THE EFFECT OF CURING AND THERMAL TREATMENT TEMPERATURE ON THE MICROSTRUCTURE OF CALCIUM ALUMINATE CEMENT BINDER WITH MICROSILICA

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SUMMARY: In this work, the effect of curing temperature (+5ºC, +20ºC, +40ºC) and thermal treatment temperature (800ºC and 1000ºC) on the microstructure and phase composition of calcium aluminate cement (CAC, Al_2O_3>70%) binder with microsilica (MS) additive (5%), when W/(CAC+SiO_2)=1 was investigated. The methods of thermal analysis, X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used. It has been found that after 3 days of hydration were formed such crystalline hydration products: at 5ºC only CAH_{10} hydrate is formed in the CAC binder, at the temperature of 20ºC – CAH_{10}, C_2AH_8 and AH_3 hydrates, at the temperature of 40ºC – C_3AH_6 and AH_3 hydrates. In the cement binder heated at 800ºC, the hydrates are decomposing, and the minerals CA, CA_2 and $C_{12}A_7$ are being formed, though the contours of the hydrate crystals' forms (prisms, plates, irregular cubes) changing slightly, when the process of heating is over. SEM tests revealed significant changes in CAC binder microstructure caused by the added 5% of the microsilica additive. Considerable changes in cement binder microstructure observed, after a heating at a temperature of 1000ºC there had been significant increase in the quantity of fine particles and pores. The results of XRD analysis showed that, at this temperature the reactions in solid state materials proceed and as a result the intensity of the diffraction maximum of mineral $C_{12}A_7$ are increasing, while those of minerals – CA and CA_2 are decreasing.
Keywords: calcium aluminate cement (CAC), hydration, microsilica, microstructure, XRD.

INTRODUCTION

Calcium aluminate cements (CACs) are a special type of hydraulic binders most commonly used in the manufacture of refractory products. It is also used in the manufacture of conventional concrete, specialized self-levelling floor screeds (SLF) and repair mortar, etc. for construction industry [1-3] for its special properties, such as high reactivity with water, high early strength, resistance to chemical agents and abrasion resistance.

Gorkal 70 cement is made of high-quality raw materials and is characterized by its Al_2O_3 content. The main phase in all CACs with high Al_2O_3 content is active mono calcium aluminate

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CA with the presence of CA_2 (grossite), CA_6 (hibonite), α- Al_2O_3 and $C_{12}A_7$ (mayenite) [4]. The formation of the afore-mentioned minerals depends on the chemical composition of CAC raw materials [5].

Unlike with Portland cement, where the types of minerals formed during concrete curing are not subject to the length of hydration process and temperature, different crystalline and amorphous hydrates are formed during the hydration process of CAC paste, depending on W/C ratio, curing time and mainly on temperature [3, 6-12]. In general, the hydration process of CACs can produce four main temperature-dependent hydrates: CAH_{10}, C_2AH_8, AH_3 and C_3AH_6 (cement notation: C = CaO, A = Al_2O_3, S = SiO_2, H = H_2O) [8, 13, 14].

In work [13] it is noted that at low hydration temperatures (below 15ºC) CAH_{10} is formed; in the temperature range 15–27ºC CAH_{10} can coexist with C_2AH_8 and AH_3; when hydration temperature is raised above 27ºC C_2AH_8 and AH_3 are dominated, but if hydration temperature exceeds 50ºC C_3AH_6 and AH_3 predominate. However the temperature ranges are not precise and in literature some divergent information, especially at about ambient temperatures, are stated.

Free water and physically and chemically bound water are released during the firing of CAC.

Bentsen, Seltveit and Sandberg [15] specify the following dehydrating temperatures: alumina gel at 100˚C, CAH_{10} at 120˚C, C_2AH_8 in the range of 170˚C–195˚C, AH_3 (gibbsite) in the range of 210˚C–300˚C, C_3AH_6 in the range of 240˚C–370˚C. Dehydration at the temperature between 500˚C–800˚C leads to the formation of $C_{12}A_7$, which converts into CA, CA_2 after firing at 1 000˚C temperature [4].

A number of recent researches have proven that different industrial waste (fly ash, silica fume etc.) can be successfully utilised in building materials [16-18]. These pozzolans can produce a retarding effect on CAC dissolution and inhibit the phase transformation of calcium aluminate hydrates.

Mineral dispersive additives, most frequently microsilica (MS), added by weight of cement to concrete mixes, can effectively modify CAC characteristics. MS is a waste generated in iron and steel industry and is widely used in refractory concretes for its low cost and the possibility to reduce the amount of cement in concrete mixes. Pozzolanic reaction between MS and CAC minerals produces hydrated aluminosilicate minerals and stratlingite [19, 20]. Research into aluminate cement and MS hydration [18] showed that only hydrates of (C-A-Hn) type crystals are formed at room temperature of 20˚C after 3 days of curing. Hydrates of CASHn type crystals are formed after 2–3 days of curing at 40˚C temperature. Author [21] states that stratlingite forms only under certain conditions or after conditioning the specimen in humid environment for a long time.

The microstructure and the development of hardened CAC paste phase composition depending on the curing temperature as well as the change of phase composition and structure during the firing of hardened cement paste must be analysed in order to use MS (5%) in the mix.

Pacewska et al. [22-25], other authors [26, 27], as well as our papers [28–30] state that XRD and SEM tests are informative methods for testing cement hydration. Therefore, the aim of the present work is to investigate the formation of microstructure and phase composition of the CAC binder with microsilica additive, made with W/(CAC+MS)=1, depending on the temperature of CAC hardening and the change of these characteristics during heating.

MATERIALS, SAMPLES PREPARATION AND METHODS

CAC, grade Gorkal 70, was produced at the interprise Gorka Cement sp. z o.o in Trzebinia (Poland). The image, particle morphology and XRD spectrum of CAC are shown in Figure 1.

The chemical composition and main phases, is shown in Table 1. As determined by XRD, the minerals monocalcium aluminate (CA) and calcium dialuminate (CA_2) were predominant. The phases α-Al_2O_3 and $C_{12}A_7$ were also identified and existed in small amounts in CAC. The Blaine fineness of CAC were 4000–4500 cm^2/g [31].

MS with the brand name RW–Fuller produced by RW Silicon GmbH (Germany) was used. Its chemical composition (mass %) is as follows: SiO_2 – 96.06; Al_2O_3 – 0.20; Fe_2O_3 – 0.05; C – 0.60; CaO – 0.25; MgO – 0.40; K_2O – 1.20; Na_2O – 0.10; SO_3 – 0.35. MS is ultra-dispersed spherical particles with diameter of ~150 nm and also less than ~50 nm [32].

Distilled water was used for making the samples.

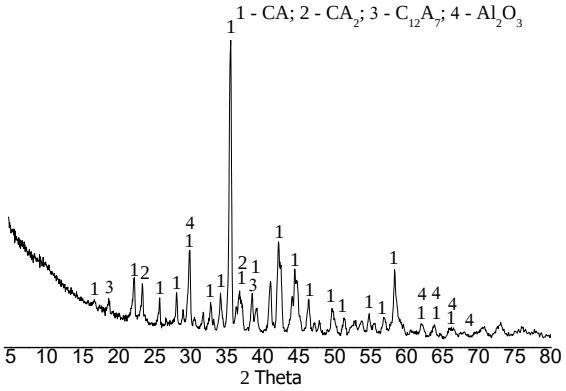

Fig. 1: *XRD pattern of CAC Gorkal 70*

Table 1: *Composition and properties of the CAC used*

Component	Typical values (%)	Main phases
Al_2O_3	69.0-71.0	CA: $CaO \cdot Al_2O_3$
CaO	28.0-30.0	CA_2: $CaO \cdot 2Al_2O_3$
SiO_2	<0.5	Additional phases:
Fe_2O_3	<0.3	$C_{12}A_7$: $12CaO \cdot 7Al_2O_3$
$Na_2O + K_2O$	<0.5	A: α-Al_2O_3

CAC and microsilica (95+5%) was mixed with water in a ratio 1:1. The paste obtained was poured into polyethylene bags. To avoid self-heating, the paste in all bags were evenly distributed so that it would make a thin, 5 mm thick, layer. Polyethylene bags were tightly closed and put into the climatic test chamber 3401 RUMED. The 1st group samples were cured at the temperature of 5ºC, the 2nd, – at 20ºC and the 3rd group samples – at 40ºC. All samples were formed, cured and heated in accordance with the standard LST EN ISO 1927-5:2013.

One control sample was taken from each group of the hardened samples. Other samples were heated at 800ºC and 1000ºC (heating speed 2.5°C/min till 700°C, further 5°C/min – 800ºC and 1000ºC, heating was done at the air condition). Both control and heated samples were tested.

The compositions of CAC with MS used for the tests described in this paper is presented in Table 2.

Table 2: *Composition (mass %) of CAC and MS*

Marking of composition	CAC (%)	MS (%)	Water (%)	Temperature (°C)
GS5C	95	5	100	5°C, 800°C, 1000°C
GS20C	95	5	100	20°C, 800°C, 1000°C
GS40C	95	5	100	40°C, 800°C, 1000°C

The microstructure of samples was investigated with the scanning electron microscopy (SEM) device SEM JEOL JSM-7600F (Oxford Instruments, High Wycombe, UK). Electron microscopy parameters: Power 10 kW, distance to specimen surface from 7 to 10 mm. Characteristics of the microstructure was identified by testing the specimen splitting surface.

Before testing, the splitting surface was coated with electrically conductive thin layer of gold by evaporating the gold electrode in the vacuum using the instrument QUORUMQ150R ES (Quorum, Laughton, UK).

The X-ray diffraction (XRD) analysis of the phase composition of materials was carried out upon applying diffractometer DRON-7 (Bourevestnik, St. Petersburg, Russia). In order to obtain X-ray radiation Cu Kα spectrum (λ = 0.1541837 nm), a graphite monochromator was used. The parameters of the tests were following: voltage - 30 kV; current - 12 mA; the range of the diffraction angle – from 4 to 60°, the detector movement step – 0.02°; the duration of the intensity measuring in a step – 0.5 s. Phase identification was carried out by decoding the XRD patterns according to International Centre for Diffraction Data (ICDD) diffraction databases. The quantitative changes in the XRD patterns were assessed according to the height of the peak of the main diffraction maximum of a mineral.

The thermal analysis was performed by thermal analyser LINSEIS STA PT-1600 (LINSEIS, Germany). The samples of 60–70 mg weight were placed in a platinum crucible and heated at the rate of 10ºC/min in the air up to 1000ºC.

RESULTS AND DISCUSION

The results of XRD analysis show (Figure 2) the formation of the following compounds in hardened cement paste at the following curing temperatures: only CAH_{10} is formed at 5°C, CAH_{10}, C_2AH_8 and AH_3 are formed at 20°C, crystalline hydrates C_3AH_6 and AH_3 are formed at 40°C. X-ray patterns also reveal the peaks of unreacted CA and CA_2 minerals during the curing of CAC paste. The intensity of CA and CA_2 peaks was seen to reduce at higher hydration temperature and $C_{12}A_7$ was seen to disappear after 3 days of curing irrespective of the curing temperature.

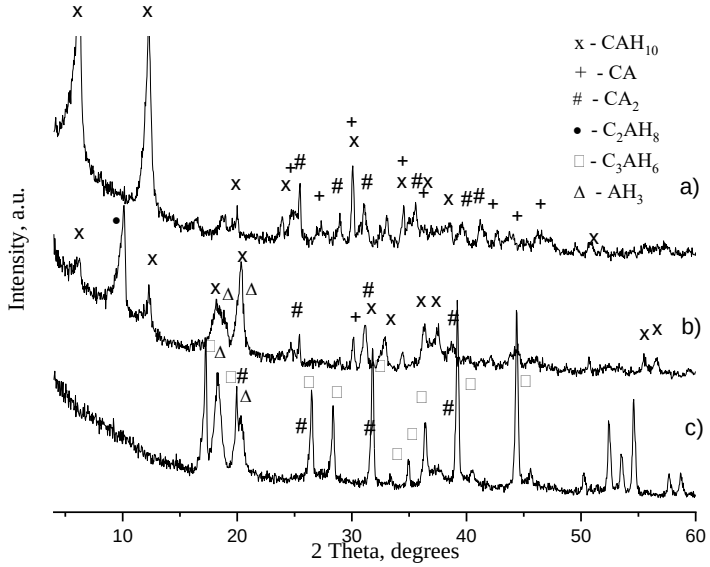

Fig 2: *XRD patterns of hardened CAC paste with MS after 3-days curing at temperatures: a) 5ºC, b) 20ºC, c) 40ºC*

The morphology of hydrates is seen in SEM images of the surface of split specimens (Figure 3). The abundance of CAH_{10} crystals is seen on the surface of the specimen cured at low temperature (5°C) (Figure 3a). CAH_{10} crystals have a form of a long hexagonal prism with the average diameter of ≥0.10μm.

When specimens are cured at 20°C temperature, plate-shaped C_2AH_8 crystals and prism-shaped CAH_{10} crystals are formed on the surface of hardened cement paste (Figure 3, b). Round fragments containing very fine crystals are also observed in the microstructure of these specimens. Presumably, these are crystalline hydrates and unreacted cement minerals that are joined by crystalline AH_3. AH_3 is formed on the surface of ultradispersed spherical particles of

microsilica. The average thickness of C_2AH_8 mineral plates is ≥0.1μm, the diameter of hexagonal CAH_{10} prisms is ≥0.1μm.

Cubic C_3AH_6 crystals with the average edge length of 8μm prevail in the structure of specimens cured at 40°C (Figure 3, c). Cubic crystals are covered in part in some places or in full in other places by a crystal material made of fine crystals about <1μm in size. These crystals encapsulate the spherical particles of microsilica. The results of previous tests [29] prove that this material is AH_3. In Figure 2 (curve c) the diffraction peaks of AH_3 (gibbsite) are clearly visible. This crystalline material is evidently gibbsite.

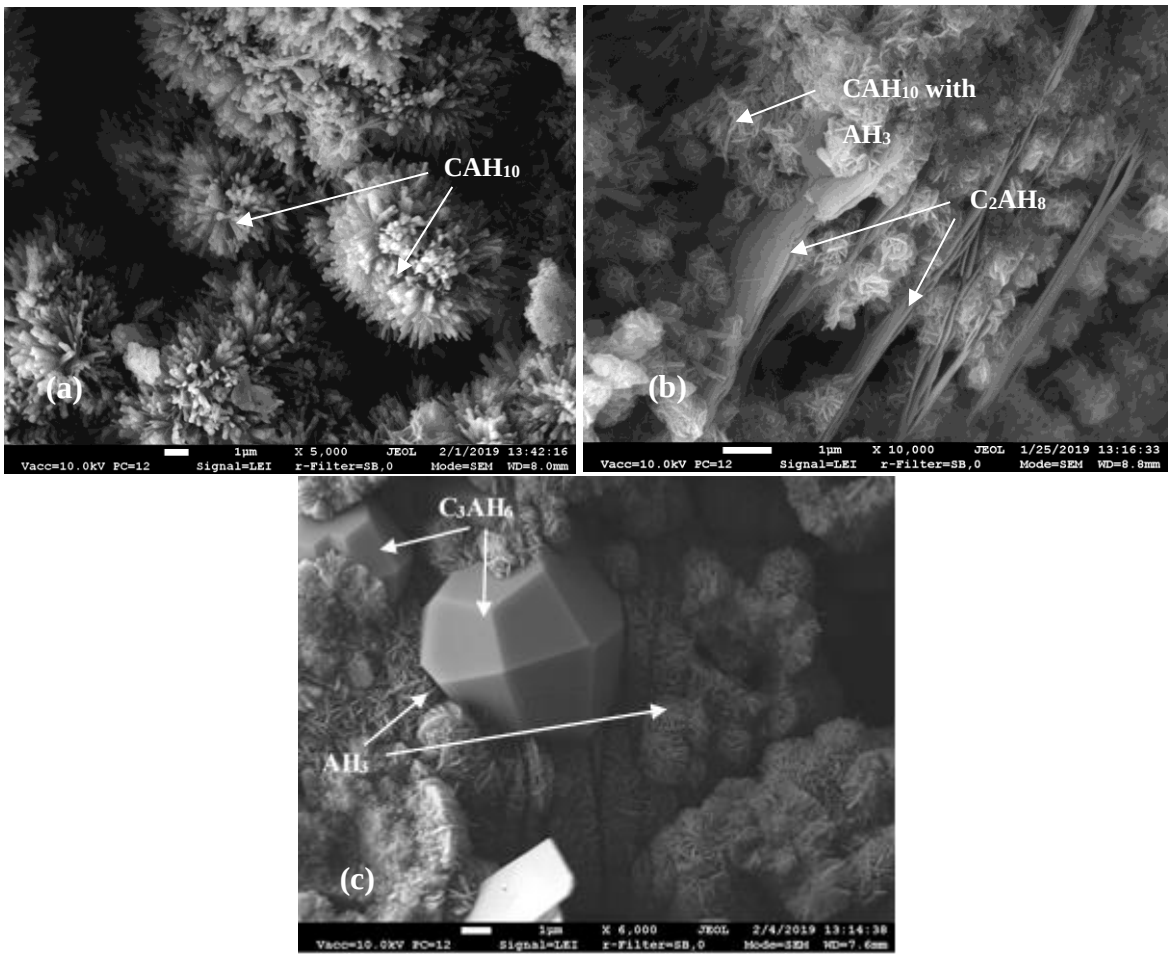

Fig. 3: *The microstructure of hardened CAC paste specimens with MS: after 3 days curing at temperatures of: a) 5°C; b) 20°C; c) 40°C.*

Stratlingite mineral is hardly identifiable it was not fixed in tested specimens after 3 days of hardening irrespective of the curing temperature.

Authors [32] state that dehydration occurs when hardened CAC paste is heated up to 800ºC temperature with subsequent conversion of hydrates: $CAH_{10} \rightarrow C_2AH_8 \rightarrow C_3AH_6$. Dehydration process in hardened cement paste ends after firing at 800°C temperature. At 800ºC temperature $C_{12}A_7$ is formed [4] and it converts into CA and CA_2 after further firing at higher temperature (1000ºC). From the pattern presented in [33] C_3AH_6 conversion may be written as follows:

$$C_3AH_6 + 2AH_3 \rightarrow C_{12}A_7 + CA + H$$

XRD patterns of specimens fired at 800ºC are presented in Figure 4 (a), SEM photos in Figure 5.

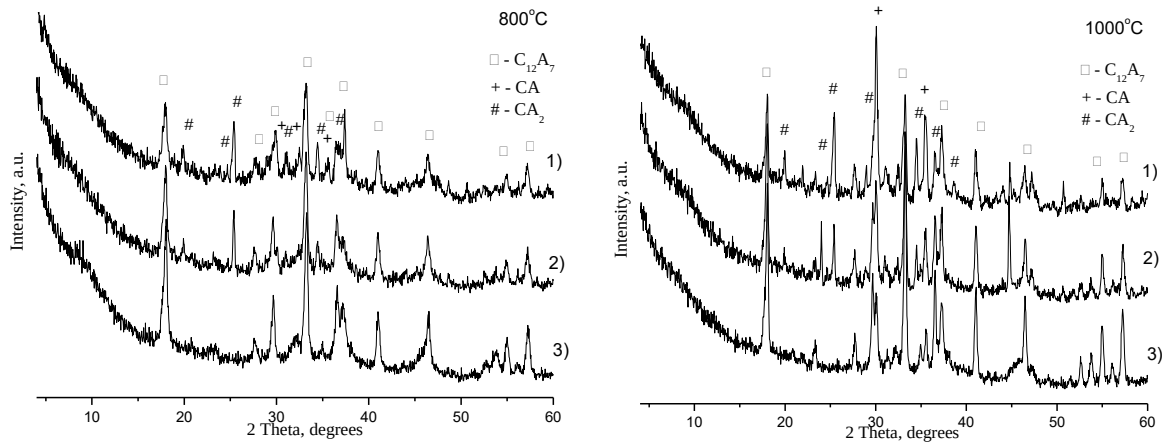

Fig. 4: *XRD patterns of hardened CAC paste with MS fired at 800ºC and 1000ºC. Curing temperature: 1) 5ºC; 2) 20ºC;3) 40ºC*

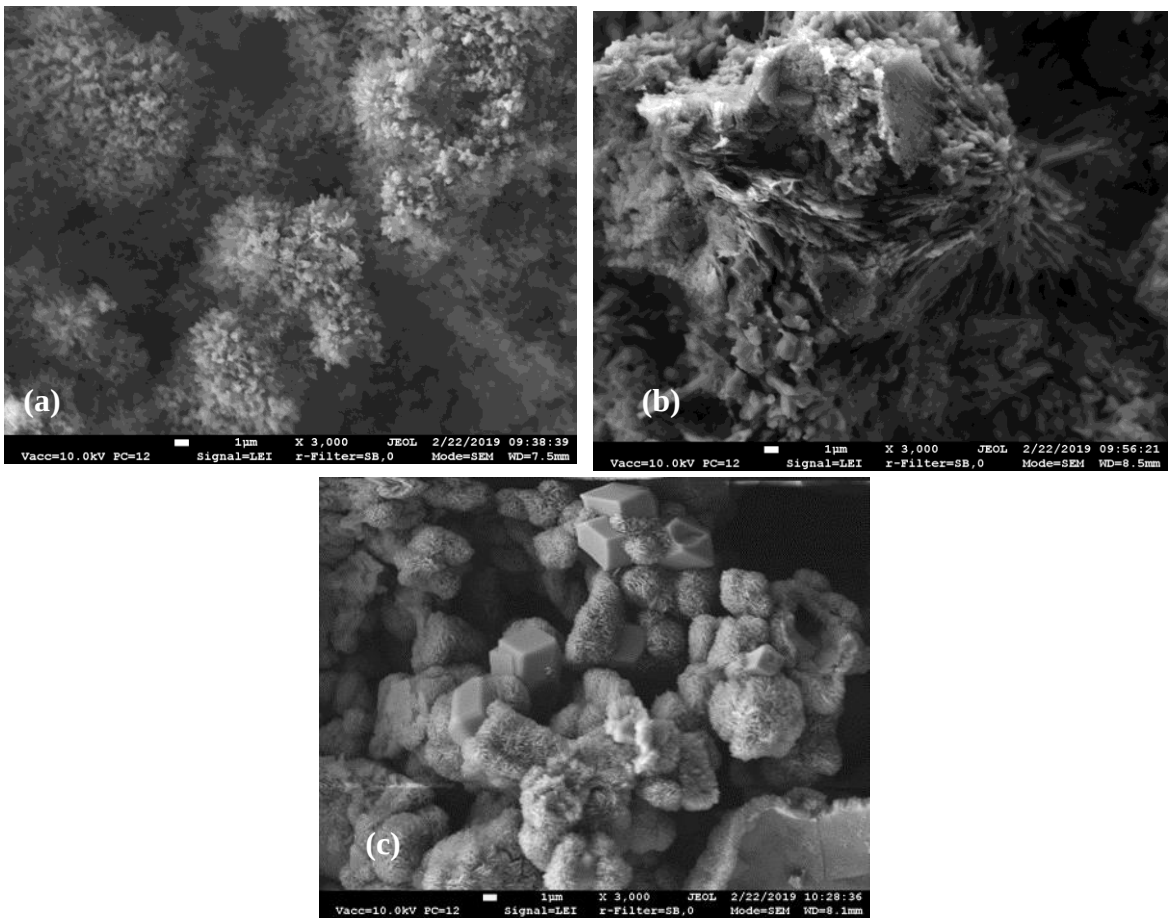

Fig. 5: *The microstructure of hardened CAC paste specimens fired at 800ºC: a) sample cured at 5ºC; b) sample cured at 20ºC; c) sample cured at 40ºC*

SEM analysis of specimens fired at 800ºC reveals the change in morphology of specimens cured at 5°C, 20°C and 40°C and then fired at 800ºC (see and compare Figure 5 (a, b and c) and Figure 3 (a, b and c) accordingly). Slight changes in the morphology of materials are observed, the crystals have a fluffier shape.

The analysis of XRD and SEM patterns of hardened CAC paste fired at 800ºC show that CAH_{10}, C_2AH_8, C_3AH_6, AH_3 decompose at this temperature but the contours of their crystal forms (prisms, plates, cubes) practically remain unchanged.

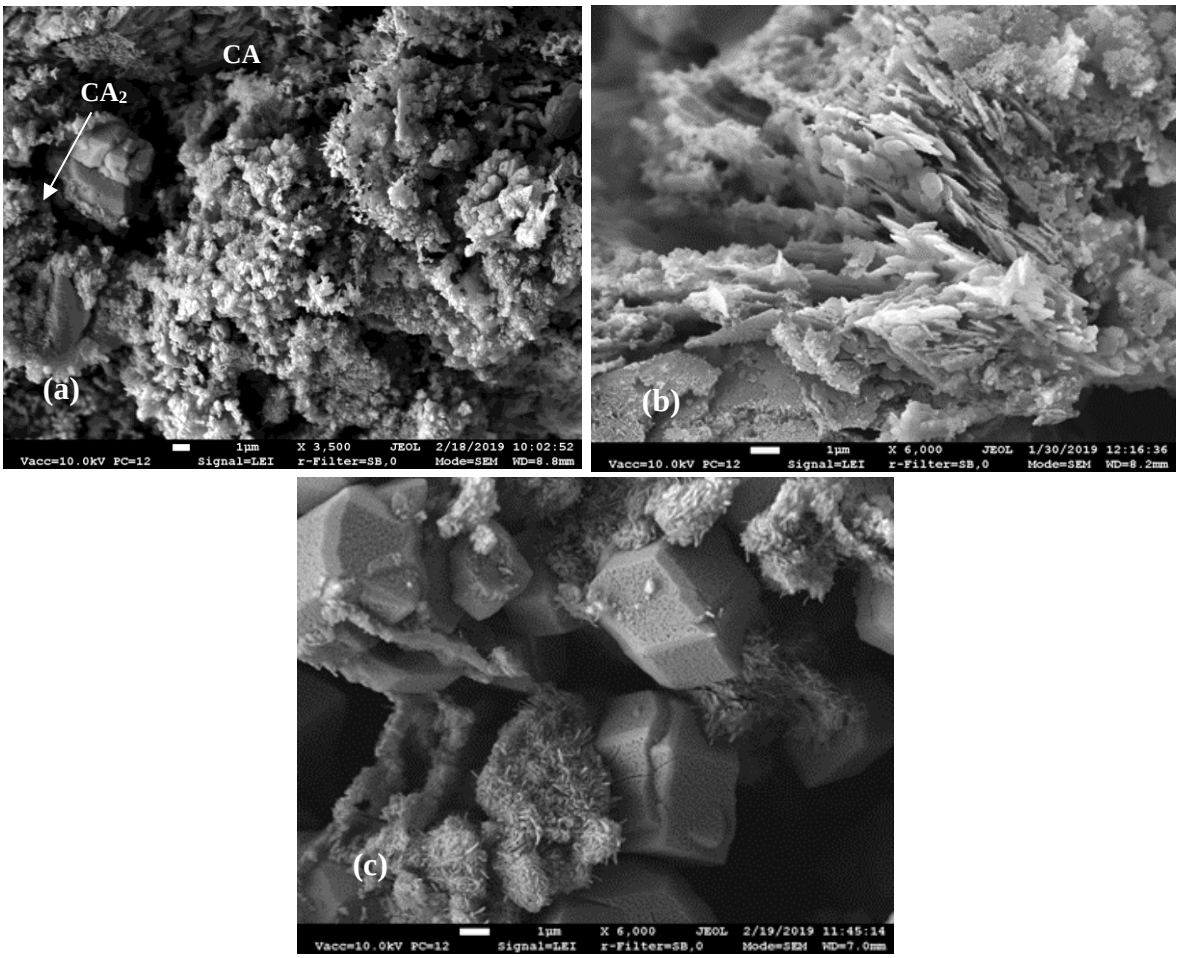

Fig. 6: *Microstructure of hardened CAC paste specimens fired at 1000ºC: a) cured at 5ºC; b) cured at 20ºC; c) cured at 40ºC*

Table 3: *Results of XRD (intensity) analysis of minerals formed in all compositions after 3-days curing and thermal treatment at different length of curing time*

Marking of composition	Temperature	CAH_{10}	C_2AH_8	C_3AH_6	AH_3	CA	CA_2	$C_{12}A_7$
GS5C	3-days hardening	841	-	-	-	272	216	-
GS20C	(5ºC, 20ºC, 40ºC)	338	474	-	250	140	149	-
GS40C		-	-	440	351	-	97	-
GS5C	800°C	-	-	-	-	132	165	230
GS20C		-	-	-	-	100	164	263
GS40C		-	-	-	-	108	160	311
GS5C	1000°C	-	-	-	-	349	201	237
GS20C		-	-	-	-	234	165	317
GS540		-	-	-	-	-	160	444

Table 3 shows the intensities of the peaks of the main minerals in order to evaluate easier the formation of hydrates in specimens after curing. The results show that unreacted minerals (CA, CA_2) have much more intensive peaks in specimens cured at the lowest temperature (5°C). At higher curing temperatures the intensities of CA and CA_2 peaks reduce, thus proving that the formation of crystallised hydrates tends to intensify at higher curing temperatures.

Lower amounts of CA, CA_2 and $C_{12}A_7$ were identified in specimens cured at higher temperatures after firing the specimens at 800ºC and 1000ºC.

The tests have proved that the curing temperature has a major effect on the composition and structure of hydrates in hardened cement paste with microsilica addition. The contours of the formed crystallised hydrates remain almost unchanged after dehydration, which occurs

during thermal treatment of hardened cement paste at 800°C, whereas the firing at 1000°C causes significant changes in the microstructure of specimens.
Thermogravimetric analysis (TGA) was done to determine the rate of degradation of hardened CAC paste specimens (Fig. 7).

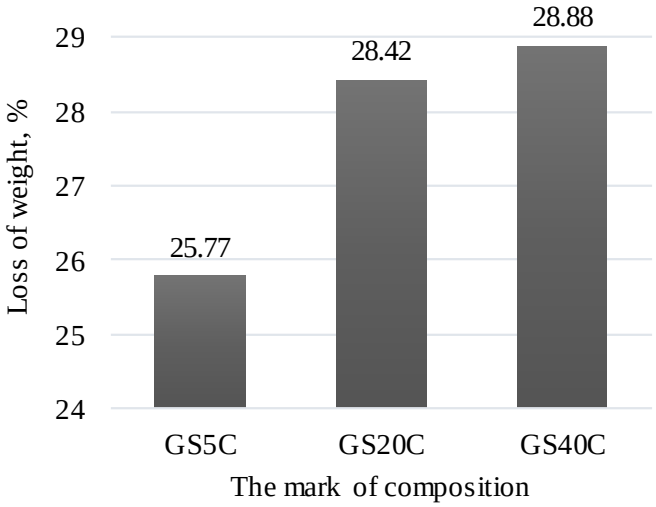

Fig 7. *Total weight loss (%) in hardened CAC paste specimens fired at 20ºC–1000ºC temperature (the diagram prepared on the basis of TG analysis results)*

The highest weight loss of 28.88% was recorded in specimens cured at the highest temperature (40°C). This degradation can be explained by coarser cubic C_3AH_6 crystals with the average edge length of 8µm in specimens GS40C. Specimens GS20C cured at a lower (20°C) temperature experienced a slightly lower weight loss of 28.42% compared to specimens GS40C. The lowest weight loss of 25.77% was observed in specimens GS5C.

CONCLUSIONS

1. The formation of hydrates in hardened cement paste where W/(CAC+MS)=1 was found to be different depending on the curing temperature: only CAH_{10} formed in specimens cured at 5°C, CAH_{10}, C_2AH_8 and AH_3 formed in specimens cured at 20°C, and C_3AH_6 and AH_3 formed in specimens cured at 40 °C. CAH_{10} crystals have a shape of a long hexagonal prism with the average diameter of ≥1µm. The average thickness of C_2AH_8 plates is ≥0.1µm, the average edge length of C_3AH_6 cubes is 8µm.
2. During the thermal treatment of hardened cement paste at 800ºC, the hydrates formed in the curing phase dissociate into CA, CA_2 and $C_{12}A_7$ minerals. However, the contours of the shapes of crystals formed (prisms, plates, cubes) change little after the firing at 800ºC temperature. Significant changes in the microstructure of hardened cement paste occur after the firing of specimens at 1000ºC temperature, which causes a significant increase in the amounts of fine particles and pores.

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