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The Influence of Zn Containing Components on the Synthesis of Z-Phase

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Abstract:

The influence of Zn containing compounds on the formation of Z-phase during hydrothermal treatment at 200 °C temperature was investigated. The molar ratio of primary mixtures was $\text{CaO}/(\text{SiO}_2 + \text{ZnO}) = 0.55$ and $\text{ZnO}/(\text{SiO}_2 + \text{ZnO}) = 0; 0.025$ (it corresponds 2.27 % ZnO in the mixture). Compounds containing Zn^{2+} ions were used: soluble in water $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and insoluble in water $5\text{ZnO} \cdot 2\text{CO}_2 \cdot 4\text{H}_2\text{O}$. It was determined that the formation of Z-phase increases approximately twice due to influence of Zn^{2+} ions from the mixture. The high crystalline compound formed after 4 hours, while in the mixtures without additives – after 8 h of hydrothermal synthesis at 200 °C temperature. Moreover, Zn^{2+} ions penetrate into Z-phase crystal lattice by exchanging Ca^{2+} ions. It was observed that insoluble $5\text{ZnO} \cdot 2\text{CO}_2 \cdot 4\text{H}_2\text{O}$ additive has no essential influence on the beginning of Z-phase formation, but it promotes Z-phase recrystallization into gyrolite. The products were characterized using X-ray powder diffraction, simultaneous thermal analysis, FT-IR spectra and scanning electron microscopy.

Keywords: Calcium silicate hydrate (CSH), Z-phase, Zinc, hydrothermal treatment.

1. Introduction

Generally structures of phyllosilicates may be regarded as stacking of alternating silicate and calcium layers which are relatively regular and consist of sixfold coordinated atoms [1,2]. The phyllosilicates are an important group of calcium silicate hydrates (CSH) that includes the gyrolite, Z-phase, reyerite, truscottite, K-phase and fedorite, tungusite, minehillite. The C/S ratio of the crystalline C-S-H phases is limited to 0.44-0.66.

The most investigated from phyllosilicate group compounds is gyrolite because it is stable at 120 – 200 °C temperatures under the saturated steam pressure. At a lower temperature, a semicrystalline having no crystal structure C-S-H gel was obtained[3,4]. At a temperature higher than 200 °C truscottite forms, although a metastable gyrolite may be obtained up to 270 °C.

During hydrothermal synthesis of gyrolite the intermediary compound is Z-phase ($\text{Ca}_9\text{Si}_{16}\text{O}_{40}(\text{OH})_2 \cdot (14+x\text{H}_2\text{O})$), the first time which was synthesized by G. O. Assarsson (1957) [5]. Synthetic Z-phase can be produced by hydrothermal treatment of either a calcium silicate hydrate gel or a mixture of lime and amorphous silica at temperatures

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varying from 140 °C to 240 °C[6,7]. J. A. Gard with co-authors estimated that the Z-phase could be produced by the decomposition of Al-substituted tobermorite. The highest content of the Z-phase was obtained from a one-year run [8]. There has been no stability field for Z-phase reported, but it may be stable at temperatures below 120 °C. No natural samples are known, although some gyrolite samples have been reported with small inclusions of intergrown Z-phase[5].

The main structural feature of Z-phase consists of pairs of mirrored single S_2 sheets (the sheet S_2 consists of six-fold rings of tetrahedra all pointing in the same direction connected to additional tetrahedra pointing in the opposite direction) alternating with calcium sheets. Between two symmetrically equivalent S_2 sheets there is an additional sheet comprising calcium atoms coordinated with water[1,9]. One structure which is easily obtained from the Z-phase is K-Phase $Ca_7Si_{16}O_{38}(OH)_2$ [10]. This may be obtained via polymerisation of two mirrored single silicate sheets to double sheets. The formation of K-phase is a process which requires either higher synthesis temperatures (350 °C), or dehydration of Z-phase at about 450 °C[11]. Moreover both Z-phase and gyrolite are converted to α - $CaSiO_3$ on heating at 700°C[1].

Despite all these studies, no detailed work has been reported on the hydrothermal formation of high cristallinity Z-phase.

A. Stumm in his dissertation shows, that both C-S-H(I) and gyrolite can incorporate Zn^{2+} ions to similar limits. Also the incorporation of Zn^{2+} ions into the interlayer of C-S-H(I) was proposed. Recently A. Stumm with co-authors have indicated that zinc incorporation into synthetic gyrolite is also possible up to $Zn/(Zn+Ca) = 1/6$, corresponding to approximately 6 wt. %. Increasing zinc content led to a gradual diminishing of the basal reflection (001) of gyrolite, as for the nanocrystalline phases [12].

In recent years, the new application fields of low base calcium silicate hydrates ($C/S = 0.44-0.66$) have been found, i. e. they can be used as sorbents to clean polluted wastewaters by heavy and radioactive metals. Calcium silicate hydrates exhibit a large number of structural sites available for cation and anion binding[13]. P. Mandaliev with co-authors [14] have investigated Nd(III) (trivalent lanthanides and actinides) binding to amorphous C-S-H phases processes. The study reveals that Nd may form several species in contact with C-S-H phases. The study suggests that, in the long term, amorphous C-S-H phases are capable of taking up Nd via exchange processes with Ca^{2+} ions in the Ca sheets and the interlayer[14].

It is known that many chemical elements ions could interrupt into calcium silicate hydrates crystal structure. In the literature is noted that influence of alkaline metals[15–19], aluminium[20–25] and other elements on the synthesis of phyllosilicates is significant.

Heavy metals commonly make little soluble (for example oxides) compounds in the wastewaters. The incorporation of heavy metals into calcium silicate hydrates is important for their potential long-term immobilisation in hardened cement pastes. The type of fixation of heavy metals in cement pastes, whether incorporation, sorption, or coprecipitation, is of major importance for safety assessment of these materials and their potential for recycling. Consequently using classical heavy metals segregation/utilization methods mentioned compounds always must be converted into ionic condition. However, this stage is very complicated (need to choose particular solvent, decomposition conditions and such things) and economically it's useless.

It is presumable that during hydrothermal synthesis is possible to insert insoluble heavy metals compounds into products structure. Meanwhile the influence of heavy metals ions on synthesis processes are less examined. Presumable, that mentioned compounds would accelerate the formation of phyllosilicates and would penetrate into their structure. In this case two task will be dissolved: heavy metals are utilized and it is presumable that heavy metals ions will have possitive influence on the Z-phase crystallization processes.

The aim of this work was to investigate the influence of Zn containing compounds on the formation of Z-phase during hydrothermal treatment at 200 °C.

2. Experimental procedure

In this paper the following reagents were used: fine-grained $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ („Reaktiv“, Russia, ignition losses 16.5 %, specific surface area $S_a = 923 \text{ m}^2/\text{kg}$ by Blaine); calcium oxide („Stanchem“, Poland, CaO additionally was burned at 950 °C for 0.5 hours, specific surface area $S_a = 828 \text{ m}^2/\text{kg}$, purity – 97.3 %). Zn containing compounds: soluble in water $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ („Reaktiv“, Russia, purity – 99 %); insoluble in water $5\text{ZnO} \cdot 2\text{CO}_2 \cdot 4\text{H}_2\text{O}$ („Reaktiv“, Russia, purity – 99 %).

The synthesis of calcium silicate hydrates has been carried out in unstirred suspensions in the vessels of stainless steel. The molar ratio of primary mixtures was $C/(S + Z) = 0.55$ and $Z/(S + Z) = 0; 0.025$ ($C - \text{CaO}$, $S - \text{SiO}_2$, $Z - \text{ZnO}$). It corresponds 2.27 % ZnO in the mixture. Water/solid ratio of the suspension was equal to 10.0. Hydrothermal synthesis has been carried out under the saturated steam pressure at 200 °C temperature; the duration of isothermal curing was 4, 8, 12, 16, 24, 48 or 72 hours. The products were filtered off, dried at the temperature of 50 ± 5 °C and sieved through sieve with a mesh width of 80 μm .

The X-ray powder diffraction (XRD) data were collected with a DRON-6 X-ray diffractometer with Bragg–Brentano geometry using Ni-filtered $\text{Cu K}\alpha$ radiation and graphite monochromator, operating with the voltage of 30 kV and emission current of 20 mA. The step-scan covered the angular range $2-60^\circ$ (2θ) in steps of $2\theta = 0.02^\circ$.

Simultaneous thermal analysis (STA: differential scanning calorimetry–DSC and thermogravimetry–TG) was also employed for measuring the thermal stability and phase transformation of samples at a heating rate of 15 °C/min, the temperature ranged from 30 °C up to 1000 °C under air atmosphere. The test was carried out on a Netzsch instrument STA 409 PC Luxx. The ceramic sample handlers and crucibles of Pt–Rh were used.

FT-IR spectra have been carried out with the help of a Perkin Elmer FT-IR Spectrum X system. Specimen were prepared by mixing 1 mg of the sample with 200 mg of KBr. The spectral analysis was performed in the range of $4000-400 \text{ cm}^{-1}$ with spectral resolution of 1 cm^{-1} .

Scanning electron microscopy (SEM) (FEI Quanta 200 instrument) of the samples was performed using 30 kV accelerating voltage and a working distance of 9.2 mm, detector – ETD.

3. Results and Discussion

In the pure $\text{CaO-SiO}_2 \cdot n\text{H}_2\text{O-H}_2\text{O}$ suspension after 4 hours of isothermal curing at 200 °C temperature semi-crystalline calcium silicate hydrate – C-S-H(I) was formed (Fig. 1, (curve 1, d -spacing: 0.306, 0.280, 0.184 nm)). It was estimated that during the first 4 hours of synthesis in the mixtures with Zn additive $5\text{ZnO} \cdot 2\text{CO}_2 \cdot 4\text{H}_2\text{O}$ it decomposes because in the X-ray diffraction pattern was not identified mentioned compound diffraction peaks while ZnO was formed (Fig. 1, (curve 2, d -spacing: 0.280, 0.248, 0.183 nm)). This compound is insoluble therefore has minor influence on compounds formation and only the traces of Z-phase (d -spacing – 1.557, 0.305, 0.280, 0.183 nm) were observed in the XRD curve.

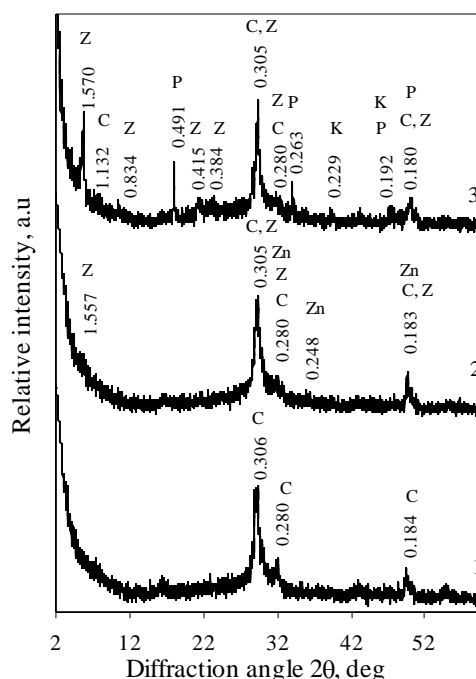


Fig. 1. X-ray diffraction patterns of the synthesis products. Duration of hydrothermal synthesis at 200 °C temperature is 4 h. 1 – pure CaO–SiO₂·nH₂O–H₂O mixture; 2 – the same, with 5ZnO·2CO₂·4H₂O; 3 – the same, with Zn(NO₃)₂·6H₂O. Indexes: C–C-S-H(I), Z–Z-phase, P–portlandite, Zn–ZnO, K–calcite.

Meanwhile, Zn(NO₃)₂·6H₂O additive accelerates the formation of Z-phase of a high crystallinity (Fig. 1, (curve 3)). It should be noted that diffraction peaks typical of Ca(OH)₂ were identified ($d = 0.491, 0.263, 0.192, 0.180$ nm) too. Apparently, during the Z-phase formation Zn²⁺ ions penetrate into this compound crystal lattice by exchanging Ca²⁺ ions. We hypothesize (Fig. 2) that zinc cations are incorporating into interlayers (Ca²⁺ and H₂O) by exchanging with calcium cations and H₂O. This process not proceed using insoluble Zn containing compound because in this case Zn²⁺ ions doesn't participate in the reaction.

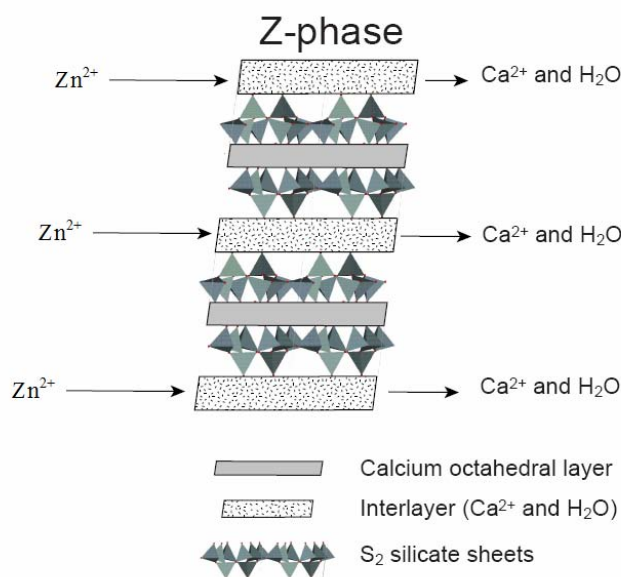


Fig. 2. Possible mechanism of Z-phase structure changes.

These results were confirmed by differential scanning calorimetry data. In the DSC curve was indicated two endothermic effects: at 141 °C temperature characteristic to dehydration of structural water from Z-phase crystals lattice and at 451 °C temperature characteristic to portlandite dissociation into CaO and H₂O. Also was identified the exothermic effect at a temperature of 854 °C which shows formation of wollastonite (Fig. 3).

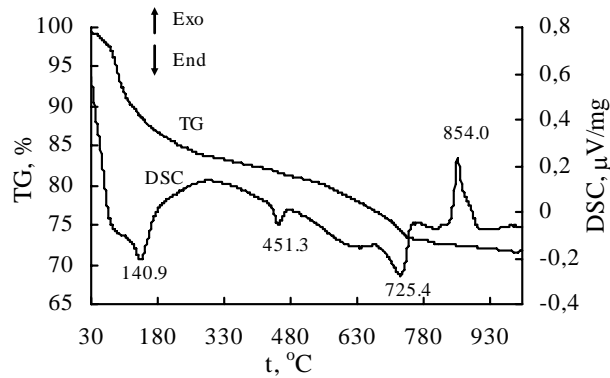


Fig. 3. DSC and TG curves of the synthesis products with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; duration of hydrothermal synthesis was 4 h.

When hydrothermal synthesis is extended to 8 hours, in the XRD curve of the pure mixture the traces of Z-phase were identified (Fig. 4, curve 1). It should be noted that in the mixtures with $5\text{ZnO} \cdot 2\text{CO}_2 \cdot 4\text{H}_2\text{O}$ additive at the beginning of the synthesis formed ZnO is not search out in the synthesis products (Fig. 4, curve 2). As after 4 hours of synthesis using $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ additive in the products together with Z-phase remain not reacted $\text{Ca}(\text{OH})_2$ (Fig. 4, curve 3).

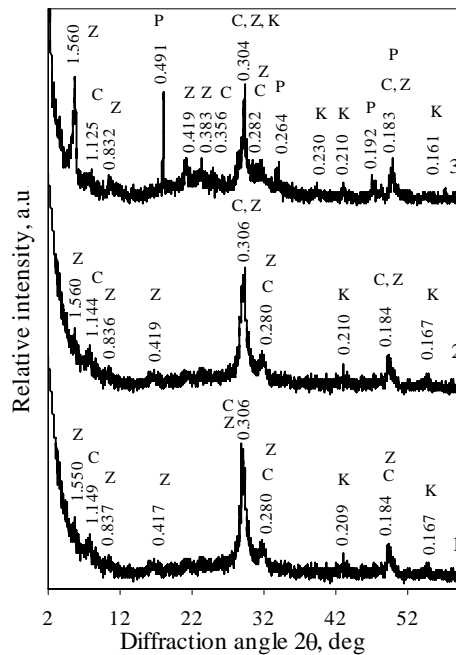


Fig. 4. X-ray diffraction patterns of the synthesis products. Duration of hydrothermal synthesis at 200 °C temperature is 8 h. 1 – pure $\text{CaO-SiO}_2 \cdot n\text{H}_2\text{O-H}_2\text{O}$ mixture; 2 – the same, with $5\text{ZnO} \cdot 2\text{CO}_2 \cdot 4\text{H}_2\text{O}$; 3 – the same, with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Indexes: C–C-S-H(I), Z–Z-phase, P–portlandite, K–calcite.

The obtained results were confirmed by SEM/EDS analysis data. In the mixture with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ additive in SEM micrographs is observable: bounded to aggregates Z-phase characteristic plate shape crystals (Fig. 5, a, spectrum 1). The results of EDS analysis indicated that in the chemical composition of mentioned crystals are 1.34 wt. % of Zn (Fig. 5, b)

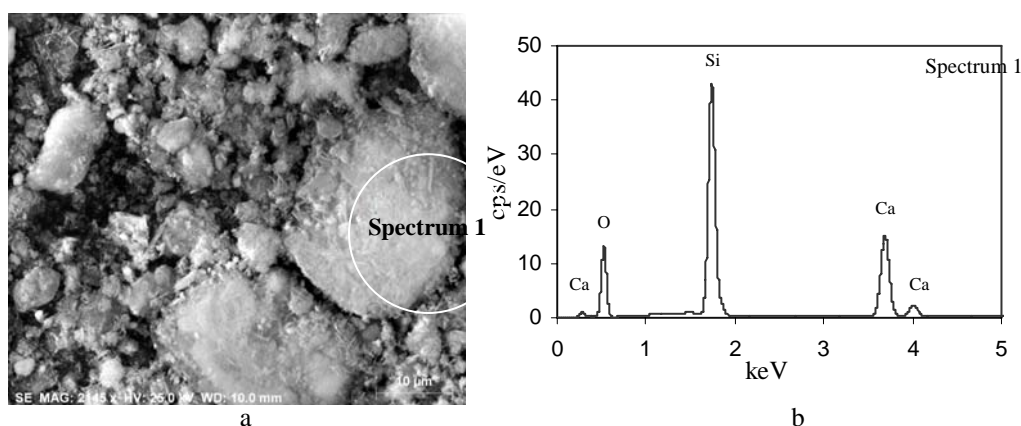


Fig. 5. Scanning electron micrographs (a) and EDS analysis curve (b) of synthesis products when the composition of the primary mixture with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ additive is equal to $\text{C}/(\text{S}+\text{Z})=0.55$ and $\text{Z}/(\text{S}+\text{Z})=0.025$. Duration of hydrothermal synthesis at 200 °C is equal to 8 h. Chemical composition of spectrum 1, wt. %: O – 58.37, Si – 19.66, Ca – 20.63, Zn – 1.34.

All of these compounds formation has been confirmed by the method of IR spectroscopy and differential scanning calorimetry (DSC) analysis data results.

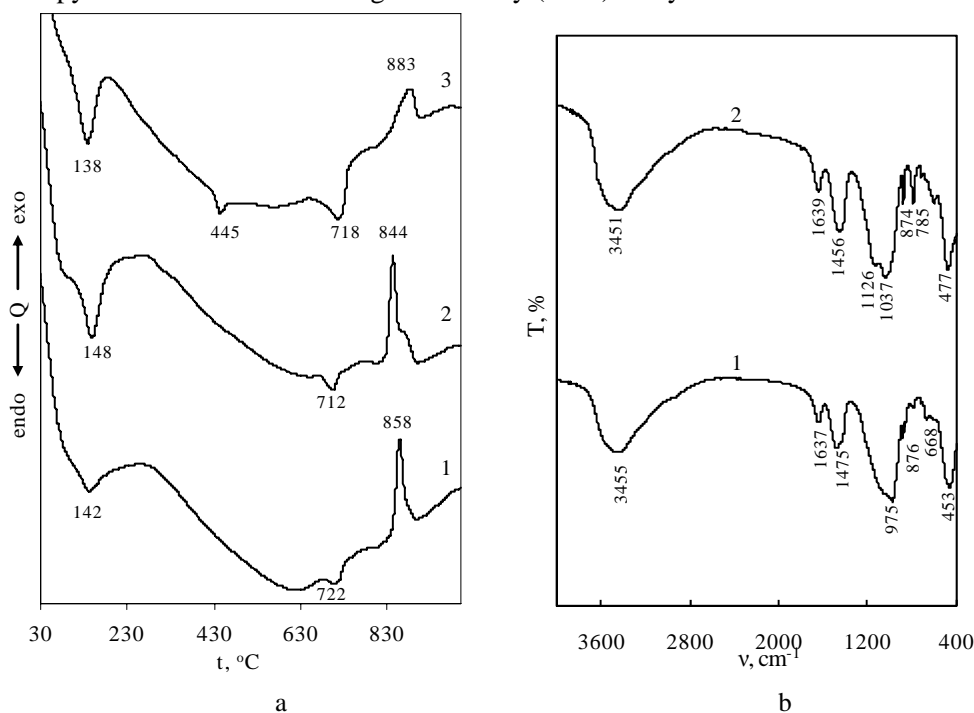


Fig. 6. DSC curves (a) and FT-IR spectra (b) of synthesis products. Duration of hydrothermal synthesis at 200 °C temperature is 8 h: 1 – pure $\text{CaO-SiO}_2 \cdot n\text{H}_2\text{O-H}_2\text{O}$ mixture; 2 – the same, with $5\text{ZnO} \cdot 2\text{CO}_2 \cdot 4\text{H}_2\text{O}$; 3 – the same, with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

The obtained FT-IR data show that in the $\delta(\text{O-Si-O})$ range of vibrations, Z-phase is characteristic of an intensive absorption band with the maximum in the frequency range of 453; 477 cm^{-1} (Fig. 6, b, curves 1–2). Moreover, in the $\delta(\text{Si-O-Si})$ range of vibrations (symmetric deformation), the Z-phase is characteristic of low intensity bands (668 and 785 cm^{-1}). In the range of 1037 cm^{-1} , the IR spectrum of Z-phase shows an intensive peak and in 1126 cm^{-1} only a “shoulder”. In the range of symmetric vibrations of OH groups ($\nu(\text{OH})$, 2900 ... 3700 cm^{-1}), the Z-phase spectrum indicates a wide band in the frequency range of 3451 cm^{-1} . This means that the positions of OH groups in the structure of this compound are not so well arranged compared to other calcium silicate hydrates.

The results of DSC analysis proved that, after 8 hours of isothermal curing in the mixture with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ additive, the endothermic effect at 445 °C temperature characterize dehydration of calcium hydroxide (Fig. 6, a, 3 curve). Z-phase with inserted Zn^{2+} ions during heating is more stable than pure compound because in this case wollastonite forms in ~ 25 °C higher temperature and exothermal peak at 883 °C temperature broad compared with pure compound

When the synthesis is continued (12 h), Z-phase remain stable in pure mixture (Fig. 7, a, curve 1). Meanwhile, $5\text{ZnO} \cdot 2\text{CO}_2 \cdot 4\text{H}_2\text{O}$ additive shorten the stability of Z-phase and the XRD curve shows the traces of gyrolite gel (Fig. 7, a, curves 2) (d -spacing – 2.205; 1.106; 0.830; 0.279 nm). $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ additive also shorten the stability of Z-phase, plus identified higher intensity gyrolite gel peaks. Also was identified still fully not reacted $\text{Ca}(\text{OH})_2$ (d – 0.492; 0.263; 0.179 nm) (Fig. 7, a, curve 3).

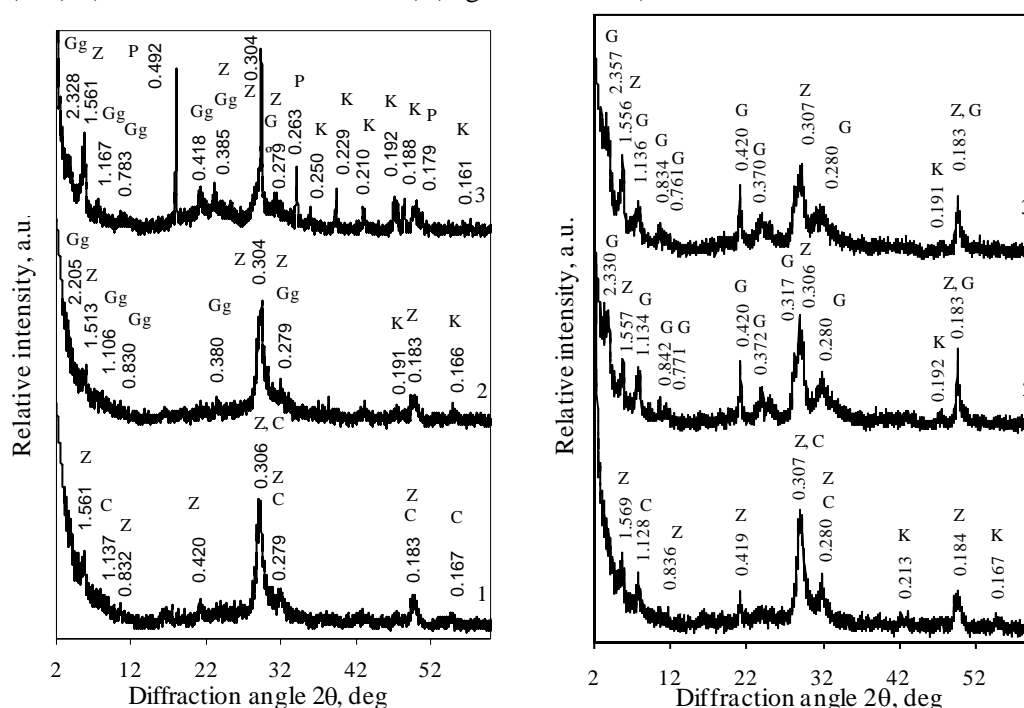


Fig. 7. X-ray diffraction patterns of the synthesis products. Duration of hydrothermal synthesis at 200 °C temperature is 12 h (a) and 16 h (b). 1 – pure $\text{CaO-SiO}_2 \cdot n\text{H}_2\text{O-H}_2\text{O}$ mixture; 2 – the same, with $5\text{ZnO} \cdot 2\text{CO}_2 \cdot 4\text{H}_2\text{O}$; 3 – the same, with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Indexes: C–C-S-H(I), Z–Z-phase, P–portlandite, K–calcite, Gg–gyrolite gel, G–gyrolite, C–C-S-H(I).

When hydrothermal synthesis is extended to 16 hours in the pure mixtures dominate Z-phase (Fig. 7, b, curve 1). As expected, in the mixture with $5\text{ZnO} \cdot 2\text{CO}_2 \cdot 4\text{H}_2\text{O}$ in the synthesis products forms gyrolite (Fig. 7, b, curves 2) (d -spacing – 2.330; 1.134; 0.842; 0.771;

0.420; 0.372; 0.317; 0.280; 0.183 nm). Also, Z-phase remains.

It should be underlined that in the mixture with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ portlandite completely reacted after 16 hours of isothermal curing. Accordingly, gyrolite starts to crystallize in the reaction products just fully reacted initial compounds. EDS analysis shows that a little bit more Zn^{2+} ions was inserted compering with double shorter duration of synthesis. Zn^{2+} ions are not released and are not passing to the solution during the process of recrystallization of Z-phase (Fig. 8).

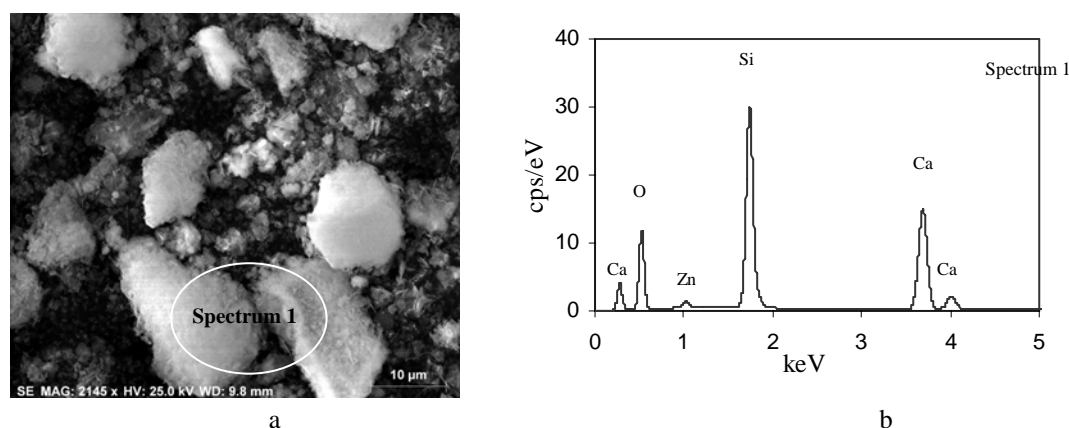


Fig. 8. Scanning electron micrographs (a) and EDS analysis curve (b) of synthesis products when the composition of the primary mixture with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ additive is equal to $\text{C}/(\text{S}+\text{Z})=0.55$ and $\text{Z}/(\text{S}+\text{Z})=0.025$. Duration of hydrothermal synthesis at 200 °C is equal to 16 h. Chemical composition of spectrum, wt. %: O – 62.44, Si – 13.82, Ca – 22.02, Zn – 1.71.

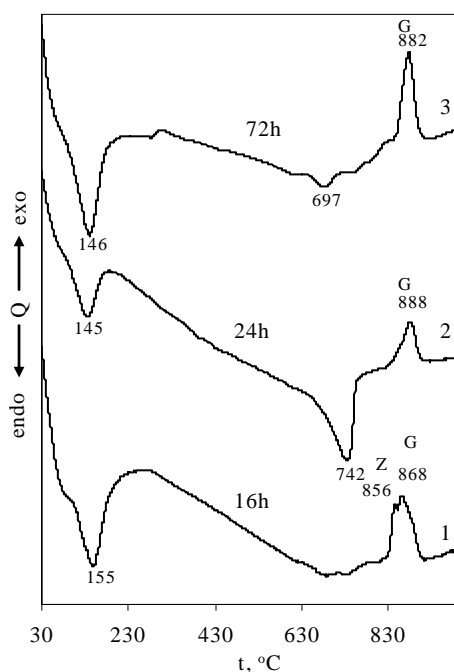


Fig. 9. DSC curves of synthesis products with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Duration of hydrothermal synthesis at 200 °C temperature, h: 1 – 16; 2 – 24; 3 – 72. Indexes: Z–Z-phase, G–gyrolite.

The XRD data were confirmed by DSC measurements as well. After 16 h of synthesis in the DSC curve the two exothermic peak were identified: at 856 °C characteristic to Z-phase and at 868 °C, associated to gyrolite (Fig. 9, curve 1). Meanwhile, after prolonging the duration of isothermal curing (24 h) Z-phase start to crystallize into gyrolite. After 72 hours of synthesis gyrolite remain stable (Fig. 9, curve 3).

After 24 hours of hydrothermal treatment in the pure mixture Z-phase already start to recrystallizes into gyrolite (Fig. 10, a, curve 1). It should be noted that this process in the mixtures with $5\text{ZnO} \cdot 2\text{CO}_2 \cdot 4\text{H}_2\text{O}$ occur faster because the intensity of 2.326 nm peak is much higher (Fig. 9, a, curve 2). Moreover, latter compound remain stable both 48 h (Fig. 10, b, curve 2) and 72 h (Fig. 11, b, curve 2). It should be noted that in the mixtures with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ additive Z-phase remain stable a longer duration of synthesis (24 h) because a low intensity peak was estimated $d = 1.550$ nm. Meanwhile after 48 h of hydrothermal treatment Z-phase completely recrystallize into gyrolite (Fig. 10, b, curve 3) which remain stable and 72 h of synthesis (Fig. 11, curve 3).

Obtained results confirmed other authors data, i. e. Z-phase is metastable, intermediate compound and always formed before gyrolite. After 48 h of isothermal curing at 200 °C temperature in the pure mixture together with gyrolite was identified only the traces of Z-phase, i. e. small intensity peak with d -spacing–1.545; 0.281; 0.183 nm (Fig. 10, b, curve 1), and Z-phase finishes to transfer into gyrolite within 72 h (Fig. 11, curve 1).

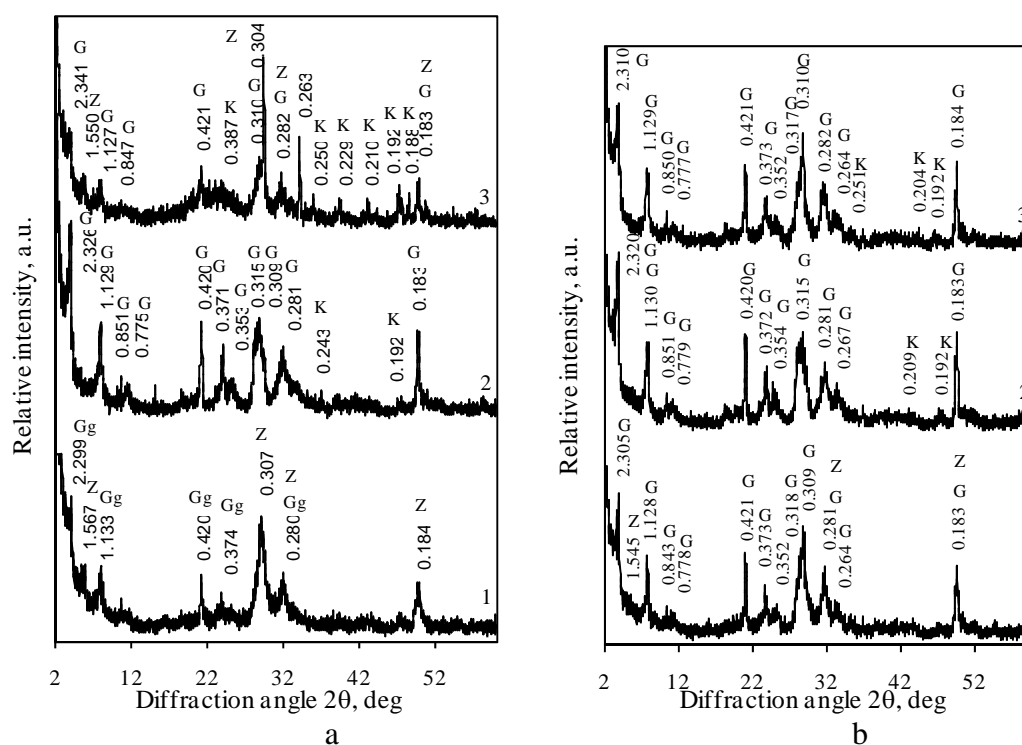


Fig. 10. X-ray diffraction patterns curves of the synthesis products. Duration of hydrothermal synthesis at 200 °C temperature is 24 h (a) and 48 h (b). 1 – pure $\text{CaO-SiO}_2 \cdot n\text{H}_2\text{O-H}_2\text{O}$ mixture; 2 – the same, with $5\text{ZnO} \cdot 2\text{CO}_2 \cdot 4\text{H}_2\text{O}$; 3 – the same, with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Indexes: Z–Z-phase, Gg – gyrolite gel, G – gyrolite, K–calcite.

Consequently, when to the initial mixture is added soluble Zn^{2+} ions containing additive the duration of the hydrothermal synthesis of Z-phase reduce ~ 2 times. By using $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ additive Z-phase remain stable longer than using $5\text{ZnO} \cdot 2\text{CO}_2 \cdot 4\text{H}_2\text{O}$. Zn^{2+}

ions additives exchange formation processes and when curing the mixture of CaO and amorphous SiO₂ in the environment of saturated water steam curing at 200 °C range the formation of new compounds occurs in the following sequence:

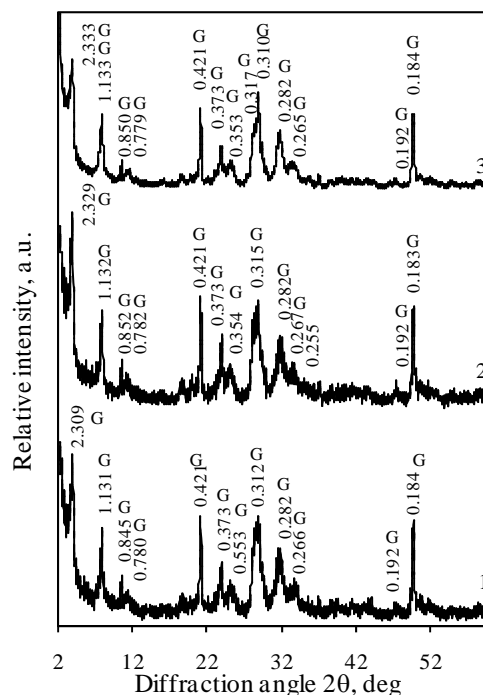
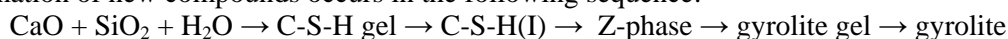


Fig. 11. X-ray diffraction patterns of the synthesis products. Duration of hydrothermal synthesis at 200 °C temperature is 72 h. 1 – pure CaO–SiO₂·nH₂O–H₂O mixture; 2 – the same, with 5ZnO·2CO₂·4H₂O; 3 – the same, with Zn(NO₃)₂·6H₂O. Indexes: G – gyrolite.

Meanwhile, zinc oxide additive did not change crystals morphology of synthesis products because in the SEM micrographs prevail both individuals or to aggregates of plate shape crystals characteristic to gyrolite (Fig. 12, a). The results of EDS analysis indicate that 1.88 % of Zn enters into the structure of these crystals (Fig. 12, b).

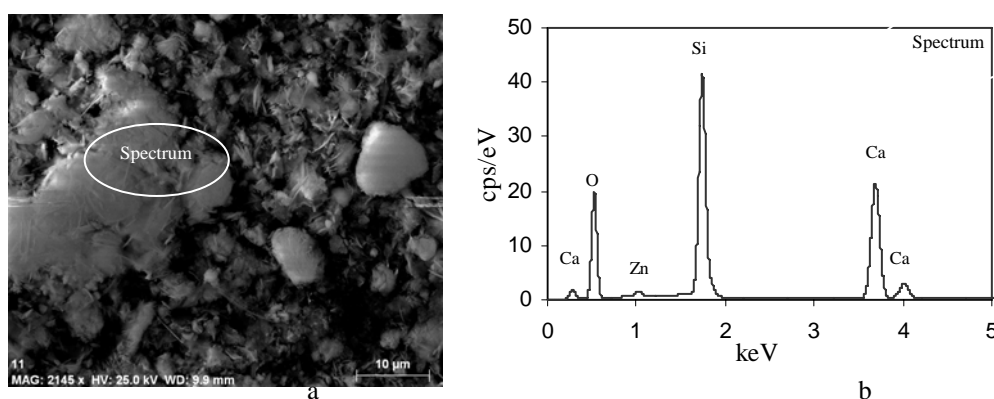


Fig. 12. Scanning electron micrographs (a) and EDS analysis curve (b) of synthesis products when the composition of the primary mixture with 5ZnO·2CO₂·4H₂O is equal to CaO/(SiO₂+ZnO)=0.55 and ZnO/(SiO₂+ZnO)=0.025. Duration of hydrothermal synthesis at 200 °C is equal to 72 h. Chemical composition of spectrum, wt. %: O – 61.28, Si – 13.63, Ca – 24.16, Zn – 0.92.

4. Conclusions

1. Soluble Zn^{2+} ions containing additive approximately 2 times reduce the duration of the hydrothermal synthesis of Z-phase. Later compound was already identified after 4 hours of hydrothermal synthesis at 200 °C temperature, while in the mixtures without additives – after 8 h.
2. Insoluble $5\text{ZnO}\cdot 2\text{CO}_2\cdot 4\text{H}_2\text{O}$ additives don't have influence on Z-phase formation processes. ZnO was formed while decomposes $5\text{ZnO}\cdot 2\text{CO}_2\cdot 4\text{H}_2\text{O}$ at the beginning of synthesis.
3. Zn^{2+} ions promote Z-phase recrystallization into gyrolite. With insoluble additive this transformation finishes after 24 h, with soluble additive – after 48 h, in the pure mixture – after 72 h.

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Садржај: Испитиван је утицај једињења које садрже Zn на формирање Z-фазе током хидротермалног третмана на 200 °C. Молски однос почетних смеша је био $\text{CaO}/(\text{SiO}_2 + \text{ZnO}) = 0,55$ и $\text{ZnO}/(\text{SiO}_2 + \text{ZnO}) = 0; 0,025$ (то одговара 2,27 % ZnO у смеши). Коришћена су једињења која садрже Zn^{2+} јоне: растворна у води $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ и нерастворна у води $5\text{ZnO} \cdot 2\text{CO}_2 \cdot 4\text{H}_2\text{O}$. Утврђено је формирање Z-фазе расте апроксимативно два пута услед утицаја јона Zn^{2+} из смеша. Високо кристалична једињења су формирана након 4 сата, док у смешама без адитива – после 8 сати хидротермалном анализом на 200 °C. Даље, Zn^{2+} јони продиру унутар кристалне решетке Z-фазе замењујући јоне Ca^{2+} . Уоћено је да нерастворни адитив $5\text{ZnO} \cdot 2\text{CO}_2 \cdot 4\text{H}_2\text{O}$ нема битног утицаја на почетак формирања Z-фазе, али промовише рекристализацију Z-фазе у гиролит. Продукти су карактерисани рендгенском дифракцијом, симултаном термијском анализом, ФТИР спектрима и СЕМ анализом.

Кључне речи: Силикатни хидрат калцијума (CSH), Z-фаза, Цинк, хидротермални третман.
