Highly Active Calcium-Silicate Phases for Application in Endodontics

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SUMMARY

Introduction Mineral trioxide aggregate (MTA) is one of the most commonly used materials in endodontics. Given its shortcomings, there is an intensive search for new materials. Calcium-silicate phase (CS phase) is a new material synthesized by the method based on a combination of sol-gel process and self-propagation synthesis which can significantly improve setting time through accelerated hydration. The aim of this study was to explain the mechanisms of hardening of CS phase in aqueous medium as similar mechanism is expected in contact with body fluids.
Materials and Methods CS phases Ca_3SiO_5 (C_3S) and $2\beta\text{-}CaSiO_4$ ($\beta\text{-}C_2S$) were synthesized from $CaCl_2\cdot5H_2O$ (Merck, Germany). To investigate the process of hydration, CS were mixed with water and kept at 37 °C for 28 days in closed polyethylene containers. Analysis of the composition of samples before and after immersion in water for 1, 3, 7 and 28 days was performed using X - ray diffractometry and IR.
Results XRD patterns for hydrated samples during 1, 3, 7 and 28 days showed that the amount of hydrated tobermorite phases relative to the amount of CS phase changes with the time of hydration. After 1 day, in addition to the hydrated phases, a significant amount of untransformed $\beta\text{-}C_2S$ and C_3S were found while after 28 days hydrated CS phase was completely transformed to tobermorite with a small amount of portlandite.
Conclusion Using combined method of sol-gel and self-propagating waves at high temperature very active nanostructured silicate phases were obtained. Hydration process of CS phases was analyzed using XRD and FTIR, the mechanism of hydration was proposed and it was pointed to the difficulties in determining the exact reaction as well as the problem of determining the exact structure of tobermorite.
Keywords: calcium-silicates; endodontics; setting time; compressive strength; XRD

INTRODUCTION

Mineral trioxide aggregate (MTA) is one of the most commonly used materials in endodontic practice for the treatment of various root canal perforations, pulpotomy and vital pulp treatment, as an apical barrier in teeth with necrotic pulp etc. After application of MTA for direct pulp capping in permanent teeth, the appearance of calcified bridge was observed after one week only [1, 2]. Several *in vitro* and *in vivo* studies have demonstrated that sealing abilities of MTA are superior to those of amalgam, IRM and super EBA [1, 3-6]. However, several important disadvantages of MTA have been pointed: long setting time, weak rheological properties and weakening of the material structure during hydration in acidic environment. Also, particle size, powder to liquid ratio, temperature and presence of air in the mixture may influence the physical properties of MTA [6]. Therefore, search for new material with similar composition which shows higher degree of activity of calcium-silicate (CS) and better mechanical properties has been continued.

In the current study, calcium-silicate phases (CS phases) were synthesized by the method, based on the combination of sol-gel process and self-propagating synthesis, which can significantly improve setting time of obtained phases through their accelerated hydration. The process of their hydration, as the most responsible for their behavior, was particularly analyzed.

The aim of this study is to understand mechanisms of cement hardening in water medium, as similar mechanism is expected in contact with body fluids.

MATERIAL AND METHODS

Synthesis and characterization methods of calcium-silicate phases

The CS phases, Ca_3SiO_5 (C_3S) and $2\beta\text{-}CaSiO_4$ ($\beta\text{-}C_2S$), were synthesized from $CaCl_2\cdot5H_2O$ (Merck, Germany) and silica sol was obtained by hydrothermal treatment [7]. The chemicals were used in stoichiometric quantities, corresponding to the ratio C_3S: $\beta\text{-}C_2S$ = 2:1, to obtain silicate active phase. $Al(C_2H_3O_2)$ was added to the mixture to provide production of small amount (~3%) of active C_3A phase.

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Firstly, the mixture of silica sol and $CaCl_2 \cdot 5H_2O$ was dried at 80 °C to obtain gel, and then heated at 150 °C to remove water among the silica particles. In order to start the combustion reaction, ammonium nitrate (NH_4NO_3), as an oxidation agent, and citric acid ($C_6H_8O_7CH_2O$), as a fuel, were added. During the strong reaction of self-propagating combustion the gel swelled into the foam and black ashes were obtained as a product of auto-ignition. After this treatment at high temperatures the sample was quickly cooled using copper plates, in order to obtain high reactivity and low crystallinity of β-C_2S and C_3S phases. Finally, the resulting black powder was calcined in air at 650°C for 4 h to remove carbon residues and obtain desired products with small crystallite sizes.

In order to investigate the process of their hydration, CS was mixed with water (water-to-powder ratio about 1:2) and compacted using a stainless steel plunger. Cement was allowed to set up to 28 days at 37°C in sealed polyethylene containers. Phase compositions of the samples before immersing in water and 1, 3, 7 and 28 days after immersion were analyzed using X-ray diffractometry, XRD (Philips PW 1050, Almelo), with Ni–filtered Cu-Ka$_{1,2}$ radiation. The patterns were registered in the 2q range 9-67° with a scanning step size of 0.02°. FTIR analysis (Nicollet 380 FT-IR, Termo Electron Corporation) was done for the samples before soaking and for the samples soaked for 7 and 28 days.

RESULTS AND DISCUSSION

Phase analysis of CS phases before and after soaking in water

XRD patterns of CS phases ($C3S$ and β-C_2S) are shown in Graph 1. Peaks corresponding to C_3S phase are registered at the angles 11.7, 23.6, 29.6, 32.5, 32.8, 33.4, 34.6 and 41.5° [with corresponding planes: (-401), (-114), (422), (-715), (224), (-424), (1004) and (-626), respectively], while the peaks corresponding to β-C_2S phase are found at the angles 23.3, 29.7, 32.3, 33.0, 34.6, 41.6, 46.9, 51.9, 56.8, 60.2 and 62.7° [with corresponding planes: (012), (120), (-121), (121), (103), (031), (024), (310), (-303), (303) and (043), respectively]. Crystallite sizes of these phases, calculated using Sherrer equation, were about 19.9 nm.

XRD patterns for samples hydrated for 1, 3, 7 and 28 days (Graph 1), show that the quantity of hydrated phase tobermorite relative to sum of CS phases changed with hydration time. For the samples hydrated 1 day, beside the presence of hydrated phase of tobermorite [planes (006), (112), (202) and (213)] and portlandite [planes (011), (012) and (001)] which showed the progress of hydration; significant amounts of β-C_2S and C_3S remained untransformed. For the samples hydrated 3 days, a few peaks of low intensity indicated that only slight amounts of CS phases were present. For the samples hydrated 7 days traces of C_3S were present, while the peaks of the main hydrated phase, tobermorite, were more pronounced. Finally, for the samples hydrated 28 days, CS were completely transformed to tobermorite, with small amounts of portlandite.
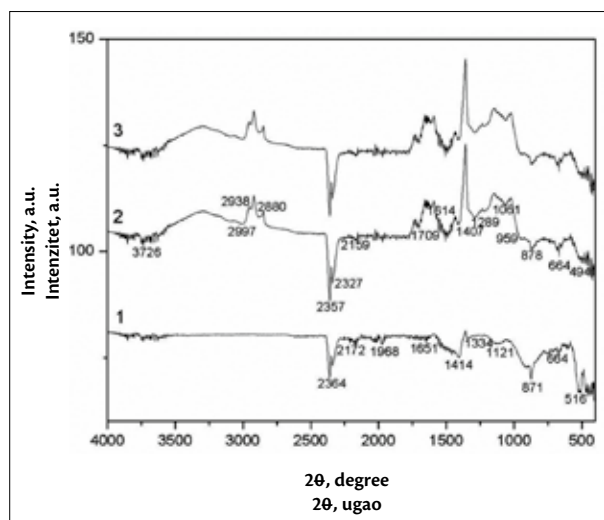
Graph 1. XRD patterns of hydrated calcium-silicates
Grafikon 1. XRD obrasci hidratisanih kalcijum-silikata

T – tobermorite; P – portlandite; 1 – nonhydrated sample; 2 – sample hydrated for 1 day; 3 – sample hydrated for 3 days; 4 – sample hydrated for 7 days; 5 – sample hydrated for 28 days

T – tobermorit; P – portlandit; 1 – nehidrirani uzorak; 2 – uzorak hidratisan tokom jednog dana; 3 – uzorak hidratisan tri dana; 4 – uzorak hidratisan sedam dana; 5 – uzorak hidratisan 28 dana
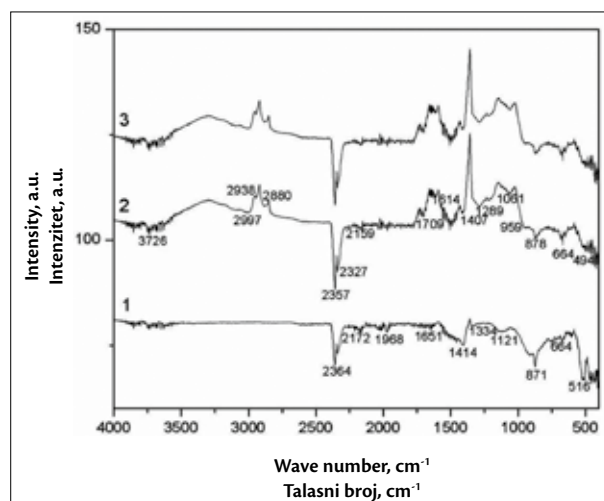
Graph 2. FTIR spectra of hydrated calcium-silicates
Grafikon 2. FTIR spektar hidratisanih kalcijum-silikata

1 – nonhydrated sample; 2 – sample hydrated for 1 day; 3 – sample hydrated for 28 days

1 – nehidrirani uzorak; 2 – uzorak hidratisan tokom jednog dana; 3 – uzorak hidratisan 28 dana

The FTIR spectrum of CS phases is shown in Graph 2. The characteristic doublet recorded between 2334 and 2364 cm^{-1} can be assigned to the stretching vibration of OH groups, and explained by the decrease in hydrogen bond length, caused by steric effects [7, 8]. The band at 2172 cm^{-1} can be assigned to SiH stretching mode in the small grains, while the band at 1968 cm^{-1} corresponds to SiO_2 vibrational modes [8]. The band at 1651 cm^{-1} can be ascribed to the liberation mode of OH, while the broad band with a minimum at 1414 cm^{-1} may be ascribed to vibrations corresponding to partially hydrated C_3S and C_2S phases. The bands at 1334 cm^{-1} region and 871 cm^{-1} cor-

respond to the asymmetric stretch and the out-of-plane bending of C-O, respectively. The band at 1121 cm^{-1} can be assigned to the vibration of C$_2$S units, while small band (shoulder) at 921 cm^{-1} can be indication of slight hydration of C$_3$S or C$_2$S. The band at 664 cm^{-1} can be attributed to the Si-O-Si symmetric vibration and band at 516 cm^{-1} to the out-of-plane bending vibration of SiO$_4$ [9, 10].

The FTIR spectra of the samples hydrated for 1 day (S-1) and 28 days (S-28) show the bands at 3726 and 3718 cm^{-1}, respectively, indicating the presence of the 1.4 tobermorite which contains poorly resolved band in the range of 2800–3700 cm^{-1} due to larger content of molecular H$_2$O, compared to the 1.1 nm tobermorite. The bands at 3726 cm^{-1} and 3718 cm^{-1} can be assigned to vibrations which involve less hydrogen bonded protons in water molecules, including intensity corresponding to Ca-OH groups in the structure. The weak bands at 3740 cm^{-1} can be also assigned to Si-OH vibrations. The bands at 2997, 2938 and 2880 cm^{-1} (S-1), and 2990, 2938 and 2872 cm^{-1} (S-28) confirmed also the presence of the 1.4 nm tobermorite [11].

The characteristic sharp and pronounced band at 2357 cm^{-1} can be assigned to the combination of bands at 959 cm^{-1} and broad band at 1407 cm^{-1}, the band at 2327 cm^{-1} to the combination of bands at 1407 cm^{-1} and 878 cm^{-1} while the band at 2364 cm^{-1} probably belongs to the combination of bands at 1489 cm^{-1} and 871 cm^{-1}. This characteristic doublet recorded between 2327 and 2357 cm^{-1} (S-1) and 2364 and 2320 cm^{-1} (S-28) can be stretching vibration of OH groups explained by corresponding decrease in hydrogen bond length, caused by steric effects. The weak bands at 1407 and 1458 cm^{-1} and its combination, and overtone bands observed at 2997, 2938 and 2880 cm^{-1} (S-1) and 2990, 2938 and 2872 cm^{-1} (S-28) and weak vibrations at 1407 and 1414 cm^{-1} indicate the presence of carbonate species in the samples. The band at 1614 cm^{-1} belongs to the water bending vibration. The bands at 2159 cm^{-1} (S-1) and 2165 cm^{-1} (S-28) can be assigned to SiH stretching mode in the small grains, gradually exposed to oxidation during combustion process at intermediate temperature during synthesis given phases. This is some kind of fingerprints of the oxidation state of silica during synthesis of these powders. The bands at 1709 cm^{-1} and 1702 cm^{-1} correspond probably to water bending vibration inside of gypsum dehydrate present in small amount in samples. The band at 1216 cm^{-1} (S-28) can be assigned to the Si-O stretching vibrations in Q3 site, characteristic for presence of the 1.1 nm tobermorite, while the bands at 1061 and 1054 cm^{-1} belong to the Si-O stretching vibrations in Q2 site of the 1.1 nm tobermorite. This proves possible combination of tobermorite 1.4 nm and 1.1 nm. The bands at 955 cm^{-1} (S-1) and 966 cm^{-1} (S-28) belong to Si-O lattice vibrations, while the bands at 878 cm^{-1} (S-1) and 871 cm^{-1} (S-28) belong to the out of plane vibrations of C-O. The bands at 664 cm^{-1} (S-1) and 671 cm^{-1} (S-28) can be assigned to Si-O-Si bending vibrations inside silica chains and v_4 SO$_4^{2-}$ bending vibrations. These bands can also be attributed to the Si-O-Si symmetric vibration, while the bands at 494 cm^{-1} (S-1) and 509 cm^{-1} (S-28) belong to the out-of-plane bending vibration of SiO$_4$.
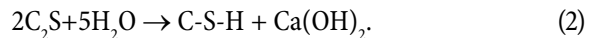
Finally, the bands at 406 cm^{-1} (S-1) and 414 cm^{-1} (S-28) correspond to the deformations of the SiO$_4$ tetrahedrons.

Hydration process of calcium-silicate pastes

The most important parameter affecting the setting and mechanical properties of CS phases is the rate of their hydration. The hydration of β-C$_2$S and C$_3$S phases is the most important process for setting of these phases during their ageing in water solutions. As it was mentioned in various references [8-12], the reaction between C$_3$S and water is the main factor in the setting and hardening of cement mixtures. During this reaction, CS grains become wet, causing rapid release of Ca^{2+} and OH$^-$ ions from each grain surface. The process of transformation of C$_3$S to amorphous calcium-silicate-hydrate (C-S-H), known as tobermorite gel, and calcium hydroxide (Ca(OH)$_2$) can be expressed by the reaction:

$$2C_3S + 7H_2O \rightarrow C\text{-}S\text{-}H + 3Ca(OH)_2. \tag{1}$$
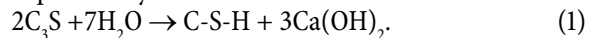
Similarly, the reaction between β-C$_2$S and water is expressed as:

$$2C_2S + 5H_2O \rightarrow C\text{-}S\text{-}H + Ca(OH)_2. \tag{2}$$

The C-S-H obtained in both reactions was the high-lime end-member of a series of hydrates assigned by Taylor as calcium-silicate hydrate (I) or CSH (1) and it can have variable composition. Bernal was the first one who tentatively assigned the structural formula Ca$_2$[SiO$_2$(OH)$_2$]$_2$ [Ca(OH)$_2$] to this compound [8-14].

Difficulties in determination of the exact reaction are joined with a huge problem of determination of the exact structure and corresponding formula of tobermorite. We assumed the ideal formula of tobermorite is 4CaO·Ca(OH)$_2$·6SiO$_2$·4H$_2$O, although it is well-known that central part of each tobermorite layer is similar to octahedral layer in a clay mineral, which could be described as a distorted calcium hydroxide sheet divested of all its hydrogen atoms (CaO$_2$). This sheet is flanked on both sides by parallel rows of wollastonite-type chains that are kinked in a plane perpendicular to the plane of the sheets [13-16].

Only two-thirds of the tetrahedrons of each chain are linked directly to the central CaO$_2$ sheet by sharing the oxygen atoms. The other third, held away from the CaO$_2$ sheet, can be observed as "bridging" tetrahedrons. The corresponding composite 2:1 sheets, so far described, have the composition Ca$_4$SiO$_4$O$_{18}$. The remaining or interlayer calcium atoms and water molecules are placed between these sheets. The distribution of hydrogen is uncertain. There are probably more SiOH groups than it is implied by the formula Ca$_4$(SiO$_4$O$_{18}$H$_2$)·Ca·4H$_2$O, with corresponding replacement of interlayer water by hydroxyl groups [15, 16, 17]. Following this, when CS paste is prepared, C$_3$S phase probably reacts very quickly and water becomes suddenly saturated with Ca(OH)$_2$ (reaction occurs within minutes). The same happens with β-C$_2$S, but more slowly. As the result of hydration, Ca(OH)$_2$ and a member of the tobermorite (G, tobermorite 11) subgroup are formed [15]. If, however, the silicates are hydrated in a large excess of water, so that the concentration of the lime in the

solution is below saturation, the C-S-H that forms is not a member of the tobermorite (G) series and, of course, no $Ca(OH)_2$ is produced in the reaction. The CaO/SiO_2 ratio in the C-S-H depends on the final concentration of the lime in the solution [the lower limit of the ratio (at a low lime concentration) is around 0.8, and the upper limit is about 1.5 (at or near lime saturation)] [16].

Taylor and Howison [17] measured densities of CSH (I), in the range of CaO/SiO_2 ratio from 0.81 to 1.50, and found no systematic trend of density increase with the ratio. They have also advanced a hypothesis for the explanation of constant density together with constant unit cell dimension. They suggested that, as the CaO/SiO_2 ratio increases, calcium replaces silicon in the lattice. The "bridging" SiO_4 tetrahedrons, which are not attached to the central CaO_2 sheet, are frequently gradually removed or, more correctly, only SiO_2 is removed because two of the oxygen ions in each tetrahedron are common to adjacent groups. The calcium ion enters the lattice, but not directly into the place of SiO_2, i.e., not into the layer, but between layers. Since the calcium ion has two positive charges and SiO_2 is neutral, two hydrogen ions must also be removed to preserve charge balance. The over-all replacement is SiO_2H_2 by Ca. Such replacement would have relatively small effect on cell dimensions. It would also explain very slow equilibration between CSH (I) hydrates and $Ca(OH)_2$ solutions. If the increase of the lime content would involve merely uptake of lime between the layers, one would not expect such a slow equilibration. Finally, the hypothesis predicts that the upper limit of the CaO/SiO_2 ratio would be 1.75, corresponding to the removal of all "bridging" tetrahedrons. Although the upper limit of the ratio for the CSH (I) subgroup is around 1.5, the upper limit for the tobermorite (G) subgroup is 1.75, as was stated before, and the upper limit for another subgroup, CSH (II), is also 1.75. It is possible that either the tobermorite (G) or CSH (II) or both of these subgroups form a continuous series with CSH (I). Brunauer and Greenberg have modified the Taylor-Howison hypothesis with the suggestion that SiO_2H_2 is replaced, not by Ca alone, but by Ca plus a water molecule. Such substitution would lead to a far better constancy of the cell dimension than the Taylor-Howison substitution; it would explain found compositions of tobermorite better; and it would also explain the constancy of the c spacing, mentioned earlier [18]. The modified Taylor-Howison hypothesis corresponds quite well for the compositions, structures, densities, and some other properties of the hydrates of the CSH (I) subgroup, possibly even of the entire tobermorite group. Besides structural variations, the CSH (I) hydrates exhibit a wide range of specific surface areas. Such differences in the structure and surface area are, doubtless, responsible for differences in the ratio between compositions of various kind of CSH, formed during the hydration process [16, 17, 18].

Otherwise, it is well-known that tobermorite (G) hydrates are poorly crystallized. Their X-ray diffraction patterns consist of three lines: a very strong and very broad reflection, with a maximum at 0.305 nm, and two weaker broad lines at 0.279 and 0.182 nm. Heller & Tay-

lor found that these spacings have indices of (110), (200), and (020) planes, respectively, and they reported the same spacings at 0.307, 0.281, and 0.183 nm for less dried CSH (I) samples prepared hydrothermally [19]. The three lines of tobermorite (G) hydrates correspond to the three of the strongest lines of all tobermorites. All three are hk0 spacings, i.e., spacings within the layers. The (020) spacing represents half the distance between neighboring Si atoms in the chains of the SiO_4 tetrahedrons of the 2:1 layers. Twice this distance, 0.364 nm is the length of the ortho-rhombic pseudo cell. Twice the (200) spacing, 0.559 nm, is the length of the pseudo cell. However, tobermorite (G) exhibits no basal spacing, so the c length can be obtained only by using slightly modified approach [19, 20].

According to this approach, it can be concluded that in the tobermorite (G) hydrate of composition $Ca_3Si_2O_7 \cdot H_2O$, one molecule of water is between layers. After drying, the molecule contains only the hydroxylic water attached to the SiO_4 tetrahedrons in layers, and this water is more firmly held than the interlayer water. On the other hand, tobermorite is often finely divided in the c direction. This dimension of crystallite is colloidal. The dimension of the particles in the b direction, i.e., along silicate chains, is quite large; it is in the order of a micron or several microns. Thus, it seems that tobermorite is colloid in the c direction but not in the b direction. It is interesting that interlayer water is lost continuously, as water is usually lost by colloids, but the water content of the silicate chains remains almost constant independently on the conditions of its setting [16, 21].

The adhesion of tobermorite particles to each other and to other bodies is responsible for the strengths of hardened pastes of tricalcium and dicalcium silicates; it is also the most important factor in the strengths of hardened portland cement pastes. Compressive strength of hardened portland cement pastes exceed their tensile strength by an order of magnitude, and compressive strengths of hardened CS pastes are about the same with those of hardened portland cement pastes. Although no data have been published on tensile strengths of CS pastes, it seems likely that they are lower than those of portland cement pastes because CS pastes are dispersed easily by ultrasonic vibrations contrary to portland cement pastes [22, 23].

CONCLUSION

The advantages of synthesis of active silicate phases by combined sol gel and high-temperature self-propagating wave method, by the first time applied in this paper, are clearly shown. The obtained nanostructured silicate phases are very active. They show significant increase of setting properties of active silicate phase, as the most important phase in any endodontic mixture.

The process of hydration of CS phases is carefully analyzed by XRD and FTIR, from the aspect of structural changes inside the mixture during its wetting for 1, 3, 7 and 28 days. After 3 days, β-C_2S and C_3S phases were mostly transformed to tobermorite, while after 7 day they

were completely transformed. The mechanism of hydration was proposed and deep insight into difficulties in determination of the exact reaction, joined with a problem of determination of the exact structure of tobermorite, was given.

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Primena vrlo aktivne kalcijum-silikatne faze u endodonciji

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KRATAK SADRŽAJ
Uvod Mineral trioksidni agregat (MTA) je jedan od najčešće korišćenih materijala u endodonciji. S obzirom na njegove nedostatke, intenzivno se traga za novim materijalima. Kalcijum-silikatna faza (CS faza) je novi materijal sintetisan prema metodi zasnovanoj na kombinaciji sol-gel procesa i samoprenosivoj sintezi koja može značajno poboljšati vreme vezivanja kroz ubrzanu hidrataciju. Cilj ove studije je bio da objasni mehanizme otvrdnjavanja CS faze u vodenom medijumu budući da se sličan mehanizam očekuje u kontaktu s telesnim tečnostima.
Materijal i metode rada CS faze Ca_3SiO_5 (C_3S) i 2β-$CaSiO_4$ (β-C_2S) su sintetisane iz $CaCl_2 \cdot 5H_2O$ (*Merck*, Nemačka). Da bismo istražili proces hidratacije, CS su pomešani s vodom i ostavljeni 28 dana na 37°C u zatvorenim polietilenskim kontejnerima. Analiza sastava uzoraka pre potapanja u vodu i jedan dan, tri, sedam i 28 dana nakon potapanja izvršena je difraktometrijom radioloških zraka i FTIR.
Rezultati XRD obrasci za uzorke hidratisane tokom jednog, tri, sedam i 28 dana pokazuju da se količina hidratisane faze tobermorita u odnosu na količinu faze CS menja s vremenom hidratacije. Kod uzorka hidratisanog jedan dan, pored hidratisane faze tobermorita, utvrđene su i značajne količine β-C_2S i C_3S koje su ostale netransformisane, da bi kod uzoraka hidratisanih 28 dana CS faza bila potpuno transformisana u tobermorit uz male količine portlandita.
Zaključak Pomoću kombinovane metode sol-gel i metode samopropagirajućih talasa na visokoj temperaturi dobijene su veoma aktivne nanostrukturne silikatne faze. Proces hidratacije CS faza je analiziran pomoću XRD i FTIR, predložen je mehanizam hidratacije i ukazano na teškoće u utvrđivanju tačne reakcije, kao i na problem utvrđivanja tačne strukture tobermorita.
Ključne reči: kalcijum-silikat; endodoncija; vreme vezivanja; otpornost na pritisak; XRD

UVOD

Mineral trioksidni agregat (MTA) je jedan od najčešće korišćenih materijala u endodonciji, u lečenju perforacije kanala, pulpotomiji, terapiji vitalne pulpe, za postizanje apeksne barijere kod nekrotičnih zuba itd. Nakon primene MTA za direktno prekrivanje pulpe kod stalnih zuba pojava kalcifikovanog mosta uočena je nakon samo nedelju dana [1, 2]. Nekoliko studija *in vitro* i *in vivo* pokazalo je da MTA obezbeđuje mnogo bolje zaptivanje u odnosu na amalgam, IRM i Super EBA materijale [1, 3-6]. Međutim, postoji nekoliko važnih nedostataka MTA: dugo vreme vezivanja, slaba reološka svojstva i slabljenje strukture materijala tokom hidratacije u kiseloj sredini. Takođe, veličina čestica, odnos praha prema tečnosti, temperatura i prisustvo vazduha mogu uticati na fizičke osobine MTA [6]. Stoga potraga za novim materijalom sa sličnim svojstvima koji pokazuje bolju aktivnost kalcijum-silikata (CS) i bolja mehanička svojstva nije završena.

U našoj studiji je sintetisana kalcijum-silikatna faza (CS faza) prema metodi zasnovanoj na kombinaciji sol-gel procesa i samoprenosivoj sintezi, što može značajno poboljšati vreme vezivanja dobijenih faza kroz njihovu ubrzanu hidrataciju. U studiji je posebno analiziran proces hidratacije, kao najodgovorniji proces za njihove osobine.

Cilj ove studije je bio da objasni mehanizme otvrdnjavanja cementa u vodenom medijumu budući da se sličan mehanizam očekuje u kontaktu s telesnim tečnostima.

MATERIJAL I METODE RADA

Sinteza kalcijum-silikatne faze i karakterizacija metode

CS faze Ca_3SiO_5 (C_3S) i 2β-$CaSiO_4$ (β-C_2S) su sintetisane iz $CaCl_2 \cdot 5H_2O$ (*Merck*, Nemačka), a silika-sol je dobijen hidrotermičkim tretmanom [7]. Hemijske supstance su korišćene po

stehiometrijskim razmerama (odnos C_3S i β-C_2S bio je 2:1), da bi se dobile silikatne aktivne faze. $Al(C_2H_3O_2)$ je dodat u ovu mešavinu da bi se omogućilo dobijanje male količine (~3%) aktivne faze C_3A.

Najpre je smesa silika-sola i $CaCl_2 \cdot 5H_2O$ osušena na 80°C da bi se dobio gel, a zatim je zagrejana na 150°C da bi se uklonila voda između silika-čestica. Da bi započela reakcija sagorevanja, dodati su amonijum-nitrat (NH_4NO_3) kao oksidans i limunska kiselina ($C_6H_8O_7CH_2O$) kao gorivo. Tokom jake reakcije samoprenosivog sagorevanja gel se pretvorio u penu a crni pepeo je dobijen kao proizvod samozapaljenja. Nakon ovog tretmana na visokim temperaturama uzorak je brzo ohlađen pomoću bakarnih ploča, kako bi se dobili visoka reaktivnost i niski kristalitet β-C_2S i C_3S faze. Na kraju, dobijeni crni prah je kalcinisan na vazduhu i 650°C četiri sata da bi se uklonio ostatak ugljenika i dobili željeni proizvodi s malim veličinama kristalita.

Da bismo istražili proces hidratacije, CS su pomešani s vodom (odnos vode i praha bio je 1:2) i potisnuti koristeći nabijač od nerđajućeg čelika. Cement se vezivao tokom 28 dana na 37°C u zatvorenim polietilenskim kontejnerima. Analiza sastava uzoraka pre potapanja u vodu i jedan dan, tri, sedam i 28 dana nakon potapanja su analizirani difraktometrijom radioloških zraka, XRD (*Philips PW 1050, Almelo*), sa Ni-filtriranim Cu-K$\alpha_{1,2}$ zračenjem. Obrasci su registrovana u rasponu 2θ 9-67° s veličinom koraka od 0,02°. FTIR analiza (*Nicollet 380 FTIR, Termo Electron Corporation*) urađena je za uzorak pre potapanja i, kao i za uzorke potopljene u vodu, 7 i 28 dana.

REZULTATI I DISKUSIJA

Analiza CS faze pre i posle potapanja u vodi

XRD obrasci CS faza (C_3S and β-C_2S) prikazani su na grafikonu 1. Vrhunci (pikovi) koji odgovaraju C_3S fazi su registrovani

na uglovima od 11,7, 23,6, 29,6, 32,5, 32,8, 33,4, 34,6 i 41,5° [s odgovarajućim ravnima: (-401), (-114), (422), (-715), (224), (-424), (1004) i (-626)], dok su vrhovi koji odgovaraju β-C_2S fazi zabeleženi na uglovima od 23,3, 29,7, 32,3, 33,0, 34,6, 41,6, 46,9, 51,9, 56,8, 60,2 i 62,7° [s odgovarajućim ravnima: (012), (120), (-121), (121), (103), (031), (024), (310), (-303), (303) i (043)]. Veličina kristalita kod ovih faza, izračunata Šererovom (*Sherrer*) jednačinom, bila je 19,9 nm.

XRD obrasci za uzorke hidratisane jedan dan, tri, sedam i 28 dana (Grafikon 1) pokazuju da se količina hidratisane faze tobermorita u odnosu na količinu faze CS menja s vremenom hidratacije. Kod uzorka hidratisanog jedan dan, pored hidratisane faze tobermorita [ravni (006), (112), (202) i (213)] i portlandita [(ravni (011), (012) i (001)], koji su pokazali napredak hidratacije, utvrđene su i značajne količine β-C_2S i C_3S koje su ostale netransformisane. Kod uzoraka hidratisanih tri dana nekoliko vrhova niskog intenziteta ukazuju na to da je samo neznatna količina CS faze bila prisutna, dok je kod uzoraka hidratisanih sedam dana C_3S nađen u tragovima, gde su vrhovi glavne hidratisane faze, tobermorita, bili izraženiji. Konačno, kod uzoraka hidratisanih 28 dana, CS faza je bila potpuno transformisana u tobermorit uz male količine portlandita.

FTIR spektar CS faza je prikazan na grafikonu 2. Tipičan dublet zabeležen između 2334 i 2364 cm^{-1} može se pripisati istežućoj vibraciji OH-grupa i objasniti padom dužine vodonične veze uzrokovane sternim efektom [7, 8]. Linija na 2172 cm^{-1} može se pripisati istežućem modusu u mala zrna, dok linija na 1968 cm^{-1} odgovara SiO_2 vibracijskom modusu [8]. Linija na 1651 cm^{-1} može se pripisati oslobađajućem modusu OH, dok široka linija s minimumom na 1414 cm^{-1} može odgovarati vibracijama delimično hidratisane C_3S i C_2S faze. Linije na 1334 cm^{-1} i 871 cm^{-1} odgovaraju asimetričnom istezanju i savijanju van ravni C-O grupe. Linija na 1121 cm^{-1} može se pripisati vibraciji C_2S jedinica, dok mala linija (rame) na 921 cm^{-1} može biti pokazatelj blage hidratacije C_3S ili C_2S. Linija na 664 cm^{-1} može se pripisati Si-O-Si simetričnoj vibraciji, dok se linija na 516 cm^{-1} pripisuje savijenoj vibraciji van ravni SiO_4 [9, 10].

FTIR spektri uzoraka hidratisanih 1 dan (S-1) i 28 dana (S-28) pokazuju linije na 3726 i 3718 cm^{-1} ukazujući na prisustvo 1,4 tobermorita koji sadrži slabo razdvojene linije u rasponu od 2800 do 3700 cm^{-1} zbog većeg sadržaja molekularne H_2O u odnosu na 1,1 nm tobermorita. Linije na 3726 cm^{-1} i 3718 cm^{-1} mogu se pripisati vibracijama koje uključuju protone vodonika vezane u molekule vode, uključujući intenzitet koji odgovara Ca-OH grupama. Slabe linije na 3740 cm^{-1} mogu se takođe pripisati Si-OH vibracijama. Linije na 2997, 2938 i 2880 cm^{-1} (S-1) i 2990, 2938 i 2872 cm^{-1} (S-28) takođe dokazuju prisustvo tobermorita od 1,4 nm [11].

Tipična oštra i izražena linija na 2357 cm^{-1} može biti dodeljena kombinaciji linija na 959 cm^{-1} i široke linije na 1407 cm^{-1}, linije na 2327 cm^{-1} i kombinaciji linija na 1407 cm^{-1} i 878 cm^{-1}, dok linija na 2364 cm^{-1} verovatno pripada kombinaciji linija na 1489 cm^{-1} i 871 cm^{-1}. Tipični dublet zabeležen između 2327 i 2357 cm^{-1} (S-1) i 2364 i 2320 cm^{-1} (S-28) može biti istežuća vibracija OH-grupe, a objašnjava se odgovarajućim smanjenjem u dužini vodonične veze izazvane sternim efektima. Slabe linije na 1407 i 1458 cm^{-1} i njene kombinacije, kao i dodatne linije na 2997, 2938 i 2880 cm^{-1} (S-1) i 2990, 2938 i 2872 cm^{-1} (S-28) i slabe vibracije na 1407 i 1414 cm^{-1} ukazuju na prisustvo ugljenika u uzorcima. Linija na 1614 cm^{-1} pripada savijajućim vibra-
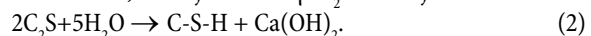
cijama molekula vode. Linije na 2159 i 2880 cm^{-1} (S-1) i 2165 cm^{-1} (S-28) mogu poticati od istegnutih modusa malih zrna SiH, postepeno izloženih oksidaciji tokom procesa sagorevanja na srednjoj temperaturi tokom sinteze datih faza. Ovo je neka vrsta otisaka prstiju oksidacijskog stanja silicijum-dioksida tokom sinteze ovog praha. Linije na 1709 cm^{-1} i 1702 cm^{-1} odgovaraju verovatno savijajućim vibracijama vode unutar dehidriranog gipsa prisutnog u maloj količini u uzorcima. Linija na 1216 cm^{-1} (S-28) može poticati od Si-O istežućih vibracija na Q3 mestu, tipičnog za prisustvo tobermorita veličine 1,1 nm, dok linije na 1061 i 1054 cm^{-1} pripadaju Si-O istežućim vibracijama na Q2 mestu tobermorita od 1,1 nm. Ovo dokazuje moguću kombinaciju tobermorita veličine 1,4 i 1,1 nm. Linije na 955 cm^{-1} (S-1) i 966 cm^{-1} (S-28) pripadaju vibracijama Si-O rešetke, dok linije na 878 cm^{-1} (S-1) i 871 cm^{-1} (S-28) pripadaju vibracijama van ravni C-O grupe. Linije na 664 cm^{-1} (S-1) i 671 cm^{-1} (S-28) mogu se pripisati Si-O-Si savijajućim vibracijama unutar silika lanaca i v_4 SO_4^{2-} savijajućih vibracija. Ove linije se takođe mogu pripisati Si-O-Si simetričnim vibracijama, dok trake na 494 cm^{-1} (S-1) i 509 cm^{-1} (S-28) pripadaju savijajućim vibracijama van ravni grupe SiO_4. Konačno, linije na 406 cm^{-1} (S-1) i 414 cm^{-1} (S-28) odgovaraju deformacijama SiO_4 tetraedara.

Proces hidratacije kalcijum-silikatne paste

Najvažniji parametar koji utiče na vezivanje i mehanička svojstva CS faza je procenat njihove hidratacije. Hidratacija β-C_2S i C_3S faza je najvažniji proces za vezivanje ovih faza tokom njihovog starenja u vodenim rastvorima. Kao što je pomenuto u različitim studijama [8-12], reakcija između C_3S i vode je glavni faktor u određivanju vezivanja i stvrdnjavanja smese cementa. Tokom ove reakcije zrna CS se navlaže i uzrokuju brzo oslobađanje Ca^{2+} i OH^- jona s površine svakog zrna. Proces transformacije C_3S u amorfni kalcijum-silika-hidrat (C-S-H), poznat kao tobermorit-gel i kalcijum-hidroksid (Ca(OH)$_2$), može se prikazati pomoću reakcije:

$$2C_3S + 7H_2O \rightarrow C\text{-}S\text{-}H + 3Ca(OH)_2. \tag{1}$$
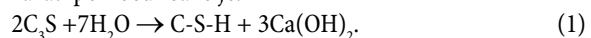
Slično tome, reakcija između β-C_2S i vode je izražena kao:

$$2C_2S + 5H_2O \rightarrow C\text{-}S\text{-}H + Ca(OH)_2. \tag{2}$$

C-S-H dobijen u obe reakcije poslednji je član u seriji hidrata koje je Tejlor (*Taylor*) opisao kao kalcijum-silika-hidrat (I) ili CSH (1) i on može biti promenljivog sastava. Bernal (*Bernal*) je prvi dodelio strukturnu formulu Ca$_2$[SiO$_2$(OH)$_2$]$_2$ [Ca(OH)$_2$] ovom jedinjenju [8-14].

Teškoće u određivanju tačne reakcije su povezane s problemom utvrđivanja tačne strukture i odgovarajuće formule tobermorita. Pretpostavili smo da je idealna formula tobermorita 4CaO·Ca(OH)$_2$·6SiO$_2$·4H$_2$O iako je dobro poznato da je centralni deo svakog sloja tobermorita sličan oktaedarskom sloju u mineralu gline, koji bi se mogao opisati kao iskrivljen kalcijum-hidroksidni sloj lišen svih atoma vodonika (CaO$_2$). Ovaj sloj je okružen na obe strane paralelnim redovima lanaca tipa volastonita, koje su prignječene u ravni upravnoj na ravni slojeva [13-16].

Samo dve trećine tetraedara svakog lanca je direktno povezano s centralnim CaO$_2$ slojem deleći atome kiseonika. Preostala trećina koja je udaljena od CaO$_2$ sloja može se posmatrati kao „premošćujući" tetraedri. Opisani kompozitni slojevi 2:1 imaju sastav Ca$_4$SiO$_4$O$_{18}$. Preostali ili međusloj čine atomi kalcijuma i

molekuli vode koji su postavljeni između ovih slojeva. Raspored vodonika je neizvestan. Verovatno ima više SiOH grupa nego što je predstavljeno formulom $Ca_4(SiO_4O_{18}H_2)\cdot Ca\cdot 4H_2O$, uz odgovarajuću zamenu vode iz međusloja hidroksilnima grupama [15, 16, 17]. U skladu s tim, kada se priprema CS pasta, C_3S faza verovatno reaguje veoma brzo i voda postaje iznenada zasićena sa $Ca(OH)_2$ (reakcija se dešava u nekoliko minuta). Isto se dešava i sa β-C_2S, ali sporije. Kao rezultat hidratacije dolazi do stvaranja $Ca(OH)_2$ i jednog člana podgrupe tobermorita (G, tobermorite 11) [15]. Ako su, međutim, silikati hidratisani u velikom višku vode, tako da je koncentracija kreča u rastvoru ispod zasićenja, C-S-H koji se formira nije član (G) serije tobermorita i onda ne dolazi do formiranja $Ca(OH)_2$. CaO/SiO_2 odnos u C-S-H zavisi od konačne koncentracije kreča u rastvoru [donja granica odnosa (pri niskoj koncentraciji kreča) je oko 0,8, a gornja granica je oko 1,5 (na ili blizu zasićenja kreča)] [16].

Tejlor i Hovison (*Howison*) [17] su merili gustinu CSH (I) u opsegu odnosa od 0,81 do 1,50 CaO/SiO_2, ali nisu našli sistematski trend povećanja gustine s porastom odnosa. Oni su takođe unapredili hipotezu za objašnjenje konstantne gustine zajedno s konstantnom dimenzijom jedinične ćelije. Ukazali su na to da kod rastućeg odnosa CaO/SiO_2 kalcijum zamenjuje silicijum u rešetki. „Premošćujući" SiO_4 tetraedri koji nisu vezani za centralni CaO_2 sloj postepeno se uklanjaju ili, tačnije, samo SiO_2 se uklanja, zato što su dva jona kiseonika u svakom tetraedru zajednički za susedne grupe. Jon kalcijuma ulazi u rešetku, ali ne direktno na mesto SiO_2, odnosno ne u sloj, već između slojeva. Pošto jon kalcijuma ima dvostruko pozitivno naelektrisanje a SiO_2 je neutralan, dva jona vodonika moraju takođe biti uklonjena da bi se očuvalo konstantno naelektrisanje. Ukupna zamena je SiO_2H_2 s kalcijumom. Takva zamena će imati relativno mali uticaj na veličinu ćelija. To bi takođe objasnilo sporu ekvilibraciju između CSH (I) hidrata i $Ca(OH)_2$ rastvora. Ako bi povećanje sadržaja kreča podrazumevalo samo apsorpciju kreča između slojeva, ne bi se očekivala tako spora ekvilibracija. Konačno, hipoteza predviđa da će gornja granica odnosa CaO/SiO_2 biti 1,75, odgovarajući uklanjanju svih „premošćujućih" tetrahedara. Iako je gornja granica odnosa za CSH (I) podgrupu oko 1,5, gornja granica za tobermorit (G) podgrupu je 1,75, kao i za drugu podgrupu, CSH (II). Moguće je da tobermorit (G) ili CSH (II) ili obe podgrupe formiraju kontinuiranu seriju sa CSH (I). Brunauer i Grinberg su modifikovali Tejlor-Hovisonovu hipotezu uz napomenu da je SiO_2H_2 zamenjen ne samo kalcijumom, već i molekulima vode. Takva zamena će dovesti do daleko bolje konstantnosti veličine ćelija nego zamena po Tejlor-Hovisonu, a takođe bi bolje objasnila pronađen sastav tobermorita, što bi dalje objasnilo konstantnost ranije pomenutog c razmaka [18]. Modifikovana Tejlor-Hovisonova hipoteza objašnjava dobro sastav, strukturu, gustinu i neke druge osobine hidrata iz CSH (I) podgrupe, možda čak cele tobermoritne grupe. Pored strukturnih varijacija, CSH (I) hidrati pokazuju širok spektar specifičnih površina. Takve razlike u strukturi i površini su, nesumnjivo, odgovorne za razlike u odnosu između sastava različitih vrsta CSH formiranih tokom procesa hidratacije [16, 17, 18].

U suprotnom, dobro je poznato da su tobermoritni (G) hidrati loše kristalizirani. Difrakcijom radioloških zraka dobijaju se tri linije: jedna s veoma jakom i širokom refleksijom, sa maksimumom na 0,305 nm, i dve mnogo slabije široke linije

na 0,279 i 0,182 nm. Heler (*Heller*) i Tejlor [19] su otkrili da ovi razmaci imaju indekse u ravnima (110), (200) i (020). Oni su takođe ustanovili rastojanja od 0,307, 0,281 i 0,183 nm za slabije osušene uzorke CSH (I) pripremljene hidrotermalnom metodom. Tri linije tobermoritnih (G) hidrata su najjače linije svih tobermorita. Sve tri su (hk0) razmaci, odnosno razmaci unutar slojeva. Razmak (020) predstavlja polovinu rastojanja između susednih Si atoma u lancima SiO_4 tetraedara u 2:1 slojevima. Dvostruko ovo rastojanje, 0,364 nm, jeste dužina ortorombične pseudoćelije. Dvostruki razmak (200), 0,559 nm, jeste dužina pseudoćelije. Ipak, tobermorit (G) ne pokazuje osnovni razmak, pa se c dužina može dobiti samo pomoću neznatno izmenjenog pristupa [19, 20].

Prema takvom pristupu, može se zaključiti da je u sastavu tobermoritnih (G) hidrata $Ca_3Si_2O_7\cdot H_2O$ samo jedan molekul vode između slojeva. Posle sušenja, molekul sadrži samo hidroksilnu vodu vezanu za SiO_4 tetraedre u slojevima, i ova voda je mnogo čvršće vezana nego voda iz međusloja. S druge strane, tobermorit je veoma često podeljen u c pravcu. Ova dimenzija kristalita je koloidna. Dimenzija čestica u b pravcu, tj. duž silikatnih lanaca, prilično je velika, reda mikrometra ili više mikrometara. Stoga se čini da je tobermorit koloid u c pravcu, ali ne i u b pravcu. Zanimljivo je da se međusloj vode stalno gubi, kako se voda obično gubi kod koloida, ali sadržaj vode silikatnih lanaca ostaje skoro konstantan nezavisno od uslova vezivanja [16, 21].

Prianjanje tobermoritnih čestica međusobno kao i sa drugim je odgovorno za snažnu vezu u stvrdnutoj pasti trikalcijum-silikata i dikalcijum-silikata. To je takođe najvažniji faktor snage stvrdnutih Portland cementa. Otpornost na pritisak Portland cementa prevazilaze njihove zatezne čvrstoće za jedan red veličine, a čvrstoća očvrslog CS je otprilike ista kao i kod Portland cementa. Iako ne postoje publikovane zatezne čvrstoće CS pasti, pretpostavlja se da su verovatno niže nego kod Portland cementa, jer CS paste se lako raspršuju pomoću ultrazvučnih vibracija za razliku od Portland cementa [22, 23].

ZAKLJUČAK

Prednosti sinteze aktivnih silikatnih faza kombinovanom sol-gel i metodom samopropagirajućih talasa na visokoj temperaturi se prvi put primenjuju u ovom radu. Dobijene su veoma aktivne nanostrukturne silikatne faze. One su postigle poboljšano vezivanje aktivne silikatne faze, kao najvažnije faze u svakoj smesi endodontskog materijala.

Proces hidratacije CS faza je pažljivo analiziran pomoću XRD i FTIR, sa aspekta strukturnih promena unutar smese tokom kvašenja od jednog, tri, sedam i 28 dana. Posle tri dana β-C_2S i C_3S faze su uglavnom pretvorene u tobermorit, a nakon sedam dana su potpuno bile transformisane. Predložen je mehanizam hidratacije i ukazano na teškoće u utvrđivanju tačne reakcije, kao i na problem utvrđivanja tačne strukture tobermorita.

ZAHVALNICA