

## Comparative study of the phase formation and interaction with water of calcium-silicate cements with dental applications

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Mineral trioxide aggregate (MTA) is based on plain Portland cement and is composed of tricalcium silicate, dicalcium silicate, tricalcium aluminate, and tetracalcium aluminoferrite. This cement is used for various dental clinical applications. The degree of solubility of calcium-silicate based cements is an object of debate among investigators. The present study was designed to compare the phase formation and evolution, as well as solubility of five different commercial calcium-silicate cements. X-ray diffraction (XRD) analysis was applied to determine the phase composition of the initial powder mix, cement compositions, and cement compositions evolution after aging the material in distilled water. Thermal analyses (TG-DTA) were also performed to confirm the XRD results. The concentrations of Ca, Na, Mg, Al, K, Fe, Ti, Bi, Ta and Zr ions passed into the solution were determined by means of ICP-MS and FAAS. The changes of elemental and phase composition were discussed.

Biodentine seems an alternative to MTA. It releases significant amounts of Ca ions and therefore stimulates tissue mineralization. The concentration of radiopaque elements in the soaking water is at trace levels in all materials studied, which makes them safe for dental applications. The obtained good results do not cancel regular safety checks.

**Key words:** calcium-silicate cements, dental application, phase evolution, solubility.

### INTRODUCTION

Calcium-silicate cements were first introduced to dentistry in 1993 by Torabinejad and co-workers [1]. Based on plain Portland cement they are composed of tricalcium silicate, dicalcium silicate, tricalcium aluminate, and tetracalcium aluminoferrite. Bismuth oxide is added as a radiopaque for clinical applications since mineral trioxide aggregate (MTA) is used as endodontic material and should be more radiopaque than its surrounding structures. According to Parirokh and Torabinejad [2] the addition of bismuth oxide affects the hydration mechanism of MTA. It must be insoluble to avoid leakage and should be as hard as possible to avoid dislodgement from the dentine wall [3]. The main requirement to this group of materials is hermetic sealing. The hermetic mechanism comes as a complex result

of several factors – marginal adaptation, adhesion, solubility and volume changes [4].

During the last years many producers developed production of calcium silicate- based cements for dental applications. Despite similar constituents, due to the variations of manufacturing processes the purity of their constituents and hydration products their behavior can be different.

The degree of solubility of calcium-silicate based cements is an object of debate among investigators. Most authors reported low solubility or solubility has not been observed, however increased solubility was reported in a long-term study. According to Frindland et al [5] calcium as hydroxide was the main chemical compound released by MTA in water. Bodanezi et al [6] reported that, in an aqueous environment MTA is more soluble than Portland cement. Calcium silicate materials *MTA Plus gel* and *MTA Angelus* showed the highest values of porosity, water sorption and solubility, according to Gandolfi [7]. Based on the findings of Saghiri and Asgar [8] storage temperature appears to play an important

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role in the properties and hence clinical outcomes of MTA. According to Gandolfi [9] solubility of *MTA Plus* is higher than that of *ProRoot MTA*. Grech [10] reported that *Biodentine* demonstrates a high wash-out, low fluid uptake and sorption values, low setting time and superior mechanical properties.

Regarding the solubility test of Vivan [11], the white *MTA-Angelus* and *MTA-Bio* cements had higher solubility than Portland cement. It is important to explain that the solubility testing standards recommend immersion of the materials only after complete setting, which is impossible to be achieved in a clinical situation, where the materials are immediately in contact with fluids and blood. Therefore, solubility values are probably even higher under clinical conditions.

The aim of the present study is to compare the phase formation and evolution as well as solubility of five different commercial calcium-silicate cements after aging the material in distilled water.

## EXPERIMENTAL

### *Samples notation*

The following cements were chosen for the study:

Sample I – white *ProRoot MTA* (*Dentsply, Tulsa, Johnson City, TN*)

Sample II – gray *MTA-Angelus* (*Angelus, Londrina, Brazil*)

Sample III – white *MTA-Angelus* (*Angelus, Londrina, Brazil*)

Sample IV – *BioAggregate* (*Innovative Bioceramix, Vancouver, Canada*)

Sample V – *Biodentine* (*Septodont, Saint-Maur-des-Fossés, France*)

### *Samples preparation*

*MTA ProRoot*, *MTA-Angelus* и *BioAggregate* were mixed according to the manufacturer's instructions on a glass slab with cement spatula to produce homogeneous paste, the mixture exhibited putty like consistency after about 30 s mixing time. The cements were prepared according to the manufacturer's recommendations in the proportion of 1 g of powder to 0.21 mL of distilled water. Powder and liquid of *Biodentine* are mixed for 30 s in a capsule in a high-speed amalgamator (*Amalga Mix 2, Gnatus, Brazil*) at 4000–4200 rpm. The test materials were placed into a cylindrical polyethylene tube (12 mm in diameter and 2 mm in height). All cements were placed on a tissue soaked with saline gauze and kept at 100% relative humidity for 24 h. After that the samples were left in open air for 48 hours and placed in desiccators till obtaining constant weight.

After drying (to constant weight) the samples were placed in a 30 ml polypropylene containers and 20 ml of de-ionized water (pH=6.3) were added. The samples were kept for 28 days at room temperature ( $22\pm 1$  °C), after which the samples were filtered and the filtrate was used for element content determination.

### *Analyses*

Powder X-ray diffraction (XRD) analysis was applied to determine the phase composition of the initial powder mix, cement compositions, and cement compositions evolution after aging the material in distilled water. The XRD patterns were collected within the range from 5 to 80° 2 $\theta$  with a constant step 0.02° 2 $\theta$  on Bruker D8 Advance diffractometer with Cu K $\alpha$  radiation and LynxEye detector. Phase identification was performed with the *Diffraplus EVA* using ICDD-PDF2 Database.

Thermal analyses (TG-DTA) were also performed to confirm the XRD results. Thermal analyses were carried out using the computerized combined thermal analysis apparatus *LABSYSEvo*, *SETARAM* Company (France) at atmospheric pressure in a flow of synthetic air (*MESSER CHIMCO GAS – OOH 1056, ADR 2, 1A*) in the temperature range 25–1000 °C with heating rate 10 °C min<sup>-1</sup>. Corundum crucibles with a volume of 100  $\mu$ l were used.

Inductively coupled plasma-mass spectrometer “X SERIES 2” – Thermo Scientific with 3 channel peristaltic pump, concentric nebulizer, Peltier-cooled spray chamber (4 °C), Xt interface option, Ni cones and forward plasma power of 1400 W was used for the determination of Ca, Na, Mg, Al, K, Fe, Ti, Bi, Ta and Zr.

Thermo SOLAAR M5 Flame Atomic Absorption spectrometer with deuterium background correction was used for the determination of Ca, Na, Mg and K.

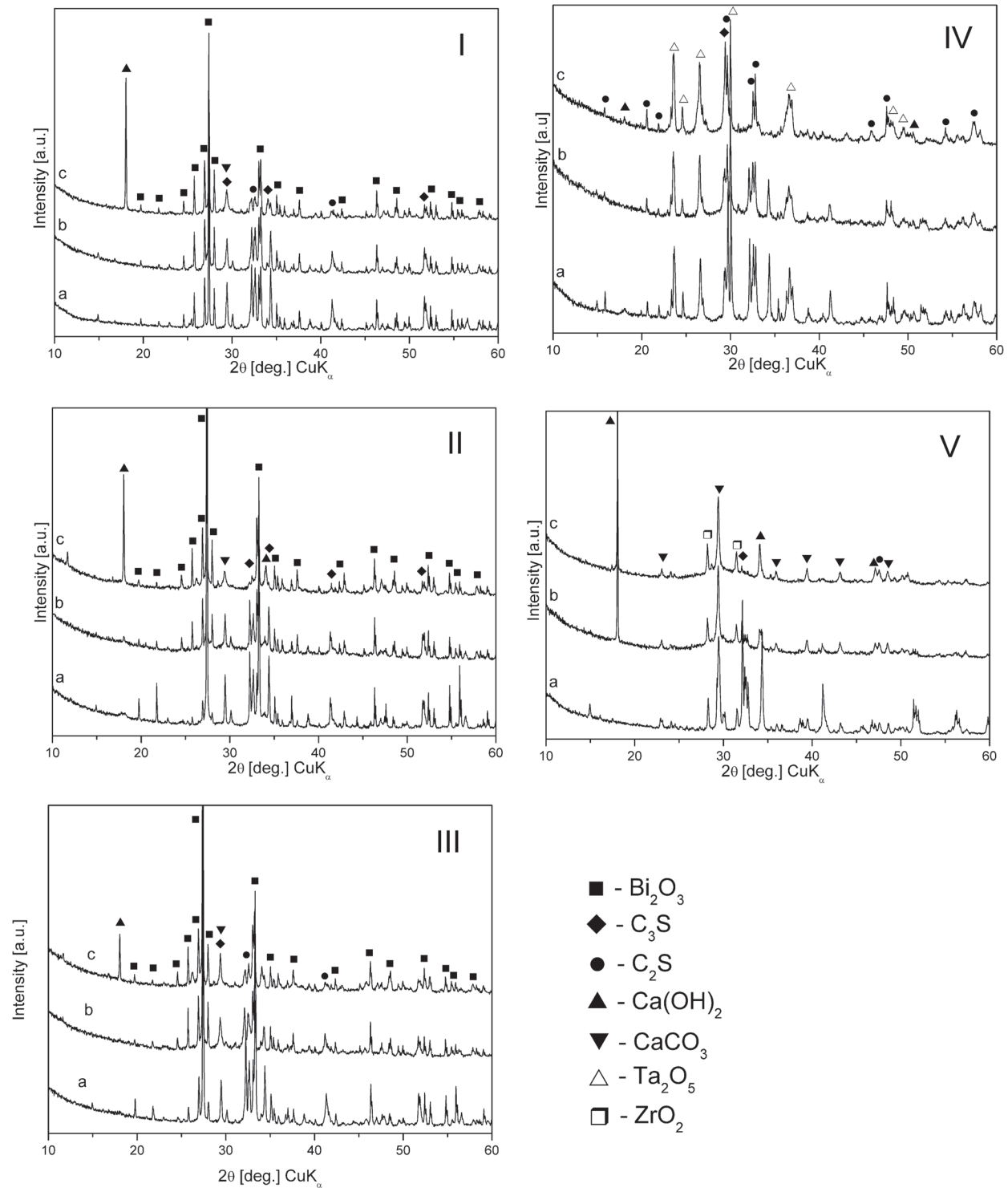
Multi-element standard solution V for ICP (Fluka, Sigma-Aldrich); 1000 mg L<sup>-1</sup> Ti (Fluka, Sigma-Aldrich); 1000 mg L<sup>-1</sup> Ta (Fluka, Sigma-Aldrich) and 1000 mg L<sup>-1</sup> Zr (Fluka, Sigma-Aldrich) were used for the preparation of diluted working standard solutions for calibration for ICP-MS measurements. Stock standard solutions of Ca, Na, Mg and K (1.000 g L<sup>-1</sup> (Merck)) were used for the preparation of diluted working standards for calibration for flame AAS.

## RESULTS AND DISCUSSION

The powder XRD patterns of five cements, currently used in dental practice are shown in Figure 1. Each figure represents initial dry mixture of calcium

silicates, the cement after hydrolysis, prepared according to the manufacturer instruction and the same cement soaked for 28 days in distilled water. The initial composition (Fig. 1, a) contains phases typical for Portland cements, such as tricalcium silicate

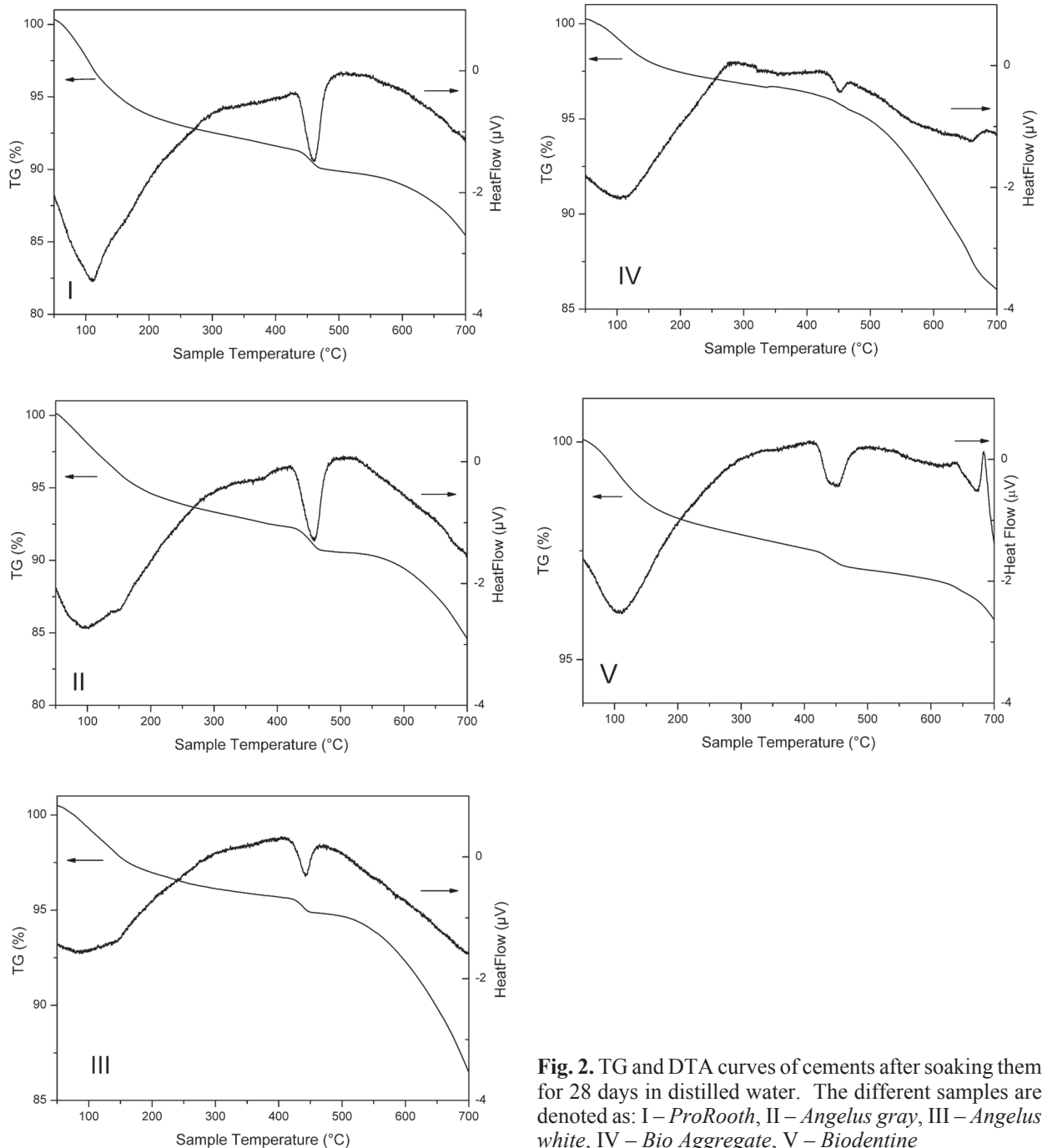
( $C_3S$ ) – main phase, usually within 50–70% mass of the composition, dicalcium silicate ( $C_2S$ ), calcium carbonate, traces of calcium hydroxide (portlandite), apatite and, depending on the manufacturer, bismuth oxide (Samples I, II and III), tantalum ox-



**Fig. 1.** Powder XRD patterns of the initial dry mixture (a), the cements after setting (b) and the cements after soaking for 28 days in distilled water (c). The different samples are denoted as: I – *ProRooth*, II – *Angelus gray*, III – *Angelus white*, IV – *Bio Aggregate*, V – *Biodentine*

ide (Sample IV) or zirconium oxide (Sample V) as a radiopaquer. The setting reaction i.e. the hydration process of the initial dry cement mixture results in increasing the mass% of the radiopaquer in the crystalline part due to the formation of amorphous calcium silicate hydrates. Increased amount of portlandite is also observed. It should be mentioned that the hydration is not complete for all samples. For some of them part of initial non-hydrated calcium silicates can be detected (Fig. 1, b). According to

the literature amorphous calcium silicate hydrates are formed on the surface of non-hydrated calcium silicates, thus providing a matrix for colloidal-type material. The matrix binds the non-hydrated calcium silicate particles. Calcium portlandite usually remains in the pores of the cement matrix [12, 13]. The soaking process for 28 days results in increased amount of portlandite for all samples with the exception of sample IV (Fig. 1, c). What is interesting is that for the hydrated and soaked samples the



**Fig. 2.** TG and DTA curves of cements after soaking them for 28 days in distilled water. The different samples are denoted as: I – *ProRooth*, II – *Angelus gray*, III – *Angelus white*, IV – *Bio Aggregate*, V – *Biodentine*

**Table 1.** Weight loss calculated from TG curves for different temperature regions for cements after soaking for 28 days in distilled water

Sample	Weight loss below 200 °C (%)	Weight loss at 450 °C (%)
I	7.65	1.6
II	8.16	1.8
III	2.81	0.83
IV	3.02	0.85
V	9.24	1.93

amount of calcium carbonate remains almost constant, indicating that this constituent of the cements is independent of treatment.

An important feature of calcium silicate-based cements is the ability to release ions, mainly calcium ions within the tooth tissue, which facilitates the dentin–restoration process. It is assumed that ion release depends on several factors such as the nature of the compositional and matrix structure related to water sorption and solubility as well as the porosity of the material, which is related to water diffusion. To investigate this type of properties thermal analyses were performed. The TG-DTA curves of the samples are presented on Fig 2. All samples show well defined weight loss below 200 °C, which is related to the amount of the adsorbed water. For all samples, an endothermic peak situated at about 450 °C is also observed accompanied by a mass loss. This peak is associated with the decomposition of portlandite presented in the samples. Table 1 represents the values of mass loss for these two cases.

The elements determined by chemical analyses of the soaking liquid were those announced by the manufacturers (Table 2). Analysis of the soaking liquid after 28 days showed that Mg, Al, Ti, Fe, Bi, Zr, and Ta concentrations are at trace levels i.e. less than  $1 \times 10^{-5}$  g. It should be mentioned that oxides used as radiopaquer ( $\text{Bi}_2\text{O}_3$ ,  $\text{Ta}_2\text{O}_5$  and  $\text{ZrO}_2$ ) do not dissolve in distilled water under the conditions described above. A certain part of the Na ions in the samples comes from the manipulation during sample preparation. In this case the content of dissolution of sodium could not be commented.

The main importance of the analyses is the calcium ions behavior during cement setting and soaking, since it is a key factor for successful endodontic and pulp capping therapies because of the action of calcium on the mineralizing cells. Gandolfi at all [14] in recent study determined the concentration of Ca ions released from *ProRoot MTA* and *Biodentine* cements within 28-day soaking in distilled water. Our results are in good agreement with the results obtained by them. *Biodentine* (Sample V) showed a markedly higher release of free calcium ions than all other cements. This may be due to the fact that calcium is presented not only in the cement powder, but it is also contained in the liquid provided by manufacturer of this cement in a form of  $\text{CaCl}_2$  solution.

## CONCLUSION

*Biodentine* seems an alternative to MTA. It releases significant amounts of Ca ions and therefore stimulates tissue mineralization. The concentration of radiopaquer elements in the soaking water is at trace levels in all materials studied, which makes them safe for dental applications. The obtained good results do not cancel regular safety checks.

**Table 2.** Contents of Na, Mg, Al, K, Ca, Ti, Fe, Bi, Zr and Ta in the solution obtained after 28 days soaking of the samples in distilled water

Elements	Sample I	Sample II	Sample III	Sample IV	Sample V
Na, $\mu\text{g g}^{-1}$	418±20	422±20	756±30		
Mg, $\mu\text{g g}^{-1}$	0.35±0.1	0.20±0.1	0.17±0.1	0.46±0.1	0.20±0.1
Al, $\mu\text{g g}^{-1}$	14.2±0.3	5.91±0.3	15.6±0.3		
K, $\mu\text{g g}^{-1}$		1575±50			
Ca, $\mu\text{g g}^{-1}$	2815±80	10300±440	25.0±1.0	955±30	22830±590
Ti, $\mu\text{g g}^{-1}$	<0.01	<0.01			
Fe, $\mu\text{g g}^{-1}$	<1.0	<1.0	<1.0		<1.0
Bi, $\mu\text{g g}^{-1}$	0.45±0.03	0.55±0.06	0.10±0.01		
Zr, $\mu\text{g g}^{-1}$					<0.01
Ta, $\mu\text{g g}^{-1}$				<0.01	



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## СРАВНИТЕЛНО ИЗСЛЕДВАНЕ НА ФАЗООБРАЗУВАНЕТО И ВЗАИМОДЕЙСТВИЕТО С ВОДА НА КАЛЦИЕВО-СИЛИКАТНИ ЦИМЕНТИ С ПРИЛОЖЕНИЕ В ДЕНТАЛНАТА МЕДИЦИНА

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(Резюме)

Минералният триоксид агрегат (МТА) е базиран на стандартния Портланд цимент и е съставен от трикалциев силикат, дикалциев силикат, трикалциев алуминат и тетракалциев алумоферит. Като контрастен материал за денталната рентгенография към цимента се добавя бисмутов оксид. Степента на разтворимост на калциево-силикатните дентални цименти е обект на дискусия между изследователите. Настоящата работа изследва фазообразуването и еволюцията на фазите, както и разтворимостта на пет различни търговски калциево-силикатни цименти. Рентгенодифракционният анализ (XRD) е използван за определяне на първоначалния фазов състав на изходната смес, състава на пригответените цименти, и развитието на фазите в циментовите състави след престой на материала в дестилирана вода. Извършени бяха и термични анализи (TG-DTA) чиито резултати корелират добре с резултатите от рентгеновата дифракция. Концентрациите на Ca, Na, Mg, Al, K, Fe, Ti, Bi, Ta и Zr йони преминали в разтвора са определени с помощта на ICP-MS и FAAS. Обсъдени са промените на елементния и фазовия състави на денталните цименти при стареене във водна среда. Установено е, че материалът Biodentine е алтернатива за МТА, защото отдава значително количество Ca йони като по този начин стимулира тъканната минерализация. Концентрацията на контрастните елементи за денталната рентгенография в разтвора е под формата на следи във всички изследвани материали, което ги прави безопасни за стоматологични приложения. Получените добри резултати не анулират редовни проверки за безопасност.