

KAUNAS UNIVERSITY OF TECHNOLOGY

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**THE HYDROTHERMAL SYNTHESIS, PROPERTIES AND
APPLICATION OF FUNCTIONAL $x\text{CaO}\cdot y(\text{Al}_2\text{O}_3, \text{SiO}_2)\cdot z\text{H}_2\text{O}$
COMPOUNDS**

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KAUNO TECHNOLOGIJOS UNIVERSITETAS

JOLANTA DONĖLIENĖ

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INTRODUCTION

Relevance of the work

Recently, functional $x\text{CaO}\cdot y(\text{Al}_2\text{O}_3, \text{SiO}_2)\cdot z\text{H}_2\text{O}$ compounds have attracted a widespread interest in potential applications, such as binding materials and adsorption. However, due to the structural inequalities and impurities, the use of natural compounds is limited. Consequently, synthetic products, which can be obtained by treating $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ mixtures under hydrothermal conditions [1], are commonly applied.

Natural calcium hydroalumosilicates (such as metakaolinite, kaoline, bentonite and others) are used in many processes; however, a wider application is limited by their physico-chemical properties, which vary in a narrow range because of additional treatment, i. e. crushing (changes the granulometric composition and the particle size but not the internal surface area), burning (increases their activity; however, due to the fluxing impurities, they sinter), and other. Other important factors which limit the use of natural compounds are the variable crystal structure and probable presence of impurities. Due to these reasons, specially made synthetic compounds are much more effective because, the specific product properties can be controlled during the synthesis. One of these methods of synthesis is hydrothermal treatment of the initial compounds in a saturated water vapor environment [2].

Hydrothermal synthesis is a facile, highly efficient, easily controllable process, during which compounds that are insoluble under normal conditions can react together in a saturated water vapor environment. It is worth mentioning that not only the composition of the resulting products, but also their physical properties can be varied by changing such conditions of hydrothermal synthesis as isothermal curing temperature, pressure and duration. The stability of these parameters and the possibility of changing them, determine a wide application of synthesis products in various industries [1, 2, 3-6].

One of them is the cement industry. In order to reduce the amount of major greenhouse gas emissions from cement production, especially the amount of CO_2 , clinker is partly replaced by a variety of mineral and/or waste additives, which allows to lower the production costs [7, 8]. This group also includes compounds which can be obtained in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ system. The synthetic products are significantly better than the natural compounds because when they partly replace clinker, the mechanism of cement hydration can be controlled and modified, depending on the composition and properties of the synthetic product: the solubility of initial cement compounds and their degree of hydration, the duration of the main hydration stages and other [9, 10, 11, 12, 13]. For this reason, in order to evaluate the effect of the synthetic calcium

hydroalumosilicate additive on the hydration of cement, firstly, it is necessary to determine the optimal hydrothermal treatment conditions for the formation of $x\text{CaO}\cdot y(\text{Al}_2\text{O}_3, \text{SiO}_2)\cdot z\text{H}_2\text{O}$ compounds.

Another application area of the mentioned compounds is CaO stabilizing additive for CO_2 adsorption. To date, in order to reduce CO_2 emissions from the industry, CaO-based solid adsorbents are widely applied for the cyclic calcination/carbonation processes [14, 15]. However, due to high temperature, the reactivity of the sorbents decreases after several cycles of calcination and carbonation [16-18]. One of the ways to solve this problem is to modify the natural adsorbents with an inert material and provide a stable solid matrix which would allow to increase the number of cycles and prevent a solid sintering of the sorbents [19, 20-29]. Among different stabilizers, the most effective is mayenite [25, 29, 30], which can be prepared by using various synthesis techniques: solid sintering, self-combustion method [31], sol-gel synthesis [32], flame spray pyrolysis [33] and oxalate precursor route [34]. However, these techniques require high temperatures or additional purification of the product, because soluble starting materials and specific media, such as nitrates and various organic solvents, is used, and often by-products are formed.

Therefore, a reasonable assumption can be made that mayenite can be obtained by thermally treating intermediate compounds $x\text{CaO}\cdot y(\text{Al}_2\text{O}_3, \text{SiO}_2)\cdot z\text{H}_2\text{O}$, which crystallize during hydrothermal synthesis [4, 35, 36]. It is worth mentioning that this production method does not result in the formation of by-products, thus, the following stages of purification can be eliminated. Supposedly, after such preparation, mayenite can be successfully used as a CaO stabilizing additive.

The aim of this work is to examine the influence of synthesis conditions on the formation and properties of functional $x\text{CaO}\cdot y(\text{Al}_2\text{O}_3, \text{SiO}_2)\cdot z\text{H}_2\text{O}$ compounds and to propose their application areas.

In order to achieve the aim of the work, we had to accomplish the following goals:

1. To examine the effect of both the Al_2O_3 additive and the hydrothermal treatment conditions on the formation and stability of compounds in CaO-SiO₂-Al₂O₃-H₂O system.
2. To perform thermodynamic calculations and validate the optimal hydrothermal treatment conditions for the formation of $3\text{CaO}\cdot \text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ by an experiment.
3. To determine the influence of synthetic calcium hydroalumosilicate additive on the hydration process of cement and the mineral composition of products.
4. To apply a synthetic calcium hydroalumosilicate additive for the stabilization of natural CaO chemisorbent in the cyclic CO_2 adsorption/desorption process.

Scientific novelty of the research

This research determined for the first time that hydrogranates which usually form during hydrothermal synthesis in CaO, SiO₂ and Al₂O₃ suspensions may not be obtained in this system, and only calcium hydroaluminates and calcium hydroalumosilicates may dominate in the products.

It was revealed that the synthetic calcium hydroalumosilicate additive changes the hydration of cement samples and accelerates the curing process: it shortens the induction period, stimulates the hydration of C₃S and increases the total amount of heat released. It was determined that mayenite can be obtained at 350°C temperature by burning hydrothermally treated calcium hydroalumosilicate.

Practical significance of the dissertation

It was examined that the synthetic mayenite additive stabilizes the natural CaO chemisorbent in the cyclic CO₂ adsorption/desorption process. The technology for the production of the mentioned synthetic additive and its application in the preparation of CO₂ chemisorbent is offered.

Approbation and publication of research results

Results of the research are presented in three scientific publications included into the Clarivate Analytics WoS database: one of them published in Romanian Journal of Materials, one in Advances in Materials Science and Engineering and one in Journal of Thermal Analysis and Calorimetry. The results of this dissertation have been reported in the proceedings of six international conferences: “Chemistry and Chemical Technology” (2015, Lithuania); 3rd Central and Eastern European conference on thermal analysis and calorimetry, CEEC-TAC3, (2015, Slovenia); “Chemistry and Chemical Technology” (2016, Lithuania); “BaltSilica” (2016, Lithuania), XV Russian and International Conference on Thermal Analysis and Calorimetry (2016, Russia); “Chemistry and Chemical Technology” (2017, Lithuania).

Structure and contents of the dissertation

The dissertation consists of an introduction, a literature survey, an experimental part, results and discussion, conclusions, lists of references and publications on the topic of the dissertation and appendixes. The list of references includes 165 bibliographic sources. The main results are discussed in 114 pages, illustrated in 2 schemes, 19 tables and 61 figures.

Statements presented for the defence

1. The mineral composition and stability of compounds which form in the CaO-SiO₂-Al₂O₃-H₂O system depend not only on the amount of Al₂O₃ additive but also on the temperature and duration of isothermal curing.
2. The synthetic products which are obtained from the mixtures containing 10.5% or 15.4% of Al₂O₃, change the hydration process of cement samples: they induce the formation of calcium silicate hydrates, the early

hydration of C_3S and the dissolution of gypsum, and also increase the total amount of heat released.

3. During the cyclic CO_2 adsorption/desorption process, the synthetic mayenite additive stabilizes the structure of CaO chemisorbent.

2. EXPERIMENTAL PART

Materials:

The following reagents were used as starting materials: fine-grained **SiO₂·nH₂O** (*Reaktiv*, Russia) ($S_a = 1047 \text{ m}^2/\text{kg}$; the loss of ignition is 7.0 mass%); **amorphous Al(OH)₃** (*Sigma Aldrich*, Germany) was burned at 475 °C for 4 h ($S_a = 513 \text{ m}^2/\text{kg}$); **Ca(OH)₂** (*Stanchem*, Poland; purity – 99 %, $S_a = 961 \text{ m}^2/\text{kg}$) burned at 500 °C for 2 h. The quantity of free CaO was equal to 99%.

Ordinary Portland cement. Samples of ordinary Portland cement were prepared with a laboratory grinding mill by grinding cement clinker (JSC Akmenes Cementas, Lithuania) with a 4.5 % of gypsum additive (*Sigma–Aldrich*, Germany) up to $S_a = 450 \text{ m}^2/\text{kg}$. The chemical analysis and phase composition of clinker are shown in Table 1.

Table 1. Chemical and mineralogical composition of clinker

Oxide	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃ ²⁻	Ignition of losses	Insoluble particles
Amount, %	1972	5.41	4.21	62.76	3.41	0.16	1.08	2.08	0.93	0.24
Minerals	3CaO·SiO ₂			2CaO·SiO ₂			3CaO·Al ₂ O ₃		4CaO·Al ₂ O ₃ ·Fe ₂ O ₃	
Amount, %	63.16			8.89			7.21		12.81	

Natural lime (JSC Naujasis Kalcitas, Lithuania) was ground for 30 s in a vibrating cup Pulverisette 9 mill at 650 rpm and sieved through a sieve with a mesh size of 80 μm ($S_a = 683.7 \text{ m}^2/\text{kg}$). The chemical composition of lime was determined according to the standard (LST EN 459-1:2010). The quantity of free CaO was equal to 81.6%.

Other pure chemical reagents: 1N HCl, acetone, sodium hydroxide, CO₂ (JSC AGA, Lithuania, purity – 99.99%), N₂ (JSC AGA, Lithuania; purity – 99.99%).

Methods [37-39]:

The preparation of primary mixtures and the conditions of hydrothermal synthesis. Dry primary mixtures with the molar ratio of CaO/(SiO₂+Al₂O₃) = 0.55; Al₂O₃/(SiO₂+ Al₂O₃) = 0.025; 0.05; 0.1; 0.15 (the amount of Al₂O₃ in primary mixtures is equal to 2.7%; 5.3%; 10.5% and 15.4%, respectively) were mixed with water to reach the water/solid ratio (W/S) of the suspension equal to 10.0. Hydrothermal synthesis was carried out in unstirred suspensions, in 25 mL volume PTFE cells which were placed in a Parr Instruments (Germany) autoclave, under a saturated steam pressure at 130°C and 200°C temperature for 4, 8, 24, 48 and 72 h (the temperature was reached within 2 h). After hydrothermal treatments, the autoclave was quenched to a room temperature. After synthesis, the suspensions were filtered, the products were rinsed with

acetone to prevent the materials from carbonising, dried at $50^{\circ}\text{C} \pm 5^{\circ}\text{C}$ for 24 h and sieved through a sieve with the width of 80 μm .

X-ray powder analysis (XRD) was performed by using the *D8 Advance* diffractometer (Bruker AXS, Karlsruhe, Germany) operating at the tube voltage of 40 kV and tube current of 40 mA. The X-ray beam was filtered with a Ni 0.02-mm filter to select the $\text{CuK}\alpha$ wavelength. Diffraction patterns were recorded in a Bragg–Brentano geometry using a fast counting detector *Bruker LynxEye* based on the silicon strip technology. The specimens were scanned over the range of $2\theta = 3\text{--}70^{\circ}$ at a scanning speed of 6°min^{-1} using a coupled two theta/theta scan type.

The thermal stability of samples was evaluated by applying In situ XRD analysis, which was performed with a high-temperature camera MTC-hightemp (Bruker AXS, Karlsruhe, Germany). The measurements were taken with a step width of 0.02° and 0.2 s/step at a heating rate of $100^{\circ}\text{C}/\text{min}$ after equilibration for 2 min at the desired temperature.

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 $15^{\circ}\text{C}/\text{min}$, when the temperature ranged from 30°C up to 950°C under air atmosphere. The test was carried out with the *Linseis instrument STA PT1000*. Ceramic sample handlers and platinum crucibles were used.

Differential scanning calorimetry (DSC) analysis was performed with the *Netzsch DSC 214 Polyma* instrument. This method was employed for measuring the thermal stability and phase transformation of samples at a heating rate of $10^{\circ}\text{C}/\text{min}$, when the temperature ranged from 30°C up to 600°C under air atmosphere. Ceramic sample handlers and Al crucibles were used.

Quantitative analysis by differential scanning calorimetry. The quantitative analysis of portlandite samples was performed by applying differential scanning calorimetry. In order to obtain a calibration curve for the evaluation of the amount of portlandite formed in cement samples, different quantities of $\text{Ca}(\text{OH})_2$ (0–30%) were mixed with SiO_2 , and the amount of absorbed heat (J/g) at $\sim 410^{\circ}\text{C}$ temperature was calculated. The latter parameter values were taken as a function of the amount of portlandite in the mixture and presented in Fig. 1. The obtained straight line correlation coefficient R^2 was equal to 0.9969, showing that the calibration curve was reliable.

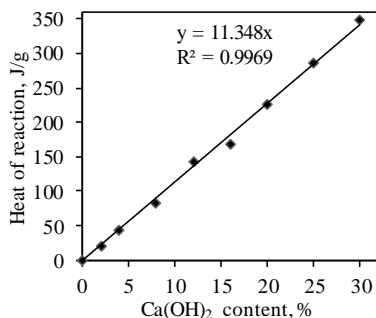


Fig. 1. The relationship between the amount of absorbed heat at $\sim 410^\circ\text{C}$ temperature and the quantity of portlandite in the mixtures with quartz

Isothermal calorimetry. An eight-channel *TAM Air III* isothermal calorimeter was used to investigate the heat evolution rate of the samples. Glass ampoules (20 ml) each containing 3 g of dry cementitious material were placed in the calorimeter along with the injection units for each ampoule filled with amounts of water equivalent to a W/(OPC and additive) ratio of 0.5. After a steady temperature of 25°C had been reached, the water was injected into the ampoules and mixed inside the calorimeter with the dry material for 20 s (frequency $2\text{--}3\text{ s}^{-1}$). The heat evolution rate was then measured over a period of 72 h. Repetition of the measurements showed deviations in total heat below 3 % for samples of similar type. Apart from the first minutes of water addition and mixing, the heat evolution rates were essentially identical. The rate of heat evolution was calculated on the basis of a unit weight of OPC.

The evaluation of mineralogical composition of compounds formed during cement hydration. In order to investigate the mineral and chemical composition of compounds formed during hydration, the heat evolution experiments were repeated at 25°C in a Grant SUB14 thermostatic absorber for different time periods (1.8, 3, 5.5, 9.5, 13, 16.5 and 24 h), which corresponded to the onset/peak/end duration of different early hydration periods. The hydration of samples was stopped by using acetone. Later, the samples were crushed to powder, dried at the temperature of $50 \pm 5^\circ\text{C}$, and put through a sieve with an $80\ \mu\text{m}$ mesh.

The preparation of chemisorbents from CaO and CaO with synthetic mayenite additive mixtures involved the following steps: firstly, calcined lime, calcined lime and synthetic Al-based stabilizer ($\text{CaO}/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.55$, $\text{Al}_2\text{O}_3/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.15$; 130°C , 8 h) were mixed in a *Turbula T2F* shaker-mixer (speed: 40 rpm) in order to homogenize the powders. The mass ratio of the obtained calcinated lime and CAH sample mixture was equal to 75:25, respectively. Secondly, the homogeneous mixtures were wet-ground for 1 min in

a vibrating cup Pulverisette 9 mill at 600 rpm. The mass ratio of water-to-solid (pure CaO or CaO with an Al-based stabilizer) was equal to 10:3. After milling, the suspensions were filtered and slowly calcined at 750°C at a rate of 0.25°C/min. The adsorbents were ground and sieved to reach a lower than 80 µm size.

The test of CO₂ adsorption was performed in a Nabertherm furnace (*Model L5/11*) operated under the atmospheric pressure at selected numbers of carbonation/calcination cycles. Approximately 500 mg of powdered adsorbent was loaded into a quartz U-tube and placed in the reactor furnace. CO₂ and N₂ flow rates were controlled by using mass flow meters. During carbonation/calcination cycles, the total gas flow rate was maintained at 60 mL/min. A complete cycle consisted of carbonation and calcination steps at 650°C and 750°C, respectively. In a typical run, the sorbent sample was heated to 650°C at a rate of 10°C/min under an atmosphere of 100% N₂. When the temperature was reached and stabilized, pure N₂ was replaced with 100% CO₂ gas. After carbonating for 30 min, the CO₂ gas was switched to pure N₂, while the reactor furnace was heated to 750°C at a rate of 10°C/min and kept at 750°C for 30 min. After complete calcination, the temperature was decreased at the rate of 10°C/min to 650°C for next cycle.

3. RESULTS AND DISCUSSION

3.1. The formation and stability of compounds in CaO-Al₂O₃-SiO₂·nH₂O-H₂O system under the conditions of hydrothermal synthesis at 200°C temperature

In order to evaluate the effect of hydrothermal treatment duration on the stability of formed compounds, the products were investigated after 4, 8, 16, 24, 48 and 72 h of synthesis.

It was determined that after 4 h of isothermal curing at 200°C temperature, a semi-crystalline C-S-H(I) (*d-spacing* – 1.25, 0.530, 0.307, 0.280, 0.183 nm) and traces of Z-phase (*d-spacing* – 1.557, 0.835, 0.507, 0.305, 0.182 nm) were formed in the CaO–Al₂O₃–SiO₂·nH₂O–H₂O mixtures with the lowest amount of Al₂O₃ (Fig. 2, a, *curve 1*). When the quantity of the aforementioned additive was increased to 5.3%, calcium hydroaluminate (*d-spacing* – 0.513, 0.444, 0.314, 0.229, 0.204 nm), labelled as C₃AH₆, was identified in the XRD patterns (Fig. 2, a, *curve 2*) alongside the previously mentioned compounds. It is worth noting that the intensity of diffraction maximums characteristic to the latter compound increased with the increasing amount of Al₂O₃ in the primary mixtures.

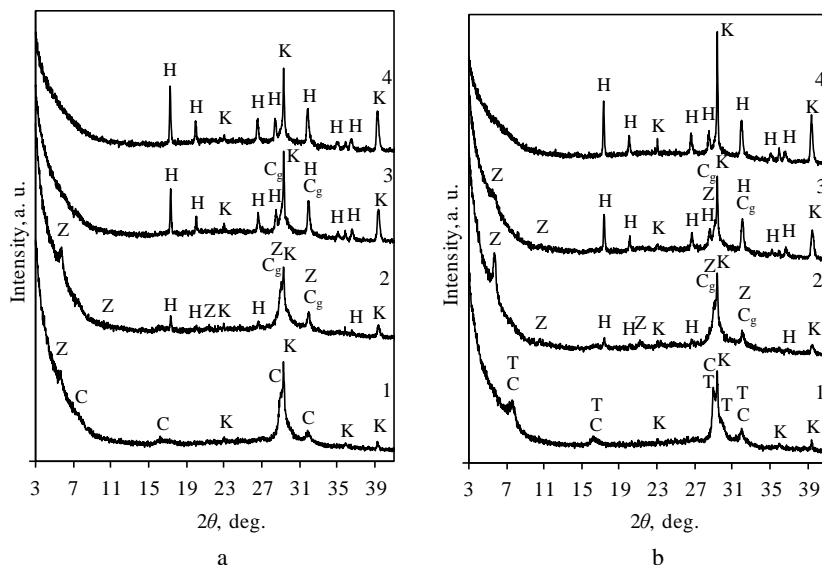


Fig. 2. XRD patterns of synthesis products after 4 h (a) and 8 h (b) of hydrothermal treatment at 200°C, when the molar ratio of primary mixtures (CaO/(SiO₂+Al₂O₃)) is equal to 0.55 and the amount of Al₂O₃ additive (%) is: *curve 1* – 2.7, *curve 2* – 5.3, *curve 3* – 10.5, *curve 4* – 15.4. Indexes: H – C₃AH₆, C – C-S-H(I), C_g – C-S-H(I) gel, Z – Z-phase, T – 1.13 nm tobermorite intercalated with Al³⁺ ions, K – CaCO₃

Besides, a higher than 5.3% of Al_2O_3 additive inhibited the formation of Z-phase, because the main diffraction peaks typical to this compound were not observed in the XRD patterns (Fig. 2, a, *curve 3* and *4*). Meanwhile, in the sample with 10.5% of Al_2O_3 , a lower crystallinity C-S-H(I) modification – C-S-H(I) gel (*d-spacing* – 0.304, 0.279, 0.182 nm) – was formed (Fig. 2, a, *curve 3*).

It should be underlined that under all experimental conditions the carbonation of synthesis products proceeded when they were dried in an air-conditioned chamber (50°C, 24 h), because a fair amount of CaCO_3 (*d-spacing* – 0.3035, 0.2284, 0.2094, 0.1912, 0.1875 nm) was formed in all of the investigated samples (Fig. 2).

Moreover, when the duration of isothermal treatment was prolonged to 8 h, 1.13 nm tobermorite intercalated with Al^{3+} ions ($\text{Ca}_5\text{Si}_3\text{Al}(\text{OH})\text{O}_{17}\cdot 5\text{H}_2\text{O}$; *d-spacing* – 1.18, 0.309, 0.2995, 0.2814, 0.1848 nm) was formed in the mixtures with the lowest amount of Al_2O_3 (Fig. 2, b; *curve 1*). In comparison with the products obtained after 4 h of synthesis, it was observed that the Z-phase was fully reacted, because the main diffraction maximum characteristic to this compound (*d-spacing* – 1.557; 0.835; 0.507; 0.305; 0.182 nm) was not noticed in the XRD patterns, meanwhile C-S-H(I) remained stable (Fig. 2, b; *curve 1*).

It should be emphasized that the formation of Z-phase was strongly affected by both the duration of synthesis and the amount of additive: when the quantity of Al_2O_3 was increased to 5.3%, a higher crystallinity Z-phase was obtained, while in the mixtures with 10.5% of Al_2O_3 only traces of this compound were formed (Fig. 2, b, *curve 2* and *3*). Besides, in the samples with a higher amount of Al_2O_3 (5.3–15.4%), the intensity of diffraction peaks characteristic to C_3AH_6 slightly decreased (Fig. 2, *curve 2, 3* and *4*).

It was determined that by extending the duration of synthesis to 24 h, 1.13 nm tobermorite intercalated with Al^{3+} ions became unstable and recrystallized to Z-phase and gyrolite gel (*d-spacing* – 2,2; 1,11; 0,3159; 0,3100; 0,1839 nm) in the mixtures with 2.7% of additive (Fig. 3, a, *curve 1*).

It should be noted that over the same duration of synthesis, the intensity of diffraction peaks characteristic to C_3AH_6 decreased when a higher quantity of Al_2O_3 (5.3–15.4%) was used. Meanwhile, the crystallinity of Z-phase was increased in the sample with 5.3% of Al_2O_3 (Fig. 3, a, *curve 2, 3* and *4*). Besides, small intensity diffraction peaks characteristic to gyrolite gel were observed in the XRD patterns of those synthesis products, in which the amount of additive varied from 5.3 to 10.5%.

Presumably, the quantity of semi-crystalline calcium silicate hydrates increased with the increasing duration of isothermal curing because C-S-H(I) gel was identified in the samples with the highest amount of Al_2O_3 (Fig. 3, a, *curve 4*).

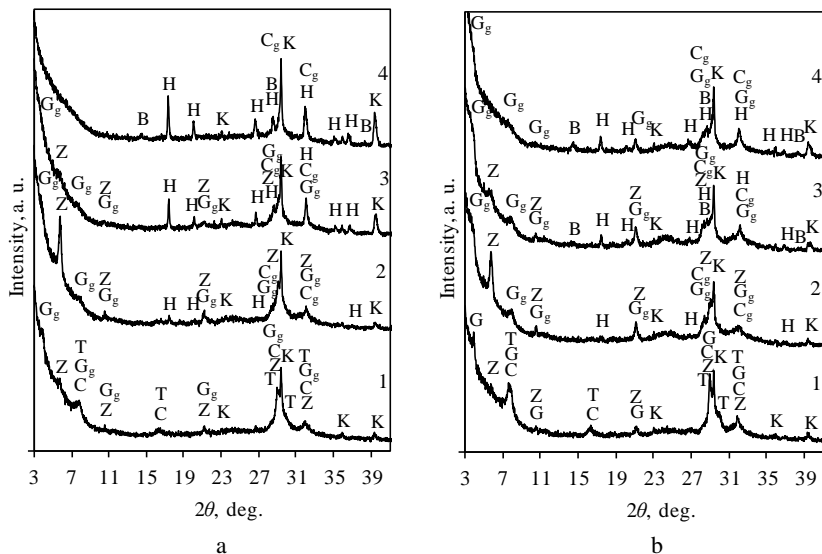


Fig. 3. XRD patterns of synthesis products after 24 h (a) and 72 h (b) of hydrothermal treatment at 200°C, when the molar ratio of primary mixtures ($\text{CaO}/(\text{SiO}_2+\text{Al}_2\text{O}_3)$) is equal to 0.55 and the amount of Al_2O_3 additive (%) is: *curve 1* – 2.7, *curve 2* – 5.3, *curve 3* – 10.5, *curve 4* – 15.4. Indexes: H – C_3AH_6 , C – C-S-H(I), C_g – C-S-H(I) gel, Z – Z-phase, K – CaCO_3 , G – gyrolite, G_g – gyrolite gel, T – 1.13 nm tobermorite intercalated with Al^{3+} ions, B – boehmite

Also, boehmite ($\text{AlO}(\text{OH})$, d -spacing – 0.6107; 0.3161; 0.2345; 0.1860; 0.1847 nm) was observed in the synthesis products (Fig. 3, a, *curve 4*).

After 72 h of hydrothermal treatment at 200°C temperature, the same compounds which characteristic diffraction peaks intensities increased with the increasing duration of isothermal curing were dominant in the mixtures with 2.7% of Al_2O_3 (Fig. 3, b, *curve 1*).

Meanwhile, when the amount of additive was increased to 5.3%, a lower crystallinity Z-phase was obtained and the intensity of diffraction maximums typical to gyrolite gel was increased (Fig. 3, b, *curve 2*).

It was examined that the intensity of diffraction peaks characteristic to C_3AH_6 was constantly decreasing with the increasing duration of synthesis. It is possible that a part of this compound decomposed to boehmite, since the latter compound was identified not only in the mixtures with the highest amount of Al_2O_3 , but also in the synthesis products containing 10.5% of the mentioned additive (Fig. 3, b, *curve 3* and *4*) after 72 h of synthesis.

Thus, according to the results of the current research, the scheme which represents the sequence of compounds formed during hydrothermal synthesis (200°C, 4–72 h) in the CaO–Al₂O₃–SiO₂·nH₂O–H₂O system was created (Fig. 4).

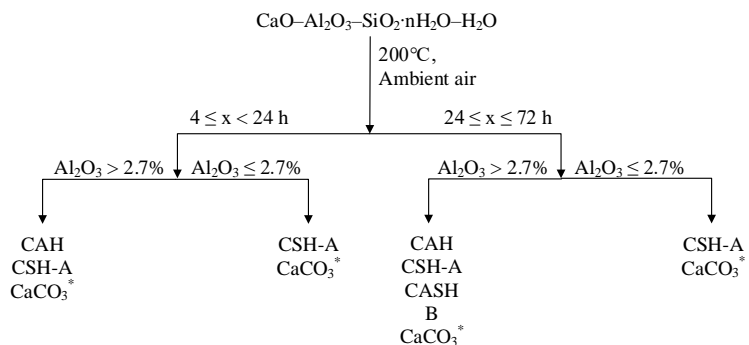


Fig. 4. The schematic representation of the sequence of compounds formed during hydrothermal synthesis (200°C, 4–72 h) in the CaO–Al₂O₃–SiO₂·nH₂O–H₂O system. Indexes: x – the duration of isothermal curing, h; CSH-A – calcium silicate hydrates intercalated with Al³⁺ ions; CAH – calcium hydroaluminates; CASH – calcium hydroalumosilicates; B – boehmite, CaCO₃* – calcite

It was determined that calcium silicate hydrates intercalated with Al³⁺ ions were formed in the samples with 2.7% of Al₂O₃ irrespectively of the synthesis duration (Fig. 4). However, when the amount of the mentioned additive was increased from 5.3 to 15.4% and the duration of isothermal curing was prolonged to 24 h, calcium hydroaluminates and calcium silicate hydrates intercalated with Al³⁺ ions were dominant in the synthesis products. Moreover, when the duration of isothermal treatment was extended from 24 to 72 h, calcium silicate hydrates intercalated with Al³⁺ ions and calcium hydroaluminates, which partly decomposed to boehmite and calcium hydroalumosilicates, were formed. In all cases, calcium carbonate forms due to the reaction with atmospheric CO₂.

The assumption that calcium hydroaluminates are only formed at the beginning of hydrothermal treatment and calcium silicates hydrates, in which a part of Al³⁺ ions is intercalated, stabilize them was made by evaluating the obtained synthesis data. Therefore, no free SiO₂ which can participate in the crystallization of hydrogarnets is present in the reaction medium.

In order to determine the optimal formation temperature of C₃AH₆ and to reduce the amount of experiments, the following part of this work evaluated the stability of C₃AH₆: the theoretical possibilities of compound decomposition during hydrothermal treatment were calculated according to the temperature of isothermal curing.

The thermodynamic parameters of reactions (Fig. 5) showed that, in the entire temperature interval, the decomposition of C_3AH_6 most likely occurs according to reaction 1 (the Gibbs free energy varies from -595 to -670 kJ/mol), during which the latter compound decomposes to calcium hydroxide and boehmite:

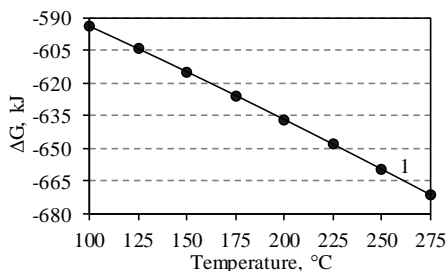
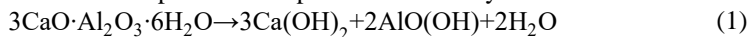


Fig. 5. The Gibbs free energy values as a function of temperature for the decomposition of C_3AH_6 (reaction 1) during hydrothermal treatment

Thus, the obtained thermodynamic results show that the possibility of the formation of C_3AH_6 and its stability increase by decreasing the temperature of isothermal curing. For this reason, the next part of this work investigates the influence of hydrothermal synthesis duration on the crystallization of C_3AH_6 at 130°C temperature.

3.2. The influence of isothermal treatment duration on the formation of calcium hydroaluminates in the $CaO-SiO_2-Al_2O_3-H_2O$ system at 130°C temperature

It was determined that not only the duration of hydrothermal synthesis but also the amount of Al_2O_3 affects the interaction between raw materials and the mineralogical composition of products. Calcium hydroaluminate was dominant in the synthesis products after 8 h of isothermal curing at 130°C when the molar ratios of primary mixtures $CaO/(SiO_2 + Al_2O_3)$ were equal to 0.55 and $Al_2O_3/(SiO_2 + Al_2O_3) = 0.05, 0.1$ and 0.15 (Fig. 6, a, curve 1). Alongside the mentioned compound, a broad basal reflection was noticed in a $18-34^\circ$ range of diffraction angles, and was assigned to compounds of amorphous structure, which mainly contain silicon, calcium and/or aluminium components (Fig. 6, a). Moreover, the amount of formed CAH depends on the quantity of Al_2O_3 additive in the primary mixtures ($Al_2O_3/(SiO_2 + Al_2O_3) = 0.15$): both, the highest intensity of diffraction maximums typical to this compound and the highest heat values of the CAH dehydration at $\sim 281^\circ\text{C}$ temperature were observed (Fig. 6, a, curve 3; Fig. 6, b, curve 2).

It is worth noting that under all experimental conditions when the products were dried in an air conditioned chamber (50°C, 24 h), carbonation occurred because the characteristic diffraction peaks for calcium carbonate were detected in the XRD patterns (Fig. 6, a). It is clearly shown in the DSC curve: the decomposition of calcium carbonate was observed in a 650–750°C temperature range (Fig. 6, b). Besides, due to a higher amount of Al₂O₃ in the synthesis products, the calculated quantity of calcium carbonate increased from 2.11 to 5.36%, which corresponded to the mass loss from 0.93 to 2.36%.

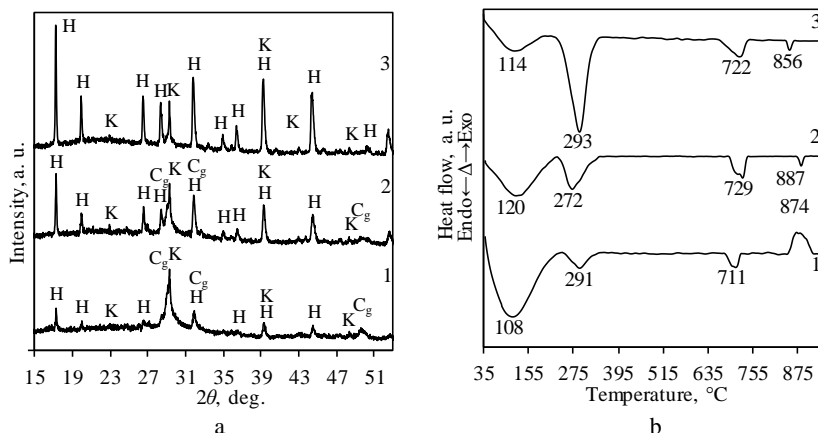


Fig. 6. X-ray diffraction patterns (a) and DSC curves (b) of synthesis products after 8 h of isothermal treatment at 130°C temperature, when the molar ratio of CaO/(SiO₂+Al₂O₃) is equal to 0.55 and Al₂O₃/(SiO₂+ Al₂O₃) was: *curve 1* – 0.05, *curve 2* – 0.1; *curve 3* – 0.15.

Indexes: H – C₃AH₆, C_g – C-S-H(I) gel, K – CaCO₃

It was determined that the formation of C₃AH₆ is inhibited when the duration of isothermal curing is extended from 16 to 72 h. It is clearly visible that, in the mixtures with Al₂O₃/(SiO₂+Al₂O₃) molar ratio of 0.05, 0.1 and 0.15, the quantity of heat absorbed during the dehydration of calcium hydroaluminates gradually decreases with the duration of isothermal curing from 28 to 21 J/g, from 106 to 22 J/g and from 245 to 91 J/g, respectively (Fig. 7).

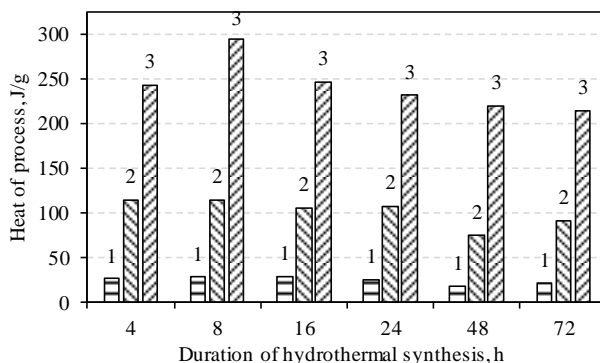


Fig. 7. The quantity of heat absorbed during CAH dehydration in a 250–330°C temperature range over different durations of synthesis (4–72 h) when the molar ratio of $\text{CaO}/(\text{SiO}_2+\text{Al}_2\text{O}_3)$ is equal to 0.55 and the amount of Al_2O_3 (wt%) is: *curve 1* – 5.3, *curve 2* – 10.5, *curve 3* – 15.4

The results show that the largest absorbed heat (~290 J/g) of calcium hydroaluminates is obtained after 8 h of hydrothermal treatment in mixtures with a higher amount of Al_2O_3 . Additionally, synthetic CAH have a similar chemical nature as the compounds which form during ordinary portland cement hydration. Presumably, they could change the mechanism of this process and influence the dissolution and interreaction of other compounds which form during cement hydration. For this reason, the effect of synthetic products on the cement hydration was investigated.

3.3. The influence of synthetic calcium hydroalumosilicate additives on cement hydration

3.3.1. The heat release kinetics of cement samples

The influence of different amounts of calcium hydroaluminate – C_3AH_6 – formed during hydrothermal treatment of synthetic calcium hydroalumosilicate additives ($(\text{CaO}/(\text{SiO}_2+ \text{Al}_2\text{O}_3) = 0.55; 8 \text{ h}; 130^\circ\text{C})$) on the early hydration of cement was investigated by performing microcalorimetric analysis. According to the amount of Al_2O_3 used in the primary mixtures, the samples obtained after synthesis were named as: CAH1 (the products containing 5.3% of Al_2O_3), CAH2 (the products containing 10.5% of Al_2O_3) and CAH3 (the products containing 15.4% of Al_2O_3).

Several types of cement mixtures were prepared by replacing a portion of portland cement with synthetic calcium hydroalumosilicate additives (5–25% by weight of the total cementitious material) for microcalorimetric analysis. The

samples were labelled as OPC-CAH1, OPC-CAH2 and OPC-CAH3, and pure portland cement sample – as OPC.

In order to determine if synthetic calcium hydroalumosilicate additives affect cement hydration, the cement mixtures with 5% of additives were first examined. The rate of heat evolution and the total amount of heat released were calculated based on a unit weight of portland cement.

It was determined that under all experimental conditions the additives induce the initial reaction, accelerate and shorten the induction period, and have a positive effect on the second (characteristic to the dissolution of C_3S) and the third exothermic (characteristic to the dissolution of C_3A and the formation of ettringite) reactions.

The highest amount of the total heat was reached in samples OPC-CAH2 and OPC-CAH3 (~310 J/g), while OPC-CAH1 and OPC showed similar values (~290 J/g).

Thus, the obtained results indicate that even a small amount of synthetic calcium hydroalumosilicate additives (5%) has a positive influence on cement hydration. For this reason, the optimal quantity of CAH was determined by replacing a portion of portland cement with a higher amount of these additives (10, 15, 20 and 25% by weight of the total cementitious material).

After 72 h of hydration, the highest quantity of the total heat (~324 J/g) was obtained in the mixtures with 10% of CAH, while in the samples with 15, 20 and 25% of synthetic calcium hydroalumosilicate additives, it only reached ~260 J/g which was lower than that obtained in pure OPC sample (~290 J/g). For this reason, only the mixtures with 10% of CAH were investigated in detail. The heat evolution curves of pure OPC samples and OPC samples with 10% of additives (CAH2 and CAH3) showed five typical stages of hydration process (the initial reaction, the induction period, the acceleration period, the deceleration period, and the period of slow continued reaction).

Synthetic calcium hydroalumosilicate additives accelerated the initial reaction (1–2 min) of cement samples because an increase in the maximum heat evolution rate was observed from 0.005 W/g (pure OPC) to 0.011 W/g (OPC-CAH3) and to 0.018 W/g (OPC-CAH2) (Fig. 7, a). Besides, the induction period, which is assigned to the growing C-S-H and CH on the surface of the particles of primary compounds, was effectively shortened: in pure OPC samples, the mentioned process lasted for 3 h, while in the cases of OPC-CAH2 and OPC-CAH3 – only for ~1.8 h (Fig. 8, b). However, the accelerating effect begun earlier, after 1.9 h of hydration in comparison with the pure OPC (Fig. 8, c). Moreover, the lower values of heat flow of the second exothermic reaction, typical to the dissolution of C_3S , were reached in OPC samples with additives, i. e. 0.0023 W/g at 5.02 h for OPC-CAH2 and 0.0023 W/g at 6.02 h for OPC-CAH3. Meanwhile, during the third exothermic reaction, which is characteristic

to the dissolution of C_3A and the formation of ettringite, the highest value of heat flow (0.0032 W/g) at 13.1 h was obtained in the OPC-CAH3 sample (Fig. 8, c).

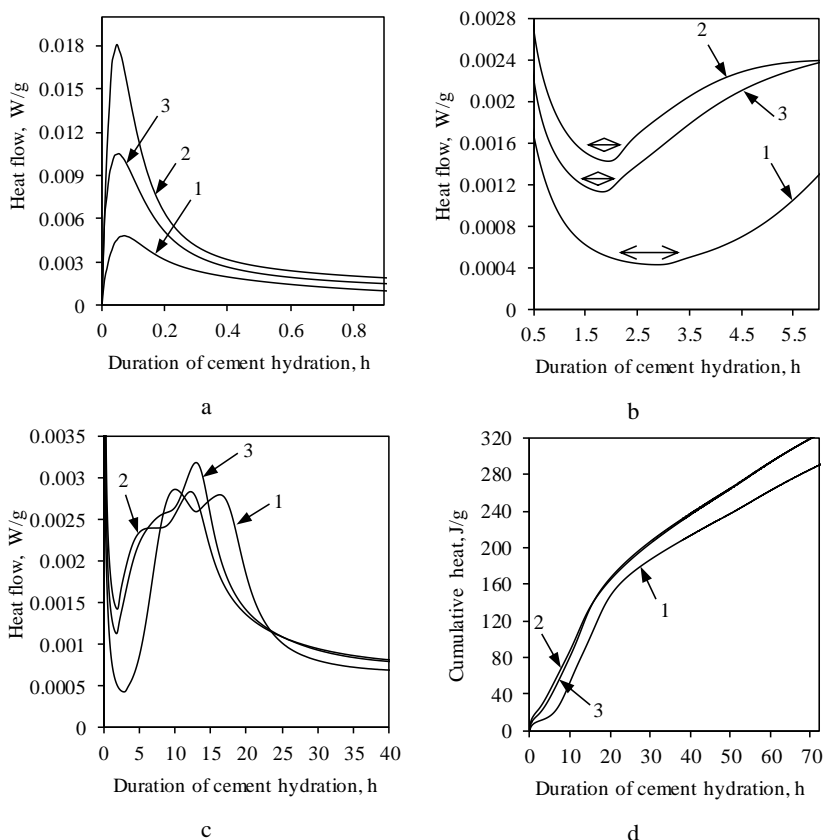


Fig. 8. The heat evolution rate (a–c) and cumulative heat (d) of OPC (1), OPC-CAH1 (2), and OPC-CAH2 (3) samples during the early stage of hydration

At later stages of hydration, the synthetic calcium hydroalumosilicate additive acts as the usual pozzolanic additive. It is worth noting that the largest value of cumulative heat was reached in the OPC-CAH2 sample (Fig. 8, d).

Thus, the research indicates that the quantity of synthetic additives significantly influences the rate of heat evolution and the total amount of heat released during cement hydration. It was found that the highest amount of total heat was obtained in the mixtures with 10% of CAH. For this reason, in the next part of this work, the effect of 10 % of synthetic additive on cement hydration was examined.

3.3.2. The influence of 10% of synthetic calcium hydroalumosilicate additives on the early hydration of cement

In order to investigate the mineral and chemical composition of compounds formed during hydration, heat evolution experiments were repeated at 25°C for different time periods (1.8, 3, 9.5, 13, and 24 h) which corresponded to the onset/peak/end duration of different early hydration periods.

It was determined that the stability and reactivity of OPC-CAH2 and OPC-CAH3 samples depend significantly on the composition of the primary mixture used for hydrothermal synthesis. In a case of OPC-CAH2 sample, one of the synthesis products, C_3AH_6 , was fully reacted after 1.8 h of hydration (Fig. 9, a, curve 2; Table 2); meanwhile, 66% of this compound is still present in sample OPC-CAH3 (Fig. 9, a: endothermic effect at ~282°C (23.4 J/g), Table 2).

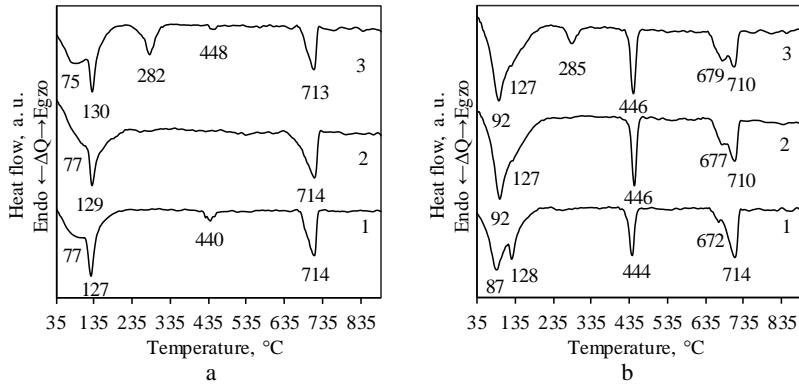


Fig. 9. DSC curves of OPC (1), OPC-CAH2 (2) and OPC-CAH3 (3) samples after 1.8 h (a) and 9.5 h (b) of hydration at 25°C temperature

However, when the duration of OPC hydration was extended to 24 h, the amount of unreacted compounds decreased (Fig. 9; Table 2).

Table 2. The main characteristics of thermal effects typical to C_3AH_6

Composition	Hydration time, h	T_{max} , °C	Heat process, J/g of	Mass loss, %	Unreacted CAH, wt. %
OPC-CAH2	0	263.7	13.13	0.62	100
	1.8–24	-	-	-	-
OPC-CAH3	0	274.2	35.69	1.03	100
	1.8	281.5	23.4	0.93	65.56
	3	275.4	21.85	1.11	61.22
	9.5	285.1	13.53	0.80	37.91
	13	293.9	14.34	0.78	40.18
	24	287.5	14.19	0.56	39.76

It appears that the syntetic additives influence the dissolution of gypsum because after 9.5 h of hydration, only a shoulder which is characteristic to gypsium, can be visible in DSC curves of OPC-CAH2 and OPC-CAH3 samples (Fig. 9, b) at ~127°C temperature. In a pure system, the latter compound fully reacted after 16.5 hours of hydration, whereas in the samples with additives – after 13 h. It is clearly visible in DSC curve: the endothermic effect disappeared in the 105–135°C temperature range, which corresponds to dehydration of gypsum (Table 3). In comparison with pure OPC samples, only smaller amounts of semicrystalline C-S-H (Fig. 8: endothermic effect at 67°C; Table 3) as well as portlandite (Fig. 9: endothermic effect at 440°C; Table 3) were obtained by prolonging the duration of OPC hydration.

Table 3. The main characteristics of thermal effects typical of CSH, gypsum, portlandite and CaCO₃

Composition	Hydration time, h	C-S-H	Gypsum		Portlandite		CaCO ₃		
		Heat of process, J/g	Heat of process, J/g	Unreacted gypsum, wt.%	Heat of process, J/g	The amount of formed Ca(OH) ₂ , %	Heat of process, J/g	Mass loss, %	The amount of formed CaCO ₃ in the sample, %
OPC	1.8	14.89	16.23	69.01	5.72	0.50	37.07	1.75	3.97
	3	17.22	16.69	70.96	6.10	0.54	46.29	2.26	5.14
	5.5	28.12	10.97	46.64	8.29	0.73	48.57	2.61	5.93
	9.5	40.88	6.86	29.15	20.97	1.85	50.95	2.89	6.57
	13	53.01	0.79	3.36	40.14	3.54	58.4	2.39	5.42
	16.5	71.84	0	0	64.63	5.70	72.06	3.09	7.02
	24	77.42	0	0	93.41	8.23	95.02	3.81	8.65
OPC-CAH2	1.8	18.61	13.63	74.93	0.97	0.09	56.79	2.27	5.17
	3	22.53	10.33	43.92	0.99	0.09	48.14	1.24	2.82
	5.5	37.6	6.02	25.57	8.39	0.74	49.82	2.03	4.61
	9.5	51.1	0.29	1.24	23.94	2.11	52.24	2.72	6.19
	13	63.13	0	0	41.86	3.69	58.81	2.28	5.17
	16.5	66.49	0	0	55.36	4.88	55.12	2.34	5.32
	24	71.74	0	0	72.08	6.35	52.82	2.41	5.48
OPC-CAH3	1.8	17.2	13.54	67.60	2.10	0.19	34.04	1.52	3.45
	3	21.1	11.15	55.67	3.10	0.27	69.67	3.44	7.83
	5.5	37.32	4.74	23.68	11.69	1.03	63.45	2.97	6.75
	9.5	54.86	0.51	2.54	26.99	2.38	55.4	2.53	5.75
	13	64.14	0	0	42.47	3.74	69.61	2.99	6.80
	16.5	58.51	0	0	58.46	5.15	64.79	3.01	6.84
	24	66.5	0	0	74.3	6.55	62.58	3.09	7.03

The amounts of unreacted C_3S after heat evolution experiments at different time periods were determined by using quantitative analysis (QXRD). The quantity of C_3S was calculated from the change in intensity of the basic reflection (d -spacing – 0.2604 nm). The measurement was repeated five times and it was determined that the data declined no more than $\pm 2\%$ from the mean (Fig. 10). The quantity of C_3S in pure OPC samples and in samples with additives before hydration was equal to 100%.

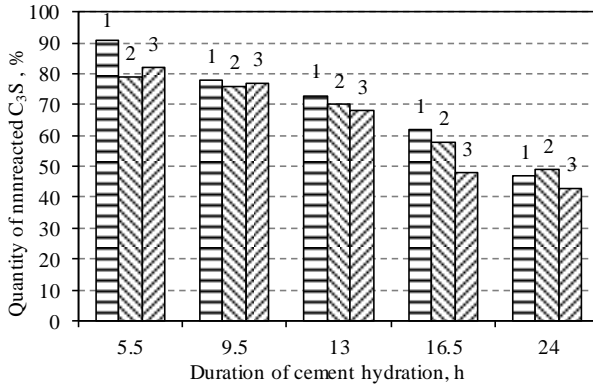


Fig. 10. The quantity of unreacted C_3S in pure OPC (1), OPC-CAH2 (2) and OPC-CAH3 (3) samples after different duration of hydration at 25°C

After 5.5 h of hydration, only 9% of C_3S reacts in pure OPC samples and further reduction of its quantity depends on the duration of hydration (Fig. 10, Table 3). Meanwhile, within the same duration of hydration, in 21% and 18% of this compound reacted in the samples with CAH2 and CAH3 additives, respectively (Fig. 10). Besides, these additives induced the earliest C_3S hydration in all samples (5.5–16.5 h).

Presumably, the synthetic CAH sample also induces the formation mechanism of ettringite. In order to prove this, the change in intensity of the basic reflection of ettringite (d -spacing, 0.972 nm) in cement samples was evaluated by X-ray diffraction analysis (XRD) according to the area of mentioned diffraction maximum per shift at different durations of hydration (Fig. 11).

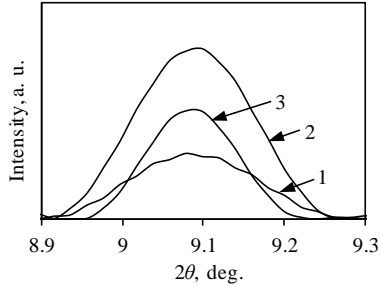


Fig. 11. The change in the main diffraction peak of ettringite in samples after 3 h of hydration: *curve 1* – OPC; *curve 2* – OPC-CAH2; *curve 3* – OPC-CAH3

The obtained results show that after 3 hours of hydration, the area of the main diffraction peak typical to ettringite increases twice in comparison with the pure OPC samples (Fig. 11). The same tendency was also observed when the duration of hydration was extended to 9.5 hours (Table 4).

Table 4. The values of the main diffraction peak area of ettringite in OPC, OPC-CAH1, and OPC-CAH2 samples

Composition	Hydration time, h							
	0	1.8	3	5.5	9.5	13	16.5	24
OPC	-	0.14	0.15	0.26	0.40	0.60	1.00	1.45
OPC-CAH2	-	0.15	0.37	0.42	0.89	0.90	1.18	1.39
OPC-CAH3	-	0.21	0.22	0.54	0.51	1.03	1.18	1.30

In addition, due to the accelerated dissolution of gypsum, a larger amount of ettringite formed in samples OPC-CAH2 and OPC-CAH3. However, after 24 h of hydration, the area of the main diffraction maximum of ettringite was slightly higher because of an excess of gypsum in pure OPC samples (Table 4).

In summary, the processes which occur during the early hydration of cement and the quantitative mineral composition of the cement hydrates are changed in the samples with calcium hydroalumosilicate additives. The additives induce the formation of CSH(I), the early hydration of the C_3S (5.5 – 16.5 h), the dissolution of gypsum as well as the formation of ettringite over 3–9.5 h of hydration. Due to these processes, the curing of cement proceeds faster in the samples with calcium hydroalumosilicate additives. Therefore, it is likely that the strength of these samples will be attained in shorter time.

3.4. The effect of synthetic mayenite additive on the properties of natural CaO chemisorbent

It is known that a natural CaO adsorbent is often used for CO₂ capture in high temperature processes (300–800°C). However, after only a few cycles of adsorption, the sintering of CaO occurs and the activity of this compound reduces [40]. In order to eliminate these drawbacks, various additives, such as calcium aluminates are used to stabilize CaO.

For this reason, the synthesis product which contains the highest amount of C₃AH₆ (CaO/(SiO₂+Al₂O₃) = 0.55; the quantity of Al₂O₃ – 15.4%; 8 h; 130°C) was used to investigate the thermal stability of synthesis products in the temperature range of 25–1050°C.

It was determined that the intensities of diffraction peaks characteristic to calcium hydroaluminates (*d*-spacing – 0.513, 0.444, 0.336, 0.204, 0.174 nm) slightly decrease with increasing the calcination temperature from 75°C to 150°C due to the dehydration of water from calcium hydroaluminates and amorphous compounds (Fig. 12).

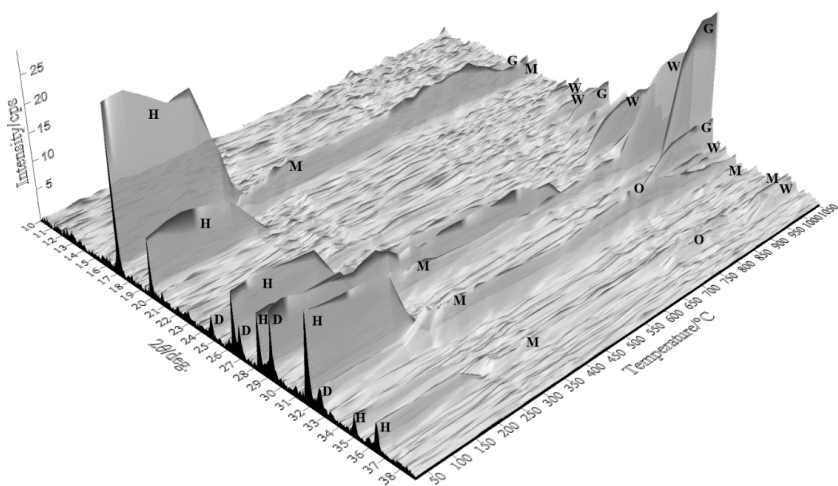


Fig. 12. In situ XRD patterns of the sample (130°C, 8 h, the amount of Al₂O₃ – 15.4 wt%) when the temperature of calcination varied in the 25–1050°C temperature range. Indexes: H – calcium hydroaluminate, C₃AH₆; M – mayenite, Ca₁₂Al₁₄O₃₃; D – calcium carbonate, CaCO₃; O – CaO; W – wollastonite, CaSiO₃; G – gehlenite, Ca₂Al₂SiO₇

It is possible to conclude that C₃AH₆ remained stable up to 225°C because the intensity of diffraction maximums characteristic to this compound was unchanged (Fig. 12). Meanwhile, at slightly higher calcination temperature (250°C), the crystalline structure of C₃AH₆ was destroyed and the mentioned

compound fully recrystallized to mayenite (*d*-spacing – 0.4910, 0.3003, 0.2690, 0.2454, 0.2196, 0.1610 nm) (Fig. 12).

It was examined that, when the calcination temperature varies in the 650–900°C range, the intensity of basic diffraction maximum which is characteristic to mayenite (*d*-spacing – 0.4910 nm) increases from ~8 to ~9.7 cps. Besides, CaCO₃ fully decomposes into CaO (*d*-spacing – 0.2778, 0.2405, 0.1701, 0.1452 nm) at 700°C temperature.

It was also determined that the solid-state reactions occurred after calcination at the temperatures above 850°C. The intensity of diffraction peaks typical to wollastonite increased up to 950°C, and up to 1000°C in the case of gehlenite (Fig. 12).

The following part of the research investigated the uptake of CO₂ by CaO/Ca₁₂Al₁₄O₃₃ chemisorbent. The chemisorbent was decarbonized at 750°C, therefore mayenite was used as additive, since it remains stable up to 800°C. Synthetic Al-based CaO chemisorbent was prepared from mixtures of natural calcined lime and synthetic CAH sample (CaO:CAH = 75:25). After wet milling, the suspension was filtered and calcined for 1 h at 750°C.

The results of STA analysis show that the difference between mass losses of the endothermic effect (630–820°C) typical to the decomposition of CaCO₃ in the investigated samples is insignificant and decreases only slightly from 26.36% (59.91% of CaCO₃) to 25.23% (57.34% of CaCO₃), respectively (Table 5; Fig. 13, b), in comparison to the first and the eighth cycle of adsorption/desorption.

Table 5. The main characteristics of thermal effects typical to the chemisorbents used for the STA analysis

Chemisorbent	Number of cycles	The characteristics of thermal conversions of products				Mass change, %
		T _{onset} , °C	T _{max} , °C	T _{ends} , °C	Heat of process, J/g	
CaO/Ca ₁₂ Al ₁₄ O ₃₃ (mass ratio 75:25)	0	35.8	37.4	150.1	62.71	0.08
		633	693.9	713	36.82	1.03
	1	37.7	92.9	182.8	38.97	0.67
		716.4	797.5	813.9	806.74	26.36
	8	35.0	93.2	169.1	48.05	0.18
		431.0	447.3	462.2	11.88	0.17
		721.7	800.2	815.6	732.99	25.23

These results are in a good agreement with the data of TG and DSC analyses. After CO₂ adsorption, the endothermic effect which is assigned to the decomposition of CaCO₃ shifted to higher temperatures (Table 5).

The previous results have also been confirmed by XRD analysis. It has determined that mayenite remains stable and CaCO₃ dominates in the products under all experimental conditions (Fig. 13, a). As expected, the uptake of CO₂ by

the prepared chemosorbent decreases only slightly from ~ 0.358 to ~ 0.337 $\text{gCO}_2/\text{g}_{\text{ads}}$. (Fig. 11, b).

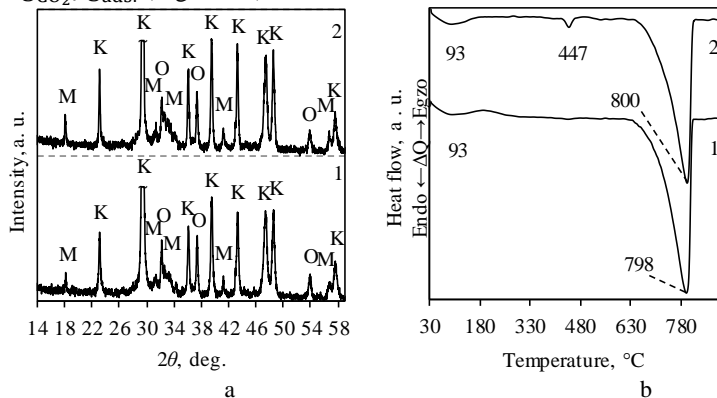


Fig. 13. XRD (a) and DSC (b) curves of $\text{CaO}/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ chemosorbent after: *curve 1* – 1 cycle, *curve 2* – 8 cycles (calcination was performed at 750°C under 100% N_2 atmosphere, carbonation – at 650°C under 100% CO_2 atmosphere)

Thus, it was determined that mayenite obtained by calcinating the synthesis product (130°C ; 8 h) has a positive influence on the adsorption capacity of CaO . Therefore, it can be used to stabilize CaO chemosorbents, which are obtained from various raw materials, and extend their exploitation. In order to apply this adsorption/desorption process in cycles at an industrial scale, the chemosorbent should be granulated or tableted. Therefore, a detailed investigation is still needed. It is unknown how additives, such as binders (to help the ingredients bind properly when the tablet is calcinated) or the size of granules/tablets and their thermal stability, the specific surface area, the compressive strength of granular/tablet and other parameters would affect chemosorption.

3.5. Technological recommendations for the production and application of synthetic calcium hydroalumosilicate additive

The optimal parameters for the production of synthetic calcium hydroalumosilicate additive were chosen according to the results of current research, in which the products with the highest amount of C_3AH_6 were obtained in CaO , amorphous $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ and Al_2O_3 mixtures, when the molar ratios of $\text{CaO}/(\text{SiO}_2 + \text{Al}_2\text{O}_3)$ and $\text{Al}_2\text{O}_3/(\text{SiO}_2 + \text{Al}_2\text{O}_3)$ are equal to 0.55 and 0.15, respectively. Hydrothermal treatment was performed in unstirred suspensions ($\text{W}/\text{S} = 10$) when the saturated water vapour temperature was equal to 130°C and the duration of synthesis was 8 h.

The hydrothermal synthesis of the aforementioned compounds includes the following steps: cleaning the autoclave, pouring the raw material suspension

into the autoclave, closing the autoclave, raising the temperature until a stable reading is obtained, isothermal treatment, decreasing the pressure to atmospheric, opening the autoclave, and unloading.

All stages comprise one work cycle, which takes 12 hours. One autoclave works on average 250 cycles per year, 5 days per week. For one cycle, the required amount of starting materials is 200 kg ($\text{CaO} = 61.3$ kg, $\text{Al}_2\text{O}_3 = 30.7$ kg, $\text{SiO}_2 \cdot n\text{H}_2\text{O} = 108$ kg), and, in order to maintain the Water/Solid ratio, 2000 kg of H_2O is necessary.

The recommended technological scheme for the production and application of synthetic calcium hydroalumosilicate additive is presented in Fig. 14.

CaO , Al_2O_3 and amorphous $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ are kept in raw materials silos 1. The required amount of starting materials is weighed 3 and transported to the mixer 5 (the volume – 3.5 m^3 , stirring speed – 170 rpm), in which the necessary amount of water is poured from the water tank 2. The mixed suspension is then fed to an autoclave 7 (the volume – 4.0 m^3 , operating temperature – $130 \pm 2^\circ\text{C}$) and, after the synthesis, the suspension is poured to an intermediate reservoir 8, where a part of excess water is removed by the pump 6 and the remaining part – by a filter 9. Then, the moist material from the filter 9 is transported to the drum dryer 10, where the heating agent is air obtained in the calorifier 11. It is worth noting that air in the calorifier supplied by the fan is heated to $90 \pm 2^\circ\text{C}$ temperature. After this process, the obtained dry product is packed and stored in a warehouse.

The manufactured synthetic calcium hydroalumosilicate additive can be used in the production of cement (1st approach) or as additive in the preparation of chemisorbents for the capture of CO_2 (2nd approach).

In the production of cement, the required amount of CEM(I) and synthesis product is weighed 3 ($\text{CEM(I)}:\text{CAH} = 90:10$) and transported to a homogenizer 5. After the mixing process, the prepared cement is packed and stored in a warehouse.

If the synthetic calcium hydroalumosilicate additive was used for the production of chemisorbent, lime and synthetic additive would be stored in raw materials silos 1, the required amount of these materials would be weighed 3 ($\text{Lime}:\text{CAH} = 75:25$) and transported to a mixer 5. The obtained mixture would be then fed to a ball mill 17 and, after milling, it would be kept in the intermediate reservoir 18. The required amount of the mixture would be then weighed 3 and transported to the granulating/tableting equipment. The obtained granules or tablets would be then packed and stored in a warehouse.

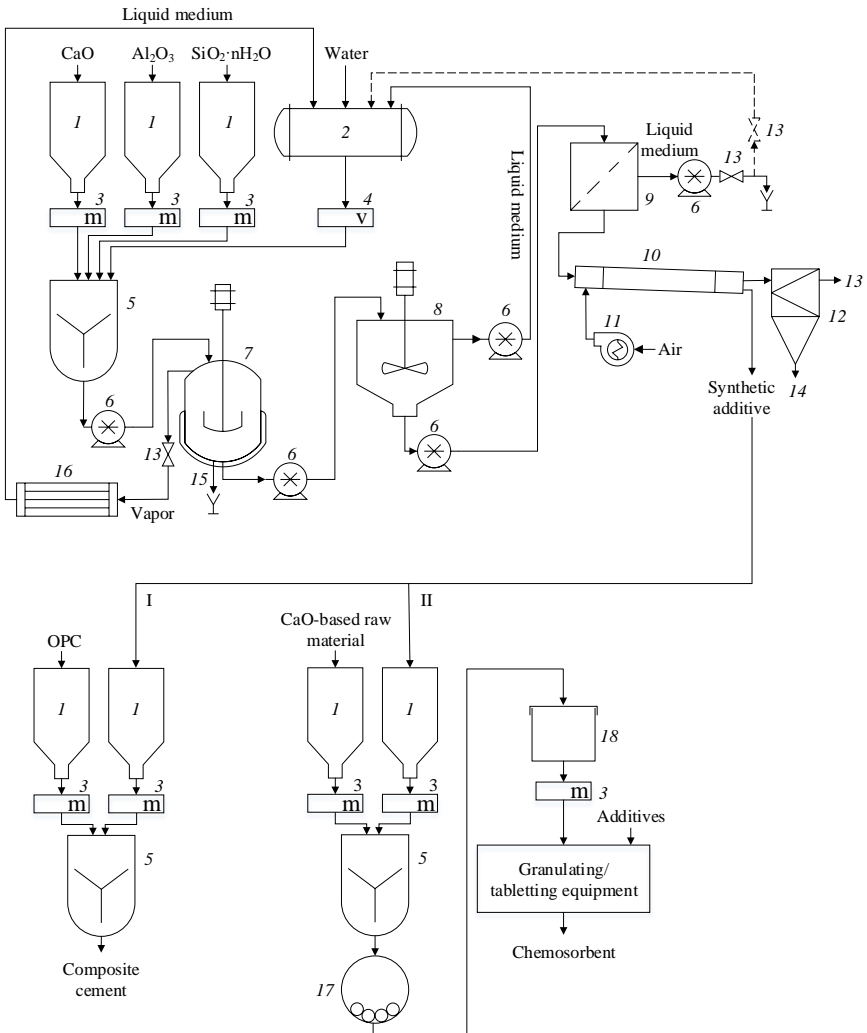


Fig. 14. The technological scheme for the production and application of synthetic calcium hydroalumosilicate additive: 1 – raw materials silos; 2 – water tank; 3 – weight dispensers; 4 – volume dispensers; 5 – mixers; 6 – pumps; 7 – autoclave; 8 – suspension reservoir; 9 – filter; 10 – drum dryer; 11 – calorifier; 12 – cyclone; 13 – cleaned air; 14 – small product fraction; 15 – solution after synthesis; 16 – condenser; 17 – ball mill; 18 – intermediate reservoir

CONCLUSIONS

1. It was determined that at 200°C, calcium silicate hydrates intercalated with Al^{3+} ions form in the mixtures with 2.7% of Al_2O_3 irrespectively of the duration of hydrothermal synthesis (4–72 h). However, when the amount of the mentioned additive increases from 5.3 to 15.4% and the duration of isothermal curing is prolonged to 24 h, calcium hydroaluminates and calcium hydrosilicates intercalated with Al^{3+} ions are the dominant products of synthesis. When the duration of isothermal treatment is extended to 72 h, higher-crystallinity calcium silicate hydrates intercalated with Al^{3+} ions are obtained and a part of calcium hydroaluminates decomposes to boehmite and calcium hydroalumosilicates.
2. The stability of C_3AH_6 increases with decreasing the temperature of hydrothermal treatment and the optimal duration for the synthesis of this compound at 130°C temperature is 8 h. When the amount of Al_2O_3 is higher than 2.7%, the quantity of C_3AH_6 increases proportionally with the amount of additive. Also, during the decomposition of this compound, the maximum amount of absorbed heat is obtained under all investigated conditions.
3. The synthetic calcium hydroalumosilicate additives obtained after 8 h of hydrothermal treatment at 130°C and containing 5.3–15.4% of Al_2O_3 increase the total amount of heat released. The research has proved that the quantitative mineral composition of the cement hydrates is changed in cement samples with 10% of mentioned additives during hydration: the additive induces the formation of CSH (I), the early hydration of the C_3S (5.5–16.5 h), the dissolution of gypsum as well as the formation of ettringite during the hydration (3–9.5 h).
4. After 8 h of hydrothermal treatment at 130°C, the dominant compound C_3AH_6 synthesized in the mixtures with 15.4% of Al_2O_3 , at higher than 250°C temperature decomposes and recrystallizes into calcium aluminate – mayenite. The latter compound remains stable up to 800°C. After the CO_2 adsorption/desorption test, it has been determined that the calcined synthesis product is suitable for the stabilization of the structure of chemosorbents having a CaO component because after the eighth cycle (650–750°C), the adsorption capacity of chemosorbent slightly decreases from ~ 0.358 to $\sim 0.337 \text{ g}_{\text{CO}_2}/\text{g}_{\text{ads.}}$ and mayenite remains stable.
5. The technological scheme for the preparation of the synthetic calcium hydroalumosilicate additive and the production of cement and chemosorbent for CO_2 adsorption was offered. The optimal parameters of technological process were determined and the right type of equipment was chosen.

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SANTRAUKA

Temos aktualumas

Pastaraisiais metais plačiai domimasi funkciniais $x\text{CaO}\cdot y(\text{Al}_2\text{O}_3, \text{SiO}_2)\cdot z\text{H}_2\text{O}$ junginiais, kurie vis labiau pritaikomi tiek rišamųjų medžiagų gamybos, tiek adsorbcijos procesuose. Gamtiniai kalcio hidroaliumosilikatai (pavyzdžiui, metakaolinitas, kaolinas, bentonitas ir kiti) naudojami daugelyje procesų, tačiau platesnį jų pritaikomumą riboja jų fizikinės cheminės savybės, kurios kinta ganėtinai siaurame intervale, papildomai juos apdorojant, t. y. smulkinant (kinta granulimetrinė sudėtis ir dalelių dydis, bet ne vidinis paviršiaus plotas), degant (didėja jų aktyvumas, bet dėl flusuojančių priemaišų prasideda sukepimas) ir t. t. Kiti svarbūs veiksniai, ribojantys gamtinių junginių naudojimą, yra kintanti kristalų gardelės struktūra ir į ją įsiterpę papildomi jonai. Dėl šių priežasčių specialiai pagaminti sintetiniai junginiai yra kur kas efektyvesni, nes sintezės metu galima valdyti tikslines produktų savybes. Vienas iš tokių sintezės būdų yra hidroterminis pradinių mišinių apdorojimas sočiųjų vandens garų aplinkoje.

Hidroterminė sintezė yra paprastas, didelio našumo, lengvai kontroliuojamas procesas, kurio metu sočiųjų vandens garų aplinkoje reaguoja įprastinėmis sąlygomis netirpūs junginiai. Keičiant hidroterminio proceso parametrus: temperatūrą, slėgį ir apdorojimo trukmę, galima kontroliuoti ne tik susidarančių produktų sudėtį, bet ir jų fizines savybes. Minėtų parametrų ir susidarančių junginių pastovumas sintezės metu bei galimybė juos keisti nulemia platų gautų junginių panaudojimą įvairiose pramonės srityse.

Viena iš jų yra cemento gamybos pramonė. Siekiant sumažinti cemento gamybos metu išmetamų pagrindinių šiltnamio efektą sukeliančių anglies dioksido dujų kiekį, dalis klinkerio yra keičiama įvairiais priedais ir / arba gamybos atliekomis, tokiu būdu sumažėja klinkerio gamybos sąnaudos. Šiai priedų grupei yra priskiriami ir $\text{CaO}\text{-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ sistemoje susidarantys junginiai, kurie lyginant su gamtiniais yra žymiai pranašesni, nes priklausomai nuo sintetinio junginio sudėties bei savybių, keičiant dalį klinkerio galima valdyti ir keisti cemento hidratacijos mechanizmą: pradinių cemento junginių tirpumą bei jų hidratacijos laipsnį, pagrindinių hidratacijos etapų trukmę ir kita. Dėl šios priežasties, norint įvertinti sintetinio kalcio hidroaliumosilikatinio priedo įtaką cemento hidratacijai, pirmiausia būtina nustatyti palankiausias $x\text{CaO}\cdot y(\text{Al}_2\text{O}_3, \text{SiO}_2)\cdot z\text{H}_2\text{O}$ junginių susidarymo hidroterminės sintezės sąlygas.

Kita $x\text{CaO}\cdot y(\text{Al}_2\text{O}_3, \text{SiO}_2)\cdot z\text{H}_2\text{O}$ junginių panaudojimo sritis – CaO stabilizuojantis priedas CO_2 adsorbcijai. Pramoninių procesų metu išsiskiriančių CO_2 dujų emisijos į aplinką mažinimui plačiai naudojama CO_2 adsorbcija iš kalcio oksido pagamintais kietais adsorbentais, kurie yra tinkami naudoti

cikliniuose kalcinavimo / karbonizavimo procesuose. Dėl aukštos temperatūros poveikio po kelių kalcinavimo / karbonizavimo ciklų adsorbento efektyvumas gerokai sumažėja. Šiai problemai spręsti gali būti panaudoti inertiniai stabilizatoriai aliuminio oksido pagrindu, kurie suformuoja patvarų kietą karkasą (matricą), kuris padidina ciklų skaičių ir stabdo adsorbento sukepimą. Iš daugelio naudojamų stabilizatorių efektyviausiais yra majenitas, kuris gali būti gaminamas įvairiais būdais: kietafazio sukepimo, savaiminio degimo, zolių-gelių, purškiamosios pirolizės, oksalatų prekursorių metodais. Tačiau minėtoms gamybos technologijoms reikalingos arba aukštos temperatūros, arba papildomas produkto gryninimas, nes dėl tirpių pradinių žaliavų ir specifinės skystosios terpės, tokių kaip nitratai ir įvairūs organiniai tirpikliai, dažniausiai susidaro pašaliniai junginiai.

Taigi, galima daryti pagrįstą prielaidą, kad majenitas gali būti gautas hidroterminėse sąlygose susintetinant tarpinius $x\text{CaO}\cdot y(\text{Al}_2\text{O}_3, \text{SiO}_2)\cdot z\text{H}_2\text{O}$ junginius ir juos termiškai apdorojant. Šio gamybos būdo metu nesusidarytų kenksmingų pašalinių junginių, todėl būtų eliminuota produkto gryninimo stadija. Manoma, kad tokiu būdu pagamintas majenitas vėliau gali būti sėkmingai panaudotas kaip CaO stabilizuojantis priedas.

Darbo tikslas ir uždaviniai

Darbo tikslas – nustatyti hidroterminės sintezės sąlygų įtaką funkcinių $x\text{CaO}\cdot y(\text{Al}_2\text{O}_3, \text{SiO}_2)\cdot z\text{H}_2\text{O}$ junginių susidarymui ir savybėms bei pasiūlyti racionalias taikymo sritis.

Siekiant užsibrėžto tikslo reikėjo išspręsti šiuos uždavinius:

1. Ištirti Al_2O_3 priedo kiekio ir hidroterminės aplinkos parametrų įtaką junginių susidarymui ir stabilumui $\text{CaO}\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$ sistemoje.
2. Termodinaminiais skaičiavimais parinkti palankiausias $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ hidroterminės sintezės sąlygas ir jas patvirtinti eksperimentiškai.
3. Nustatyti sintetinio kalcio hidroaliumosilikatinio priedo įtaką cemento hidratacijos procesui ir produktų mineralinei sudėčiai.
4. Pritaikyti sintetinį kalcio hidroaliumosilikatinį priedą gamtinio CaO chemosorbento stabilizavimui cikliniame CO_2 dujų adsorbcijos/desorbcijos procese.

Mokslinis naujumas

Pirmą kartą nustatyta, kad hidrotermiškai apdorojant CaO, SiO_2 ir Al_2O_3 suspensijas, įprastiniai sintezės produktai – hidrogranatai – gali nesusidaryti, o vyrauti vien tik kalcio hidroaliuminatai bei kalcio hidrosilikatai. Ištirta, kad sintetinis kalcio hidroaliumosilikatinis priedas keičia cemento bandinių hidrataciją ir spartina kietėjimo procesą: sutrumpina indukcinį periodą, skatina

C₃S hidrataciją ir didina bendrą išsiskyrusios šilumos kiekį. Nustatyta, kad majenitą galima gauti 350 °C temperatūroje išdegant hidroterminėse sąlygose susintetintą kalcio hidroaluminatą.

Praktinė vertė

Nustatyta, kad sintetinis majenito priedas stabilizuoja gamtinį CaO chemosorbentą cikliniame CO₂ dujų adsorbcijos / desorbcijos procese ir pasiūlyta minėto priedo gavimo ir CO₂ dujų chemosorbento gamybos technologinė schema.

Darbo aprobavimas ir publikavimas

Disertacijos tema paskelbtos 3 mokslinės publikacijos leidiniuose su citavimo indeksu įtrauktuose į Clarivate Analytics WoS duomenų bazę: Romanian Journal of Materials, Advances in Materials Science and Engineering bei Journal of Thermal Analysis and Calorimetry.

Disertacijoje atliktų tyrimų rezultatai paskelbti šešiuose pranešimuose dalyvaujant šešiose tarptautinėse konferencijose: „Chemistry and Chemical Technology“ (2015, Lietuva); „3rd Central and Eastern European conference on Thermal Analysis and Calorimetry“, CEEC-TAC3, (2015, Slovėnija); „Chemistry and Chemical Technology“ (2016, Lietuva); „BaltSilica“ (2016, Lietuva); „XV Russian and International Conference on Thermal Analysis and Calorimetry“ (2016, Rusija); „Chemistry and Chemical Technology“ (2017, Lietuva).

Darbo apimtis

Disertaciją sudaro įvadas, literatūros analizė, metodinė dalis, tyrimų rezultatai ir jų aptarimas, išvados, 165 literatūros šaltinių sąrašas, 3 publikacijų disertacijos tema ir 6 pranešimų mokslinių konferencijų medžiagoje sąrašas bei 3 priedai. Pagrindinė medžiaga išdėstyta 114 puslapių, įskaitant 2 schemas, 19 lentelių ir 61 paveikslą.

Ginamieji disertacijos teiginiai

1. CaO-SiO₂-Al₂O₃-H₂O sistemoje susidarančių junginių mineralinė sudėtis ir jų stabilumas priklauso ne tik nuo Al₂O₃ priedo kiekio, bet ir nuo hidroterminio apdorojimo temperatūros ir trukmės.
2. Sintetiniai produktai, gauti iš mišinių, kurių sudėtyje yra 10,5 arba 15,4 % Al₂O₃ priedo, keičia cemento bandinių hidratacijos procesą: skatina kalcio hidrosilikatų susidarymą, ankstyvąją C₃S hidrataciją, gipso sureagavimą ir padidina bendrą išsiskyrusios šilumos kiekį.
3. Ciklinio CO₂ dujų adsorbcijos / desorbcijos proceso metu sintetinis majenito priedas stabilizuoja gamtinio CaO adsorbento struktūrą.

IŠVADOS

1. Nustatyta, kad hidrotermiškai 200 °C temperatūroje apdorojant pradinį mišinį, kuriame yra 2,7 % Al_2O_3 priedo, nepriklausomai nuo trukmės (4–72 val.) formuojasi kalcio hidrosilikatai su įsiterpusiais Al^{3+} jonais. Esant 5,3–15,4 % Al_2O_3 priedo kiekiui, kai izoterminio išlaikymo trukmė yra ne ilgesnė nei 24 val., sintezės produktus sudaro kalcio hidroaliuminatai ir kalcio hidrosilikatai su įsiterpusiais Al^{3+} jonais. Tuo tarpu pailginus hidroterminio apdorojimo trukmę iki 72 val. susidaro didesnio kristališkumo kalcio hidrosilikatai su įsiterpusiais Al^{3+} jonais, o dalis susidariusių kalcio hidroaliuminatų skyla susidarant bemitui.
2. Mažinant hidroterminio išlaikymo temperatūrą, didėja C_3AH_6 stabilumas, o palankiausia susidarymo 130 °C temperatūroje trukmė yra 8 valandos. Esant didesniai nei 2,7 % Al_2O_3 priedo kiekiui, sintezės produktuose šio junginio daugėja proporcingai priedo kiekiui. Vykstant C_3AH_6 skilimui nustatytas didžiausias absorbuotas šilumos kiekis visomis tirtomis sąlygomis.
3. Nustatyta, kad naudoti sintetiniai kalcio hidroaliumosilikatiniai priedai, gauti po 8 val. hidroterminio apdorojimo 130 °C temperatūroje, kuriuose yra 5,3–15,4 % Al_2O_3 , didina bendrą išsiskyrusios šilumos kiekį. Įrodyta, kad cemento bandiniuose su 10 % sintetinių kalcio hidroaliumosilikatinių priedų hidratacijos metu pasikeičia kiekybinė mineralinė cemento hidratų sudėtis: priedas skatina C-S-H(I) susidarymą, ankstyvąją (5,5–16,5 val.) C_3S hidrataciją, spartina gipso sureagavimą, o 3–9,5 val. hidratacijos laikotarpiu ir etringito susidarymą.
4. Įstirta, kad po 8 val. izoterminio išlaikymo 130 °C temperatūroje vyraujantis produktas yra C_3AH_6 , susintetintas iš mišinio, kuriame Al_2O_3 priedo kiekis yra lygus 15,4 %, aukštesnėje nei 250 °C temperatūroje skyla ir persikristalizuoja į kalcio aluminatą – majenitą, kuris išlieka stabilus iki 800 °C. Atlikus CO_2 adsorbcijos / desorbcijos testą nustatyta, kad degtas sintezės produktas yra tinkamas CaO komponentą turinčių chemosorbentų struktūros stabilizavimui, nes po 8 adsorbcijos / desorbcijos 650–750 °C temperatūroje ciklų chemosorbento adsorbcinė geba sumažėja labai nežymiai: nuo ~0,358 iki ~0,337 $\text{g}_{\text{CO}_2} / \text{g}_{\text{ads}}$, o majenitas išlieka stabilus.
5. Pasiūlyta sintetinio kalcio hidroaliumosilikatinio priedo gamybos ir sudėtinio cemento bei CO_2 dujų chemosorbento gamybos technologinė schema. Nustatyti palankiausi technologinio proceso parametrai ir parinkta tinkama įranga.

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