Synthesis and physicochemical investigation of calcium silicate hydrate with different stoichiometric composition

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Abstract. Calcium silicates are considered as promising components of materials for hard tissue repair. The main attention is paid to the crystalline forms of these substances. In the present study, a series of amorphous calcium silicate hydrates with molar coefficient Ca/Si = 0.65 - 1.45 was prepared by precipitation in aqueous solutions. The samples were analysed using X-ray diffraction, FT-IR spectroscopy, SEM, TGA, BET. The dynamics of calcium silicate hydrates dissolution in Tris-buffer solution with pH = 7.40, corresponding to the acidity of human plasma, was compared with wollastonite and apatite. It is shown that calcium silicate hydrates actively dissolve in a slightly alkaline medium, ensuring the appearance of calcium ions in the solution in amounts that exceed the cation concentrations in systems with $\beta$-CaSiO$_3$ и Ca$_{10}$(PO$_4$)$_6$(OH)$_2$.

1. Introduction

To date, a very wide range of synthetic materials has been proposed for medical use to repair damaged areas of human hard tissues. Among them there are Ca$_{10}$(PO$_4$)$_6$(OH)$_2$, Ca$_{10}$(PO$_4$)$_6$F$_2$, ($\alpha$-, $\beta$-)Ca$_3$(PO$_4$)$_2$, CaHPO$_4$·2H$_2$O, Ca$_4$H$_2$(PO$_4$)$_5$·5H$_2$O, Ca$_2$P$_2$O$_7$, CaCO$_3$, CaSO$_4$, Ca(OH)$_2$, CaSiO$_3$ and some other substances [1-6]. They are successfully used in traumatology, orthopedics, maxillofacial surgery, dentistry, because they can provide local replacement of the cavities and defects, as well as stimulate the formation of new bone due to the gradual dissolution and release into the environment of Ca$^{2+}$ ions which can involve in the mineral formation processes.

A special place among the listed substances is occupied by calcium silicates. These include CaSiO$_3$ – calcium metasilicate, Ca$_2$SiO$_4$ – calcium orthosilicate, Ca$_3$SiO$_7$ – calcium pyrosilicate, Ca$_3$SiO$_5$ – tricalcium silicate and group of compounds with the general formula $r$CaO·$m$SiO$_2$·$n$H$_2$O – calcium silicate hydrates (CSH). These salts contain Ca$^{2+}$ cations – building elements of bone mineral, as well as anions of SiO$_3^{2-}$. In work [7] it is noted that the latter participate in the formation of the organic matrix of bone at the initial stages of its calcification, act as a catalyst for the processes of calcium assimilation (at its low content), initiate mineralization. In this regard, it seems promising to use materials based on calcium silicates in medicine.

While materials based on crystalline forms of calcium silicates have been successfully used in dental practice (see the paper [8] about the mineral trioxide aggregate (MTA) containing up to 75 wt.% of Ca$_2$SiO$_4$ and Ca$_3$SiO$_3$) and are being actively investigated in terms of the possibility of their using in bone tissue engineering [9–11], amorphous CSHs (as independent therapeutic compositions) have not yet found wide application in medicine, despite the high bioactivity [12, 13]. They are mainly used in industry as fillers of building materials and are studied as hardening products that ensure the strength of portland cement [14–16].

Industrial calcium silicates are derived from a variety of natural raw materials and/or technological
wastes that has accumulated in significant quantities [14]. The resulting products often contain chemically and mechanically incorporated impurities, which can cause negative reactions of the organism during materials biomedical application. In this connection, the methods for CSH synthesis from commercial reagents are more preferable, since it is possible to obtain powders free from unwanted phases with uniform morphology and dispersion. Individual studies are related to the salts synthesis under specific parameters of the reaction system [13, 17-20] and a comparison of the bioactivity of the obtained amorphous product and its crystalline form [13]. It is known that there are about 30 hydrates of acidic and basic calcium silicates of variable composition [21]. They differ from each other by the content of crystallization water, the stoichiometric ratio of the oxides forming them and the structure [21]. It is expected that the properties of the different CSHs are not the same, because the interconnection of the composition - structure - properties exists for many substances. Therefore, it seems important to establish a correlation between the form of calcium silicate precipitated under certain conditions and its characteristics, in particular solubility in media modelling extracellular fluids of the human body.

2. Problem formulation
The task of this work is the synthesis and physicochemical investigation of calcium silicate hydrates with various stoichiometric composition, as well as the kinetic study of their degradation in solutions modelling extracellular fluids of the human body.

3. Materials and methods
It is known that calcium silicate hydrates are poorly soluble compounds and can be obtained by precipitation from aqueous solutions of reagents containing Ca$^{2+}$ and SiO$_3^{2-}$ ions according to the scheme:

$$r \text{CaX}_2 + m \text{M}_2\text{SiO}_3 + n \text{H}_2\text{O} \rightarrow r\text{CaO} \cdot m\text{SiO}_2 \cdot n\text{H}_2\text{O} \downarrow + \text{MX}$$

The process conditions (temperature, speed of reagents mixing, etc.) and the medium composition (components concentration, pH) influence on the composition, amount, crystallinity, and morphology of the synthesis product.

On the basis of the earlier studies [22], the conditions for obtaining a series of calcium silicate hydrates with the molar ratio Ca/Si = 0.65 - 1.45 have been chosen (table 1). Crystalline β-CaSiO$_3$ (β-wollastonite) and Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ have been chosen as the comparison samples.

| Ca/Si     | C$_{\text{Ca(NO}_3)_2}$, mol/l | C$_{\text{Na}_2\text{SiO}_3}$, mol/l | pH  | $\omega$, ml/min$^1$ | $\tau$, h | $t$, °C$^2$ | $T$, °C$^3$ |
|-----------|-------------------------------|-----------------------------------|-----|---------------------|----------|-----------|-----------|
| 0.65      | 0.05                          | 0.1                               | 12  |                     |          |           | 105$^4$   |
| 0.85      | 0.1                           | 0.1                               | 11  |                     |          |           |           |
| 1.00      | 0.1                           | 0.1                               | 12  |                     |          |           |           |
| 1.20      | 0.15                          | 0.1                               | 12  | 4 - 5               | 24       | 25        |           |
| 1.45      | 0.2                           | 0.1                               | 12  |                     |          |           |           |
| CaSiO$_3$ | 0.1                           | 0.1                               | 12  |                     |          |           |           |
| Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ | 0.1$^6$                    | 0.06$^6$                        | 12  |                     |          |           | 1000$^5$ |

$^1$ $\omega$ – speed of reagents mixing,

$^2$ $t$ – temperature at which the suspension obtained after initial reactants mixing is maintained,

$^3$ $T$ – temperature at which the obtained solid phases were dried,

$^4$ – drying to constant weight,

$^5$ – calcination in air at 1000 °C for 2 hours pre-dried at 105 °C powder,
– concentrations of Ca(OH)₂ and H₃PO₄ - initial reagents used for Ca₁₀(PO₄)₆(OH)₂ synthesis.

The solutions of the initial reagents were prepared before the experiment. The Na₂SiO₃ solution was added at a rate of 4 – 5 ml/min to an equivalent volume of the Ca(NO₃)₂ solution, stirred with a magnetic stirrer. After complete mixing of the reagents, the pH of the medium was adjusted with HNO₃ (1:1) or 20% NaOH to the desired value. The resulting suspension was left at room temperature for 24 hours. The precipitates was separated from the mother liquids by filtration and washed with distilled water to remove the reaction by-products. Samples were dried on air at 105 °C to constant weight, and ground in a porcelain mortar to a powder state. In this study, each experiment was carried out in triplicate.

The samples and products of their calcination were examined using a group of physicochemical methods. Powder diffraction investigations were carried out with the diffractometer «XRD-7000» (Shimadzu), using CuKα (λ = 1.54 Å) radiation as an X-ray source. Identification of the crystalline phases was carried out in the «Sieve+» software package using «PDF-4» data base. FTIR spectra were scanned on IR-spectrometer «FT-801» (Simex) using the KBr pellet technique for the range of 500 – 4000 cm⁻¹ with 4 and 32 times scanning resolution. The program «ZaIR 3.5» was used to obtain and process of the spectra. Scanning electron microscopy (SEM) analysis of the samples was carried out using the microscope «JCM-5700» (JEOL), equipped with an energy dispersive X-ray spectrometer «JED-2300» in a high vacuum mode.

The powders texture characteristics were determined by the adsorption method using nitrogen adsorption-desorption isotherms at (77.4 K) obtained on the analyzer «Gemini VII» (Micromeritics Instrument Corporation). Before adsorption measurements, the samples were trained in a vacuum at 140 °C for 10 – 12 hours. The powders specific surface area was determined by the BET method [23]. Calcination of solid phases was carried out in porcelain crucibles in the air atmosphere in the muffle furnace «EKPS-5» (Smolensk «SKTB SPU»).

Thermal analysis of the solid phases was carried out on the analyzer «DHG-60» (Shimadzu). Calcination of the samples was carried out in corundum crucibles. Analysis conditions: air speed – 70 ml/min, temperature range – from 25 to 1000 °C, rate of heating – 10 °C/min. Sample’s weight was around 38 mg. According to the obtained thermogravimetric (TG), differential-thermal (DTG) curves, the mass losses of the samples upon heating were determined.

The chemical composition of the precipitated solid phases was determined from the difference in the initial and final Ca²⁺ and SiO₃²⁻ ions concentrations in the mother liquors. Residual concentrations of ions in solutions were determined using photometric techniques on a spectrophotometer «UV-1200» (EcoView). Calcium was determined photometrically by reaction with Arsenazo III in an alkaline medium, the silicates were detected in a yellow form of molybdosilicic acid [RD 52.24.433-2005]. The resorption of CSH with different stoichiometry in Tris-buffer solution (pH 7.40 ± 0.05) was investigated. The kinetic dependences of Ca²⁺ and SiO₃²⁻ ions concentrations in solutions at different time of powders and liquid phase contact were determined. Powders with particle sizes from 40 to 70 μm were used for the study. This fraction was produced by powders sieving through laboratory sieves. The powder / liquid ratio equal to 1/200 g/ml. All experiments were carried out at 22 °C under static conditions. At certain intervals (from 1 day to 3 months) Ca²⁺ and SiO₃²⁻ ions concentration were determined by the methods described above.

4. Results

White solid phases were formed as a result of all series of syntheses. The powders composed of micrometer sizes particles with various shapes (fig. 1). The mass of samples increases with the growth of the molar Ca/Si coefficient (table 2). All freshly deposited samples are characterized by high values of specific surface area (table 2). The value of specific surface area varies nonmonotonically with increasing Ca/Si. The maximum value is fixed for the powder with the stoichiometric ratio of the elements (1.00).
Figure 1. Micrographs of CSH with (a) Ca/Si = 0.65, (b) Ca/Si = 1.00, (c) Ca/Si = 1.00 (phase – CaSiO$_3$)

Table 2. Samples characteristics

| Ca/Si | m, r | S, m$^3$/g | Δm, wt.% $^1$ |
|-------|------|------------|--------------|
| 0.65  | 1.64 ± 0.08 | 86         | 23.3 ± 0.5  |
| 0.85  | 2.65 ± 0.05  | 92         | 22.9 ± 0.1  |
| 1.00  | 2.79 ± 0.08  | 105        | 21.8 ± 0.2  |
| 1.20  | 3.04 ± 0.02  | 79         | 21.9 ± 0.1  |
| 1.45  | 3.15 ± 0.08  | 65         | 23.5 ± 0.3  |

$^1$ Δm – samples weight loss during two-hour calcination on air at 1000 °C.

Precipitated calcium silicate hydrates are amorphous, according to XRD data (Fig. 2a). Their presence in the samples composition was established by FTIR spectroscopy (Fig. 3a). Absorption bands at 1030, 970 and 670 cm$^{-1}$, corresponding to the vibrations of Si-O group bonds and Si-O-Si siloxane bridges in the CSH composition [24], and the modes of deformation vibrations of the bonds H-O-H in crystallization water molecules appear in the FTIR spectra of samples. In the spectra of freshly precipitated samples, absorption maxima at 712, 875, 1430, and 1470 cm$^{-1}$, characteristic for vibrations of C-O bonds in the composition of calcium carbonate (CC), are also recorded.

Figure 2. X-ray patterns of freshly precipitated (a) and calcined (b) calcium silicates samples.
○ calcite, □ aragonite, ◊ CaO, Δ SiO₂, ◦ β-CaSiO₃

The XRD results confirm the FTIR data and indicate that only CaCO₃ polymorphs (calcite (the trigonal CaCO₃) and aragonite (the rhombic CaCO₃)) are present in the crystalline form in the samples (Fig. 2a). There are no carbonates in the composition of the reagents used in the experiment. Obviously, their source is CO₂ of air absorbed by the open water system. H₂CO₃, which formed as a result of H₂O and CO₂ interaction, has stronger acid properties than H₂SiO₃, and able to displace the metasilicic acid from its salts. Due to this, a partial conversion of the initially precipitated CSH to the CC is possible.

It is established that the solid phases lose about 20 % of their mass during calcination due to the removal of volatile components and decomposing impurities (Table 2, Fig. 4). The adsorbed H₂O molecules that are weakly bound with samples surface evaporate at t ≈ 100 °C. In the range 100 - 200 °C water (in a state of capillary condensation in the aggregates pores) removed. The loss of mass occurring at 450-600 °C is due to the release of crystallization water from the CSH composition [13]. The minimum on the curve of DTG in the range 650-750 °C corresponds to the decomposition of the CC. Mass losses at this stage indicate that the samples contain about 25 wt.% of CC.
Figure 4. Thermogravimetric (1) and differential thermogravimetric (2) curves for sample with Ca/Si = 1.00

As a result of samples calcination at 1000 °C, crystalline phases of $\beta$-CaSiO$_3$ and SiO$_2$ (in samples with Ca/Si = 0.65 and 0.85), $\beta$-CaSiO$_3$ (sample with Ca/Si = 1.00), $\beta$-CaSiO$_3$ and CaO (in samples with Ca/Si = 1.20 and 1.45) are formed (Figures 2b, 3b). The composition of powders obtained after thermal treatment of freshly precipitated samples confirms the conclusions about the composition and stoichiometry of CSH formed during the synthesis.

An important property of substances considered as biomaterials for bone tissue engineering is their ability to dissolve in contact with biological fluids. To evaluate this characteristic of CSH with different stoichiometric composition, synthetic powders were soaked in Tris-buffer solution (an aqueous solution with pH = 7.40 ± 0.05, corresponding to the human blood pH). $\beta$-CaSiO$_3$ and Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ were also used as reference samples. Fig. 5 shows the dependence of the Ca$^{2+}$ and SiO$_3^{2-}$ ions concentrations from the time of the solid and liquid phases contact. In the process of interaction with an aqueous solution all samples gradually dissolve. The ions entering into their composition pass into solution. The Ca$^{2+}$ concentrations at each period of time depend on the samples nature. The lowest cations content in the medium is in the case of hydroxyapatite resorption. Significantly large amounts of metal ions accumulate in the systems during the calcium silicates dissolution. Amorphous CSHs dissolve more intensively, as a result Ca$^{2+}$ ions concentration in the medium contacted with the samples in 1.5-2 times more than in solution contacted with the crystalline form of salt ($\beta$-CaSiO$_3$). The Ca/Si value in the samples correlates with the calcium concentration in the system at the end of experiment. Thus, as the molar ratio increases, the content of metal ions in solutions increases.

Figure 5. Dependence of (a) Ca$^{2+}$ and (b) SiO$_3^{2-}$ ion concentrations from the time of soaking of the samples in the Tris-HCl buffer

In all studied systems, the calcium concentration at each period of time exceeds the silicates amount. The silicate ions concentrations in solutions do not reliably differ for samples of different composition and vary within the limits of 1.7 – 2.7 mmol/L.

5. Discussion

In the article [25] it is reported that at room temperature and normal pressure CSH with variable composition are formed in dilute aqueous Ca(NO$_3$)$_2$ and Na$_2$SiO$_3$ solutions by the ion exchange reaction. The Ca/Si ratio in these substances can vary from 0.66 to 1.5 due to structural defects. In this paper, a series of CSH samples with the molar coefficient Ca/Si from 0.65 to 1.45 is obtained. The synthesis of these compounds in an open system does not allow to prepare a solid phase containing only CSH without impurities. Thus, the CO$_2$ absorption by aqueous solutions leads to the replacement of silicate ions in the composition of CSH by carbonates, as a result up to 25 wt.% of the precipitated calcium silicate is transformed in CC.
When the obtained powders are maintained in Tris-buffer solution, the synthetic materials gradually dissolve in a slightly alkaline medium. Thus, Ca$^{2+}$ and SiO$_3^{2-}$ ions are found in solutions that come into contact with the samples (Fig. 5). The correlation between the Ca/Si value and the current cation concentration in the system is observed, while the silicates amounts in the medium differ insignificantly. Consequently, the cations pass into the solution faster than the anions. It is important to note that calcium content in systems with amorphous CSHs exceeds in several times the cation concentration in media interacting with crystalline phases, apatite and wollastonite. The active dissolution of CSH and the release of significant amounts of calcium ions into the liquid phase allow us to consider these substances as promising components of medical materials.

6. Conclusion
A series of CSH samples with the molar coefficient Ca/Si = 0.65 - 1.45 was obtained by deposition in an open aqueous system. The dynamics of dissolution of amorphous calcium silicates, wollastonite and apatite differs significantly. CSHs actively dissolve in a slightly alkaline environment of Tris-buffer solution. As a result of calcium silicate resorption high concentrations of calcium ions appeared in the liquid phase. These free cations can be involved in the process of the hard tissues mineral component formation in vivo.

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References
[1] Daculsi G 2016 History of Development and Use of the Bioceramics and Biocomposites Handbook of Bioceramics and Biocomposites (Switzerland: Springer International Publishing) p 3-22
[2] Saska S 2015 Implant Dent. 2 158-167
[3] Hughes E, Yanni T, Jamshidi P and Grover L M 2015 Advances in Applied Ceramics 114 65-76
[4] Dizaj S M, Barzegar-Jalali M, Zarrintan M H, Adibkia K and Lotfipour F 2015 Pharmaceutical Sciences 20 175-182
[5] Kazeko L A and Fedorova I N 2009 Modern stomatology 2 4-9
[6] Torabinejad M and Chivian N 1999 Journal of endodontics 25 197-205
[7] Grosser A V, Matelo S K and Kupec T V 2009 Journal « Prevention today » 10 6-14
[8] Parirokh M and Torabinejad M 2010 JOE 36 400-3
[9] Liu X, Morra M, Carpi A and Li B 2008 Biomedicine & Pharmacotherapy 62 526-9
[10] Xu S, Lin K, Wang Z, Chang J, Wang L, Lu J and Ning C 2008 Biomaterials 29 2588-96
[11] Sun M, Liu A, Ma C, Shao H, Yu M, Liu Y, Yan S and Cou Z 2016 The Royal Society of Chemistry 6 586-96
[12] Niu L 2014 Journal of dentistry 42 517-33
[13] Wan X, Chang C, Mao D, Jiang L and Li M 2005 Materials Science and Engineering C 25 455-61
[14] Richardson I G The 1999 Cement and Concrete Research 29 1131-47
[15] Gallucci E, Zhang X and Scrivener K L 2013 Cement and Concrete Research 53 185-195
[16] Macphee D E, Lachowski E E and Glasser F P 1988 Advances in Cement Research 1 131-7
[17] Gordienko P S, Yarusova S B, Suponina A P, Krisenko G F, Bulanova S B, Kolzunov V A and Barinov N N 2009 DVO RAS herald 2 30-33
[18] Baltakys K, Jauberthie R, Siauciuunas R and Kaminskas R 2007 Materials Science-Poland 25 663-670
[19] Foley E M, Kim J J and Taha M M R 2012 Cement and Concrete Research 42 1225-32
[20] Sasaki K, Masuda T, Ishida H and Mitsuda T 1996 J. Am. Ceram. Soc. 80 472-6
[21] Richardson I G 2008 Cement and Concrete Research 38 137-158
[22] Solonenko A P, Blesman A I, Polonyankin D A and Bel’skaya L V 2017 Glass Physics and Chemistry 43 452-8
[23] Brunauer S, Emmett P H and Teller E 1938 J. Am. Chem. Soc. 60 309-319
[24] Yu P, Kirkpatrick R J, Poe B, McMillan P F and Cong X 1999 J. Am. Ceram. Soc. 82 742-8
[25] Chen J J, Thomas J J, Taylor H F W and Jennings H M 2004 Cement and Concrete Research 34 1499