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Hydraulic Cements for Various Intra-coronal Applications: Part 1

Abstract: Hydraulic cements are unique materials that set in the presence of water and do not deteriorate when wet and, as such, they lend themselves to be used in a range of endodontic procedures. Various products are available, and a classification is helpful to guide the clinician. Hydraulic cements may be used in three different locations namely: intra-coronally (pulp capping and barrier regenerative endodontics); intra-radicular (root canal sealer and apical plug); and extra-radicular (perforation repair and root-end filler). This article is the first of two parts and reviews the chemistry of these materials and their intra-coronal use.

CPD/Clinical Relevance: Hydraulic cements are indicated for several procedures in clinical endodontics and their efficacy is supported by an increasing body of evidence.

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Hydraulic cements are a unique type of material that sets in the presence of water and does not deteriorate when wet. They originate from the construction industry and the Portland cement used as a binder for concrete. Portland cement is composed of tricalcium silicate, dicalcium silicate, tricalcium aluminate and calcium sulphate. The first reports of the use of Portland cement in dentistry date back to the 19th century when it was used as an endodontic filler.^{1,2} However, this invention was not taken further until it was re-introduced by Torabinejad in 1993^{3,4} as a root-end filling material⁵ and for perforation repair.⁶ This material was called mineral trioxide aggregate (MTA) and, as suggested by the patent, was made up of a mixture of Portland cement and bismuth oxide in a 4:1 proportion. It was the hydraulic nature of

Portland cement that initiated the interest in its use in endodontics.

The first MTA to be marketed was ProRoot MTA (Dentsply-Sirona, Tulsa, OK, USA). This material was the only one in clinical use for several years until the development of MTA Angelus (Angelus, Londrina, Brazil) in 2001. These materials were originally indicated for root-end surgery and the repair of root perforations, but, with time, MTA was extended for other uses in endodontics,⁷ which have subsequently led to various material developments (Figure 1). The newer materials were developed to address key challenges with the clinical use of these materials.

Over the years, both components of MTA have been changed and the newer materials use alternatives to both the Portland cement and bismuth oxide. The main shortcoming of

Portland cement is in its manufacture, which results in the inclusion of trace elements, such as chromium, arsenic and lead, all of which have been shown to be present in a number of commercially available dental cements.^{8–13} The inclusion of trace elements can be counteracted by using cements made in-house whereby laboratory grade raw materials are burnt under controlled conditions, for example, materials made by Angelus (personal communication). Furthermore, the aluminium contained in the calcium aluminate component of Portland cement may be leached in solution and has been shown to be detrimental to organ function when tested in small animals.^{14–16} The elimination of trace elements and aluminium can be achieved by the use of pure tricalcium silicate, and this has brought forward several new materials that are based on tricalcium silicate rather than Portland cement. These developments are shown in Figure 1.

As bismuth oxide is unstable and changes colour from yellow to light brown and black on contact with various solutions used in endodontics, it has been linked with tooth discolouration.^{17,18} Furthermore, it interacts with collagen in tooth structure,¹⁹

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Figure 1. A timeline showing the key material developments for hydraulic cements showing the introduction of materials such as iRoot (Bioceramix Inc. Vancouver, Canada), Biodentine (Septodont, Saint Maur de Fossés, France) and the Endosequence/Totalfill range (Brasseler, Savannah, GA, USA/FGK, La Chaux-de-Fonds, Switzerland), commonly known as bioceramics.

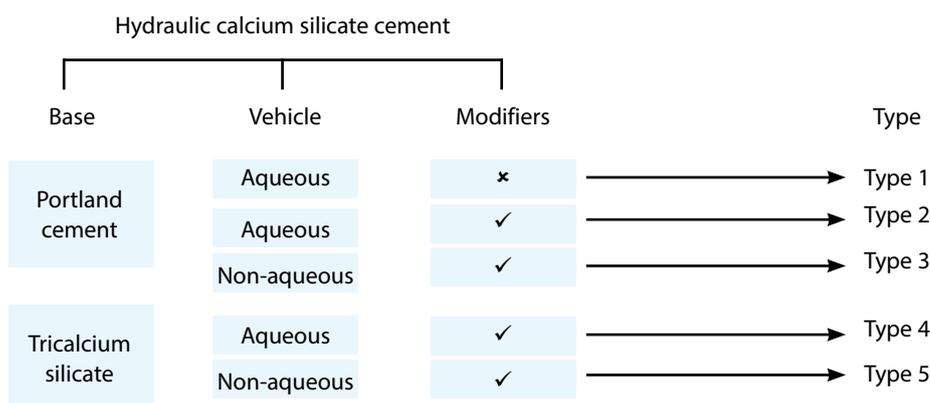


Figure 2. Classification of hydraulic calcium silicate cements based on their chemistry (adapted from Camilleri²⁷ classification) showing the five different material types available clinically.

formaldehyde formed as part of resin setting²⁰ and blood²¹⁻²³ to form a dark precipitate. Light,^{17,24,25} a lack of oxygen^{24,25} or the presence of carbon dioxide¹⁷ can all contribute to the colour change. The migration of bismuth oxide from the material to the tooth structure also results in tooth discolouration.²⁶ The newer materials are mostly bismuth oxide-free and use alternative radiopacifiers to enable visualization of the materials radiographically. Such materials include MTA Angelus (Angelus), which includes calcium tungstate as an alternative radiopacifier and Totalfill BC (FGK Dentaire, La Chaux-de-Fonds, Switzerland) and Biodentine/BioRoot (Septodont, Saint Maur de Fossés, France) with zirconium oxide instead of bismuth oxide.

Product development has seen additives being included in the materials to modify their handling and improve their physical properties, thus enabling the optimal characteristics for each specific use. As there are a number of materials now available, a classification would be helpful to guide the clinician. One proposed classification subdivides the materials based on the

chemistry of the cement base,²⁷ which can be Portland cement or synthetic tricalcium silicate, whether the cement is mixed with water (aqueous) or a non-aqueous vehicle and sets by interaction with environmental fluids. It also subclassifies materials depending on whether additives are included. This produces five types of clinically available materials as shown in Figure 2.

Section summary

MTA, a derivative of Portland cement, was the first hydraulic material to be introduced for use in endodontics. Subsequent product development, which includes changes to the cement, radiopacifier and the inclusion of additives, has led to the number of products now available to the clinician.

Material chemistry and hydration

The most important feature of these materials is the setting mechanism and their interaction with the clinical environment. When the cement is mixed with water, hydration reactions ensue

and, in the case of Portland cement, which consists of both silicates and aluminates, three concurrent hydration reactions lead to the material setting (Figure 3).

The materials based on pure tricalcium silicate only undergo the first equation shown in Figure 3. The end product of the hydration of tricalcium silicate is calcium silicate hydrate and calcium hydroxide, while that of Portland cement also includes ettringite and monosulphate. It is the formation of calcium hydroxide that has widened the scope of use of hydraulic cements in endodontics because it renders the material very reactive, particularly with the substrate with which it is in contact. This, however, varies depending on the specific material use. The main substrates include dentine, where elemental migration occurs at the tooth to material interface,²⁸⁻³⁰ with the alkalinity of the material permitting the elemental exchange, and also material penetration into the dentinal tubules.^{30,31} The interaction with blood and tissue fluids, often termed bioactivity, has been postulated to result in the deposition of calcium phosphate crystals resulting from the reaction of calcium hydroxide with phosphates in blood and tissue fluids.³² This is similar to the interaction of bioglass.³³ The formation of calcium phosphate can only happen *in vitro* with synthetic tissue fluids. Clinically, the formation of calcium carbonate is preferred³⁴⁻³⁶ because of the availability of carbon dioxide in the blood formed during the respiratory cycle.

Clinical uses

The hydraulic calcium silicate cements have a variety of uses in clinical endodontics. Different materials have been developed to enable specific use. The materials also interact differently depending on the substrate with which they are in contact. These cements can be used in three different locations namely intra-coronally, intra-radicularly and extra-radicularly as shown in Figure 4.

Section summary

The interaction of the hydraulic cements with the environment into which they are placed makes them ideal materials to be used in the three endodontic locations namely intra-coronally, intra-radicularly and extra-radicularly.

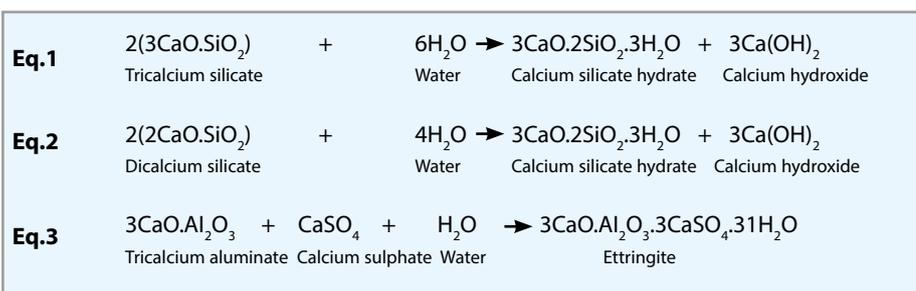


Figure 3. Chemical equations representing the three concurrent hydration reactions that occur when Portland cement sets.

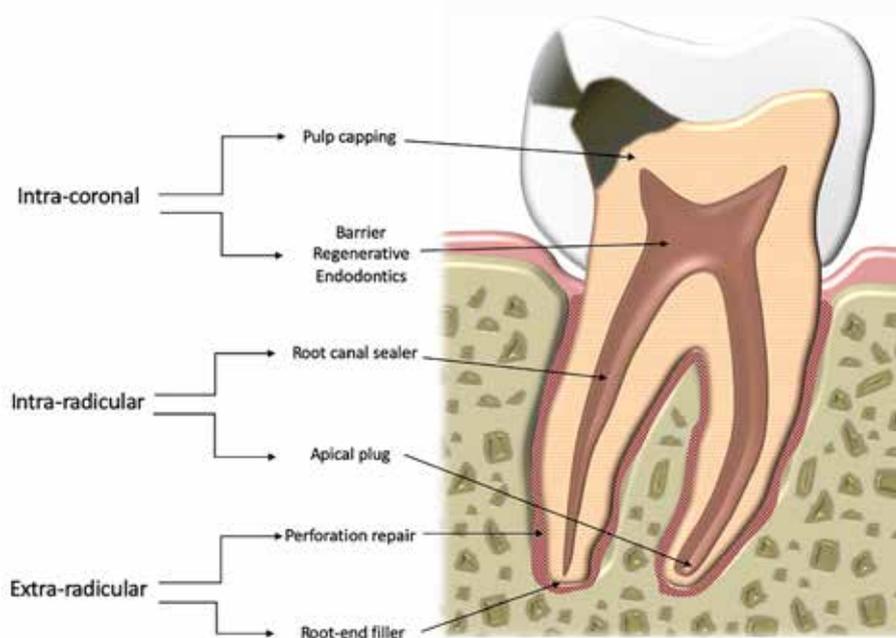


Figure 4. Specific uses of hydraulic cements in clinical endodontics. (Reproduced with permission from Camilleri.²⁷)

Intra-coronal materials

Intra-coronal materials are used for pulp-capping procedures and as barrier materials in regenerative endodontic therapy. They are in contact with coronal tooth structure, blood and restorative materials. Their use for these procedures is also suggested by the European Society of Endodontology (ESE) for vital pulp therapy³⁷ and regenerative procedures.³⁸ The requirements of such materials are listed in Table 1. One material that may be used for both indications is Biodentine (Septodont).

Material chemistry

Biodentine comprises a powder (80% tricalcium silicate, 15% calcium carbonate

and 5% zirconium oxide³⁹) and a liquid (water, calcium, chlorine, sodium and magnesium⁴⁰). The specific surface area of this product is higher than that of other commercial hydraulic cements because the powder is finer.³⁹ Biodentine is classified as a Type 4 cement because its cement base is tricalcium silicate, includes reaction modifiers and is mixed with water for hydration.

The setting reaction of Biodentine is similar to that of tricalcium silicate cement with the formation of calcium silicate hydrate and calcium hydroxide. However, there are some modifications due to the presence of calcium carbonate, which acts as a nucleating agent and also enables the early release of

calcium ions into solution. The hydro-soluble polymer reduces the water demand and this leads to improved physical and mechanical properties of the material,⁴¹ and also its handling. Calcium chloride accelerates the setting reaction,⁴¹ thus making Biodentine suitable as a pulp-capping material.

The phase composition of Biodentine gives it a very specific ordered microstructure.⁴² This is due to a hydration reaction product being formed and deposited around the calcium carbonate particles (Figure 5).

Material properties

Although Biodentine may have restricted moisture availability when used as a pulp-capping material, it has been shown that the hydration proceeds normally.⁴³ The presence of calcium hydroxide produced from the hydration of the material⁴⁴ is important for pulp healing. Biodentine has been shown to cause specific pulpal reactions⁴⁵ with favourable cell proliferation and alkaline phosphatase activity of human dental pulp cells,^{46–48} allows the expression and release of dentine matrix proteins,⁴⁹ has an anti-inflammatory potential,⁵⁰ induces pulp regeneration capacity⁵⁰ and enhances mineralized tissue formation.^{51–53} This product also allows reactionary and reparative dentinogenesis⁵⁴ and has been shown to enhance proliferation and odontoblast differentiation of human stem cells.^{54,55}

- Compressive and flexural strengths sufficient to support the overlying restorative material
- Elastic modulus similar to that of dentine
- Dimensionally stability
- Coefficient of thermal expansion close to that of dentine
- Adequate radiopacity
- Ability to form a seal with dentine
- Non-irritant to the pulp (biocompatible)
- Antimicrobial
- Easy to mix and handle
- Quick setting
- Chemically and physically compatible with the restorative material used to restore the cavity

Table 1. Requirements of materials that may be used for intra-coronal indications.

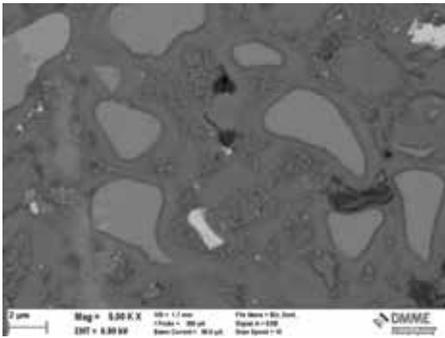


Figure 5. Scanning electron micrograph of Biodentine showing the material microstructure. The calcium carbonate particles can be seen as nucleating agents with the hydration product of calcium silicate hydrate around the particles. Zirconium oxide is also visible as discrete particles. (Reproduced with permission from Grech *et al.*⁴²)

The calcium-releasing ability of Biodentine contributes to its antimicrobial properties.⁵⁶ Prior dentine cleansing by an antimicrobial solution, such as sodium hypochlorite, is suggested and supported by the ESE position statement³⁷ as Biodentine has been shown to be rendered ineffective against multispecies microcosm biofilm⁵⁷ indicating the need to reduce the microbial load prior to application of the material over the dentine. This also enhances the bond strength of the Biodentine to caries-affected dentine.⁵⁸ The use of 17% ethylene diamine tetra-acetic acid (EDTA) applied for 1 minute resulted in a reduction in the gap at the tooth to material interface.³⁰

The interaction of Biodentine with tooth structure leads to chemical bonding of the material to dentine. The alkalinity created by the calcium hydroxide produced as the Biodentine hydrates results in mineral exchange at the tooth–material interface.³¹ Phosphorus from the tooth structure is released, and calcium phosphate has been shown to be deposited at the interface.^{29,30} Calcium carbonate formation on the material surface, as a result of the interaction between the calcium hydroxide and carbon dioxide present in any contacting blood, has been demonstrated.³⁶

Biodentine uses zirconium oxide as a radiopacifier, so tooth discolouration is prevented, unlike materials containing bismuth oxide.

The restoration of the tooth with composite resin over Biodentine requires



Figure 6. (a) Presentation of Biodentine with the powder in a capsule and the liquid in a vial. (b) The liquid is introduced to the powder. (c) The mixed homogeneous material.

fastidious clinical technique because Biodentine should not be etched directly. The etch destroys the surface microstructure and results in enhanced leakage through the Biodentine resin–composite interface.⁵⁸ Selective etching of the tooth structure and bonding to enamel and dentine is thus suggested. The use of self-etch does not improve bond strengths and self-etch primers should be avoided.^{58,60–61} Alternatively, Biodentine can be used as a temporary filling material and the tooth can be restored in a second visit.⁶²

Presentation

Biodentine is supplied as a powder and a

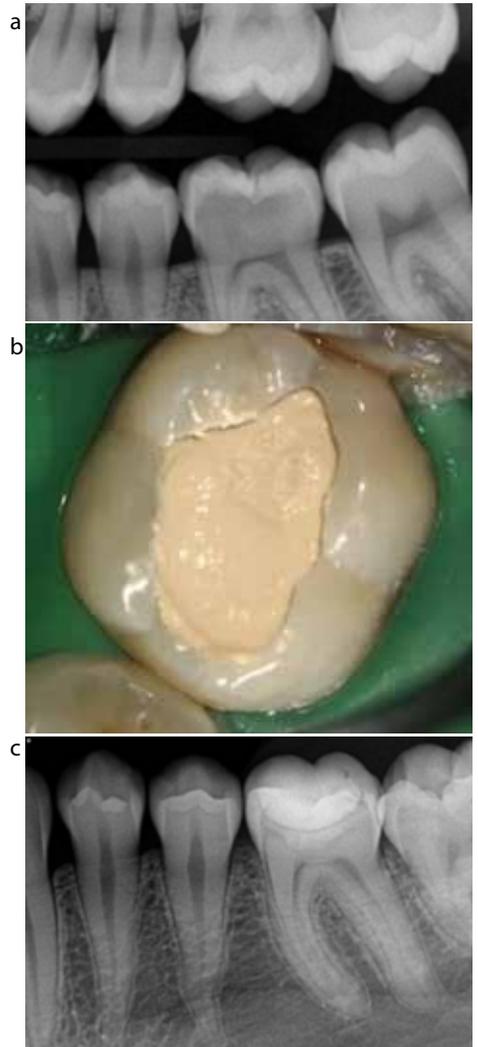


Figure 7. (a) Left horizontal bitewing radiograph. Note the radiolucency in the crown of LL6. (b) Biodentine immediately after placement in LL6 and in its setting phase. (c) A peri-apical radiograph of LL6 taken 2 years post-operatively to monitor the peri-radicular tissues for any sign of peri-radicular breakdown.

liquid that must be mixed (Figure 6a). Five drops of liquid from the vial are added to the powder in the capsule (Figure 6b). The challenge is to achieve the correct powder–liquid ratio owing to the potential variability arising from the size of the drops expressed from the vial. The manufacturer’s instructions should be followed fastidiously. The capsule is then closed, placed into a mechanical mixer and agitated at 4500rpm for 30 seconds to achieve a homogeneous mixture (Figure 6c).



Figure 8. (a) Pre-operative peri-apical radiograph of UL1 prior to its treatment using a barrier regenerative endodontic technique as described in the text. (b) The post-operative peri-apical radiograph. (c) The follow up peri-apical radiograph taken 12 months post-operatively showing resolution of the peri-radicular radiolucency. (Case courtesy of Dr Matthias Widbillier, University of Regensburg.)

Section summary

Two shortcomings of hydraulic cements, namely slow set and poor handling properties have been overcome by the inclusion of additives, such as in Biodentine, thus permitting it to be used in the intra-coronal situation.

Clinical cases

Pulp capping

A 19-year-old female presented having been diagnosed with Ewing's sarcoma and was about to embark on chemotherapy. Clinically, there was a shadow in the occlusal surface of LL6 consistent with a carious lesion, although no cavitation of the enamel was evident (Figure 7a). From the radiograph, it was judged that some pulpal involvement was likely because of the potential extent of the lesion. After the administration of local anaesthetic (LA), a rubber dam (RD) was placed pre-operatively to create a controlled bacteriological environment. The cavity was prepared, the amelodentinal junction cleared and stepwise excavation of dentinal caries proceeded, leaving some caries-affected dentine over the pulp. Biodentine was mixed and placed into cavity (Figure 7b). In this situation, the material may be placed as a dressing by filling the entire cavity,⁶² in which case, the patient should be

recalled within 4 weeks so that the outer part of the material may be reduced to accommodate an overlaying definitive restorative material. Alternatively, Biodentine may be placed as a lining material and once set, covered with resin composite at the same appointment. This latter approach is considered to be preferable. It has been shown that the placement of a definitive restoration within the first 2 days after pulp exposure contributed significantly to increased pulpal survival rate,⁶³ and so, particularly in view of the patient's medical history, this approach was chosen.⁶⁴ Clinical and radiographic follow up was undertaken to monitor pulp vitality and 4 years post-operatively, no further operative intervention had been necessary. A follow up radiograph is shown in Figure 7c.

Clinical outcomes

The use of Biodentine has been shown to reverse irreversible pulpitis when used as a dressing over partial or full pulpotomies in permanent teeth.^{65,66} When used for indirect pulp capping, higher success rates were shown when healing was evaluated by cone beam computed tomography (CBCT).^{67,68} A product of this type is considered the material of choice in this situation.

Barrier regenerative endodontics

An 11-year-old female patient was referred by her general dental practitioner (GDP) with pulpal necrosis in UL1. Although she presented asymptotically, there was a history of trauma whereby the tooth had suffered a luxation injury and had an incomplete apex when viewed on a radiograph (Figure 8a).

The treatment was performed under LA and RD, the root canal of UL1 was irrigated with 2.5% sodium hypochlorite solution and 17% EDTA and sterile isotonic saline with only necrotic and infected tissue removed as per the ESE protocol.³⁸ The excess irrigant was removed using sterile paper points prior to the use of a size 25.02 Hedström file into pulp stump (which was visible under the operating microscope) to induce bleeding. The blood clot was allowed to form at the level of the amelocervical junction and covered with an absorbable collagen sponge (Parasorb Cone, Resorba Medical GmbH, Nürnberg, Germany) prior to the placement of Biodentine. A coronal seal was established with a resin-modified glass polyalkenoate cement (Vitrebond Plus, 3M, Seefeld, Germany) and the access cavity restored with resin composite (Figure 8).

Section summary

The adoption of barrier regenerative techniques is more commonplace in contemporary endodontics. This has been made possible by the availability of hydraulic cements, such as Biodentine, whose chemical and handling properties are conducive for this indication.

Conclusion

The use of hydraulic cements is becoming more commonplace in contemporary endodontics because they set in the presence of water and do not deteriorate when wet. As a guide to the clinician, a classification has been proposed which refers to the three different locations in which they may be used namely: intra-coronally (pulp capping and barrier regenerative endodontics); intra-radically (root canal sealer and apical plug); and extra-radically (perforation repair and root-end filler). Their efficacy and clinical performance are supported by an increasing body of evidence.

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Compliance with Ethical Standards

Conflict of Interest: The authors declare that they have no conflict of interest.

Informed Consent: Informed consent was obtained from the patient whose case is included in the present paper.

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