INFLUENCE OF CURING TEMPERATURE ON THE PHYSICO-MECHANICAL, CHARACTERISTICS OF CALCIUM ALUMINATE CEMENT WITH AIR-COOLED SLAG OR WATER-COOLED SLAG

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Microstructure and phase compositions

The nature, sequence, crystallinity and microstructure of hydrated phases were analyzed using differential scanning calorimetry (DSC), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results showed that the formation of different hydrated phases was temperature dependence. The physico-mechanical and microstructural characteristics were investigated after curing at 20, 40 and 60° C. The results indicated that for the substitution of calcium aluminate cement (CAC) by air-cooled slag (AS) or water-cooled slag (WS) at 20 C, the compressive strength increases with slag content up to 10 wt.%, then followed by a decrease with further slag substitution up to 25 wt.%; but the values are still higher than those of the neat CAC pastes at different curing ages up to 60 days. After 28 days of hydration at 40-60 C, the compressive strength increases with the slag content. This is attributed to the prevention of the conversion reaction, which was confirmed by XRD, DSC and SEM techniques, and the preferential formation of stratlingite (gehleinte-like) phase. The SEM micrographs showed a close texture of hydrated CAC/slag blends made with AS or WS at 40°C due to the formation of C_2ASH_8 *and C-S-H phases.*

INTRODUCTION

Modern construction requires advanced concretes, which have high strength, cost effectiveness and durability. Calcium aluminate cement, by virtue of its early rapid strength development, high temperature resistance, and resistance to a wide range of chemically aggressive conditions, has many specialized industrial applications including structural repair. It is used in the refractory industries, pipes and sewer constructions, industrial floors, dam spillways, cold concreting and repair constructions in general [1].

High early strength is one of the major advantages of calcium aluminate cement (CAC) over Portland cement. This high early strength may mislead designers into ignoring the conversion effect during its service life. The compressive strength of CAC can however be adversely affected by temperature. This is due to the crystalline conversion from the hexagonal CAH_{10} or C_2AH_8 to cubic C_3AH_6. The CAH_{10} and C_2AH_8 crystals are not stable at moist conditions with temperatures higher than about 20°C. They will eventually convert to C_3AH_6 in a humid environment at elevated temperature. The conversion markedly increases the porosity of CAC hydration products, because the density of C_3AH_6 is higher than that of CAH_{10} or C_2AH_8 [2]. The strength and durability of CAC decrease as a consequence. This is sufficient to cause strength reduction due to microcracks created during conversion. Strength reduction due to conversion was believed to be one of the contributions to the structural damage [3]. Midgley and Rao used hydrated Portland cement as an additive for CAC to produce stratlingite; but was not successful [4]. A comparative study of the hydration of CAC in the presence of C-S-H gel or β-C_2S with varying degrees of fineness was reported [5]. It was observed that the metastable calcium aluminate hydrates could react with C-S-H gel to form stratlingite. The amount of stratlingite formed was dependent on the availability of CSH gel for reaction.

The use of a siliceous material in combination with a sodium salt in CAC was recently reported to be more effective than the siliceous material alone in promoting formation of stratlingite instead of hydrogarnet [6-13]. Siliceous materials, including natural zeolites, fly ash, slag and silica fume were effective in inhibiting hydrogarnet formation and preventing strength reduction in CAC products when added in combination with a sodium salt. Silica fume have been reported to favour the formation of stratlingite (C_2ASH_8) [14,15]. Microsilica reacts to form silicates in a high pH environment. This reaction is accelerated in the presence of an increased amount of alkali ions that may act as a catalyst activating microsilica surfaces. Silicate anions then react with hydrated calcium aluminates to produce stratlingite. The incorporation of slag was suggested as a way of preventing the conversion reaction [16-22]. The prevention of the reaction was attributed to stratlingite formation in preference to the hydrogarnet. Strength reduction due to conversion was eliminated in the CAC/slag blends at later ages; the 1-day strength was, however, significantly lower than that for neat CAC [16,18,20].

The effect of curing temperature on the compressive strength of CAC or modified CAC concretes was studied [23]. Ground-granulated blastfurnace slag, natural zeolite or silica fume in combination with sodium sulfate were used to inhibit the strength reduction of the CAC.

In a previous work, the variations of electrical conductivity to monitor the change occurring during the initial setting from zero time (3 minutes) up to 7 days as well as, reflecting the hydraulic activity of AS in comparison with WS, for prevention of the conversion reaction have been studied [24].

The present work aimed to study the effect of curing temperatures on morphology and phase composition as well as the physico-mechanical properties of some special types of blended cements containing AS or WS slag produced in Egypt as additives to the calcium aluminate cement (CAC) that can be safely used in special applications in the climate prevails in Egypt, such as lining for centrifuged concrete pipes as well as centrifuged lining of ductile iron pipes used for wastewater and concrete structures exposed to some aggressive salts. The climatic temperature in Egypt is 15-25°C in winter where, it ranges between 30-40°C in summer.

EXPERIMENTAL

Materials

The materials used in this investigation are calcium aluminate cement (CAC), Egyptian air-cooled (AS) and water-cooled (WS) slags provided by the Iron and Steel Company, Helwan, Egypt. The chemical composition of these raw materials is given in table 1. WS is produced by rapid quenching in water. AS is produced by slow cooling in air due to inadequate facilities. The slags were ground in a ball mill to attain a Blaine surface area of 350 m^2/g. XRD pattern of air-cooled slag reveals the presence of gehlenite (C_2AS) and quartz. The water-cooled slag shows a hump existing between 20-35° 2θ indicating the presence of amorphous glassy phases.

Preparation and Testing of Specimens

The mix proportions are shown in table 2. Each blend was mixed in a porcelain ball mill with four balls for 1 hour to assure complete homogeneity. The CAC was partially substituted by 5, 10, 15, 20 and 25 wt.% of AS or WS. Different mixes were mixed with the required water of normal consistency given in table 2. The mix compositions of the prepared mixes are given in table 2. The fineness was checked using the Blaine air-permeability apparatus, according to the ASTM method (ASTM Designation C204-79) [25]. The surface areas of the starting materials are also shown in table 1.

The required amount of mixing water was mechanically mixed for three minutes and the paste was then poured into one-inch cube moulds, which were compacted several times, and their surfaces smoothened.

Table 1. Chemical analysis of the starting materials.

Oxides (wt.%)	CAC	AS	WS
SiO_2	4.59	32.69	37.21
Al_2O_3	53.68	8.17	10.45
Fe_2O_3	1.24	1.89	1.27
CaO	35.52	33.57	35.70
MgO	n.d	1.35	2.05
SO_3	n.d	0.01	0.15
L.O.I	n.d	--	--
K_2O	n.d	0.43	0.71
Na_2O	n.d	1.47	1.60
TiO_2	2.92	0.46	0.35
MnO	Nil	4.48	3.50
BaO	--	6.63	3.11
S^{2-}	Nil	0.01	3.62
Blaine surface area (m^2/g)	350	350	350

Table 2. Mix compositions and the required water of normal consistency of CAC-slag blends.

Mix. no.	CAC	AS	WS	W/C, (wt.%)*
M.0	100	--	--	25.5
M.5	95	5	--	24.9
M.10	90	10	--	24.5
M.15	85	15	--	24.3
M.20	80	20	--	24
M.25	75	25	--	23.8
C.5	95	--	5	25.2
C.10	90	--	10	24.9
C.15	85	--	15	24.6
C.20	80	--	20	24.3
C.25	75	--	25	24

* Required water for standard consistency

The required water of standard consistency is represented in table 3. The moulds were cured in a humidity chamber at 100 % relative humidity at 20°C for the first 24 hours, then demoulded and cured under water up to 60 days at three thermostatic temperatures of 20, 40 and 60°C.

The compressive strength measurements were conducted for a set of at least 3 (2.54 × 2.54 × 2.54 cm) cubes of each mix at any given curing period. The required water for standard consistency and setting times were determined in accordance with B.S. 4550 sections 3.5 and 3.6, respectively. The bulk density and apparent porosity of the hardened blended CAC-slag pastes were determined on samples using the water displacement methods [26]. The evaporable water (uncombined water), W_e, of the hydrated samples was removed using the method described elsewhere [27].

The phase compositions of the hydration products were determined using X-ray diffraction analysis with a Ni-filtered Cu-Kα radiation Philips diffractometer with a scanning speed of 1° 2θ/min. Differential scanning calorimetry runs were conducted using a Shimadzu DSC-50 thermal analyzer at a heating rate of 10°C/min. The microstructure of the selected samples was examined using a JEOL JXA-840 high-resolution scanning electron microscope.

RESULTS AND DISCUSSION

Physico-Mechanical Properties

Compressive Strength

Figure 1 shows the compressive strength of CAC/AS and CAC/WS as a function of slag content for the samples cured for different periods at 20°C. The compressive strength increases with slag content (AS or WS) up to 10 wt.%, then it decreases with the further increase of the slag content. As the curing time increases the compressive strength increases in the same trend. The compressive strength of CAC/AS pastes shows somewhat higher values than those of CAC/WS pastes; this indicates that the unhydrous parts of AS grains contribute strongly to the compressive strength as compared to WS grains; AS grains are much harden than WS grains.

The compressive strength values of different cement pastes cured at 40°C are illustrated in figure 2; the specimens are cured first at 20°C for 24 hours and 100 % relative humidity, and then cured under water at 40°C. After 3 and 7 days, the compressive strength increases with the slag content up to 10 wt.%, and then decreases slightly up to of slag content up to 25 wt.%. The compressive strength values obtained for the paste containing 25 wt.% are similar to those obtained for the neat CAC pastes. The compressive strength of the neat

Table 3. Bulk density (BD) and apparent porosity (AP) of CAC/AS and CAC/WS pastes cured for 28 days at 20, 40 and 60°C.

curing temperatures	slag content (wt.%)	AS BD (g/cm^3)	AS AP (%)	WS BD (g/cm^3)	WS AP (%)
20°C	0	2.048	19.88	2.048	19.88
	5	2.056	18.92	2.054	19.02
	10	2.058	18.58	2.056	18.65
	15	2.061	18.11	2.059	18.24
	20	2.052	19.62	2.048	19.82
	25	2.049	19.82	2.046	19.98
40°C	0	1.986	25.69	1.986	25.69
	5	2.035	21.60	2.030	22.01
	10	2.058	20.07	2.046	20.87
	15	2.077	18.99	2.056	19.25
	20	2.089	18.55	2.061	18.66
	25	2.091	18.25	2.065	18.39
60°C	0	2.167	16.16	2.167	16.16
	5	2.180	15.49	2.173	15.93
	10	2.183	15.38	2.176	15.81
	15	2.188	15.25	2.179	15.75
	20	2.191	15.19	2.181	15.69
	25	2.194	15.02	2.183	15.65

CAC paste decreases very sharply after 28 and 60 days of hydration, whereas the pastes made of CAC/AS or CAC/WS blends showed a progressive increase with increasing slag content. The compressive strength of CAC paste was about 68 MPa at 7 days; it, however, dropped to about 12.6 MPa at 28 days. A further little decrease in strength occurred with the increase of the hydration time to 60 days (12.0 MPa). The strength of CAC containing AS or WS increases with the slag content up to 10 wt.% up to 7 days of hydration and then deteriorated. Evidently, the strength values after 7 days were 68.0, 72.9, 77.1, 73.8, 72.2 and 70.4 MPa for the pastes containing AS and the corresponding values for those the containing WS were 68.0, 72.5, 76.5, 73.3, 71.8 and 70.0 MPa for the paste containing 0, 5, 10, 15, 20 and 25 wt.% slag, respectively. On the other hand, the strength values after 28 days of hydration were lowered. The strength values of the pastes containing 15-25 wt.% of slag after 28 days of hydration are significantly improved. This indicates that the additions of 15-25 wt.% of slag to CAC were sufficient to suppress the strength reduction as a result of conversion reaction [23]. The compressive strength was further developed after 60 days of hydration which confirm the optimum constitution of CAC/slag blends of (85-75)/(15-25) when curing was carried out at 40°C.

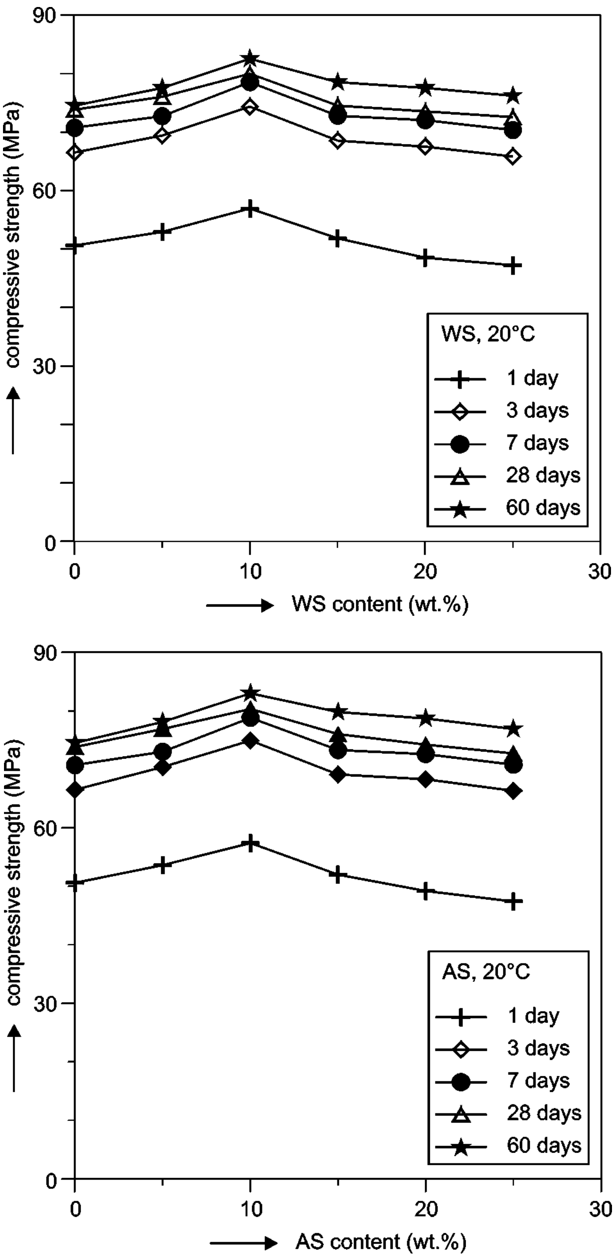

Figure 1. Compressive strength of neat CAC, CAC/AS and CAC/WS cement pastes cured at 20°C up to 60 days.

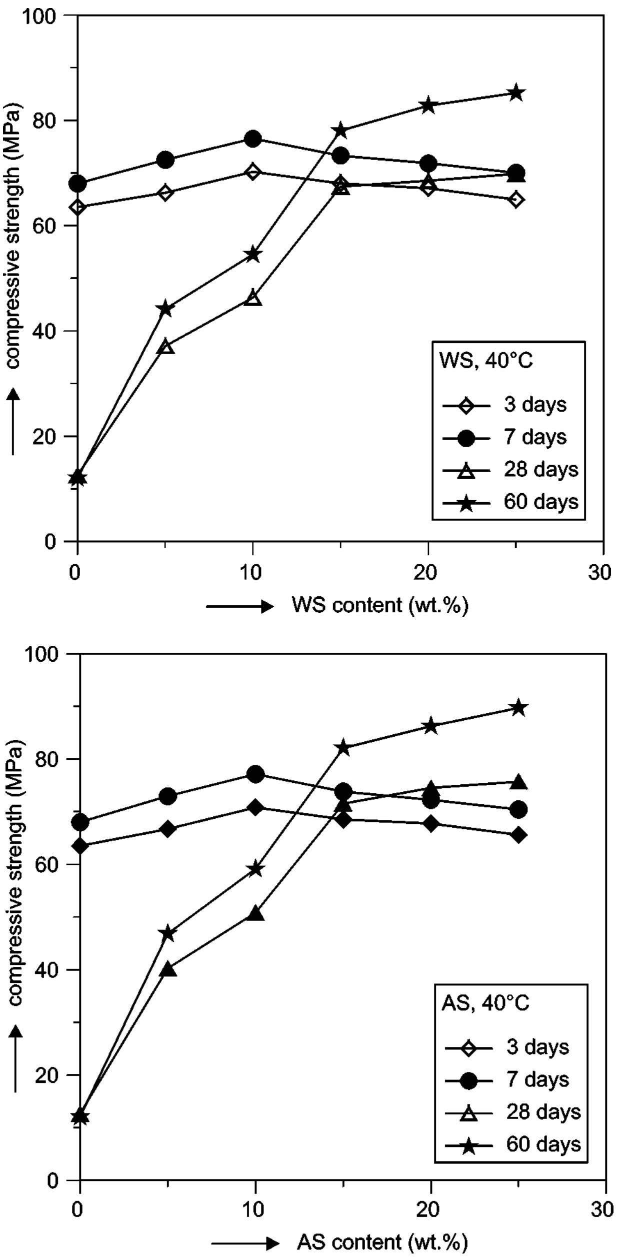

Figure 2. Compressive strength of CAC, CAC/AS and CAC/WS cement pastes cured at 40 C up to 60 days.

For curing at 60°C, the specimens were cured first for 24 hours at 20°C and 100 % relative humidity, followed by curing under water at 60°C. The compressive strength increases with slag content (figure 3). The increase of curing time from 3 to 28 days is accompanied by a notable strength decrease; this is due to the formation of C_3AH_6. The stable C_3AH_6 phase is formed straight away at a temperature of 60°C. The strength beyond 24 hours at 60°C will be lower than that obtained when hardening was carried out at lower temperatures. The hydrates that are formed, on the other hand, are much more stable. After 60 days, the strength of CAC/AS and CAC/WS increases over those obtained at other curing ages; this is due to the formation of stratlingite (C_2ASH_8) phase at longer hydration ages. The relatively low early strength is attributed to the direct formation of C_3AH_6 at early ages. Also, the degree of strength reduction is due to the phenomenon of conversion at later ages.

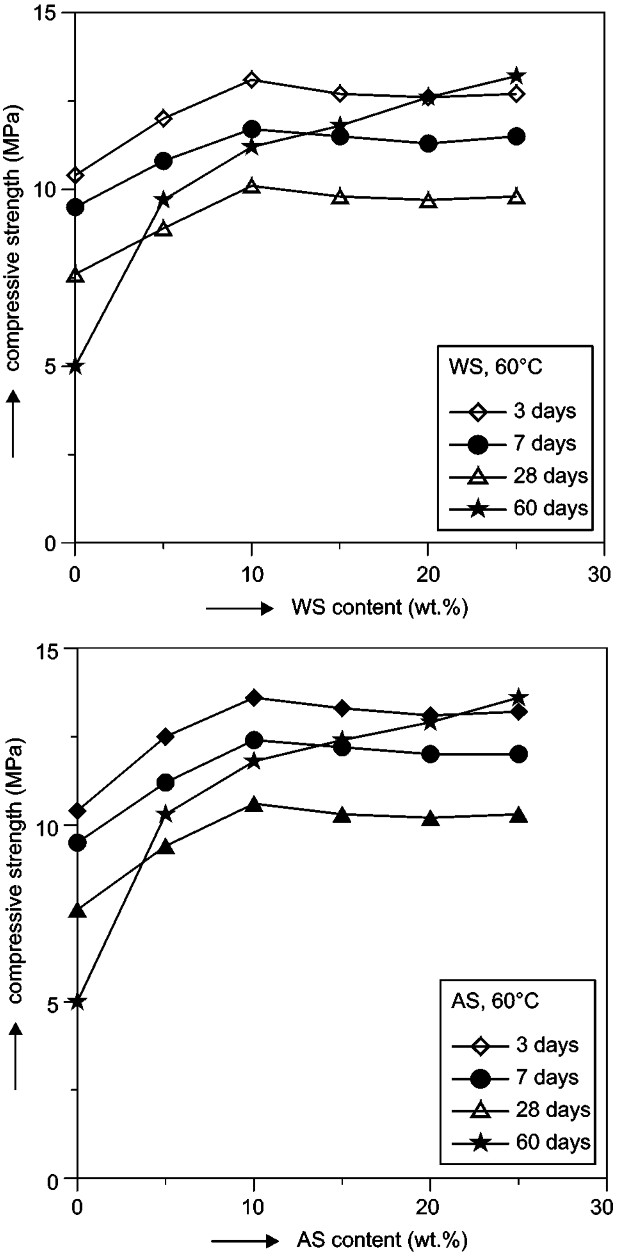

Figure 3. Compressive strength of CAC, CAC/AS and CAC/WS cement pastes cured at 60 C up to 60 days.

High early strength of CAC cement at lower ambient temperatures is attributed to the formation of CAH_{10} and C_2AH_8 as the dominant hydration products. However the strength of CAC pastes may decreases when the ambient temperature increases due to the conversion reaction of CAH_{10} and C_2AH_8 to C_3AH_6. One important outcome of substitution of CAC with slag is the formation of stratlingite (C_2ASH_8) phase [20,21,28]. At elevated temperatures, the cubic phase (C_3AH_6) is formed initially, and then started to diminish in amounts after 28 days with the formation of C_2ASH_8 as the major crystalline hydrate after 60 days. From the strength results it was shown that the formation of C_2ASH_8 at the expense of calcium aluminate hydrates is the main factor in the elimination of progressive strength loss of the paste made of CAC/slag blends. However, the progress of strength enhancement of CAC/slag blends is more complex because of the presence of large amounts of gels in the hydrated products [5]. As a result, the examination of the microstructure looks to be useful as shown later.

Physical Properties

The bulk density and apparent porosity of CAC and CAC containing AS or WS slag are presented in table 3. The determination of porosity of CAC was problematic; the difficulty arises because the procedures normally adopted necessitates drying of the hydrated cement specimens before measuring their porosity, either by heating or by solvent extraction of non-evaporable water or by vacuum drying, affects the obtained results. Heating of CAC pastes beyond about 30°C will induce rapid "conversion". Solvent extraction or evacuation, on the other hand, will remove some structurally held water from calcium aluminate hydrate phases such as CAH_{10} and probably from the amorphous gel material as well [28].

For a given curing age, at 20°C, the bulk density of the pastes made of CAC/slag blends increases slag content up to 15 wt.% of AS or WS slag, followed by a decrease with further substitution of CAC by slag up to 25 wt.%. On the other hand, the apparent porosity behaves in the opposite direction, it decreases with increasing slag content up to 15 wt.%, and then increases with slag content up to 25 wt.%. The increase of slag content up to 10 wt. % is accompanied by an increase of the compressive strength and bulk density; this due to the formation of gehlenite-like (C_2ASH_8) hydrates, whereas the increase of the slag content increases the dilution effect of CAC.

Increase of the curing temperatures to 40°C, the bulk density of CAC decreases where the apparent porosity increases. Higher curing temperature enhances the conversion reaction to proceed leading to the formation the stable C_3AH_6 phase from metastable phases CAH_{10} and C_2AH_8. The cement hydrates CAH_{10} and C_2AH_8 that are formed are metastable at temperatures above 20°C; in due course they are converted into C_3AH_6. During the conversion process the existing cement hydrates CAH_{10} and C_2AH_8 release some of their combined water, as a result of which more and more voids are created in the cement material. The porosity of cement material consequently increases substantially. New reaction products are formed upon conversion to C_3AH_6 and water release. The results of table 3 showed also that the porosity decreases with the increase of the slag content (AS or WS) of CAC/slag pastes. The results indicated that apparent porosity of the pastes containing AS were lower than those containing WS; this result is coincident with the results of compressive strength.

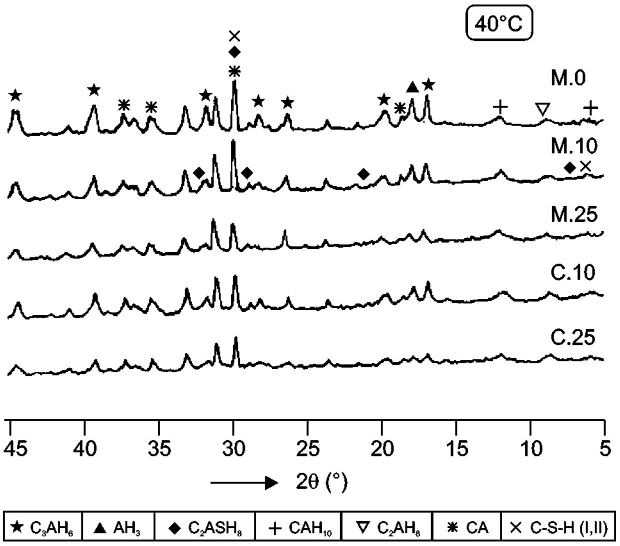

Figure 4. XRD patterns of M.0, M.10, M.25, C.10 and C.25 cured at 40 C for 28 days.

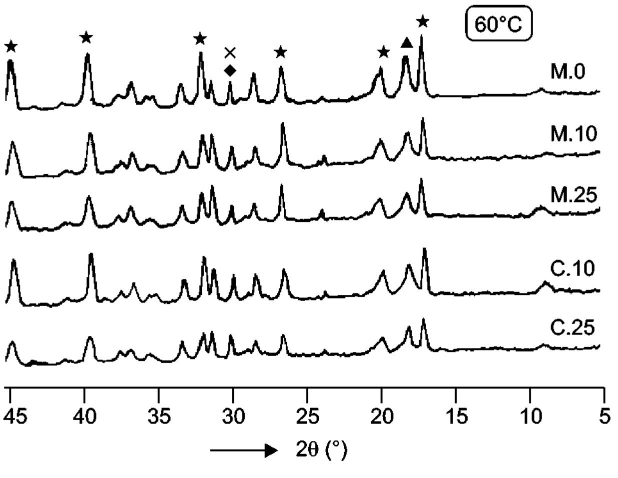

Figure 5. XRD patterns of M.0, M.10, M.25, C.10 and C.25 cured at 60 C for 28 days.

On curing at 60°C, the results of bulk density and apparent porosity show unexpected values. The bulk density values at 60°C are higher than those measured at 20 and 40°C; whereas, the apparent porosity values are lower than those at 20 and 40°C. This indicated that the reaction proceeds via the direct formation of stable crystalline C_3AH_6 phase rather than that of the conversion reaction.

At higher temperatures, the stable C_3AH_6 phase is formed early during the hydration process. It has been claimed that the formation of C_3AH_6 is always preceded by the transitory formation of some C_2AH_8, even at temperature up to 90°C [29], but the direct formation of C_3AH_6 during CAC hydration can take place when C_3AH_6 has been nucleated to some extent. This phase rapidly becomes the only hydrate present when hydration occurs at temperatures above 50°C. The crystallization of AH_3 gel to gibbsite (γ-AH_3) is also highly temperature dependent and sluggish at ambient temperature [30]. The density of C_3AH_6 and γ-AH_3 are 2.52 and 2.40, where the density of CAH_{10} and C_2AH_8 are 1.72 and 1.95 respectively [31].

Phase Composition

XRD Analysis

XRD analysis of hydrated pastes made of CAC and CAC/slag blends containing 10 and 25 wt.% of AS and WS carried out on the pastes cured under water at temperatures of 40 and 60°C up to 28 days of hydration. The XRD patterns of the pastes made of mixes M.0, M.10, M.25, C.10 and C.25 cured for 28 days at 40 and 60°C are shown in figures 4 and 5 respectively. Figure 4 shows that the characteristic peaks of hydrogarnet (C_3AH_6) and AH_3 are found, which decrease with the increase of the amount of slag present especially for mixes containing 25 wt.% of slag (WS and AS) with their less intensed peaks. This indicates that the presence of both slag types may prevent the conversion process of the hexagonal calcium aluminate phases to the stable cubic form of hydrogarnet (C_3AH_6) by the reaction of slag phases with the hydrated calcium aluminate phases to form the stratlingite (C_2ASH_8) compound (22). The hydration of the slag portions could be detected by the appearance of relatively small characteristic peaks of the CSH phases together with a little change of the peaks found at 2θ between 30-32° due to the overlapping that characteristic peaks of calcium silicate hydrate with those of CAC hydrated phases. This behaviour is almost similar to the XRD patterns of pastes cured at 60°C but it looks to be more obvious than that for the pastes cured at 40°C (figure 5). The characteristic peaks of hydrogarnet (C_3AH_6) and AH_3 are found and their intensity are relatively more intense than those for figure 4 (40°C) which indicate that the conversion process is greatly affected by high curing temperature. The degree at which these peaks are decreased by the increase of the slag portions is relatively lower than that of pastes cured at 40°C. The high temperature of curing may enhance the hydration reaction of both slag types (33) which is clear as shown in figure 5 by the great changes monitored in the XRD patterns of the hydrated phases especially in the 2θ range between 30-32° and the enhancement of the characteristic peaks of the stratlingite compound (C_2ASH_8) and calcium silicate hydrate phases.

Differential Scanning Calorimetry

DSC thermograms of selected hydrated samples of CAC (M.0) and CAC/slag pastes containing 10 and 25 wt.% AS and WS namely, M.10, M.25 and C.10, C.25, respectively, cured at 20, 40 and 60°C up to 28 days are depicted in figure 6. Figure 6A shows the thermograms of CAC cured for one day of hydration at 20°C. The peak located at 100-110°C is mainly attributed to the decomposition of CAH_{10} and AH_3 gel. After 28 days of hydration at 20°C (figure 6B), there are three peaks located at 100, 180 and 254°C. The enthalpy of peak located at 100°C of CAC increases with curing time from 109.22 to 138.79 J/g. The second peak is due to decomposition of C_2AH_8. On curing at 40°C for 28 days (figure 6C), the thermogram of the neat pastes CAC shows four peaks located at 100, 180, 225 and 279°C. The enthalpy of the first peak (100°C) increases from 138.50 J/g after 28 days of hydration at 20°C to 68.96 J/g at 28 days of hydration at 40°C; this is due to the conversion reaction and deformation of AH_3 gel to γ-AH_3, which appeared at 225°C (6.22 J/g). The peak, which located at 279 C is attributed to the decomposition of C_3AH_6 (182.37 J/g). On increasing the curing temperature to 60°C (figure 6D), the thermogram show only two endothermic peaks located at 235 and 278°C attributed to γ-AH_3 and C_3AH_6 respectively. The enthalpy of the peak corresponding to C_3AH_6 increases from 182.37 J/g at 40°C to become 260.01 J/g at 60°C. At 60°C the main reaction product is the formation of C_3AH_6.

The initial hydration products of CAC paste below 20°C is CAH_{10}; above this temperature C_2AH_8 and AH_3 gel are formed [32]. These hydrates (CAH_{10} and C_2AH_8) are metastable hydrates and slowly converted to cubic stable phase (C_3AH_6). On substitution of CAC with AS or WS (one day-20°C), the enthalpies of the peak located at 100-110°C decreases with increasing slag content; this is due to the dilution of CAC. The enthalpies of these peaks were 109.22, 94.85, 83.78, 109.50 and 62.37 for M.0, M.10, M.25, C.10 and C.25, respectively (figure 6A). With the increase of curing time (28 days-20°C), the main hydration product is still CAH_{10} but show traces of C_2AH_8, AH_3 and C_3AH_6 (figure 6B). The enthalpies of the peak located at 100-110°C, which is attributed to CAH_{10} and AH_3 gel phases as a result of the overlap between these phases, were 138.79, 107.97, 121.20, 122.55 and 132.10 J/g for mixes M.0, M.10, M.25 C.10 and C.25.

At 40°C, a rapid hydration reaction takes place producing crystalline C_2AH_8 together with some amorphous materials. The hydration at 40°C is completely different (figure 6C); the C_2AH_8 was first crystallized rather than C_3AH_6. The amount of C_2AH_8 began to decrease after 7 days of hydration and C_3AH_6 appeared together with AH_3. The conversion reaction is completed after 28 days, where C_2AH_8 had disappeared. The enthalpies of the peak located at 100-110°C were 68.96, 80.21, 76.92, 89.45 and 86.96 for M.0, M.10, M.25 C.10 and C.25, respectively. The enthalpies of this peak for the pastes containing AS and WS show higher values than those of the neat CAC pastes; this is may be due to the formation of CSH (I and II) [27]. The enthalpies of the peak located at 270-280°C, which is attributed to the decomposition of C_3AH_6 were 182.37, 125.48, 99.61, 135.22 and 79.94 J/g. The enthalpies of the decomposition of C_3AH_6 decrease with the increase of slag content. The traces of C_2ASH_8 phase formed that in the hydration of CAC/AS or CAC/WS pastes are indicated in the range 180-200°C and also at approximately 220°C.

DSC thermograms of M.0, M.10, M.25 C.10 and C.25 pastes cured at 60 C for 28 days (figure 6D) show the three endothermic peaks located at 40-60, 225-235 and 275-285°C. The peak located at 40-60 appears only with the pastes containing AS or WS. The enthalpies of the peak located at 275-285°C, due to the decomposition of C_3AH_6, were 260.44, 242.02, 246.01, 257.99 and 199.48 J/g. The presence of AS and WS slags decreases the enthalpies of decomposition of C_3AH_6, i.e., decreases the conversion reaction.

Also, monocarboaluminate can be formed in this system at 20 and 40°C; this may be due to the atmospheric carbon dioxide attack [20].

The consumption of liberated Ca^{2+} ions, as a result of CAC hydration; in the slag activation inhibits the formation of calcium-rich hydrates. The reaction with silica present in slag produces C_2ASH_8. The formation of these hydration phases removes Ca^{2+} ions from the pore solution and hence restricts the conversion of CAH_{10} and C_2AH_8 to the stable cubic hydrate C_3AH_6 [21]; i.e., suppressing the extent of the conversion reaction. This is reflected on the strength development of CAC/AS or CAC/WS pastes cured at 40 and 60°C, which was greater than that of the neat CAC pastes after curing for 28-60 days.

Scanning Electron Microscopy

High-resolution SEM provides useful information on the morphology of the hydration products. The morphology and microstructure of hydrated CAC and CAC containing 25 wt.% of AS and WS cured at 20, 40 and 60°C up to 28 days are shown in figures 7-9. The micrograph of CAC paste shown in figure 7 (20°C) illustrates the presence of relatively massive areas of CAH_{10} as well as the presence of small amounts of hexagonal plates of C_2AH_8. The strong and very dense close structure of CAH_{10} and C_2AH_8 are responsible for high

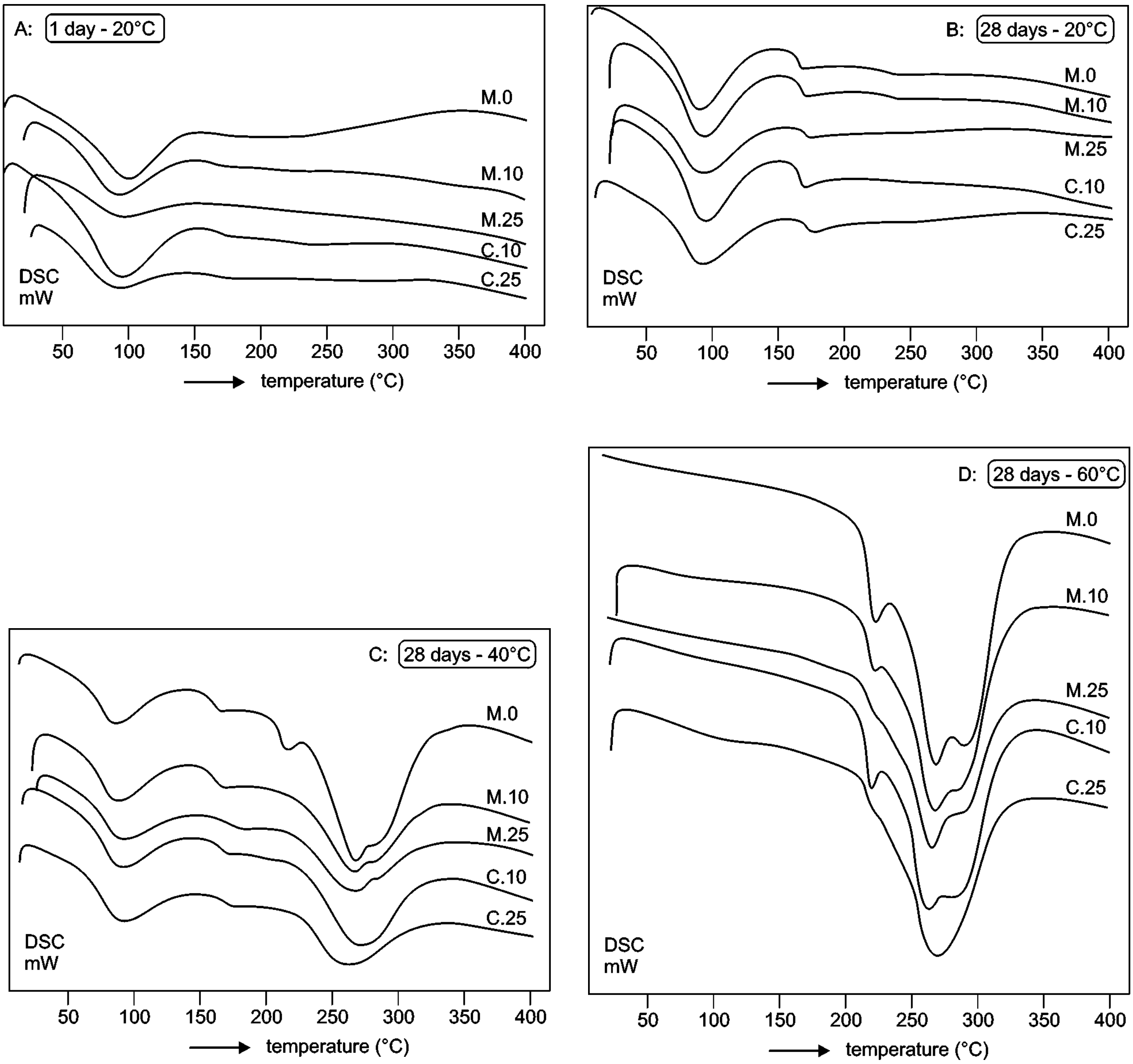

Figure 6. DSC thermograms of M.0, M.10, M.25, C.10 and C.25 cured at 20, 40 and 60°C for 28 days.

strength of CAC at the early ages of curing at 20°C. Since CAH_{10} and C_2AH_8 are thermodynamic less stable, they are converted into the stable C_3AH_6 phase at temperatures above 20°C.

The micrograph shown in figure 7 (40°C) indicates the presence of poor cubic and granular crystals of C_3AH_6 as well as AH_3 gel. The micrograph 7 (60°C) shows the presence of well-crystallized C_3AH_6. On

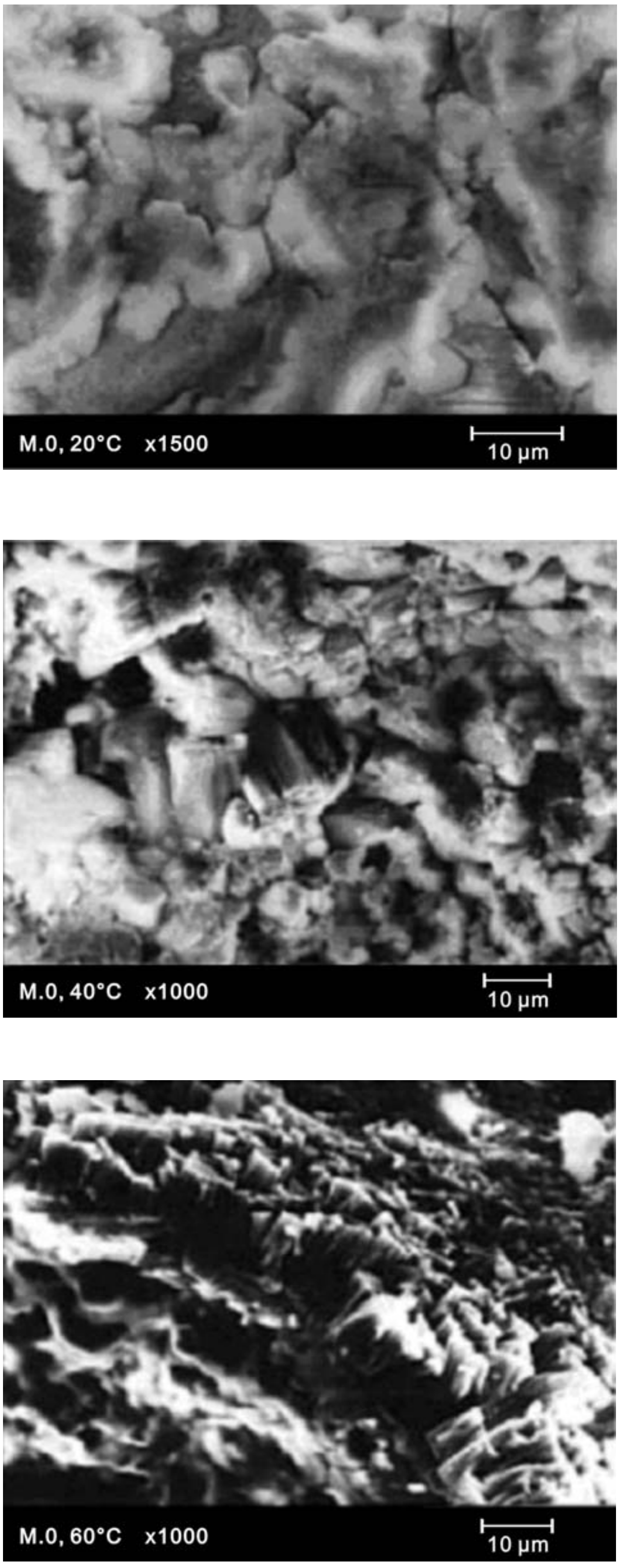

Figure 7. SEM micrographs of CAC (M.0) cured for 28 days at 20, 40 and 60°C.

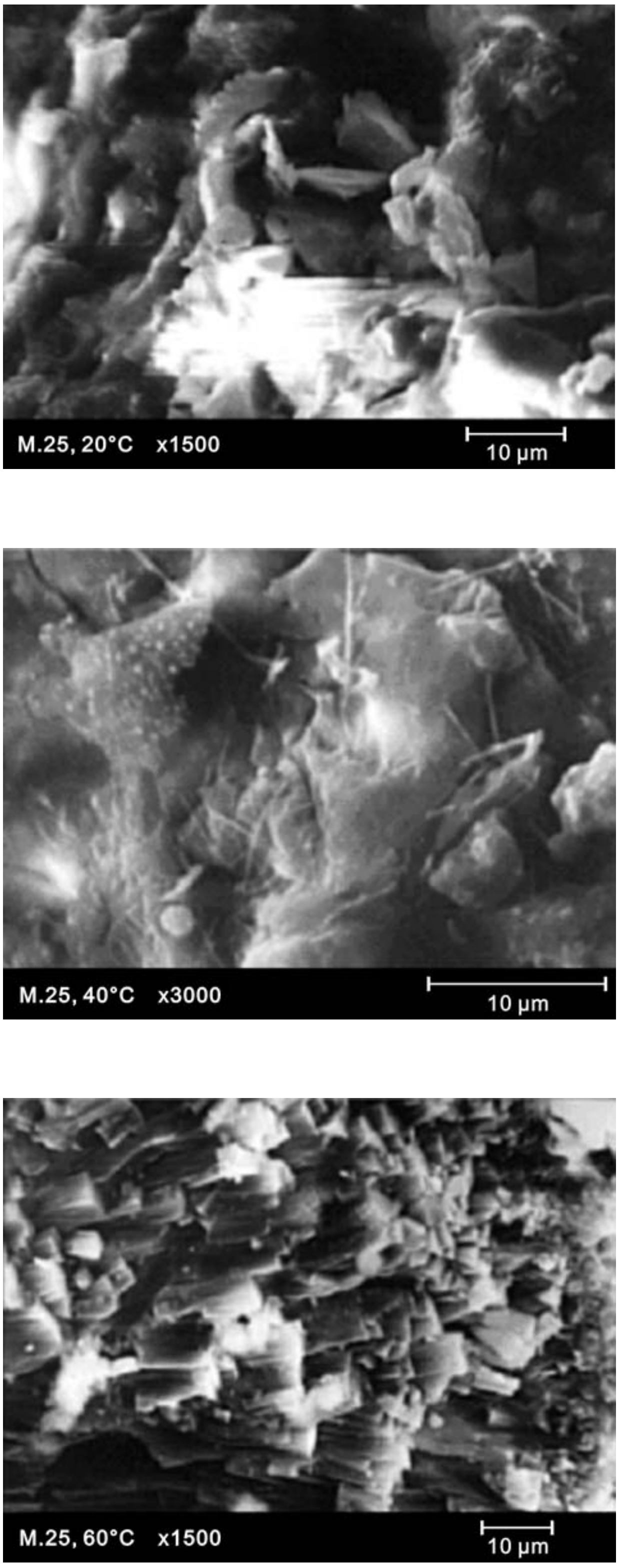

Figure 8. SEM micrographs of CAC containing 25 wt.% of AS (M.25) cured for 28 days at 20, 40 and 60°C.

increasing of the curing temperature, the conversion is faster. During the conversion process, the existing cement hydrates CAH_{10} and C_2AH_8 release water; as a result, more and more voids are formed. Consequently the porosity of the cement material consequently increases substantially. At 60°C new reaction products are formed from the anhydrous materials upon conversion to C_3AH_6 and water release. The partial transformation and well stabilization of the initial hydrates into other hydrates leads to a decrease in the compressive strength; this is due to the fact that CAC hydrated phases (CAH_{10} and C_2AH_8) undergo the conversion reaction. The structure contains pores and spaces between the hydrated products; the highly porous and weak structure may be responsible for the low strength at 40 and 60°C. The porosity of the pastes increases as indicated from the results given in table 3.

The microstructures of CAC/AS and CAC/WS are shown in figures 8 and 9. For the samples cured at 20°C, the micrograph showed a thin flaky-plate like morphology of stratlingite hydrates (C_2ASH_8) together with considerable amounts of amorphous AH_3 gel and thin fibrous particles of C-S-H; these gel compounds appeared to cover the hexagonal crystals of CAH_{10} and C_2AH_8.

The micrographs shown in figures 8 and 9 for CAC/slag samples cured at 40°C display a massive structure of well crystalline stratlingite hydrates (C_2ASH_8) as sheets of thin flaky plate like morphology which are stacked as parallel layers; which reflects a relatively more closed compact texture having plates of C_2ASH_8 together with the hexagonal crystals of the main hydrated phases of CAC and semi-crystalline fibers of C-S-H phases. The microstructure obtained at temperature of 40°C displayed the formation of dense masses of hydration products having micro and narrow pores. The plates of C_2ASH_8 are deposited within the pore system, which can accommodate larger amounts of hydration products leading to relatively higher compressive strength values of these CAC/slag pastes as compared with those of the neat CAC paste. In the presence of slag, silica fume or Portland cement clinker, the hydration of calcium aluminate cement results in the formation of stratlingite compound (C_2ASH_8) in accordance to the following equations [33]:

$$2CAH_{10} \xrightarrow{S} C_2ASH_8 + AH_3 + 9H$$

$$CAH_{10} + CSH \longrightarrow C_2ASH_8 + 3H$$

$$CAH_{10} + CSH \longrightarrow C_2ASH_8 + 2H$$

$$C_2AH_8 \xrightarrow{S} C_2ASH_8$$

$$C_2AH_8 + 2CSH + AH_3 + 3H \longrightarrow 2C_2ASH_8$$

$$C_2AH_8 + AH_3 \xrightarrow{S} C_2ASH_8 + 3H$$

Stratlingite (C_2ASH_8) was formed in significant quantities in preference to C_3AH_6 as well as little amounts of hexagonal crystals with CSH gel. Stratlingite formation is apparently promoted and hydrogarnet

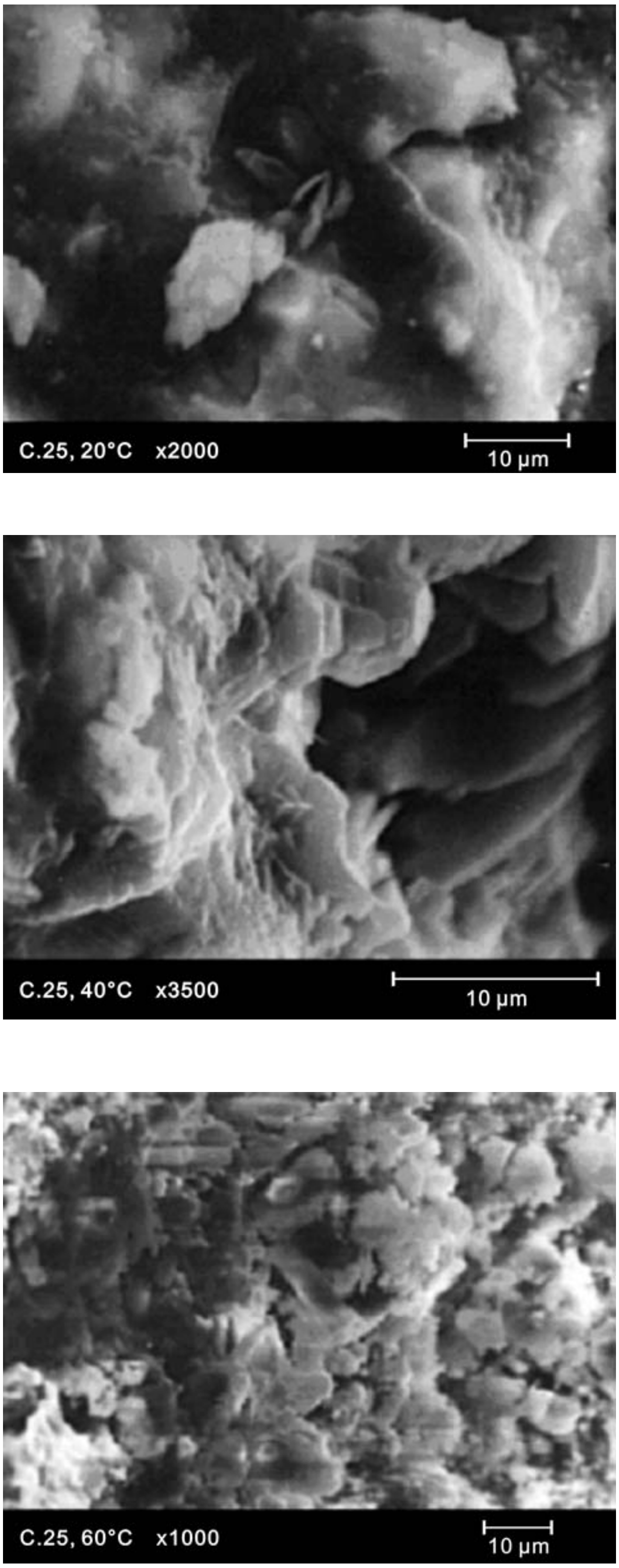

Figure 9. SEM micrographs of CAC containing 25 wt.% of WS (C.25) cured for 28 days at 20, 40 and 60°C.

formation is significantly inhibited by the addition of slag. The consumption of Ca^{2+} ions in the activation of slag inhibits the formation of calcium-rich hydrates; thus suppressing the extent of conversion reaction. Figures 7 and 8 for CAC/slag samples cured at 40°C showed that amorphous gel materials are formed around stratlingite, which may or may not crystallize eventually to C_2ASH_8. This gel may be responsible for inhibiting the formation of hydrogarnet.

As the curing temperature of for CAC/slag samples increases (figures 8 and 9 at 60°C) the micrograph showed that the cubic C_3AH_6 are embedded and covered by AH_3 gel in addition to the plates of C_2ASH_8 are deposited within the pore system but the still compact structure of CAC could be clearly distinguished as shown in the figure 7 (60°C).

CONCLUSIONS

From the above findings, it can be concluded that:

1. At 20°C the compressive strength increases with increasing slag content (AS or WS) up to 10 wt.%, then it decreases. On the increase of the curing temperature up to 40°C, the compressive strength of the neat CAC paste decreases very sharply between 7 and 28 days; whereas the pastes made of CAC/AS or CAC/WS show a progressive increase in strength with the increase of slag content. In the presence of 15-25 wt.% of slag at 28 days, there is no strength reduction and the results show nearly the same strength values obtained at 7 days. This indicates that the additions of 15-25 wt.% of slag in CAC/slag blends are sufficient to suppress the strength reduction as a result of conversion reaction.
2. The increase of slag contents up to 10 wt.% increases the bulk density. On the other hand, by increasing of curing temperature to 40°C, the bulk density of CAC decreases where the apparent porosity increases. The increase of curing temperature enhances the proceeding conversion reaction to form the stable C_3AH_6 phase from the metastable phases (CAH_{10} and C_2AH_8). As the slag content increases, the bulk density increases, whereas the porosity decreases. The bulk density values at 60°C are higher than those at 20 and 40°C, whereas, the apparent porosity values are lower than the values measured at 20 and 40°C.
3. The micrographs of CAC/AS or CAC/WS blends cured at 40°C show a massive structure of well crystalline stratlingite hydrates (C_2ASH_8) which appeared as sheets of thin flaky plate like morphology stacked as parallel layers, which reflects a relatively more closed-textured structure. C_2ASH_8 are deposited within the pore system, which can accommodate larger amounts of hydration products leading to relatively higher compressive strength values of CAC/slag pastes as compared with those of the neat CAC paste.

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VLIV TEPLOTY TUHNUTÍ NA FYZIKÁLNĚ MECHANICKÉ CHARAKTERISTIKY VÁPENATOHLINITÉHO CEMENTU S PŘÍDAVKEM STRUSKY

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Metodami diferenční skanovací kalorimetrie (DSC), rentgenové difrakční analýzy (XRD) a skanovací elektronové mikroskopie (SEM) byla sledována povaha, posloupnost tvorby, krystalinita a mikrostruktura hydratovaných fází. Výsledky ukázaly, že tvorba odlišných hydratovaných fází je teplotně závislá. Studium fyzikálně mechanických a mikrostrukturálních charakteristik provedených po tuhnutí při 20, 40 a 60°C ukázalo, že při náhradě vápenatohlinitého cementu (CAC) struskou chlazenou na vzduchu (AS) nebo ve vodě (WS) při 20°C roste pevnost v tlaku do obsahu 10 hmot.%. Při vyšších obsazích strusky (do 25 hmot.%) pevnost v tlaku klesá; je však pro různé doby tuhnutí (do 60 dní) stále vyšší než pro čistý CAC. Po 28 dnech hydratace při 40-60°C roste pevnost v tlaku s obsahem strusky. To je způsobeno zabráněním konverzní reakce, která byla potvrzena XRD, DSC a SEM a preferencí tvorby stratlingitu gehleintového typu. SEM fotografie ukázaly uzavřenou texturu hydratovaných CAC směsí následkem tvorby C_2ASH_8 a C-S-H fází.