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# Investigation of the hydration and bioactivity of radiopacified tricalcium silicate cement, Biodentine and MTA Angelus

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ABSTRACT

*Objective.* Novel root-end filling materials are composed of tricalcium silicate (TCS) and radiopacifier as opposed to the traditional mineral trioxide aggregate (MTA) which is made up of clinker derived from Portland cement and bismuth oxide. The aim of this research was to characterize and investigate the hydration of a tricalcium silicate-based proprietary brand cement (Biodentine™) and a laboratory manufactured cement made with a mixture of tricalcium silicate and zirconium oxide (TCS-20-Z) and compare their properties to MTA Angelus™.

*Methods.* The materials investigated included a cement containing 80% of TCS and 20% zirconium oxide (TCS-20-Z), Biodentine™ and MTA Angelus™. The specific surface area and the particle size distribution of the un-hydrated cements and zirconium oxide were investigated using a gas adsorption method and scanning electron microscopy. Un-hydrated cements and set materials were tested for mineralogy and microstructure, assessment of bioactivity and hydration. Scanning electron microscopy, X-ray energy dispersive analysis, X-ray fluorescence spectroscopy, X-ray diffraction, Rietveld refined X-ray diffraction and calorimetry were employed. The radiopacity of the materials was investigated using ISO 6876 methods.

*Results.* The un-hydrated cements were composed of tricalcium silicate and a radiopacifier phase; zirconium oxide for both Biodentine™ and TCS-20-Z whereas bismuth oxide for MTA Angelus™. In addition Biodentine™ contained calcium carbonate particles and MTA Angelus™ exhibited the presence of dicalcium silicate, tricalcium aluminate, calcium, aluminum and silicon oxides. TCS and MTA Angelus™ exhibited similar specific surface area while Biodentine™ had a greater specific surface area. The cements hydrated and produced some hydrates located either as reaction rim around the tricalcium silicate grain or in between the grains at the expense of volume containing the water initially present in the mixture. The rate of reaction of tricalcium calcium silicate was higher for Biodentine™ than for TCS-20-Z owing to its optimized particle size distribution, the presence of $CaCO_3$ and the use of $CaCl_2$. Tricalcium calcium silicate in MTA hydrated even more slowly than TCS-20-Z as evident from the size of reaction rim representative of calcium silicate hydrate (C-S-H) around tricalcium silicate grains and the calorimetry measurements. On the other

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hand, calcium oxide contained in MTA Angelus™ hydrated very fast inducing an intense exothermic reaction. Calcium hydroxide was produced as a by-product of reaction in all hydrated cements but in greater quantities in MTA due to the hydration of calcium oxide. This lead to less dense microstructure than the one observed for both Biodentine™ and TCS-20-Z. All the materials were bioactive and allowed the deposition of hydroxyapatite on the cement surface in the presence of simulated body fluid and the radiopacity was greater than 3 mm aluminum thickness.

*Significance*. All the cement pastes tested were composed mainly of tricalcium silicate and a radiopacifier. The laboratory manufactured cement contained no other additives. Biodentine™ included calcium carbonate which together with the additives in the mixing liquid resulted in a material with enhanced chemical properties relative to TCS-20-Z prototype cement. On the other hand MTA Angelus™ displayed the presence of calcium, aluminum and silicon oxides in the un-hydrated powder. These phases are normally associated with the raw materials indicating that the clinker of MTA Angelus™ is incompletely sintered leading to a potential important variability in its mineralogy depending on the sintering conditions. As a consequence, the amount of tricalcium silicate is less than in the two other cements leading to a slower reaction rate and more porous microstructure.



## 1. Introduction

Mineral trioxide aggregate (MTA) is composed of Portland cement clinker (80%) and bismuth oxide (20%) [1]. As a consequence the main constituent and most reactive phase of mineral trioxide aggregate (such as ProRoot MTA) is tricalcium silicate which comprises about 68% of the Portland cement component [2–4]. The percentage of tricalcium silicate in Portland cement can vary largely between brands due to the manufacturing process and the type of raw material used. Moreover the raw materials used in Portland cement production and the type of fuels used for the kiln contain minor elements that can be incorporated to tricalcium silicate leading to the stabilization of different polymorphs that hydrate with different kinetics. As a consequence, daily variations between cement batches can lead to different reactivity and final properties. Conversely dental cements only based on tricalcium silicate are likely to be more reliable. Indeed adequate quantities of tricalcium silicate can be manufactured with pure raw materials in controlled conditions [5] leading to constant properties.

Tricalcium silicate has been used as a bone cement and has shown adequate biocompatibility and bioactivity [6]. The apatite forming ability is enhanced with the addition of calcium fluoride [7]. Composite materials based on tricalcium silicate, which include calcium and sodium carbonate [8,9], calcium sulphate hemihydrate [10] and monocalcium phosphate monohydrate [11] result in accelerated cement with improved physical properties.

Tricalcium silicate is bioactive and hydrates into calcium silicate hydrate (C-S-H) and calcium hydroxide (Portlandite) which reacts in the presence of physiological fluids producing hydroxyapatite mostly at the surface of the tricalcium silicate paste [3]. Tricalcium silicate paste is biocompatible and induces differentiation of human dental pulp cells in a similar method as calcium hydroxide [12]. The addition of calcium chloride to tricalcium silicate used for a dental application resulted in an accelerated cement which exhibited enhanced bioactivity and biocompatibility when exposed to L929 cells [13]. Attempts at replacing the Portland cement component of MTA with tricalcium silicate resulted in a material of adequate physical properties [14].

Dental materials based on tricalcium silicate have been developed. These materials are synthesized in the laboratory from high purity raw materials unlike the Portland cement in MTA. One such formulation is Biodentine™ (Septodont) which was developed as dentin replacement material. Other uses for this material include restoration of deep and large coronal carious lesions, restoration of deep cervical and radicular lesions, pulp capping and pulpotomy, repair of root perforations, furcation perforations, perforating internal resorptions, external resorption, apexification and root-end filling in endodontic surgery. Biodentine™ is presented as a powder consisting of tricalcium silicate (main component), dicalcium silicate (second main component) and calcium oxide; calcium carbonate (filler material); and zirconium oxide as a radiopacifier. The liquid for mixing with the cement powder consists of calcium chloride (decreases the setting time) and a hydrosoluble polymer (water reducing agent) in order to keep a good flowability with a low water/solid ratio [15]. Biodentine has been shown to be biocompatible [16]. Biodentine™ caused the uptake of Ca and Si in the adjacent root canal dentin in the presence of physiological solution [17].

The aim of this research was to characterize MTA Angelus™, Biodentine™ and a laboratory made radiopacified tricalcium silicate cement named TCS-20-Z and then to investigate their hydration in order to first, define the difference between clinker based dental materials compared to tricalcium silicate based ones and secondly, compare Biodentine™ that is an optimized tricalcium silicate-based dental material to laboratory made mixture of tricalcium silicate and zirconium oxide. These results are expected to demonstrate the advantage of using tricalcium silicate-based dental cement as these systems can be efficiently tuned to achieve the required performance on account of all research that has been conducted on this mineral in the field of cement chemistry for more than one century.