium aluminate with water is decreased by the incorporation of sodium, but evidence suggests that its early reactivity is increased[75]. Tricalcium aluminates can be manufactured by sol-gel[88], solid state reaction[89], combustion synthesis[90,91], and polymeric precursor processes[92].

Calcium aluminoferrite has little effect on the physical properties and hydration of calcium silicate cements, but precipitation of an insoluble layer of hydrated iron oxide upon the calcium aluminoferrite crystal surface, forms a barrier to further the hardening without any contribution to the strength.

In single-phase, tricalcium silicate has several undesirable shortcomings including setting time (3–4 h), similar to MTA, and low mechanical strength at the early stage[59]. The effect of tricalcium aluminates on physical and *ex vivo* biological properties of the tricalcium silicate/tricalcium aluminate mixtures derived from MTA was investigated by adding tricalcium aluminate into tricalcium silicate[93]. The addition of tricalcium aluminate to tricalcium silicate accelerated the hydration process, reduced setting time and improved the compressive strength. Tricalcium aluminate both in regular and nano form enhanced the osseous reaction of the implanted material may be due to its high calcium content[40]. The order of main constitutes of Portland cement and MTA base materials hydration rate during the first few days are: C3A>C3S>C2S.

Strontium salts

Incorporation of a small amount of strontium into bone cements can create or increase bioactivity and bioconductivity properties[94,95]. Strontium fluoride, strontium oxide or hydroxides are used in fast setting MTA formulations[96].

The ingredient strontium carbonate improves osteopromotive properties, and bio-activeness of the dental cement, while preventing agglomeration or clustering of the nanoparticle constituents. The difference between the constituent elements of NWMTA and WMTA was related to the presence of strontium with its uniform distribution on the surface[12,54]. Micrographs from the back scattered electron mode illustrated hydrated products, better interlocking solid and better nucleation of calcium silicate hydrate needle in NWMTA than that observed in WMTA. However, other compounds were not significantly different[54].

Strontium shares the same physiological pathway as calcium in the human body and can be deposited in the bone mineral structure[97]. Strontium carbonate has a solubility close to that of calcium carbonate, making strontium carbonate resorbable. Strontium was found to exert beneficial effects on the osteoblastic activity[98], and enhancing cell viability and differentiation[99]. The main limitation with using strontium appears to be the high cost.

Calcium sulfate

Calcium sulfate hemihydrate and dehydrate are widely recognized as safe and bioactive implant materials and have been successfully used in bone substitution[100–102]. The hemihydrate form of calcium sulfate reacts with water and creates a resorbable phase. The reaction results in the growth of interlocking needle-like crystals that form the set cement.

Besides serving as a bone filler, calcium sulfate has also been used as a drug delivery material[100,103].

Calcium sulfate, typically in the form of dehydrate (gypsum), may be incorporated as a mean of controlling the rate of setting reaction[104]. Comparatively, Portland cement contains approximately double the amount of calcium sulfate as that found in MTA[105,106]. ProRoot MTA containing calcium sulfate has a much longer setting time (3–4 h) than MTA Angelus (about 15 min) without calcium sulfate because the calcium sulfate, as a setting retarder, preferentially reacts with tricalcium aluminate to produce a layer on the cement surface and delays the hydration process[107].

Radiopacifier

Calcium silicate cements have intrinsic radiopacity values ranging from 0.86–2.02 mm aluminium (Al)[26,108,109], while higher than the 3 mm Al is recommended by the International Standards for dental root canal sealing materials (ISO 6876 Section 7.8 2002). Radiopacifying agents need to be added to make the cement distinguishable from the surrounding anatomical structures[110,111]. The first radiopacifier used in MTA was bismuth oxide, while alternative radiopacifiers with a high relative molecular mass have been suggested including gold powder, silver/tin alloy[112], barium sulfate[112–114], iodoform[113,114], zirconium oxide[113,114], zinc oxide[112,114], and calcium tungstate[114].

Bismuth oxide

Bismuth oxide size affects physical properties of the hydrated MTA like cements[52]. Strong linear correlations were observed between relative porosity, dry and strut densities and bismuth oxide content. Bismuth oxide drastically affected the strength of Portland cement, varying the compressive strength from 82.1 to 28.7 MPa as the bismuth concentration increased from 0 to 40% by weight[20]. In addition, other studies have failed to observe undesirable effects associated with the addition of bismuth oxide to Portland cement in terms of biocompatibility[108,115,116], compressive strength[109], cytotoxicity and genotoxicity[117].

Radiopacifiers such as gold and silver/tin alloys added to Portland cement were considered suitable substitutes for bismuth oxide[118], as their chemical characteristics and physical properties were similar to those of ProRoot MTA. Other radiopacifying agents, such as calcium tungstate and zirconium oxide, have also been considered as potential radiopacifiers in combination with Portland cement[114].

Zirconium oxide

Investigation of the replacement of bismuth oxide with zirconium oxide in MTA, and evaluation of the radiopacity and physical properties of varying zirconium oxide levels (0 to 50%) were performed. The materials' microstructures, radiopacity, strength, setting time, water uptake, solubility, sorption and porosity of the specimens were evaluated[119]. These studies indicated that Portland cement with replaced 30% zirconium oxide resulted in optimum combination of properties. This material exhibited radiopacity, compressive strength, setting time, water uptake, solubility and sorption comparable to ProRoot MTA.

Both microscopy and the evaluation of porosity from the solubility and sorption experiments indicated a degree of porosity consisting mainly of capillary pores and entrapped air voids[119]. The same group investigated the hydration characteristics of 30% zirconium oxide in Portland cement and reported that it acted as an inert filler and did not react with the hydration by-products of Portland cement[120]. Zirconium oxide is used as radiopacifier with glass ionomer cements[121], and Biodentine (Septodont). Similar efficacies in the clinical setting were observed when the clinical, radiographic, and histologic responses of the pulp-dentin complex after direct capping with the Biodentine and MTA in human teeth were investigated[122].

Tantalum pentoxide

Bismuth can induce discoloration when used as a radiopacifying agent. In order to avoid discoloration, tantalum pentoxide or zirconia of non-discoloration induced radiocifying material were used[123]. Zirconia is used in other BioAggregate family products to increase the radiopacity. However, tantalum pentoxide is used as a radiopacifying agent in BioAggregate for more biocompatible properties.

Barium sulfate

Barium sulfate is a compound characterized by an extremely low solubility and is clinically used as a radio-contrast agent for X-ray imaging and other diagnostic procedures[124]. The addition of barium sulfate to glass ionomer cement at low concentrations reduced working and initial setting times, but further addition delayed the setting reaction of glass ionomer cements. However, both compressive strength and surface hardness decreased with increasing concentrations of the radiopacifier[125]. The effects of barium sulfate on the physiochemical properties of Portland cement are yet to be investigated.

Barium sulfate is used as a radiopacifi in composite resins and novel endodontic cements (*e.g.*, Epiphany; Pentron, Wallingford, CT, USA), and has the advantage of its white color. Cathers *et al.*[126] have reported barium sulfate to be nondegradable, with possibly toxic effects. Smith *et al.*[127] found that barium ions are not biocompatible, and severe foreign body reactions occurred in tissues contacting this material. Up to 20% barium sulfate mixed with Portland cement showed poor radiopacity, thus greater amounts of radiopaque agent should be added to meet the ISO recommendations. This may negatively affect the already poor biocompatibility of the material[113].

Methylcellulose

The addition of methylcellulose to these cements improves the tensile strength properties, while degrading the compressive properties and thermal stability. The larger the methylcellulose content, the greater is the effect[128]. Higher concentrations of methylcellulose have the capacity to entrap air and retain higher amounts of H_2O, altering Portland cement strength and retarding the setting reaction. Both of these effects are a function of concentration[129].

The methylcellulose anti-washout admixture binds water molecules within the cement, accomplishing two things. First, the addition of methylcellulose to cement increases the

cohesiveness and plasticity of the material, making it easier to handle. Second, using an admix of methylcellulose should increase the washout resistance, a benefit when placed in a contaminated site. This rate of washout resistance increases as the amount of anti-washout admixture is increased[129].

Calcium chloride

Calcium chloride ($CaCl_2$) is one of the most effective accelerators of hydration and setting in tricalcium silicate and Portland cement pastes[130]. The accelerative power of $CaCl_2$ may come, at least in part, from its ability to flocculate hydrophilic colloids, such as calcium silicate hydrate, facilitating diffusion of ions and water through the initial calcium silicate hydrate layer due to an increased mean pore diameter, and thus allowing a higher rate of hydration during the early diffusion-controlled period[131]. The accelerative power of this salt increases with increasing concentration, with a practical dosage being 1–2% by weight of cement[131,132]. A percentage greater than 2% $CaCl_2$ adversely affects the cement by increasing the risk of drying shrinkage and reducing ultimate strength[133].

MTA materials and Portland cement have been mixed with $CaCl_2$[134–136], and with methylcellulose[137]. Ber *et al.*[137] illustrated that the combination of methylcellulose and $CaCl_2$ significantly reduced the setting time of the Portland cement. Most importantly, the 1% methylcellulose/$CaCl_2$ combination had a significantly shorter setting time while the methylcellulose had a tendency to retard the setting reaction of Portland cement. In a study by Kogan *et al.*[27], the setting time of MTA was found to decrease to 20–25 min if sodium hypochlorite (NaOCl) gel, K-Y jelly, and 5% $CaCl_2$ were used as additives, but the compressive strength was also found to be much lower than MTA mixed with water.

Researchers examining the effects of salts on Portland cement and C3S hydration have arrived at the following sequences of cations and anions, ranked in order of their effectiveness as accelerators[138–140]:

$$Ca^{2+} > Sr^{2+} > Ba^{2+} > Li^{+} > \mathrm{K}^{+} > Na^{+} \overline{Cs}^{+} > Rb^{+}$$
$$Br^{-} \overline{Cl}^{-} > \mathrm{SCN}^{-} > \mathrm{I}^{-} > NO^{-3} > \mathrm{ClO}^{-4}$$

CONCLUSIONS

According to the studied overviewed, the role of major and minor constituents of calcium silicate-based cements the following conclusions can be drawn (Fig. 3):

- Tricalcium silicate and dicalcium silicate are the main constituents of the calcium silicate based cements that are believed to be promising biomaterials with applications in several aspects of endodontic surgery. Tricalcium silicate hydration greatly influences the setting and development of early strength. While dicalcium silicate hydrates much more slowly and is responsible for the latter's strength. In addition to formulation of the calcium silicate-based materials, some other parameters including setting reaction, liquid to powder mixing ratio, and particle's morphology should be considered when engineering an ideal material.

Further studies are necessary to determine the influence of its constituents on the final properties and shortcomings of the base material.

- Although the effects of various constituents and additives on Portland cement-like materials have been investigated, there is no one superior material that impacts on the ideal properties of these materials. The literature review indicates that a large volume of research is focused on developing the main drawbacks of MTA, the handling characteristics, degradability, and setting time[10,11,27,40,42,134–136,141–146]. However, the concern would always remain that additives may adversely affect biocompatibility, physical properties, and clinical applications of MTA.
- Applying nanotechnology and new synthesizing methods for powders positively affected the cement properties. Moreover, there are still many chemical components that could be used to improve the base formulation of the currently used materials. Realistic and detailed studies of the mechanism of each ingredient action in the mixture will enable advances in the properties of these materials.

ACKNOWLEDGMENTS

This publication is dedicated to the memory of Dr. Hajar Afsar Lajevardi, a legendry Iranian Pediatrician (1955–2015) who passed away during the writing of this article. We will never forget Dr. H Afsar Lajevardi's kindness and support. She was the only clinician-scientist with a particular focus on infectious diseases of children in Iran. The authors also acknowledge the unrestricted award from Research to Prevent Blindness to the Department of Ophthalmology and Visual Sciences, Retina Research Foundation, P30 EY016665, P30 CA014520, EPA 83573701, and EY022883. In addition, we thank Drs. Ali Mohammad Saghiri and Mona Momeni Moghadam for their assistance with the manuscript. Also, none of the supporters have had any role in direction of this project.

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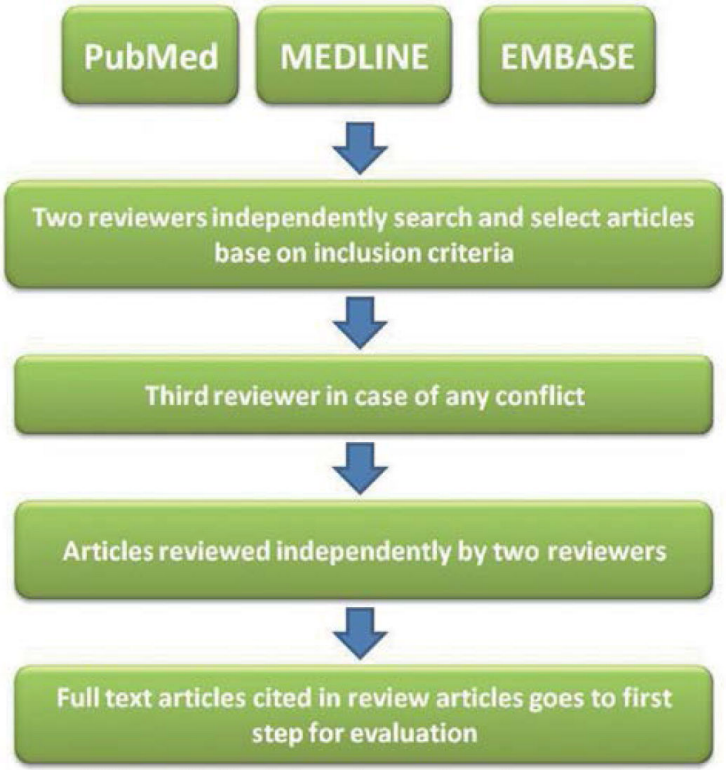

Fig. 1.
Process used to select and review articles.

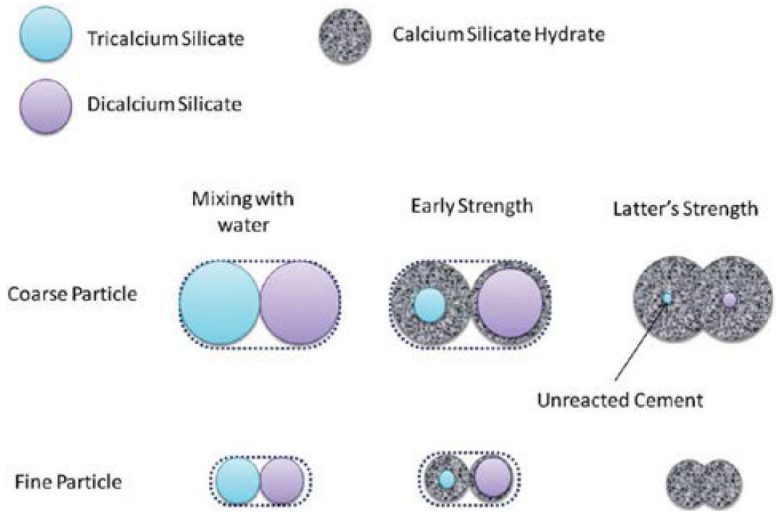

Fig. 2.

Hydration sequence and the effect of particle size on hydration of C3S and C2S.

C3S hydration greatly influences the setting and development of early strength. On the other hand, C2S contributes to late strength due to its lower reactivity.

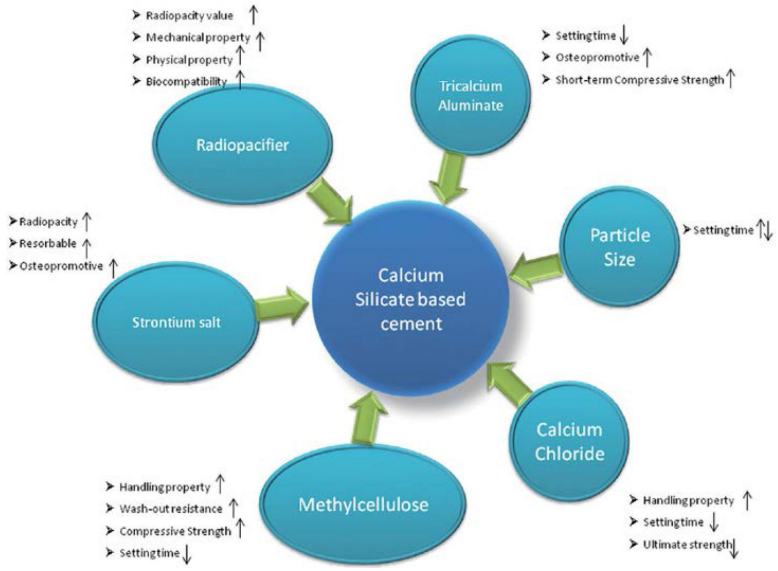

Fig. 3.

Components added to calcium silicate-based cements to improve their intrinsic properties. The effect of each component is briefly presented here.

Table 1

The calcium silicate cement constituents used in endodontics[12–15)]

Name of Ingredients (%)	Portland cement	Bioden-tine	MTA	Angelous MTA	White MTA	Nano WMTA	Biaoaggr-egate	Grey MTA	Grey Angelous MTA
Calcium silicate oxides (Ca_3SiO_5 and Ca_2SiO_4)	94.9	80.1	75.6	74.5	34.1	65	65	30.3	30.1
Magnesium phosphate ($Mg_3(PO_4)_2$)	***	***	***	***	0.9	***	***	2.3	***
(Bi_2O_3)	***	***	21.6	14.0	56.7	17	***	58.8	38.8
Calcium carbonate ($CaCO_3$)	***	14.9	***	***	0.9	***	***	***	3.9
Calcium phosphate ($Ca_3(PO_4)_2$)	***	***	***	***	1.6	***	6	1.0	***
Calcium silicate (Ca_2SiO_4)	***	***	***	***	1.7	***	***		1.0
Calcium magnesium aluminum ($Ca_2MgO.\ 2AlFeO.\ 6SiO.2O_5$)	***	***	***	***	***	***	***	2.9	4.2
Barium zinc phosphate ($BaZn_2(PO_4)_2$)	***	***	***	***	***	***	***	***	3.4
Tantalum Pentoxide (Ta_2O_5)	***	***	***	***	***	***	25	***	***
Silicon Oxide (SiO_2)	***	***	***	0.5	***	***	4	***	***
Zirconium Oxide (ZrO_2)	***	5.0	***	***	***	***	***	***	***
Tricalcium Aluminate ($Ca_3Al_2O_6$)	0.8	***	***	2.0	***	4	***	***	***
Calcium oxide (CaO)	***	***	***	8.0	***	***	***	***	***
Strontium carbonate ($SrCO_3$)	***	***	***	***	***	3	***	***	***
Gypsum ($CaSO_4•2H_2O$)	***	***	***	***	***	5	***	***	***