COMPORTAREA IN-VITRO A SILICATULUI DICALCIC OBȚINUT PRIN METODA SOL-GEL
IN-VITRO BEHAVIOR OF DICALCIUM SILICATE OBTAINED THROUGH THE SOL-GEL METHOD

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In the sol-gel synthesis of dicalcium silicate (Ca_2SiO_4 – C_2S) the calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$) and trietoxysilane ($C_6H_{16}O_3Si$ - TEOS) were used as precursors. The C_2S was obtained at 800-1100°C.

Thermal analysis methods (DTA/TG), X-ray diffraction (XRD) and scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDX) were used to investigate the formation of dicalcium silicate.

The in-vitro behavior was also investigated by soaking of the dicalcium silicate powder in simulated body fluid (SBF) for 7 days. Our results indicated that dicalcium silicate formed in SBF hydrosilicates as principal mineralogical phases and bound a small proportion of the phosphor from liquid as phosphate phases.

Precursorii utilizați în vederea sintezei silicatului dicalcic (Ca_2SiO_4 – C_2S) prin metoda sol-gel au fost: azotatul de calciu tetrahidrat ($Ca(NO_3)_2{\cdot}4H_2O$) şi trietoxi silanul ($C_6H_{16}O_3Si$ - TEOS). C_2S a fost obținut în intervalul de temperatură 800-1100°C.

Tehnicile utilizate în vederea invesigării formării silicatului dicalcic au fost: analiza termică complexă (ATD/TG), difracția de raze X şi microscopia electronică de baleiaj cuplată cu spectroscopie de energie dispersivă de radiație X (MEB/EDX).

Comportarea in-vitro a fost de asemenea investigată prin scufundarea pulberii de silicat dicalcic în lichid fiziologic simulat/sintetic pentru 7 zile. Rezultatele noastre indică că silicatul dicalcic în lichid fiziologic simulate arată că faze mineralogice principale hidrosilicați, iar o cantitate mică de fosfor din lichid se leagă ca faze fosfatice.

Keywords: *dicalcium silicate; sol-gel synthesis; in-vitro behavior*

1. Introduction

Mineral trioxide aggregate (MTA) was developed as a root-end filling material in endodontology [1-6]. MTA was shown to be superior to other commonly used root-end filling materials such as amalgam, zinc oxide-eugenol cement (IRM) and Super-EBA in studies of marginal adaptation and leakage. Recently, some studies have compared MTA with Portland cement (PC) and the findings suggest that PC has major ingredients in common with MTA [3-6].

Portland cement consists of four main phases: $3CaO{\cdot}SiO_2$ (C_3S), $2CaO{\cdot}SiO_2$ (C_2S), $3CaO{\cdot}Al_2O_3$ (C_3A), $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$ (C_4AF). The silicate compounds are responsible for development of mechanical strength, while the aluminate compounds are mainly responsible for setting of cement [7]. It is indicated to know the behaviour of these pure phases in-vitro conditions.

The conventional preparation of pure cement phases is performed through solid-state reactions and involves the sintering of stoichiometric mixtures of oxides or carbonates at high temperatures for prolonged time or repeated calcinations [7, 8].

Instead of solid-state sintering, alternative low temperature techniques such as sol-gel [9, 10] and combustion [11] were also proposed.

In this study a modified sol-gel process was used to synthesize dicalcium silicate. The in-vitro behavior of the as-prepared C_2S was then evaluated by soaking in SBF.

2. Experimental

2.1. Preparation of $2CaO{\cdot}SiO_2$ powders

The dicalcium silicate was synthesized by the sol-gel method, using $Ca(NO_3)_2{\cdot}4H_2O$ and TEOS as raw materials with a CaO/SiO_2 molar ratio of 2 – Figure 1

The nitrate salt was dissolved in 100 ml ethanol and magnetically stirred until a clear solution was obtained. The TEOS was hydrolysed, the molar ratio TEOS: water was 1:4. The clear solutions was continuously stirred at 60°C, 1 hour, than was kept at 60°C up to 72 hours, to facilitate the alcohol evaporation and to accelerate the polycondensation reaction, resulting in the formation of a viscous gel. This gel was then dried at 120°C, 24 hours resulting in the formation on a white powder.

Based on the results of thermal analysis (DTA/TG) performed on the dried gel, this one was thermally treated at 600°C/3h for the dissociation of polymer network, burning of the organic material and completion of all decomposition processes. The synthesized powder was then calcined in different conditions: 800°C/1h; 1000°C/1h, 2h; 1050°C/1h; 1100°C/1h, and subjected to a rapid cooling in air. The resulted oxide powders were investigated by XRD and SEM.

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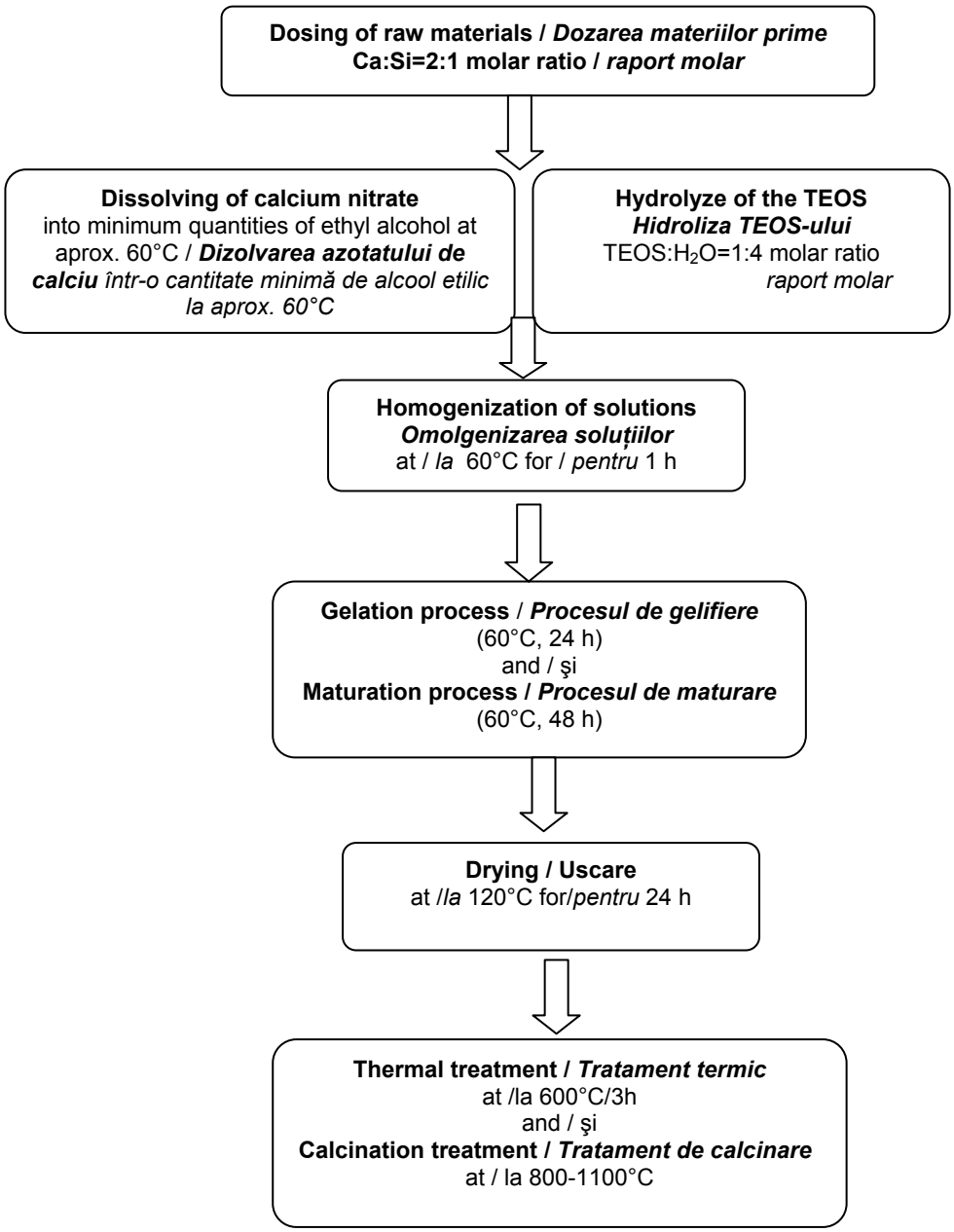


Fig. 1 - The obtaining of the dicalcium silicate by sol-gel method / *Obținerea silicatului dicalcic prin metoda sol-gel.*

The free calcium oxide (CaO_{free}) was determined by an analytical method, *i.e.* the titration of calcium (II) with hydro chloric acid 0.1 N, using characteristic indicator (mix formed phenolphthalein with naphtolphtaleine).

2.2. Soaking in SBF

The SBF is similar to that of human blood plasma (table 1). The dicalcium silicate powder obtained at 1100°C/1h was soaked in SBF solution into a bath at 37°C for 7 days at a solid/liquid ratio of 0.5 mg/ml, without refreshing the soaking medium. After the preselected soaking time, the powders were filtrated and dry at 40°C/24 h. After drying, the powder was characterized by SEM coupled with EDX.

The differential thermal analysis coupled with thermo gravimetric analysis (DTA/TG) was performed on a Shimadzu DTG-TA- 50H, at a heating rate of 10°C /min, in static air to 1000°C.

X-ray diffraction analysis was performed using a SHIMADZU XRD 6000 diffractometer, using Ni-filtered CuKα radiation, with scan step of 0.02° and counting time of 0.6 s/step, for diffraction

Table 1

Composition of SBF/*Compoziția SBF-lui*

Ionic concentration/*Concentrația ionică* (mM)									
Solution SBF /*Soluție de SBF*	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	HCO_3^-	HPO_4^{2-}	Buffer/*Soluție tampon*	pH
	142	5	1.5	2.5	148.8	4.2	1		7.25

angles 2 theta ranged between 20 and 65°, at room temperature.

SEM images were obtained by using a HITACHI S2600N equipment coupled with EDX probe, the samples being covered with a silver layer.

3. Results and discussion

Figure 2 shows the DTA, TG and DTG curves of the dried gel. The total weight loss of the sample is 65.18% (w/w). Three endothermic effects accompanied by mass loss were recorded on the DTA/TG curves: at 84°C for loss of physic water, at 565-584°C for dehydroxylation of calcium hydroxide and 663°C for decarbonation of calcium carbonate formed accidental by carbonation in during of synthesis. One small exothermic effect accompanied by mass loss was recorded on the DTA/TG curves can be attributed to the dissociation of polymer network and burning of the organic material.

Figure 3 presents the XRD patterns of the calcined masses at different temperatures. It can be seen that the identified crystalline phases were dicalcium silicate and calcium oxide.

The free calcium oxide values (CaO_{free}) are showed in table 2. These data are in concordance with the diffraction data.

The powder resulted after calcination at 1100°C/1h was used to study the in-vitro behavior. Microstructural characteristics of this powder are presented in Figure 4 which showed polyhedral particles with sizes below 500 nm and with a pronounced tendency to form agglomerates.

The SEM images and EDX data of the sample after soaking for 7 days are presented in Figures 5a-c and Table 4, respectively.

Table 2

CaO_{free} (%) values for dicalcium silicate obtained in different thermal treatment conditions
Valorile de CaO_{liber} (%) pentru silicatul dicalcic obținut în diferite condiții de tratament termic

Thermal treatment conditions *Condiții de tratament termic*	1050°C/1h	1100°C/1h
CaO_{free} / CaO_{liber} (%)	0.85	0.75

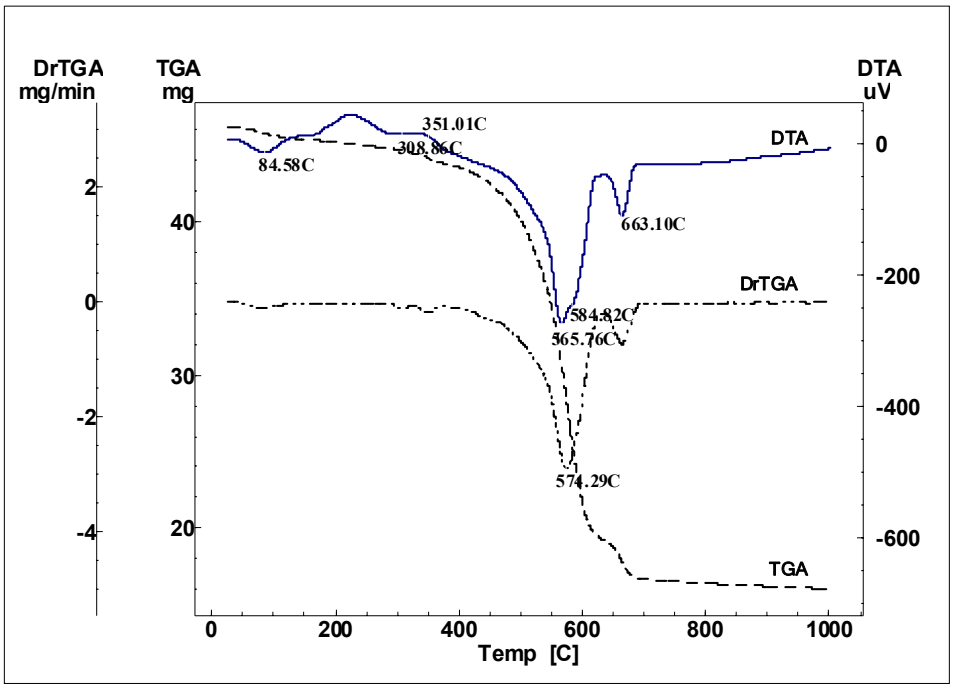


Fig. 2 - The DTA, TG and DTG curves of dried gel / *Curbele ATD, TG şi DTG pentru gelul uscat.*

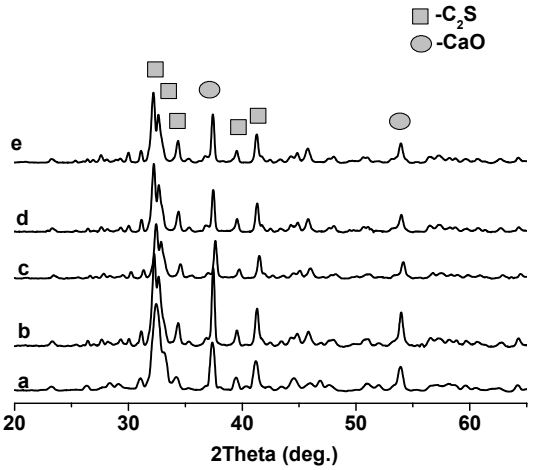
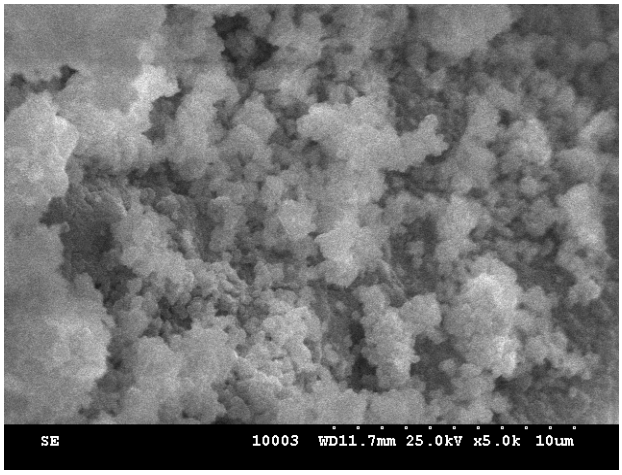
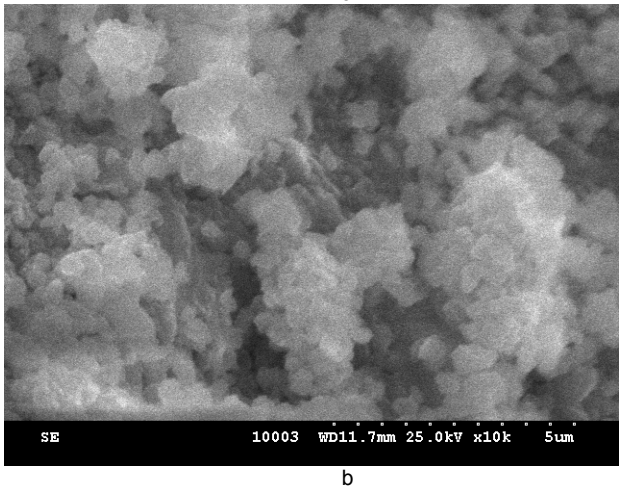


Fig. 3 - The XRD patterns of the dried gel, treated at 600°C/3h and then calcined at different temperature / *Imaginile de difracție de raze X pentru gelul uscat, tratat termic la 600°C/3h şi apoi calcinat la diferite temperaturi*: a - 800°C/1h; b - 1000°C/1h; c - 1000°C/2h; d - 1050°C/1h; e - 1100°C/1h.



a



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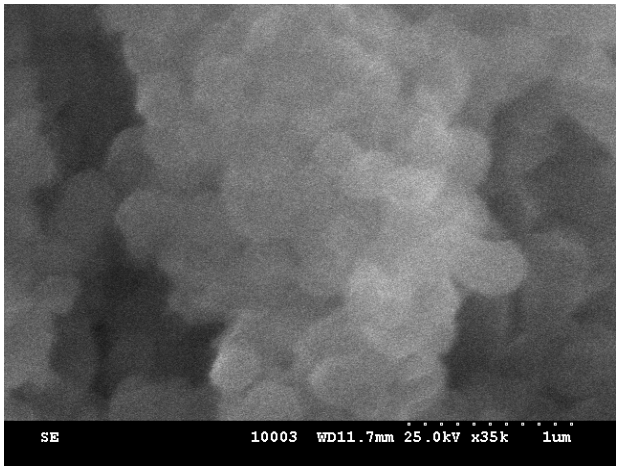

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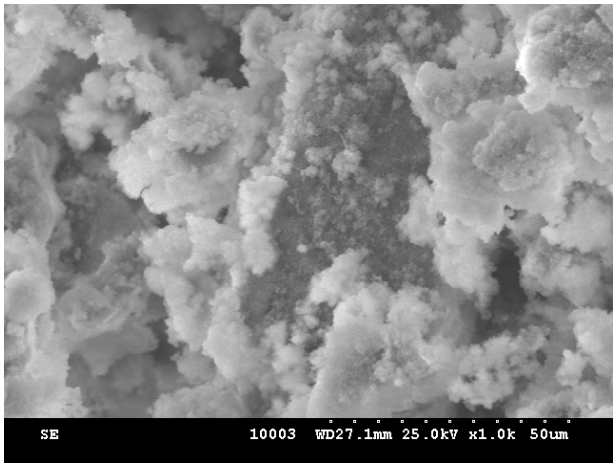
Fig. 4 - SEM images for C_2S powder obtained at 1100°C/1h / *Imaginile MEB pentru pulberea de C_2S obținută la 1100°C/1h:* a – x5000; b- x10000; c- x35000.



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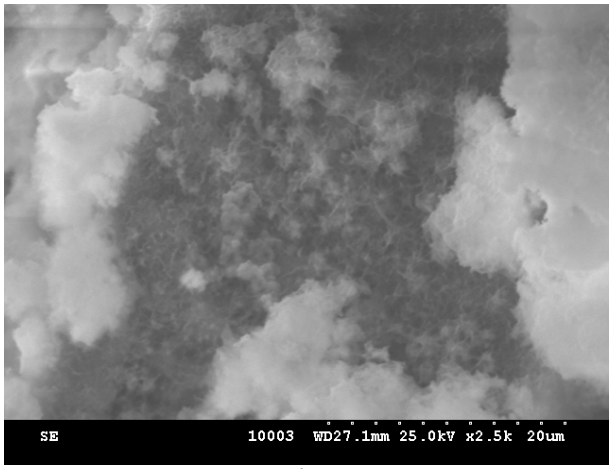

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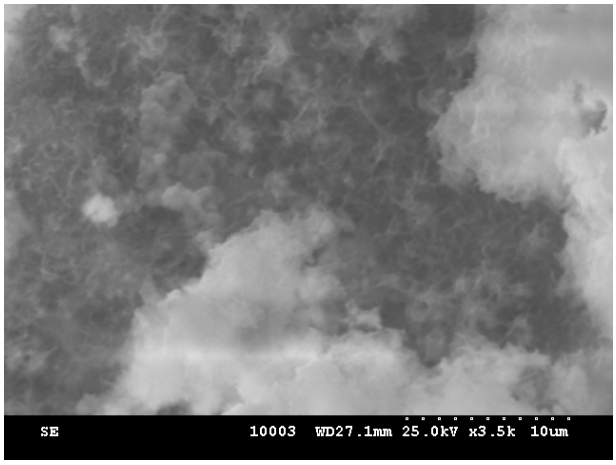

c

Fig. 5 - SEM images for C_2S powder obtained at 1100°C/1h after soaking for 7 days in SBF / *Imaginile MEB pentru pulberea de C_2S obținută la 1100°C/1h după scufundarea timp de 7 zile în lichid fiziologic simulat/sintetic:* a – x1000; b- x2500; c- x3500.

The SEM images (Fig. 5) revealed that after soaking in SBF, the surface of the C_2S particles was covered mainly with foils and fine needles of calcium hydrosilicates.

EDX data (table 3) indicate that phosphorus from SBF was incorporated in at least one of the crystalline phases of the powdered samples. The formation of some phosphates can not be excluded, but because of their low concentration and crystallinity degree (below the XRD accuracy), their detection is difficult.

Table 3

The EDX data of C_2S obtained at 1100°C/1h and soaked in SBF for 7 days

Datele EDX pentru C_2S obținut la 1100°C/1h şi scufundat în lichid fiziologic simulat/sintetic pentru 7 zile

Element / *Element*	Ca	Si	P
Concentration / *Concentrație* (%)	81.47	16.92	1.61

4. Conclusions

The sol-gel synthesis represents a better approach for synthesis of pure C_2S. This synthesis method is more effective than the conventional preparation involving high temperatures, prolonged plateaus and / or multi-step calcinations with intermediate grinding.

After soaking of C_2S powder in SBF, the appearance of hydrosilicates as principal mineralogical phases and bound a small proportion of the phosphor from liquid as phosphate phases.

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