

SINTEZA HIDROTERMALĂ A ALUMINOSILICAȚILOR DE CALCIU HIDRATAȚI CU APLICAȚII ÎN HIDRATAREA CIMENTULUI PORTLAND THE HYDROTHERMAL SYNTHESIS OF CALCIUM ALUMINIUM SILICATE HYDRATES AND ITS APPLICATION ON PORTLAND CEMENT HYDRATION

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In this work the influence of Al₂O₃ on the formation of calcium aluminium silicate hydrates under hydrothermal conditions and the effect of this additive on the early hydration of Ordinary Portland cement (OPC) were investigated. The primary mixtures with molar ratios CaO/(SiO₂+Al₂O₃) of 0.55 and Al₂O₃/(SiO₂+Al₂O₃) of 0.05, 0.1 and 0.15 were mixed with water to obtain the water/solid ratio of the suspension equal to 10.0. Meanwhile, the hydrothermal synthesis of C-A-S-H has been carried out in air atmosphere at 130 °C temperature for 4–72 hours. It was determined that not only the amount of Al₂O₃ additive, but also the duration of hydrothermal synthesis strongly affect the formation of mentioned compounds. The largest amount of calcium aluminium silicate hydrates was obtained after 8 h of hydrothermal treatment, in the mixtures with a higher amount of Al₂O₃ (A/(S+A) = 0.15). Meanwhile, the formation of mentioned compounds is inhibited, when the duration of isothermal curing is extended from 16 to 72 h. It was determined that calcium aluminium silicate hydrates affect the early hydration of OPC. These compounds effectively shorten the induction period and accelerate the dissolution of C₃S, C₃A and the formation of ettringite.

Keywords: Calcium aluminium silicate hydrates, Hydrothermal synthesis, Portland cement hydration, Additives

1. Introduction

Recently, supplementary cementitious materials, including geopolymers, have attracted a great scientific attention due to their low CO₂ footprint, high early strength, thermal and chemical stability, and excellent durability with respect to Ordinary Portland Cement (OPC), when employed in building and ceramic industries [1-9]. Geopolymers which are based on aluminosilicate materials presents a viable alternative for replacing OPC and are a novel eco-friendly construction material. This group of compounds are fabricated with natural raw materials and industrial wastes that have a rich silico-aluminate composition and can be defined by the empirical formula $M_n\{-(SiO_2)_z-AlO_2\}_n \cdot wH_2O$, where M is K⁺, Na⁺, Ca²⁺; n – the degree of polycondensation and z ($z = 1, 2, 3$) indicates the number of siloxane bonds [10-16].

Indeed a series of solid solutions, of general formula $Ca_3Al_2(SiO_4)_{3-x}(OH)_{4x}$, can be located in the CaO–Al₂O₃–SiO₂–H₂O system, where the existing series with the end members known as grossular for $x = 0$ and hydrogarnet for $x = 3$ [17-18]. This group of compounds, also named as calcium aluminosilicate hydrates (C-A-S-H), have been

synthesized by various preparative methods including aging of precipitated gels and sol-gels processes, hydrolysis of complex oxides, and hydrothermal method [19-21]. However, each of these methods has its own limitation: the high temperature-pressure hydrothermal method is complicated and has strict pressure conditions, while for the other preparative methods, firing is an essential crystallization step, which usually results in particle agglomeration [19]. For this reason, the mild hydrothermal synthesis below 240°C and under homogeneous pressure has been a promising route for preparing these novel inorganic compounds [19-22].

In hydrothermal systems the formation of new structures with certain characteristics (the structural and physical properties) is mainly effected by the preparation conditions (used raw materials, chosen duration and temperature of synthesis, C/S ratio etc. [22-27]. Meller et al. investigated the hydrothermal reactions of an oil well cement with added silica and alumina, hydrated at temperatures from 200 to 350 °C and the formation of phases in CaO–Al₂O₃–SiO₂–H₂O system [23-26]. They found that the stability of obtained phases can be altered radically even by

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small amounts of additive and the phase formation strongly depends on the synthesis temperature. Furthermore, in Rios et al. work, the quantity of obtained hydrogarnets were reduced with increasing hydrothermal synthesis (175 °C; 0-24 h) duration [27].

It is well-known that calcium aluminium silicate hydrates are a major products of the hydration of calcium aluminate cements, and occur in high-aluminum cement and to a lower extent in Portland cement [17, 28]. Aluminum may substitute silicon in calcium silicate hydrate, C-S-H and this substitution is expected to play a significant role in many aspects of the chemical behavior of cement paste, including the cation and anion exchange behavior, solubility, and the progress of the reactions that occur during delayed ettringite formation [29, 30]. Despite considerable study, the structural mechanisms of this substitution and its effect on the chemical behavior of cement systems still remains a topic of considerable discussion [30]. For this reason, in a perspective of cost and production time reduction, it is of a great importance to evaluate the reaction mechanism, which occurs during the formation of hydrogarnets in pure alumina-rich systems.

Thus, the aim of this work was to investigate the influence of Al_2O_3 on the formation of calcium aluminium silicate hydrates under hydrothermal conditions and evaluate their effect on the early hydration of OPC.

2. Materials and methods

In this work the following reagents were used: fine-grained $SiO_2 \cdot nH_2O$ (ignition losses 5.19 %); calcium oxide which has been produced by burning calcium hydroxide at 550 °C for 1 hour; γ - Al_2O_3 , which has been obtained after burning at $Al(OH)_3$ for 5 hour at 475 °C.

Samples of ordinary Portland cement were prepared in a laboratory grinding mill by grinding cement clinker (JSC "Akmenes cementas", Lithuania) with a 4.5 % additive of gypsum ("Sigma-Aldrich", Germany) up to $S_a=450$ m²/kg, which was determined by Blaine method. The chemical analysis and phase composition of clinker are shown in Table 1.

The primary mixtures with molar ratios $C/(S+A) = 0.55$ and $A/(S+A) = 0.05, 0.1$ and 0.15

($C-CaO, S - SiO_2, A - Al_2O_3$) were mixed with water to obtain the water/solid ratio of the suspension equal to 10. The hydrothermal synthesis has been carried out in unstirred suspensions in 25 ml volume polytetrafluoroethylene (PTFE) cells, which were placed in „Parr instruments“ (Germany) autoclave, under saturated steam pressure in argon atmosphere at 130 °C temperature for 4, 8, 16, 48 and 72 hours by applying extra argon gas (10 bar). 130 °C temperature was reached within 2 h. The suspensions after synthesis were filtered, products rinsed with acetone to prevent carbonation of materials, dried at $50 \text{ °C} \pm 5$ temperature for 24 h, and sieved through a sieve with a size width of 80 μ m.

The X-ray powder diffraction (XRD) data were obtained with a D8 Advance (Bruker AXS) X-ray diffractometer with Bragg-Brentano geometry using Ni-filtered CuK_α radiation and a graphite monochromator, operating with a voltage of 40 kV and emission current of 40 mA. The step-scan covered an angular range of 3–70° (2θ) in steps of $2\theta = 0.02^\circ$.

Simultaneous thermal analysis (STA) was used to measure 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. Ceramic sample handlers and crucibles of Pt-Rh were used.

Isothermal calorimetry - an eight channel (TAM Air III) isothermal calorimeter was used to investigate the heat evolution rate of OPC and OPC blended with 5% or 10% by weight of C-A-S-H ($C/(S+A) = 0.55$ and $A/(S+A) = 0.15$, 8 h, 130 °C). Glass ampoules (20 ml) each containing 3 g dry cementitious material were placed in the calorimeter and the injection units for each ampoule filled with amounts of water equivalent to a $W/(OPC+additive)$ 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 2–3 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 additive and mixing, the heat evolution rates were essentially identical.

Table 1

Chemical and mineralogical composition of clinker.

Oxides	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃ ²⁻	Loss on Ignition (LOI)	Insoluble particles
Amount, %	19.72	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, %	63.19		8.89		7.21			12.81		

3. Results and discussions

It was determined that the quantity of Al₂O₃ additive in the initial mixture significantly effects the formation of calcium aluminium silicate hydrates in CaO–SiO₂·nH₂O–Al₂O₃–H₂O system. After 4 hours of isothermal curing at 130 °C temperature, when the molar ratio of A/(S+A) was equal to 0.05, the semi-crystalline C-S-H(I)-type calcium silicate hydrate (*d*-spacing–0.304, 0.279, 0.182 nm) are dominating in the synthesis products and only the

traces of calcium aluminium silicate hydrates (*d*-spacing–0.513, 0.444, 0.336, 0.204, 0.174 nm) are observed in XRD patterns (Fig. 1, a, curve 1, Table 2). It should be noted that many compounds from this group of minerals have nearly the same interplanar distances *d*, resulting in the overlapping peaks. This makes it almost impossible to distinguish one compound from the other and for this reason, in this work, the formed products will be named as C-A-S-H (Table 2).

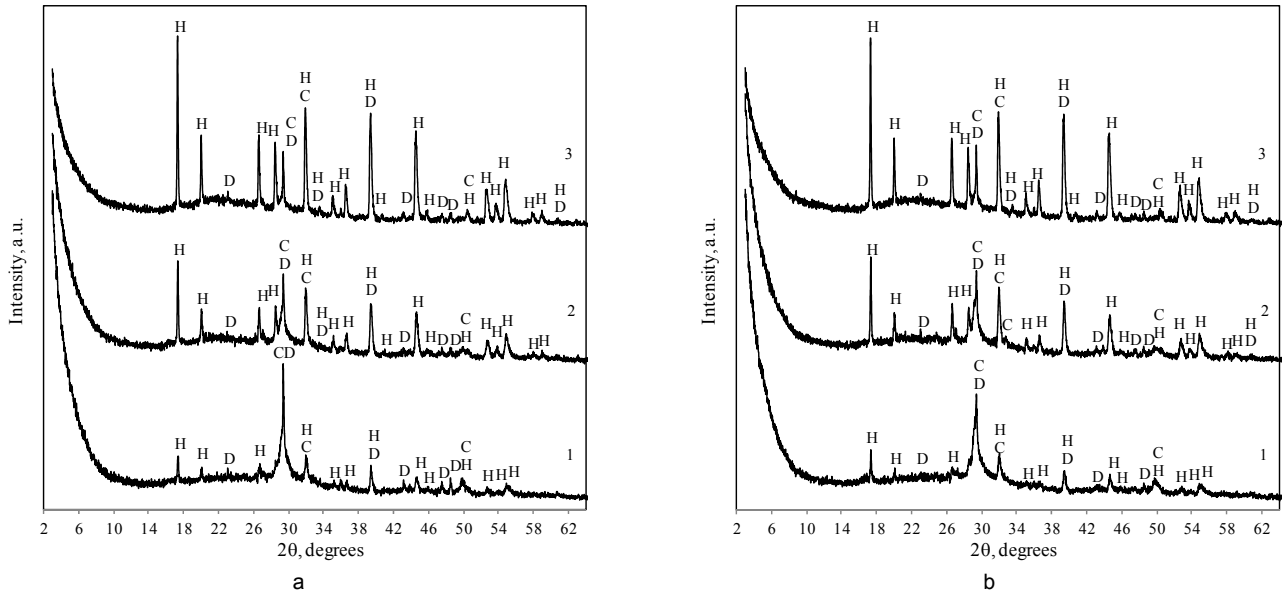


Fig. 1 - X-ray diffraction patterns of synthesis products after 4 h (a) and 8 h (b) of hydrothermal treatment at 130 °C temperature, when A/(S+A) molar ratio is equal to: 1 – 0.05, 2 – 0.1, 3 – 0.15. Indices: H – C-A-S-H, C – C-S-H (I), D – CaCO₃

Table 2

d-spacing, nm	The interlayer distances of CASH from PDF-4 database					
	Bicchulite (PDF No. 83-1321)	Hydrogarnet (PDF No. 76-557)	Hydrogrossularite (PDF No. 2-1124)	Hydrogarnet (PDF No. 84-1354)	Hydrogrossulare (PDF No. 71-735)	Hydrogrossular (PDF No. 3-125)
0.51		0.5137	0.5140	0.5129	0.5134	
0.44		0.4444		0.4442	0.4446	0.4470
0.36	0.3603					
0.34		0.3359		0.3358		
0.33						0.3300
0.31		0.3143		0.3141	0.3144	
0.29		0.2811				
0.28	0.2791			0.2809	0.2812	0.2810
0.26				0.2565		
0.25	0.2548					
0.23			0.2280		0.2296	0.2300
0.21	0.2080					
0.20		0.2039	0.2030	0.2038		0.2040
0.17		0.1743	0.1672	0.1742	0.1680	0.1680
0.16	0.1560		0.1590			0.1570

The diffraction peaks (*d*-spacing: 0.304, 0.249, 0.229, 0.187 nm) typical to calcium carbonate are also identified, indicating that carbonation of synthesis products proceeded (Fig. 1, a, curve 1). It should be noted that, in the mixtures with a higher amount of Al₂O₃ (*A*/(*S*+*A*) = 0.1 and 0.15), almost all Al₂O₃ participate in the formation of C-A-S-H, because the intensities of diffraction maximums characteristic to the latter compounds are markedly increased (Fig. 1, a, curve 2). While, a decrease in the intensities of

diffraction peaks typical to semi-crystalline C-S-H(I) are noticed after 4 and 8 h of synthesis. Moreover, regardless of the enhanced reactivity of raw materials, CaCO₃ was obtained in the system.

The given results were confirmed by STA analysis data. It should be noted that after 4 hours of hydrothermal synthesis, four endothermic effects are observed in all investigated samples, which: 1) at ~ 160 °C temperature can be assigned to the dehydration of C-S-H(I); 2) at ~ 300 °C temperature – to the dehydration of C-A-S-H; 3) at

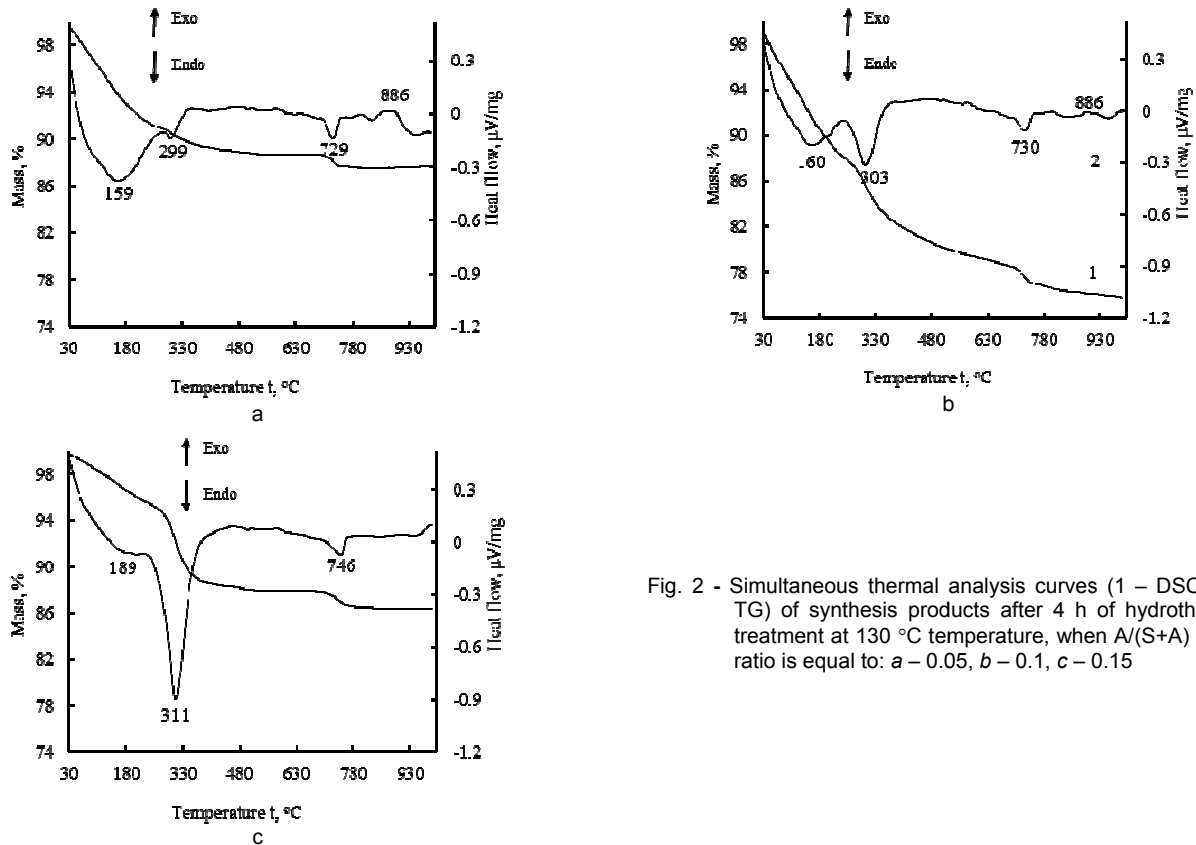


Fig. 2 - Simultaneous thermal analysis curves (1 – DSC, 2 – TG) of synthesis products after 4 h of hydrothermal treatment at 130 °C temperature, when *A*/(*S*+*A*) molar ratio is equal to: a – 0.05, b – 0.1, c – 0.15

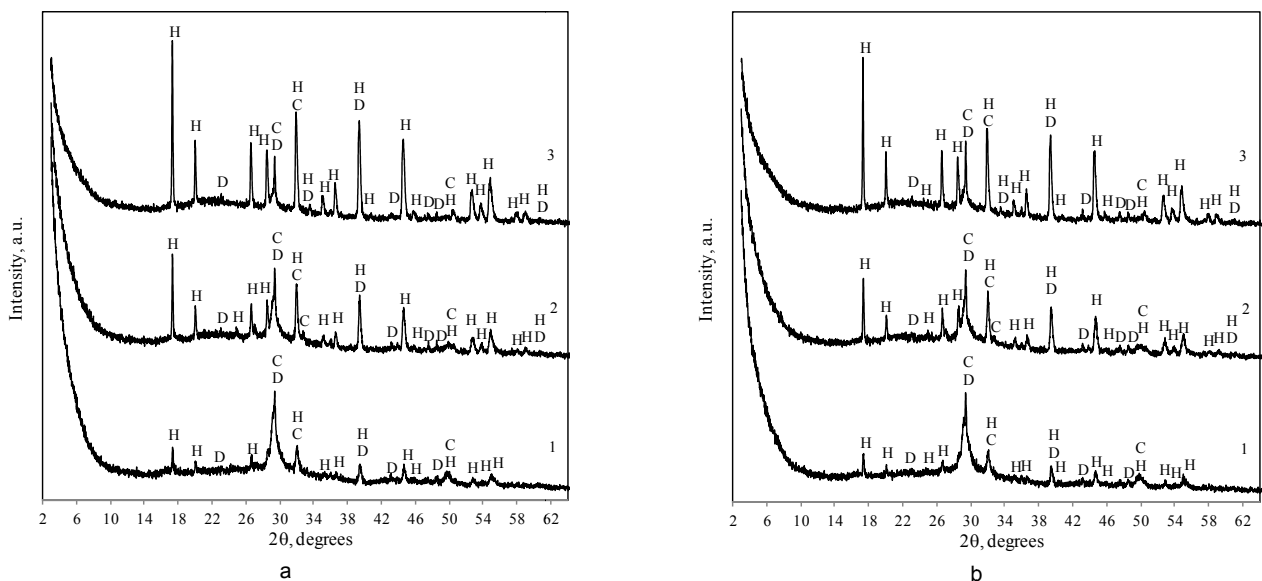


Fig. 3 - X-ray diffraction patterns of synthesis products after hydrothermal treatment at 130 °C temperature for 16 h (a) and 72 h (b), when *A*/(*S*+*A*) molar ratio is equal to: 1 – 0.05, 2 – 0.1, 3 – 0.15. Indices: H – C-A-S-H, C – C-S-H (I), D – CaCO₃

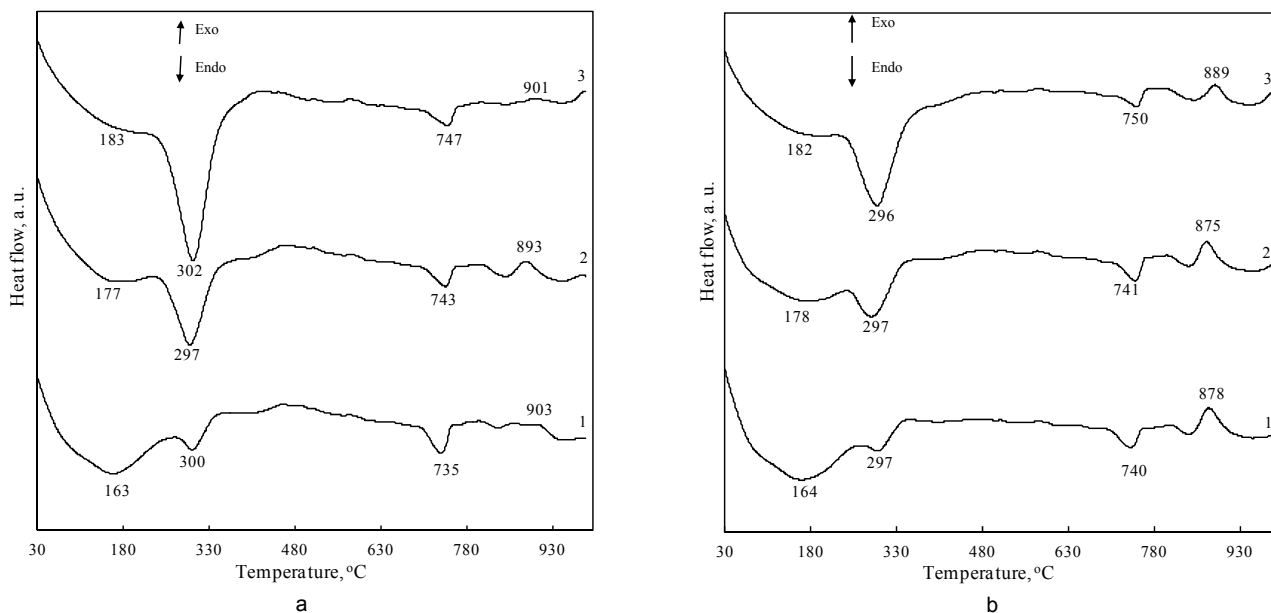


Fig. 4 - Differential scanning calorimetry curves of synthesis products after 8 h (a) and 72 h (b) of hydrothermal treatment at 130 °C temperature, when $A/(S+A)$ molar ratio is equal to: a-0.05, b-0.1, c-0.15

~ 730 °C temperature – to the decomposition of calcium carbonate; and 4) at ~ 886 °C temperature – to the recrystallization of C-S-H(I) into wollastonite (Fig. 2).

In the systems with a larger amount of Al_2O_3 , the formation of C-S-H(I) is inhibited, because the intensities of thermal effects related with its dehydration and recrystallization to wollastonite are markedly decreased. Besides, during the dehydration of C-A-S-H, the quantity of absorbed heat is 8 times larger (60.58 J/g) in the mixtures with $A/(S+A)$ molar ratio of 0.1 and 26 times greater (190.6 J/g) in the mixtures with $A/(S+A)$ molar ratio of 0.15 than in the samples with a lower $A/(S+A)$ ratio (7.17 J/g).

It was also determined that not only the amount of Al_2O_3 additive, but also the duration of hydrothermal synthesis strongly affects the interaction between raw materials and the mineralogical composition of products. However, in the mixtures with $A/(S+A)$ molar ratio of 0.05, the formed C-A-S-H remain stable even by prolonging the duration of synthesis from 8 to 72 h, because no significant change in the intensities of diffraction maximums typical to C-A-S-H were observed in XRD patterns (Fig. 2b, Fig.3b). Meanwhile, in the samples with a higher Al_2O_3 content ($A/(S+A)=0.1, 0.15$), the formation of mentioned compounds are inhibited, when the duration of isothermal curing is extended from 16 to 72 h, because the intensities of diffraction peaks characteristic to C-A-S-H are slightly decreased (Fig. 3).

These data coincide with the results of STA analysis (Fig. 4). It is clearly visible, that in the mixtures with $A/(S+A)$ molar ratio of 0.05, the area of endothermic peak characteristic to the dehydration of calcium aluminium silicate hydrates almost does not change even after continuing the

synthesis to 72 h. However, the loss of OH groups from the structure of C-A-S-H is more intense in the samples with a higher amount of Al_2O_3 ($A/(S+A) = 0.1$ and 0.15), because 2-4 times greater intensities of endothermic effects at ~ 300 °C temperature are observed. Moreover, it was determined that after 72 h of hydrothermal synthesis the area of exothermal effects from 878 to 889 °C temperature related with the recrystallization of C-S-H(I) to wollastonite are markedly increased in all investigated samples, showing that after long-term isothermal exposure C-A-S-H are unstable and decompose to form C-S-H (I).

The influence of both the amount of Al_2O_3 additive and the duration of synthesis is also noticed during an evaluation of the quantity of absorbed heat (assessed by isothermal calorimetry analysis). It was determined, that, during the dehydration of calcium aluminium silicate hydrates (292 – 311 °C), in a case of the samples of $A/(S+A)$ equal to 0.05, the quantity of mentioned heat varied in a 12–16 J/g range, when the synthesis duration was prolonged from 8 to 72 h. Meanwhile, in the samples with a higher Al_2O_3 content, the quantity of absorbed heat gradually decreased within the same duration of isothermal curing: 1) from 91 to 45 to J/g, when the $A/(S+A)$ molar ratio was equal to 0.1; and 2) from 196 to 114 to J/g, when the $A/(S+A)$ molar ratio was equal to 0.15 (Table 3).

The relationship between the quantity of absorbed heat and the mass loss during C-A-S-H dehydration (250-330 °C) as well as the decomposition of calcium carbonate were confirmed by TG analysis data (Table 4). It was determined that the calculated quantity of calcium carbonate decreased from 2.25 % to 3.98 %,

Table 3.

The quantity of absorbed heat during the dehydration of C-A-S-H

Duration of hydrothermal synthesis, h	The quantity of absorbed heat (J/g) during C-A-S-H dehydration (250-330 °C), when the molar ratio of $Al_2O_3/(SiO_2+Al_2O_3)$ is equal to		
	0.05	0.1	0.15
4	7.17	60.58	190.6
8	15.87	91.32	196.3
16	14.18	76.38	164.2
48	13.24	56.81	130.8
72	12.31	45.09	113.8

Table 4

TG mass losses of the dehydration of C-A-S-H (280–340 °C) and the decomposition of calcium carbonate (700–760 °C)

Duration of hydrothermal synthesis, h	TG mass losses of the dehydration of hydroganates and the decomposition of calcium carbonate, when the molar ratio of $Al_2O_3/(SiO_2+Al_2O_3)$ is equal to					
	0.05		0.1		0.15	
	280 –340 °C	700 –760 °C	280 –340 °C	700 –760 °C	280 –340 °C	700 –760 °C
4	1.21	0.99	6.16	1.43	7.07	1.20
8	1.72	1.56	4.87	1.44	9.62	1.75
16	1.56	1.51	4.07	1.24	7.87	1.73
48	1.31	1.09	3.78	1.11	7.15	1.52
72	2.34	1.71	4.30	1.54	5.30	1.11

which corresponds to the mass loss from 0.99 % to 1.75 % in TG curve (Table 4).

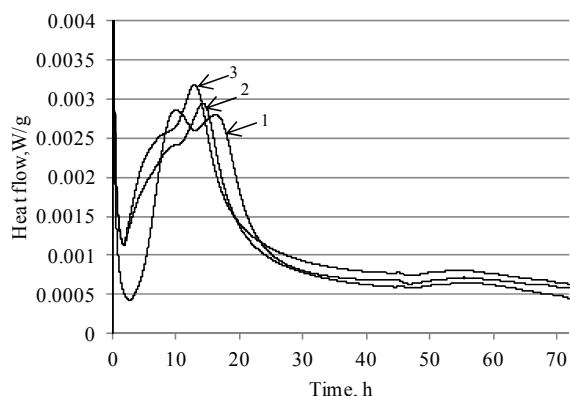
Thus, the presented results showed, that the largest quantity of calcium aluminium silicate hydrates was obtained after 8 h of hydrothermal treatment, in the mixtures with a higher amount of Al_2O_3 ($A/(S+A) = 0.15$). Presumably, this additive can affect the early hydration of OPC samples. As these reactions are exothermic, isothermal calorimetry is among the most accurate methods to monitor the global reaction process through the rate of heat production [31-33]. For this reason, synthesis product ($C/(S+A) = 0.55$ and $A/(S+A) = 0.15$, 8 h, 130 °C) was added as a partial replacement of the OPC at levels of 5% and 10% by weight of the total cementitious material.

Therefore, in the next stage of experiment, the rate of heat evolution was calculated on the basis of a unit weight of ordinary Portland cement (OPC).

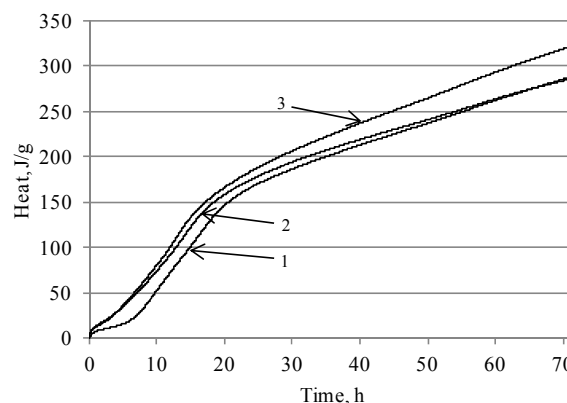
Thus, the rates can be compared with each other, and the contribution from the amount of C-A-S-H can be separated. The rate of heat evolution (W/g_{OPC}) and the cumulative heat of hydration (J/g_{OPC}) data of the binary blended pastes are presented in Figure 5.

It was determined that in the samples with additive, the induction period, which is assigned to the growing C-S-H and CH on the surface of the particles of primary compounds [32], is effectively shortened. In pure OPC paste, hydration takes about 2.8 h, while with an additive – only 1.5 h (Fig. 5, a).

Moreover, the rate of heat evolution of the second exothermic reaction – typical to the dissolution of C_3S [33-34] – decreases as the amount of C-A-S-H increases in the samples, but the accelerating effect begins earlier: from 1.9 hours in the samples with an additive, and from 3.2 hours in a pure OPC samples (Fig. 5, a).



a



b

Fig. 5 - Heat evolution rate (a) and cumulative heat (b) of OPC samples for the following amounts of additive ($C/(S+A) = 0.55$ and $A/(S+A) = 0.15$, 8 h, 130 °C), wt. %: 1 – 0; 2 – 5; 3 – 10.

It is known that the third exothermic reaction is characteristic to the dissolution of C_3A and the formation of ettringite [35]. Thus, the hydration at this stage is accelerated by the amount of C-A-S-H, because the peak of all samples with an additive produces an increase of the maximum heat evolution rate similar to OPC, and this effect grows as level of C-A-S-H increases (Fig. 5).

Moreover, it was determined that, in the OPC samples with 5 % of additive, the amount of cumulative heat started to decrease (until it reached ~58 h) and achieved the same level as pure OPC samples (Fig. 5, a, 1-2 curves). Meanwhile, the OPC samples with 10 % of synthetic C-A-S-H shows similar effects to those of the usual pozzolanic additives, because the amount of cumulative heat grows with the increasing duration of hydration (Fig. 5, a, 1,3 curves).

The presented results are only in a partial agreement with the data of Mostafa and Brown [36], which examined the influence of natural pozzolan on OPC hydration. In our case, the influence of additives is very similar, but the total amount of released heat is significantly higher in the sample with 10% of C-A-S-H.

Thus, the given data show that the use of this additive is purposive due to the strong influence on the hydration properties of ordinary Portland cement at early stages and the further research is needed in order to understand their hydration kinetics parameters and peculiarities of the process mechanism.

4. Conclusions

1. The quantity of Al_2O_3 additive strongly affects the reaction between raw materials in $CaO-SiO_2-nH_2O-Al_2O_3-H_2O$ system. During the first hours of hydrothermal treatment (4 h), when the molar ratio of $A/(S+A)$ was equal to 0.05, the semi-crystalline C-S-H(I)-type calcium silicate hydrate are dominating in the synthesis products and only traces of calcium aluminium silicate hydrates are obtained. In the mixtures with a higher amount of Al_2O_3 ($A/(S+A) = 0.1$ and 0.15), almost all Al_2O_3 participate to the formation of C-A-S-H.

2. The duration of hydrothermal synthesis also influences the formation of calcium aluminium silicate hydrates. The largest amount of calcium aluminium silicate hydrates was obtained after 8 h of hydrothermal treatment, in the mixtures with a higher amount of Al_2O_3 ($A/(S+A) = 0.15$). The formation of mentioned compounds is inhibited, when the duration of isothermal curing is extended from 16 to 72 h. It should be noted that the

carbonation of synthesis products proceeded under all experimental conditions.

3. The presence of calcium aluminium silicate hydrates affects the early hydration of OPC. These compounds effectively shorten the induction period and accelerate the dissolution of C_3S , C_3A and the formation of ettringite. Moreover, the mentioned effects increase as the C-A-S-H level increases in the OPC samples. Meanwhile, only the OPC samples with 10 % of calcium aluminium silicate hydrates shows similar effects to those of the usual pozzolanic additives, because the amount of cumulative heat increases with the increase of duration of hydration.

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