Structure, microstructure and thermal stability characterizations of C_3AH_6 synthesized from different precursors through hydration

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Abstract

In this paper, the influence of precursors (CA, C_7A_3Z , $C_{12}A_7$, C_6SrA_3Z , C_7A_2FZ and commercial calcium aluminate cement ‘Gorkal 70’) on the structure, microstructure and thermal stability characterizations of C_3AH_6 through hydration was investigated. The materials were characterized by X-ray diffraction, differential thermal analysis–thermogravimetric analysis–evolved gas analysis and scanning electron microscopy combined with energy-dispersive spectroscopy 24 h and 72 h after starting the hydration process. Results of investigation confirmed the influence of precursor on shape and grain size of C_3AH_6 . The CaO/ Al_2O_3 mass ratio of precursors before the hydration process affects the size of C_3AH_6 crystals: the higher the CaO/ Al_2O_3 value, the larger the size of the crystals of C_3AH_6 . Moreover, the presence of Sr and Fe affects the formation of stable C_3AH_6 crystals.

Keywords Tricalcium aluminate hexahydrate (C_3AH_6) · Microstructure · Hydration · Calcium aluminate cement

Introduction

The main phases in calcium aluminate cements are CA^* , CA_2 and $C_{12}A_7$. The most predominant hydration products are CAH_{10} , C_2AH_8 , C_3AH_6 and AH_3 . However, the hydration of CAC strongly depends on the conditions of the process. At ordinary temperature, the only stable hydrates are C_3AH_6 and AH_3 . At temperatures below 50 °C, the metastable phases are formed [1–4].

Some authors noted that CAH_{10} and $C_4AH_{(11-19)}$ are formed at low hydration temperatures (below 15 °C). In the temperature range of 15–27 °C, CAH_{10} can coexist with C_2AH_8 and AH_3 . When the hydration temperature is raised above 27 °C, C_2AH_8 and AH_3 dominate. As the temperature exceeds 50 °C, C_3AH_6 and AH_3 predominate. Moreover, it was found that elevated humidity is favorable to the formation of C_3AH_6 and $Al(OH)_3$ [2, 3, 5–12].

The conversion reactions are shown schematically below:

The formation of metastable hydrates in the form of hexagonal platelets is unfavorable because they have a tendency to transform into C_3AH_6 -equiaxed crystals. During conversion, the lower density hydrates: CAH_{10} (density: 1.74 g cm⁻³), C_4AH_{19} (density: 1.81 g cm⁻³) and C_2AH_8 (density: 1.95 g cm⁻³) convert to denser C_3AH_6 (density: 2.52 g cm⁻³) [13, 14].

Some authors have found that it is possible to obtain C_3AH_6 with a specific structure. The cubic form was produced from $C_{1-x}Sr_xAl_2O_4$ (the product of hydration was Sr-doped C_3AH_6), $Ca_7ZrAl_6O_{18}$ (formation of C_3AH_6 was strongly dependent on particle size and surface area), C_2AH_8 (in the presence of polycarboxylic acid type water-reducer), in the presence of two doped nano-additives Fe–TiO₂ and V–TiO₂, C_4AF , mixture of Portland cement and CAC, industrial CAC containing CA and CA_2 , C_2AH_8 and CAH_{10} with different amount of Al_2O_3 . Fine nodules of C_3AH_6 were obtained from C_2AH_8 ; the granular-shaped crystals from C_2AH_8 (in the presence of alumina powder)

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and 10–100 nm layered nano-particles [4, 8, 15–23]. Moreover, some authors reported that the presence of gypsum, deflocculants on the basis of polycarbonate ethers and the carbonation process was a favorable factor to give C_3AH_6 [24–28].

The aim of this study was to gain C_3AH_6 from different precursors. CA, $C_{12}A_7$ and commercial calcium aluminate cement ‘Gorkal 70’ were widely used and selected as reference materials. Three phases containing Zr were tested: C_7A_3Z and C_7A_3Z were modified in two ways: C_6SrA_3Z (in which 1 mol of CaO was replaced by 1 mol of SrO) and C_7A_2FZ (in which 1 mol of Al_2O_3 was replaced by 1 mol of Fe_2O_3).

The precursors were selected in terms of potential property for cubic C_3AH_6 formation and to test the influence of foreign ions on the properties of C_7A_3Z . Moreover, the authors aimed to recognize the tendency of each precursor to form stable hydrates and explain the tendency of precursors to form C_3AH_6 with different grain sizes and shapes (qualitative and quantitative aspects).

Various analytical methods and scanning electron microscopy were used to investigate the progress of phase generation in six systems at 50 °C during hydration by stopping the chemical reaction after 24 and 72 h.

*Cement chemist’s abbreviation notation is used; thus, C = CaO, A = Al_2O_3 , H = H_2O , Sr = SrO, Z = ZrO_2 , F = Fe_2O_3 , $\bar{C}$ = CO_2 .

Experimental

Samples preparation

CA, C_7A_3Z and $C_{12}A_7$ were synthesized from stoichiometric mixtures of calcium carbonate (Chempur 98.81%), aluminum oxide (Acros Organic 99.7%) and zirconium dioxide (Merck 98.08%). C_6SrA_3Z was synthesized from the stoichiometric mixtures of strontium carbonate (Merck 99.0%), calcium carbonate (POCH 99.5%), aluminum oxide (Acros Organic 99.0%) and zirconium dioxide (Acros Organic 98.5%). C_7A_2FZ was synthesized from the stoichiometric mixtures of aluminum oxide (Acros Organic 99.0%), calcium carbonate (POCH 99.999%), zirconium dioxide (Acros Organic 98.5%) and iron (III) oxide (Chempur 96.0%). In either case, substrates in the form of powders were mixed with appropriate molar ratio of CaO, Al_2O_3 , ZrO_2 , Fe_2O_3 and SrO oxides. A test sample of commercial calcium aluminate cement ‘Gorkal 70’ was approved.

The prepared mixtures were homogenized in a zirconium ball mill for 2 h, then formed roller-shaped samples with a diameter of 20 mm under pressure 80 MPa and

calcined at 1200 °C for 10 h (CA, C_7A_3Z and $C_{12}A_7$), at 1300 °C for 10 h (C_6SrA_3Z) and at 1000 °C for 10 h (C_7A_2FZ). The samples were cooled in the furnace, ground down in agate mortar to a grain size below 63 μm , homogenized in a zirconium ball mill for 2 h, then formed in roller-shaped samples with a diameter of 20 mm under pressure 80 MPa and fired at 1400 °C for 10 h (CA), at 1500 °C for 30 h (C_7A_3Z), at 1350 °C for 10 h ($C_{12}A_7$), at 1420 °C for 15 h (C_6SrA_3Z) and at 1300 °C for 10 h (C_7A_2FZ). After, firing samples were ground down again in agate mortar and milled in zirconium ball mill for 2 h to a grain size below 63 μm .

Methods of the investigation

The precursors before the hydration process were investigated by X-ray diffraction analysis in terms of chemical composition. Hydration products and their thermal stability were investigated by X-ray diffraction analysis, differential thermal analysis–thermogravimetric analysis–evolved gas analysis (DSC–TG–EGA(MS)) and scanning electron microscopy–energy-dispersive spectroscopy (SEM–EDS). In order to that, the neat cement pastes were composed. Each sample was homogenized with water by hand with w/c ratio 1.0, in a glass beaker. Samples in the form of pastes were placed in a sealed polyethylene bag and cured up to 72 h in a climatic chamber with the relative humidity maintained at 95% and the temperature of 50 °C. Subsequently, samples were dried by acetone quenching after 24 h and after 72 h since homogenization. The conditions for the hydration (temperature of 50 °C and w/c ratio of 1.0) of the precursors were adopted to create the most favorable conditions for gaining C_3AH_6 . Dry powders were then analyzed by X-ray diffraction (X’pert ProPANalytical X-ray diffractometer) and simultaneous DSC–TG–EGA(MS) method (NETZSCH STA 449 F5 Jupiter coupled to QMS 403 D Aëolos) at a heating rate of 10 °C min^{-1} under a flow of AR (50 mL min^{-1}). The containers for samples were corundum crucibles. The initial sample mass was 25 mg.

The description of microstructure evolution of cement pastes by SEM was carried out on the freshly broken surfaces of the hydrated cement pastes after 24 h and 72 h of curing duration. The samples were coated by carbon, which enables to remove any charge.

Results

The X-ray diffraction pattern of precursors before the hydration process is presented in Fig. 1. The results of X-ray diffraction analysis of the hydrated cement pastes 24 and 72 h after starting the hydration process are presented

Fig. 1 Results of X-ray diffraction analysis of precursors before hydration process

in Figs. 2–7. The TG, DSC and EGA curves as a result of the simultaneous DSC–TG–EGA(MS) method of 24-h and 72-h samples are presented in Figs. 8–11, respectively. Figures 12, 14, 16, 18, 21, 24 show the morphologies of 24-h cement pastes, whereas Figs. 13, 15, 17, 19, 22, 25 show the SEM images of their fracture surface after 72 h. The EDS spectrum of selected samples (C_6SrA_3Z , C_7A_2FZ , ‘Gorkal 70’) is presented in Figs. 20, 23, 26–28, respectively. The decomposition temperatures of CAC hydration products are presented in Table 1. Crystallographic data of hydrates detected by XRD are presented in Table 2. The obtained results have been extended to study the evolution of phase composition during the hydration process of different precursors.

Characteristics of precursors before the hydration process

The results of X-ray diffraction analysis of precursors before the hydration process are presented in Fig. 1. In the sample CA, pure-phase $CaAl_2O_4$ was identified. The sample C_7A_3Z included the main phase $Ca_7ZrAl_6O_{18}$ with a dope of $CaZrO_3$. The sample $C_{12}A_7$ contained pure-phase $Ca_{12}Al_{14}O_{33}$. The sample C_6SrA_3Z identified $Ca_7ZrAl_6O_{18}$ —its peaks were moved toward lower values of 2θ after

Fig. 2 X-ray diffraction pattern of CA after 24 h (a) and after 72 h (b), prepared with $w/c = 1$ at 50 °C. Black circle: $CaAl_2O_4$ [JCPDS card No. 98-018-0997 ($2\theta = 30.043^\circ$, $d = 2.97207 \text{ \AA}$)], black diamond: C_3AH_6 [JCPDS card No. 98-009-4630 ($2\theta = 17.262^\circ$ (the highest intensity XRD peak), $d = 5.13291 \text{ \AA}$)], plus sign: $C_3A \cdot A \cdot CaCO_3 \cdot 11H_2O$ [JCPDS card No. 01-087-0493 ($2\theta = 11.706^\circ$, $d = 7.55376 \text{ \AA}$)], white triangle: AH_3 [JCPDS card No. 98-024-5301 ($2\theta = 18.268^\circ$, $d = 4.84770 \text{ \AA}$)]

substitution for Sr and $CaZrO_3$. The sample C_7A_2FZ contained main phases: $Ca_7ZrAl_6O_{18}$ and Ca_2AlFeO_5 (brownmillerite) and dope of $CaZrO_3$. In the sample ‘Gorkal 70’, the identified phases were $CaAl_2O_4$ and $CaAl_4O_7$.

An overview of thermal analysis of the hydrated cement pastes

The thermal decomposition of hydrated cement pastes was characterized by two major temperature regions of mass loss (Fig. 8, Table 3): first an insignificant loss in the temperature range 25–200 °C (about 2.69–10.29% mass loss takes place in this region for all the samples) and, second, a sharp loss in the temperature range 200–350 °C (more than 10.45% mass loss takes place for all the samples). On the base of these data, the phases in the samples were identified.

Fig. 3 X-ray diffraction pattern of C_7A_3Z after 24 h (a) and after 72 h (b), prepared with $w/c = 1$ at 50 °C. Asterisk: C_7A_3Z [JCPDS Card No. 98-015-7989], black diamond: C_3AH_6 [JCPDS card No. 98-006-2704 ($2\theta = 39.208^\circ$, $d = 2.29587 \text{ \AA}$)], white triangle: AH_3 (reference data: JCPDS card No. 98-024-5301 ($2\theta = 18.268^\circ$, $d = 4.84770 \text{ \AA}$)), plus sign: $C_3A \cdot CaCO_3 \cdot 11H_2O$ [JCPDS card No. 01-087-0493 ($2\theta = 11.706^\circ$, $d = 7.55376 \text{ \AA}$)], degree sign: CZ [JCPDS card No. 98-009-7465 ($2\theta = 31.513^\circ$, $d = 2.83666 \text{ \AA}$)]

The gel phases presented as a hydrated amorphous alumina gel-phase AH_3 or as a calcium aluminum hydrate (C-A-H)-type gel were dehydrated over a broad temperature range, probably in the temperature range of 25–200 °C and could partially overlap with dehydration of crystalline calcium aluminate hydrates. Mass losses at higher temperatures were associated with the loss of the structural water from the numerous calcium aluminate hydrates of the defined composition (Fig. 8). As can be seen from Figs. 9 and 10, the maxima of EGA peaks corresponded to the minima of DSC peaks.

Since the main reaction peaks could be clearly identified in the EGA curves, the temperature of EGA peaks of cement pastes was used for the peak assignment. For clarity of the figure, the temperature of EGA peaks of 72-h hydrated cement pastes is presented in Fig. 10 (marked in blue).

Fig. 4 X-ray diffraction pattern of $C_{12}A_7$ after 24 h (a) and after 72 h (b), prepared with $w/c = 1$ at 50 °C. Modifier letter down arrow head: $Ca_{12}Al_{14}O_{33}$ [JCPDS card No. 98-024-1001 ($2\theta = 18.058^\circ$, $d = 4.90102 \text{ \AA}$)], black diamond: C_3AH_6 [JCPDS card No. 98-009-4630 ($2\theta = 17.262^\circ$, $d = 5.13291 \text{ \AA}$)], plus sign: $C_3A \cdot CaCO_3 \cdot 11H_2O$ [JCPDS card No. 01-087-0493 ($2\theta = 11.706^\circ$, $d = 7.55376 \text{ \AA}$)], white triangle: AH_3 [JCPDS card No. 98-024-5301 ($2\theta = 18.268^\circ$, $d = 4.84770 \text{ \AA}$)]

The MID curves for all the hydrated samples (Fig. 11) revealed an increase in ion intensity for $m/z = 44$ in the temperature ranges from ca. 250 to 300 °C and above 600 °C. This increase in ion intensity for $m/z = 44$ could be attributed to the carbon dioxide fragment ion CO_2^+ of calcium aluminate carbonate hydrates, especially mono-carboaluminate hydrate $C_3A \cdot CaCO_3 \cdot 11H_2O$ [29].

Hydration of CA

24 h after starting the hydration process, the following products were identified (XRD, Fig. 2a): C_3AH_6 , AH_3 , $C_4A\bar{C}H_{11}$ and unhydrated CA. On the base of gas evolution curves (DSC–TG–EGA(MS)) (Fig. 10), the main products of hydration were C_3AH_6 (decomposition temperature: 310 °C) and AH_3 (decomposition temperature: 284 °C) [23–28]; no effect from $C_4A\bar{C}H_{11}$ was recorded. SEM

Fig. 5 X-ray diffraction pattern of C_6SrA_3Z after 24 h (a) and after 72 h (b), prepared with $w/c = 1$ at 50 °C. Black diamond: C_3AH_6 [JCPDS card No. 98-009-4630 ($2\theta = 17.262^\circ$, $d = 5.13291$ Å)], degree sign: Sr-doped CZ (similar to JCPDS Card No. 98-009-7465), asterisk: Sr-doped C_7A_3Z (similar to JCPDS Card No. 98-015-7989), white triangle: AH_3 (reference data: JCPDS card No. 98-024-5301 ($2\theta = 18.268^\circ$, $d = 4.84770$ Å)), plus sign: $C_3A \cdot CaCO_3 \cdot 11H_2O$ [JCPDS card No. 01-087-0493 ($2\theta = 11.706^\circ$, $d = 7.55376$ Å)], circled times: C_4AH_{19} [JCPDS card No. 00-042-0487 ($2\theta = 10.64350^\circ$, $d = 8.301$ Å)] and C_2AH_8 [JCPDS card No. 00-011-0205 ($2\theta = 10.7000^\circ$, $d = 8.257$ Å)]

observations confirmed the presence of cubic C_3AH_6 with a grain size of 8 μm (Fig. 12).

72 h after starting the hydration process, XRD patterns (Fig. 2b) confirmed the presence of hydration products and the consumption of the CA during hydration. Results of gas evolution curves were not changed significantly (decomposition temperature of AH_3 : 283 °C and the decomposition temperature of C_3AH_6 : 307 °C) (DSC) [30–35]. SEM observations confirmed the presence of cubic C_3AH_6 with a grain size of 8–9 μm (Fig. 13).

Fig. 6 X-ray diffraction pattern of C_7A_2FZ after 24 h (a) and after 72 h (b), prepared with $w/c = 1$ at 50 °C. Black diamond: C_3AH_6 [JCPDS card No. 98-006-2704 ($2\theta = 39.208^\circ$, $d = 2.29587$ Å)], degree sign: CZ [JCPDS card No. 98-009-7465]

Hydration of C_7A_3Z

24 h after starting the hydration process, the following products were identified on the basis of the strongest '100' peaks (XRD, Fig. 3a): C_3AH_6 , AH_3 , $C_4\bar{A}CH_{11}$, CZ, and C_7A_3Z . On the base of gas evolution curves (DSC–TG–EGA(MS)) (Fig. 10), the main products of hydration were C_3AH_6 (decomposition temperature: 309 °C) and AH_3 (decomposition temperature: 269 °C); no effect from $C_4\bar{A}CH_{11}$ was recorded [30–35]. SEM observations confirmed the presence of C_3AH_6 in the shape of a truncated octahedron with a grain size of 20 μm , hexagonal platelets of metastable hydrates and residue of AH_3 (Fig. 14).

72 h after starting the hydration process, XRD patterns (Fig. 3b) confirmed the presence of $C_4\bar{A}CH_{11}$ and CZ and the absence of C_7A_3Z . Results of gas evolution curves showed the increase in ionization current for C_3AH_6 (decomposition temperature: 312 °C) and AH_3 (272 °C) [30–35]. SEM observations confirmed the presence of C_3AH_6 in the shape of truncated octahedron with a grain

Fig. 7 X-ray diffraction pattern of 'Gorkal 70' Cement after 24 h (a) and after 72 h (b), prepared with $w/c = 1$ at 50 °C. Plus sign: $C_3A \cdot CaCO_3 \cdot 11H_2O$ [JCPDS card No. 01-087-0493 ($2\theta = 11.706^\circ$, $d = 7.55376$ Å)], white square: $CaAl_4O_7$ [JCPDS card No. 00-046-1475 ($2\theta = 25.318^\circ$, $d = 3.51500$ Å)], black diamond: C_3AH_6 [JCPDS card No. 98-009-4630 ($2\theta = 17.262^\circ$, $d = 5.13291$ Å)], white triangle: AH_3 [JCPDS card No. 98-024-5301 ($2\theta = 18.268^\circ$, $d = 4.84770$ Å)]

size of 15–20 μm , hexagonal platelets of metastable hydrates and residue of AH_3 (Fig. 15).

Hydration of $C_{12}A_7$

24 h after starting the hydration process, the following products were identified the phases on the basis of the strongest '100' peaks (XRD, Fig. 4a): C_3AH_6 , AH_3 , $C_4\bar{A}CH_{11}$ and unhydrated $C_{12}A_7$. On the base of gas evolution curves (DSC–TG–EGA(MS)) (Fig. 10), the main products of hydration were C_3AH_6 (decomposition temperature: 299 °C), AH_3 (decomposition temperature: 272 °C) and $C_4\bar{A}CH_{11}$ (decomposition temperature: 152 °C) [30–35]. SEM observations confirmed the presence of cubic C_3AH_6 with a grain size of 1–7 μm , hexagonal platelets of metastable hydrates and residue of AH_3 (Fig. 16).

Fig. 8 TG profiles of the cementitious binder samples 24 and 72 h after starting hydration process, measured in situ by online coupled DSC–TG–EGA(MS) system (Ar flow 50 mL min^{−1}, heating rate 10 °C min^{−1})

72 h after starting the hydration process, XRD patterns (Fig. 4b) confirmed the consumption of the $C_{12}A_7$ during hydration, higher content of $C_4\bar{A}CH_{11}$ and the same amount of AH_3 . Results of gas evolution curves were not changed significantly (decomposition temperatures: of C_3AH_6 : 300 °C; AH_3 : 272 °C, $C_4\bar{A}CH_{11}$: 152 °C) [30–35]. SEM observations confirmed the presence of cubic C_3AH_6 with a grain size of 1–7 μm , hexagonal platelets of metastable hydrates and residue of AH_3 (Fig. 17).

Hydration of C_6SrA_3Z

24 h after starting the hydration process, the following products were identified the phases on the basis of the strongest '100' peaks (XRD, Fig. 5a): two types of C_3AH_6 —Ca-rich and Sr-rich on the grounds of displaced XRD peaks, AH_3 , $C_4\bar{A}CH_{11}$, C_4AH_{19} , which can also be assigned to C_2AH_8 and probably Sr-doped C_7A_3Z and Sr-doped CZ. It was found that with the presence of SrO in cement a shift in the lines corresponds to a somewhat larger cell for the 'pure' undoped C_7A_3Z in comparison with Sr-

Fig. 9 DSC profiles of the cementitious binder samples 24 and 72 h after starting hydration process, measured in situ by online coupled DSC–TG–EGA (MS) system (Ar flow 50 mL min^{-1} , heating rate $10 \text{ }^\circ\text{C min}^{-1}$)

doped C_7A_3Z solid solutions since the substitution of Sr^{2+} ion is larger than Ca^{2+} [28, 29].

On the base of gas evolution curves (DSC–TG–EGA(MS)) (Fig. 10), the main products of hydration were C_3AH_6 (decomposition temperature: $263 \text{ }^\circ\text{C}$), Sr-rich $(C,Sr)_3AH_6$ (decomposition temperature: $343 \text{ }^\circ\text{C}$) and probably C_2AH_8 (decomposition temperatures: $82 \text{ }^\circ\text{C}$ and $154 \text{ }^\circ\text{C}$) rather than $C_4\bar{A}CH_{11}$ (probability of multistage decomposition of C_2AH_8) [30–35]. SEM observations confirmed the presence of C_3AH_6 in the shape of a truncated octahedron with a grain size of $10 \text{ }\mu\text{m}$, hexagonal platelets of metastable hydrates and residue of AH_3 (Fig. 18).

72 h after starting the hydration process, XRD patterns (Fig. 5b) confirmed probably the presence of Ca-rich $(C,Sr)_3AH_6$, content of CZ Sr-doped, AH_3 and $C_4\bar{A}CH_{11}$ (only by 2 peaks). Results of gas evolution curves confirmed the presence of AH_3 (decomposition temperature: $268 \text{ }^\circ\text{C}$) and Ca-rich $(C,Sr)_3AH_6$ (decomposition temperature: $303 \text{ }^\circ\text{C}$) [30–35]. SEM observations confirmed the presence of C_3AH_6 in the shape of a truncated octahedron

Fig. 10 Gas evolution curves for representative mass spectroscopic fragments of H_2O ($m/z = 18$) vapor during the thermal decomposition of the cementitious binder samples in flowing argon 24 and 72 h after starting hydration process, measured in situ by online coupled DSC–TG–EGA(MS) system (Ar flow 50 mL min^{-1} , heating rate $10 \text{ }^\circ\text{C min}^{-1}$)

with a grain size of $8\text{--}10 \text{ }\mu\text{m}$, hexagonal platelets of metastable hydrates and residue of AH_3 (Fig. 19).

The X-ray microanalysis was performed with SEM/EDS and gave direct evidence that Sr ions were presented in a significant amount in the chemical composition of the stable hydrate crystals (Fig. 20 EDS spectrum obtained from point 1). With respect to the results of the XRD and the shift of the main diffraction lines of C_3AH_6 toward the lower values of 2θ , the formation of a solid solution $(C,Sr)_3AH_6$ was confirmed [35–37].

Hydration of C_7A_2FZ

24 h after starting the hydration process, the following products were identified on the basis of the strongest ‘100’ peaks (XRD, Fig. 6a): C_3AH_6 and CZ. Phases contained Fe were undetectable. On the base of gas evolution curves (DSC–TG–EGA(MS)) (Fig. 10), the main products of hydration were C_3AH_6 (decomposition temperature:

Fig. 11 Gas evolution curves for representative mass spectroscopic fragments of CO_2 ($m/z = 44$) vapor during the thermal decomposition of the cementitious binder samples in flowing argon 24 and 72 h after starting hydration process, measured in situ by online coupled DSC–TG–EGA(MS) system (Ar flow 50 mL min^{-1} , heating rate $10 \text{ }^\circ\text{C min}^{-1}$)

Fig. 12 SEM images of the fracture surface of 24-h hydrated CA

Fig. 13 SEM images of the fracture surface of 72-h hydrated CA

Fig. 14 SEM images of the fracture surface of 24-h hydrated $\text{C}_7\text{A}_3\text{Z}$

$310 \text{ }^\circ\text{C}$) [30–35]. SEM observations confirmed the presence of cubic C_3AH_6 with a grain size of $20 \text{ }\mu\text{m}$, hexagonal platelets of metastable hydrates and residue of AH_3 (Fig. 21).

72 h after starting the hydration process, XRD patterns (Fig. 6b) confirmed the same composition than after 24 h after starting the hydration process. Phases contained Fe were undetectable. Results of gas evolution curves were not changed significantly—the main products of hydration were C_3AH_6 (decomposition temperature: $309 \text{ }^\circ\text{C}$) [30–35]. SEM observations confirmed the presence of cubic C_3AH_6 with a grain size of $16\text{--}20 \text{ }\mu\text{m}$ (Fig. 22), the presence of C_3AH_6 in the shape of a truncated octahedron with a grain size of $18\text{--}21 \text{ }\mu\text{m}$, hexagonal platelets of metastable hydrates and residue of AH_3 . The X-ray microanalysis was performed with SEM/EDS and gave

Fig. 15 SEM images of the fracture surface of 72-h hydrated C_7A_3Z

Fig. 17 SEM images of the fracture surface of 72-h hydrated $C_{12}A_7$

Fig. 16 SEM images of the fracture surface of 24-h $C_{12}A_7$

Fig. 18 SEM images of the fracture surface of 24-h hydrated C_6SrA_3Z

direct evidence that Fe ions could be incorporated in C_3AH_6 crystals (Fig. 23 EDS spectrum obtained from point 1). Fe was presented in chemical composition, and it was confirmed on the EDS spectrum.

Nevertheless, as mentioned before, there was no clear evidence of the presence of a $C_3(A,Fe)H_6$ solid solution based on XRD studies, but in the literature sources, it was reported [38].

Hydration of calcium aluminate cement 'Gorkal 70'

24 h after starting the hydration process, the following products were identified on the basis of the strongest '100' peaks (XRD, Fig. 7a): C_3AH_6 , AH_3 , $C_4\bar{A}CH_{11}$, little

quantity of CA_2 and a lack of CA . On the base of gas evolution curves (DSC–TG–EGA(MS)) (Fig. 10), the main products of hydration were C_3AH_6 (decomposition temperature: 307 °C), AH_3 (decomposition temperature: 283 °C) and $C_4\bar{A}CH_{11}$ (decomposition temperature: 152 °C) [23–28]. SEM observations confirmed the presence of cubic C_3AH_6 with a grain size of 1.5–3 μm, hexagonal platelets of metastable hydrates and residue of AH_3 (Fig. 24).

72 h after starting the hydration process, XRD patterns (Fig. 7b) confirmed the presence of C_3AH_6 , AH_3 and $C_4\bar{A}CH_{11}$ and lack of CA_2 . Results of gas evolution curves were not changed significantly (decomposition temperatures: of C_3AH_6 : 303 °C, of AH_3 : 283 °C, of $C_4\bar{A}CH_{11}$: 150 °C) [23–28]. SEM observations confirmed the

Fig. 19 SEM images of the fracture surface of 72-h hydrated C_6SrA_3Z

Fig. 20 EDS spectrum and quantitative composition analysis of point 1 region ($(Ca,Sr)_3AH_6$) in Fig. 19

Fig. 22 SEM images of the fracture surface of 72-h hydrated C_7A_2FZ

Fig. 23 EDS spectrum and quantitative composition analysis of point 1 region (Fe-doped C_3AH_6) in Fig. 22

Fig. 21 SEM images of the fracture surface of 24-h C_7A_2FZ

presence of cubic C_3AH_6 with grain size about 2 μm (Fig. 25), the presence of C_3AH_6 in shape of truncated octahedron with a grain size of 3.5–6 μm (Fig. 26 EDS spectrum obtained from point 1), hexagonal platelets of metastable hydrates (Fig. 27 EDS spectrum obtained from point 2) and residue of AH_3 (Fig. 28 EDS spectrum obtained from point 3). Moreover, the mass CaO/Al_2O_3 ratio of C_3AH_6 was higher than for hexagonal hydrates,

Fig. 24 SEM images of the fracture surface of 24-h hydrated calcium aluminate cement 'Gorkal 70'

and it was visible on the EDS spectra. (A higher peak of Ca was recorded for C_3AH_6 than for hexagonal platelets in point 2).

Fig. 25 SEM images of the fracture surface of 72-h hydrated calcium aluminate cement 'Gorkal 70'

Fig. 26 EDS spectrum and quantitative composition analysis of point 1 region (C_3AH_6) in Fig. 25

Fig. 27 EDS spectrum and quantitative composition analysis of point 2 region (metastable hydrate—hexagonal platelets) in Fig. 25

Fig. 28 EDS spectrum and quantitative composition analysis of point 3 ($Al(OH)_3$) region in Fig. 25

Discussion and conclusions

The C_3AH_6 was successfully synthesized from various precursors. The other phases of hydration products of all precursors were: aluminum hydroxide $Al(OH)_3$ (except sample C_7A_2FZ) and calcium monocarboaluminate $C_4A\bar{C}H_{11}$ (except sample C_7A_2FZ). Depending on the type of precursor, two different types of C_3AH_6 were obtained. In the case of C_7A_3Z and C_7A_2FZ , X-ray diffraction patterns of C_3AH_6 were identified in agreement with reference data,

i.e., JCPDS card No. 98-006-2704 ($2\theta = 39.208^\circ$, $d = 2.29587 \text{ \AA}$). For other precursors ($C_{12}A_7$, C_6SrA_3Z , CA and Gorkal 70), C_3AH_6 was identified in agreement with different reference data, i.e., JCPDS card No. 98-009-4630 ($2\theta = 17.262^\circ$, $d = 5.13291 \text{ \AA}$). In all of the samples (except C_7A_2FZ), $Al(OH)_3$ was identified in agreement with reference data: JCPDS card No. 98-024-5301 ($2\theta = 18.268^\circ$, $d = 4.84770 \text{ \AA}$). $C_4A\bar{C}H_{11}$ was identified in large part of samples (except sample C_7A_2FZ) in agreement with reference data: JCPDS card No. 01-087-0493 ($2\theta = 11.706^\circ$, $d = 7.55376 \text{ \AA}$).

At a broad temperature range, probably in the temperatures of 25–200 °C, the phases presented as a hydrated amorphous alumina gel-phase $Al(OH)_3$ or as a calcium aluminum hydrate (C-A-H)-type gel were dehydrated and could partially overlap with dehydration of crystalline calcium aluminate hydrates. At higher temperatures, mass losses were associated with the loss of the structural water from the numerous calcium aluminate hydrates of the defined composition (Fig. 8). Moreover, the maxima of EGA peaks corresponded to the minima of DSC peaks (Figs. 9, 10).

The results of the investigation confirmed the influence of precursor on the shape and grain size of C_3AH_6 . The smallest grain size of C_6AH_3 was obtained for $C_{12}A_7$ and Gorkal 70 (grain size $\sim 1\text{--}4 \text{ \mu m}$), medium grain size for CA and C_6SrA_3Z (grain size $\sim 10 \text{ \mu m}$) and the biggest grain size for C_7A_2FZ and C_7A_3Z (grain size $\sim 20 \text{ \mu m}$). In the case of samples containing zirconium, C_3AH_6 was obtained in truncated octahedron shape, while in the other samples C_3AH_6 was obtained in cubic shape. Probably the presence of zirconium is conducive to obtaining C_3AH_6 in truncated octahedron shape and with a bigger size. Grains formed after 24 h did not increase during the hydration process up to 72 h.

Some general conclusion can be drawn as follows:

1. The key novelties of this work lie in the precursor-controlled synthesis of C_3AH_6 and its structure, microstructure and thermal stability.
2. From the presented XRD, DSC–TG–EGA(MS) and SEM–EDS results, it is clear that the type of precursor, i.e., pure single-cementitious phases CA, $C_{12}A_7$ and C_7A_3Z ($C = CaO$, $A = Al_2O_3$, $Z = ZrO_2$), calcium aluminate cement, Fe-doped C_7A_3Z and Sr-doped C_7A_3Z are used to study the hydration which is influenced by the properties of the final cement pastes.
3. The size of C_3AH_6 crystals can be formed depending upon the precursor used; the smallest grain size of C_3AH_6 was obtained for $C_{12}A_7$ and Gorkal 70 (grain size $\sim 1\text{--}4 \text{ \mu m}$), medium grain size for CA and C_6SrA_3Z (grain size $\sim 10 \text{ \mu m}$) and the biggest grain size for C_7A_2FZ and C_7A_3Z (grain size $\sim 20 \text{ \mu m}$).

Table 1 Decomposition temperatures of CAC hydration products in °C according to various studies, obtained by thermal analysis methods

Reference	Year	Method	Decomposition temperature/°C				
			C ₂ AH ₈	C ₃ AH ₆	C ₄ AH ₁₉	C ₄ A $\bar{C}$ H ₁₁	AH ₃ (cryst.)
[32]	1983	–	170				
[32, 33]	1983, 2001	DTA		300–330			
[31]	2015	DTA/TG			200–280		
[35]	1985	DTA				160–200	
[32, 34]	1983, 1984	DTA					275–280 ± 10–20
[30]	2007	DTA/TGA	110 175 295				

Table 2 Crystallographic data of hydrates detected by XRD

Crystallographic parameters	C ₃ AH ₆ (reference data: JCPDS Card No. 98-009-4630)	C ₄ A $\bar{C}$ H ₁₁ (reference data: JCPDS Card No. 01-087-0493)	C ₂ AH ₈ (reference data: JCPDS Card No. 00-011-0205)	C ₄ AH ₁₉ (reference data: JCPDS Card No. 00-042-0487)	Al(OH) ₃ (reference data: JCPDS Card No. 98-024-5301)
Crystal system	Cubic	Anorthic	*Not provided by the reference card	Hexagonal	Monoclinic
Space group	I a–3 d	P1		*	P 1 21/c 1
Space group number	230	1		*	14
<i>a</i> /Å	12.5730	5.7747		5.7470	8.6750
<i>b</i> /Å	12.5730	8.4689		5.7470	5.0690
<i>c</i> /Å	12.5730	9.9230		63.8500	12.5086
Alpha/°	90.0000	64.7700		90.0000	90.0000
Beta/°	90.0000	82.7500		90.0000	129.1860
Gamma/°	90.0000	81.4300		120.0000	90.0000
Calculated density/g cm ^{−3}	2.53	2.18		*	2.43
Volume of cell (10 ⁶ pm ³)	1987.54	433.02		1826.31	426.34

Table 3 Mass loss in % in the temperature ranges 25–200 °C and 200–350 °C from heated hydrated samples determined using TG

Sample	Hydration time/h	% mass loss below 200 °C	% mass loss in the temperature range 200–350 °C
C ₇ A ₃ Z	24	5.77	16.30
	72	4.67	18.70
C ₁₂ A ₇	24	4.90	20.26
	72	4.47	21.39
C ₆ SrA ₃ Z	24	10.29	10.45
	72	5.15	16.09
C ₇ A ₂ FZ	24	5.11	14.66
	72	3.60	15.15
CA	24	3.02	23.34
	72	2.69	23.94
‘Gorkal 70’	24	4.36	21.19
	72	3.95	22.33

4. The mass CaO/Al_2O_3 ratio of precursors before the hydration process affects the size of C_3AH_6 crystals in cementitious pastes. The higher the CaO/Al_2O_3 value, the larger the size of the crystals of C_3AH_6 .
5. Direct evidence for the formation of Sr-doped C_3AH_6 and Fe-doped C_3AH_6 crystals came from the chemical composition analysis in micro-areas, which was performed by means of the scanning electron microscope (SEM-EDS). The formation of $(Ca,Sr)_3AH_6$ solid solution was confirmed by XRD.
6. Under given hydration condition (temperature above 50 °C and w/c ratio 1), the most stable hydration structure was formed from Fe-doped C_7A_3Z , whereas the least stable hydration structure was formed from Sr-doped C_7A_3Z .

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