Available online at www.sciencedirect.com

SCIENCE DIRECT®

Cement and Concrete Research 35 (2005) 1601–1608

Cement and Concrete Research

Hydration characteristics of tricalcium aluminate phase in mixes containing β-hemihydate and phosphogypsum

M.M. Radwan[a], M. Heikal[b,*]

[a]National Research Center, Dokki, Cairo, Egypt
[b]Chemistry Department, Faculty of Science, Zagazig University, Benha Branch, Benha, Egypt

Received 19 November 2002; accepted 14 June 2004

Abstract

The tricalcium aluminte phase was prepared from pure chemicals on a laboratory scale. Five mixes were formulated from the prepared C_3A phase, β-hemihydate, phosphogypsum, calcium hydroxide and quartz. Different mixes were hydrated at various time intervals, namely, 6, 24, 72 and 168 h. The kinetics of hydration was measured from chemically combined water and combined lime contents. The phase compositions and microstructures of the hydrated products were studied by X-ray diffraction (XRD), differential thermal analysis (DTA)/TG, scanning electron microscopy (SEM) techniques and FT-IR spectroscopy. This work aimed to study the effect of partial to full substitution of phosphogypsum by β-hemihydate on the hydration characteristics and microstructures of tricalcium aluminte phase. The results showed that the combined lime slightly increases with the increase of amounts of phosphogypsum. The XRD patterns showed the increase in the intensities of monosulphate and different forms of calcium aluminate (C_4AH_{13} and C_4AH_{19}) with phosphogypsum content. Ettringite is less stable than monosulphoaluminate, so it transformed into monosulpho-aluminate after 24 h, which persisted up to 168 h. The mechanism of the hydration process of C_3A phase in the presence of phosphogypsum proceeds in a similar path as with β-hemihydate. Phosphogypsum reacts with C_3A in the presence of $Ca(OH)_2$ forming sulphoaluminate hydrates, which are responsible for setting regulation in cementitious system.

Keywords: Phosphogypsum; Tricalcium aluminate; Hydration kinetics; X-ray diffraction and microstructure

1. Introduction

Large quantities of industrial by-products are produced every year by chemical and agricultural industrials. These materials have dual problems of disposal and health hazards. In Abo-Zaabal, Cairo, Egypt, a few factories produces phosphatic fertilizer and chemical industries, which generate large quantities of phosphogypsum that are currently being disposed by damping into pond or wastelands. In Egypt, phosphogypsum is produced from phosphoric acid manufacture by dihydrate process. The annual production of phosphogypsum is about 300,000 tons, which causes serious storage and environmental pollution. Due to increasing concerns about environmental pollution, it is important to utilize these wastes as building materials to save the environmental from degradation. The use of phosphogypsum is of interest for many researchers [1–6].

Attempts have been made by several authors [7–9] to use phosphogypsum and fluorogypsum in the manufacture of cement. The impurities of P_2O_5, F^-, organic matter and alkalis present in the gypsum adversely affect the setting and hardening of cement [10]. The effect of waste phosphogypsum and fluorogypsum on the properties of Portland cement and Portland slag cement was studied. The natural gypsum was blended with by-product gypsum to reduce the adverse effect of impurities of P_2O_5 and F^- present in this type of gypsum.

This work aimed to study the possibility of using phosphogypsum as a set controller to the hydration process of C_3A in the presence and in the absence of β-hemihydate.

---

* Corresponding author. Tel./Fax: +2 013 222578.
E-mail address: ayaheikal@hotmail.com (M. Heikal).

doi:10.1016/j.cemconres.2004.06.037

Although the proportion of C_3A in OPC is relativity low, it exerts a very significant role on the setting property and heat of hydration during hydration. In a previous study, it has been shown that the presence of phosphogypsum in cement pastes did not adversely affect the setting times and improves the workability of cement pastes. Phosphogypsum enhances the kinetics of hydration and mechanical properties as well as the rate of hydration as indicated from differential thermal analysis (DTA) up to 90 days [11].

In the system $CaO \cdot Al_2O_3 \cdot H_2O$, different hydration products of calcium aluminate hydrates have been identified. CAH_{10}, C_2AH_8 and C_4AH_{19} were formed at temperatures below 50 °C. It was found that the metastable hydration products of C_3A were C_2AH_X and C_4AH_X. In saturated lime solution, the formation of C_4AH_{13} or C_3AH_6 formation depends on the condition of hydration reactions [12,13].

It was stated that the role of gypsum in the retardation of the reaction of C_3A is mainly due to the reduction of the solubility of C_3A as a result of the sulphate reaction. The formation of thin layer of ettringite on the surface of anhydrous C_3A crystal will control the diffusion of SO_4^{2-} ions through this layer. The formation of ettringite directly on the C_3A grains produces a sort of crystallization pressure, which leads to bursting of the ettringite layer caused by the pressure of crystallization. This burst section is sealed by newly formed ettringite. When the sulphate content is depleted (insufficient sulphate ions to allow formation of ettringite), on further hydration of the C_3A, ettringite converts to monosulphate [14,15].

A comparison study of the hydration characteristics of C_3A in the presence of raw gypsum and phosphogypsum was done.

2. Materials and experimental

2.1. Preparation of tricalcium aluminate (C_3A)

C_3A had been prepared at the laboratory by firing at appropriate temperatures the stoichiometric composition of this phase using highly pure limestone (99.0% $CaCO_3$) and technically pure $A1_2O_3$ (99.0%) with molar ratio 3:1, CaO/Al_2O_3, respectively; then, the mixture was pressed under 100 kg/cm^2 pressure. The prepared specimens were calcined at 1000 °C for 2 h. After cooling, they were crushed and ground in absolute ethanol to complete homogeneity, then remoulded and fired at 1350 °C for 3 h. Firing of the mix was repeated until nearly complete formation of this phase occurred. The final product was tested for their free lime and insoluble residue contents. The fired products were crushed and finely ground to a Blaine surface area of 3000 cm^2/g. The XRD traces of the prepared C_3A are shown in Fig. 1. The chemical composition of the utilized phosphogypsum was shown in Table 1. DTA thermograms of β-hemihydrate and phosphogypsum are represented in Fig. 2. The thermogram of β-hemihydrate shows endothermic peak located at 200 °C. On the other hand, phosphogypsum shows two endothermic peaks, the first located at 170 °C, which is due to dehydroxlation of 1.5 molecules of water of phosphogypsum to form β-hemihydrate and the second peak at 200 °C is due to the decomposition of β-hemihydrate to $CaSO_4$.

2.2. Preparation of the anhydrous mixes and hydrating pastes

Table 2 shows the prepared mixes of C_3A phase with other ingredients. For each mix, these were thoroughly mixed in a porcelain ball mill to ensure complete homogeneity. β-hemihydrate was prepared form the nearly pure alabaster gypsum sample (99% $CaSO_4$). It was preground to a Blaine surface area of ≈3000 cm^2/g. The required amount of mixing water was added to each mix and the ingredients were mixed for 3 min and the pastes then moulded into 1-in. cubes which were compacted to remove air bubbles and then in a 100% RH at 23±2 °C for 24 h. After demoulding, the cubes were stored under water until time of testing.

In this study, β-hemihydrate was used instead of gypsum because of the relatively higher solubility of β-hemihydrate than that of raw gypsum to detect the different hydration reaction rates of phosphogypsum and β-hemihydrate. The main target of this work is the investigation of the acceleration effect of the impurities that is present in phosphogypsum, which was emphasized in this investiga-

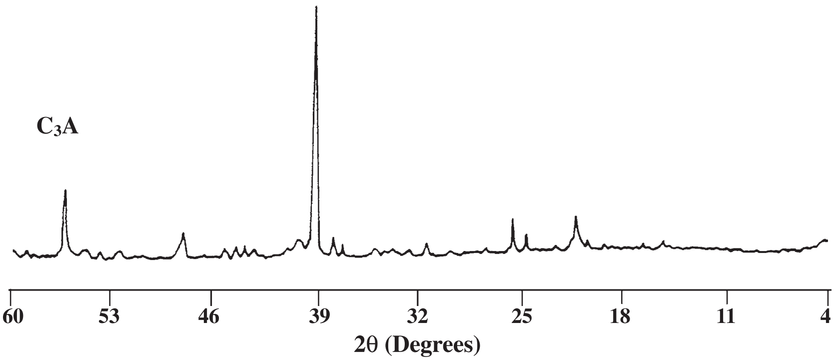

Fig. 1. XRD patterns of the prepared anhydrous C_3A phase.

Table 1
Chemical oxide composition of phosphogypsum (mass%)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	P_2O_5	F^-	Cl^-	L.O.I
Phosphogypsum	8.78	0.29	0.35	32.13	0.09	37.60	1.82	0.80	–	18.25

tion as being found in the results of combined water. $Ca(OH)_2$ was added to maintain the condition as in the case of OPC clinker as it is incorporated in the reaction of the aluminate phase with the calcium sulphate (especially with the free excess C_3A phase) [13]. Finely ground quartz silica was added to mixes at a constant proportions (10 mass%). The presence of finely ground quartz affects the crystallization of ettringite and helps to maintain the system in similar conditions to which cement is used [16].

2.3. Methods of investigation

In this investigation, the compressive strength was not considered as the hydration products are expansive and have no mechanical properties but we mean only the crushing and grinding of the sample for the rest of tests. Pulverizing 10 g of representative sample after each hydration period stopped the hydration reaction; this was placed in a beaker containing 1:1 methanol–acetone mixture, and then mechanically stirred for 1 h. The mixture was filtered through a gooch crucible, G4, and washed with ether. The solid was then dried in a CO_2-free atmosphere at 70 °C for 30 min to evaporate the alcohol.

The combined water is the percent of ignition loss of dried samples on the ignited weight basis. Approximately 2 g of the predried sample was gradually ignited up to 1000 °C for 30 min soaking time. The results of combined water were corrected for the water contents of free lime and the raw materials (phosphogypsum and β-hemihydate).

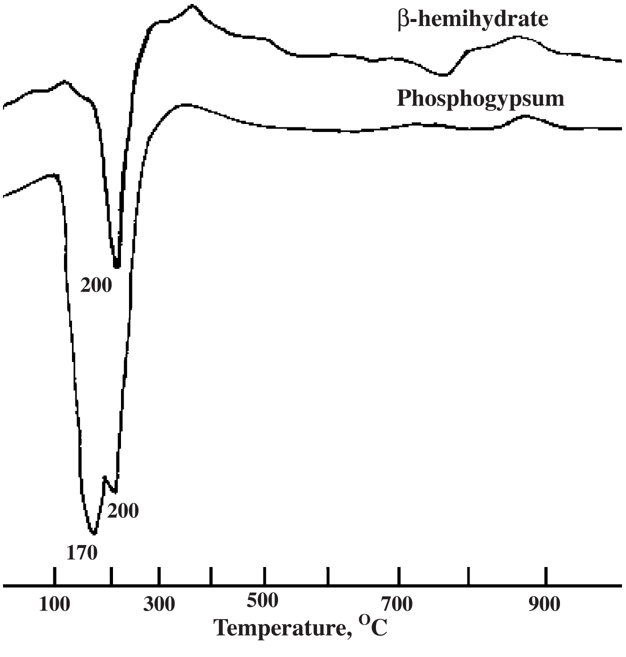

Fig. 2. DTA of phosphogypsum and β-hemihydrate.

The determination of $Ca(OH)_2$ is based on extraction of Ca^{2+} by ethylene glycol method [17]. Free lime present in the sample will react with ethylene glycol, forming calcium glycolate. This glycolate was titrated with standard hydrochloric acid. About 0.5 g of sample is placed in small conical flask with 25 ml of ethylene glycol. The flask is closed with air reflux and shaken in a water bath at 60–70 °C for 1 h. The sample was filtered through filter paper on a porcelain crucible; the filter paper was washed three times with about 15 ml ethylene glycol. The filtrate was titrated with standardized 0.1 N aqueous HCl by using phenolphthalein as indicator until the pink colour just disappeared (end point). The combined lime was calculated from the difference between lime added at zero time (15 mass%), and the residual free lime at the prescribed time.

The crystalline phases present were identified using X-ray diffraction (XRD) technique. This technique was also carried out for some selected samples of the hydrated cement pastes. Ni-filtered Cu–k_α radiation at 40 kV and 25 mA with a scanning speed 2θ of °2 min^{-1} was used in a Philips diffractometer (PW 1050/70). The sample was finely ground to pass a 200-mesh sieve. The XRD patterns were converted to a series of lattice spacings d Å and the relative intensities were visually estimated.

Some selected hydrated samples were investigated using a differential thermal analyzer of the type Schimaduz DTA-30 thermal analyzer (Co-Kyoto, Japan). A sample of 20 mg was housed in a small Pt–Rh crucible with a heating rate of 10 °C/min, using α-Al_2O_3 as a reference sample.

Infrared spectral analysis was carried out on some selected samples of hydrated pastes to provide additional information on the hydrated products. One milligram of the powder sample was ground with 99 mg of potassium bromide in an agate mortar to produce a homogeneous mixture. The infrared spectral analysis was recorded from KBr-discs using Genesis-II FT-IR spectrometer in the range 300–4000 cm^{-1}.

Table 2
Mix design of the investigated mixed of C_3A, β-hemihydrate, phosphogypsum, $Ca(OH)_2$ and quartz (mass%)

Mix no.	mass%				
	C_3A	$Ca(OH)_2$	β-hemihydrate	Phosphogypsum	Quartz
C.0	55	15	20	0	10
C.5	55	15	15	5	10
C.10	55	15	10	10	10
C.15	55	15	5	15	10
C.20	55	15	0	20	10

3. Results and discussion

3.1. Chemically combined water contents

Chemically combined water contents of the prepared pastes from different mixes of tricalcium aluminate, β-hemihydrate and phosphogypsum are depicted in Fig. 3 as a function of curing time up to 168 h. Investigation of the results indicates that, the values of chemically combined water contents generally increase with the curing time from 6 up to 168 h. At early hydration period (6 h), chemically combined water contents decrease with the phosphogypsum content; this is due to the impurities present in the phosphogypsum, such as P_2O_5, F^- and organic matter. As shown in Fig. 3, the behavior of C.0, C.5 and C.10, which contain 0, 5 and 10 mass% phosphogypsum, respectively, is almost nearly the same. With an increase of the amount of phosphogypsum at the expense of β-hemihydrate in Mixes C.15 and C.20 (15 and 20 mass% phosphogypsum), the values of chemically combined water contents decrease at 6 h. The presence of phosphogypsum decreases the rate of hydration of tricalcium aluminate during the first few hours. However, chemically combined water content shows sharp increase from 24 up to 72 h, which indicates an acceleration in the process of hydration. During the course of hydration reaction, there is a great tendency for the chemical reaction between C_3A phase and β-hemihydrate as well as phosphogypsum in the presence of $Ca(OH)_2$ which already exists in each mix composition (15 mass%) to give high and low forms of calcium sulphoaluminate, i.e., $C_3A \cdot 3CaSO_4 \cdot 32H_2O$ and $C_3A \cdot CaSO_4 \cdot 12H_2O$, respectively. In addition, C_3A phase will hydrate to form different calcium aluminate hydrate phases. However, the increase of the combined water contents of the hydrated pastes of C.15 and C.20 after 24 h of hydration may be attributed to the enhancement of ettringite formation [18].

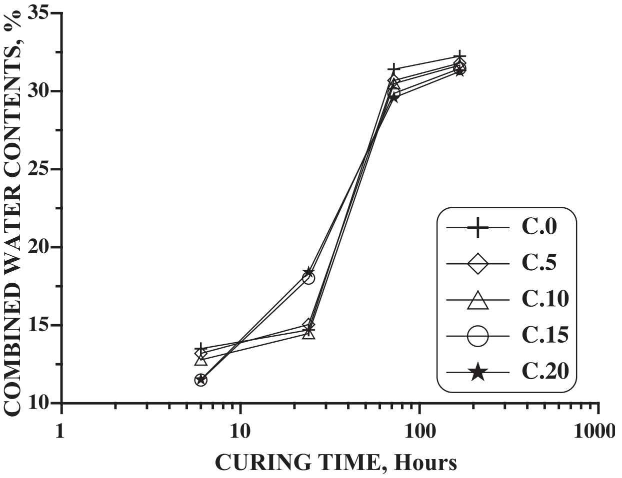

Fig. 3. Chemically combined water contents of tricalcium aluminate hydrated as a function of curing time and phosphogypsum contents up to 20 mass%.

Due to the relatively high solubility of β-hemihydrate compared with the raw gypsum, it was expected that the reaction between phosphogypsum and C_3A will proceed via lower rate than that between C_3A and β-hemihydrate; but as was found in the study, there is a great similarity in the rate of reaction of both materials used and C_3A which is connected with the expected acceleration effect of the impurities contaminated with phosphogypsum on the rate of its reaction with C_3A phase. The presence of impurities (F^- and/or P_2O_5) activates the formation of ettringite. Ettringite is less stable, which transformed to more stable phase (monosulphate) at longer hydration ages resulting to a decrease in the chemically combined water of these two mixes after 72 and 168 h. This result will be confirmed by investigating the samples by DTA and XRD in addition to the combined lime contents.

3.2. Combined lime contents

It was mentioned before that a fixed percent of $Ca(OH)_2$ (15 mass%) was added to each mix to furnish a suitable condition for the formation of sulphoalumintes. As was mentioned before, the presence of $Ca(OH)_2$ maintain the same alkaline condition as in the case of OPC clinker and is incorporated in the hydration reaction of C_3A in the presence of $CaSO_4$. The lime was partially consumed during the reaction of C_3A on one side and on the other side with $CaSO_4$. The consumed lime content (combined lime) can be calculated and considered as an indication of the extent of hydration reactions to form the above mentioned phases, which formed within the five different mixes. These are graphically represented as a function of curing time and the amount of phosphogypsum substituted in Fig. 4. It is well known that the reaction between $CaSO_4$ and C_3A phase proceeds in the presence of $Ca(OH)_2$ in the reaction medium. Fig. 4 shows that at all curing ages, the combined lime slightly increases with the amounts of phosphogypsum. Mixes C.15 and C.20 that contain the higher proportion of phosphogypsum (15 and 20 mass%) have higher combined lime content than the other mixes. This indicates that there is a little acceleration effect on the hydration reaction of C_3A phase due to the presence of phosphogypsum, which confirms the results of combined water. This acceleration effect leads to the consumption of more lime as the amount of phosphogypsum increases, and increases the probability of the formation of C_4AH_{13}.

3.3. Differential thermal analysis

The paste samples of all mix compositions hydrated for 7 days have been investigated by DTA. The thermal effect on the DTA curves obtained for the hardened pastes are illustrated in Fig. 5. Investigation of the DTA curves shows characteristic endotherms at about or around 130, 225, 310, 425, 515 and 825 °C, representing dehydration, dehydroxylation or calcination of residual ettringite, monosulphoa-

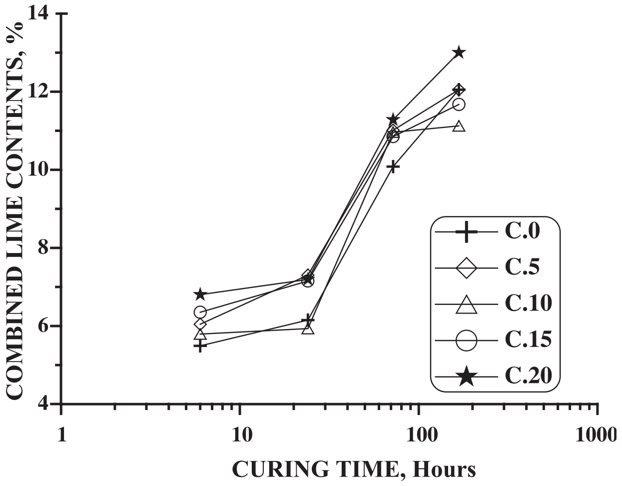

Fig. 4. Combined lime content of tricalcium aluminate hydrated as a function of curing time and phosphogypsum contents up to 20 mass%.

luiminate, C_3AH_6 and C_4AH_{13}, $Ca(OH)_2$ and calcium carbonate. As can be seen from Fig. 5, the endothermic peak at about 130–140 °C, characterizing the dehydration of ettringite, is sharply diminished with the increase of the amount of phosphogypsum substituted for β-hemihydrate from Mix C.0 to C.20. This means that the ettringite transformed to monosulphoaluminate. The strong endothermic effect appears at about 225 °C, characteristic of monosulphoaluminate. The endothermic shoulder at about 310 °C is due to C_3AH_6. These peaks show slight increase with the phosphogypsum content. Ettringite is less stable than monosulphoaluminate; thus, it is transformed into monosulphoaluminate after 24 h, which persisted up to 168 h [19]. The endothermic peak at 425 °C illustrates the decomposition of C_3AH_6 and C_4AH_{13} [12]; this shoulder shows a little increase with phosphogypsum, which is confirmed later by XRD technique.

As can be seen in the present paper, the main material in all mix compositions is C_3A which represents about 55 mass% and the maximum amounts of both hemihydrate and phosphogypsum represent about only one third of the amount of C_3A; the maximum ratio at which the reaction between C_3A and $CaSO_4$ is 1:1, which means that there will be an excess free C_3A phase that will be hydrated with the excess mixing water in the presence of $Ca(OH)_2$ added to form the C_4AH_{13} phase. During the hydration of the free excess C_3A, there will be a possibility for the formation of CAH_{10}, which is not a stable phase, and will be converted to the more stable C_3AH_6 phase [13].

The peak at 525 °C represented the dehydration of residual hydrolime ($Ca(OH)_2$). The intensity of the endotherm due to residual hydrolime in the thermograms slightly varies as it is partially entered in the hydration reaction of C_3A in the presence of both gypsum and phosphogypsum. The last endothermic peak, which is located at 835 °C, is attributed to the calcination of calcium carbonate present as contaminated by impurities with β-hemihydrate and/or by partial carbonization of the added hydrolime.

By comparing Fig. 2 with Fig. 5, it can be seen that the characteristic endotherms of both β-hemihydrate and phosphogypsum show endothermic peak located at 200 °C, which was not detected in the DTA curves of the tested pastes shown in Fig. 5. This indicates that nearly all of the amounts of β-hemihydrate and phosphogypsum were consumed in the hydration reaction of C_3A phase forming the sulphoaluminate phases as the maximum amount of both materials added represents only one third of the quantity of C_3A phase present in each mix composition.

3.4. X-ray diffraction

Fig. 6 shows the XRD patterns of Mixes C.5, C.10 and C.15 hydrated for 72 h. The patterns show the presence of ettringite, monosulphate, $Ca(OH)_2$, quartz, C_4AH_{13}, C_4AH_{19} and C_3AH_6. The presence of finely ground quartz in the prepared mixes does not play any role in the hydration reaction but only affects ettringite crystallization [16]. Quartz surfaces counteract the retardation of SO_4^{2-} on the hydration of C_3A by presenting additional sites for ettringite crystallization or by influencing the nucleation of the hydration products.

At early stages of hydration, the ettringite phase started to form with the consumption of lime and sulphate while the combined water increases. As long as SO_4^{2-} diffused between the ettringite crystals towards C_3A, the ettringite remains stable. If, however, no SO_4^{2-} reaches the C_3A, ettringite is converted into monosulphate and C_4AH_{19} [16].

It has been mentioned that the trisulphoaluminate (ettringite) in this system is less stable than monosulphoaluminate; hence, it is transformed into monosulphoaluminate after 24 h and it persisted up to 168 h. As the content of phosphogypsum increases, the intensity of ettringite peaks

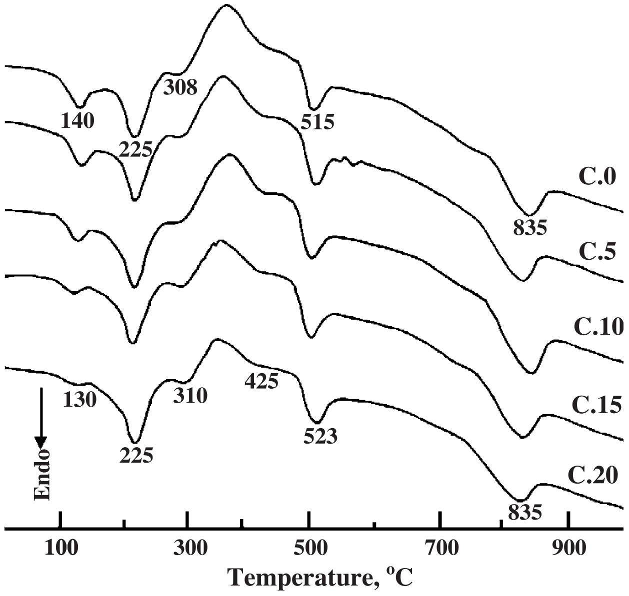

Fig. 5. DTA of tricalcium aluminate hydrated at 7 days (168 h) in the presence or absence phosphogypsum.

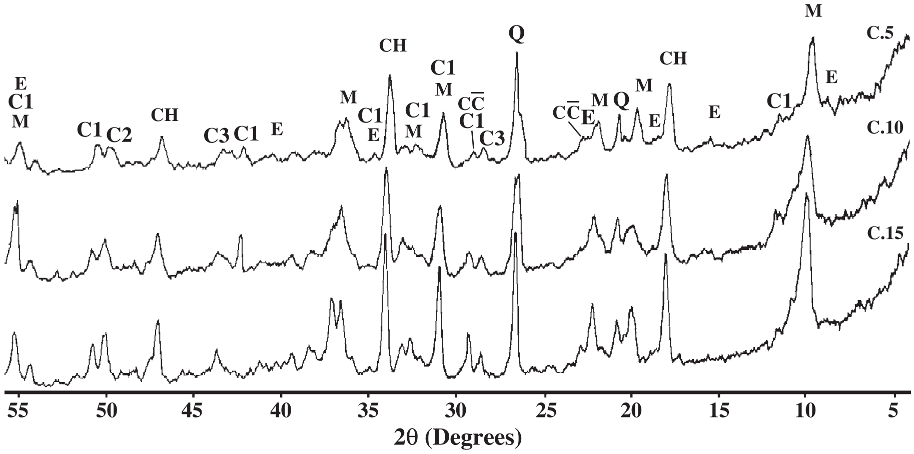

Fig. 6. XRD patterns of Mixes C.5, C.10 and C.15 hydrated at 168 h (5, 10 and 15 mass% phosphogypsum); E, ettringite; M, monosulphoaluminate; CH, $Ca(OH)_2$; C1, C_4AH_{13}; C2, C_4AH_{19}; C3, C_3AH_6; $C\bar{C}$, $CaCO_3$.

decrease as a result of the transformation to monosulphate. The patterns also showed an increase in the intensities of different forms of calcium aluminate (C_4AH_{13}, C_4AH_{19} and C_3AH_6). The intensity of these forms of calcium aluminates increases with the content of phosphogypsum. This is due to the larger amounts of C_3A (55%) compared with SO_4^{2-} content. In addition, the peak intensities representing the monosulphate increase with the prolongation of curing time and phosphogypsum content. The characteristic peaks of $CaCO_3$ were detected by XRD patterns.

3.5. *FT-IR spectroscopy*

FT-IR spectroscopy is one of the most powerful techniques normally used for molecular characterization. In particular, the FT-IR results have been used to resolve the hydroxyl bonds and to monitor the dynamics changes in the sulphate region during hydration reactions. In addition, the effect of atmospheric carbon dioxide on the hydration can be characterized. Fig. 7 shows FT-IR spectra of the hydrated samples of different mixes for 6 h. The spectral data are seen in three regions: the water region (>1000 cm^{-1}), the sulphate region ($\approx$1100–1160 cm^{-1}) and the region (<1000 cm^{-1}).

The water regions give information about the mechanism of early hydration reaction. There are three bands in the range of 3700–3100 cm^{-1}. $Ca(OH)_2$ gives a peak at 3640 cm^{-1}; ettringite has one at 3420 cm^{-1} and a weaker one at 3600 cm^{-1}; and monosulphate has one at 3100, 3500 (broad), 3540 and 3675 cm^{-1}. The broad band centered at 3400 cm^{-1} is due to symmetric and asymmetric (υ_1 and υ_2) stretching vibration of O–H water molecule. The water

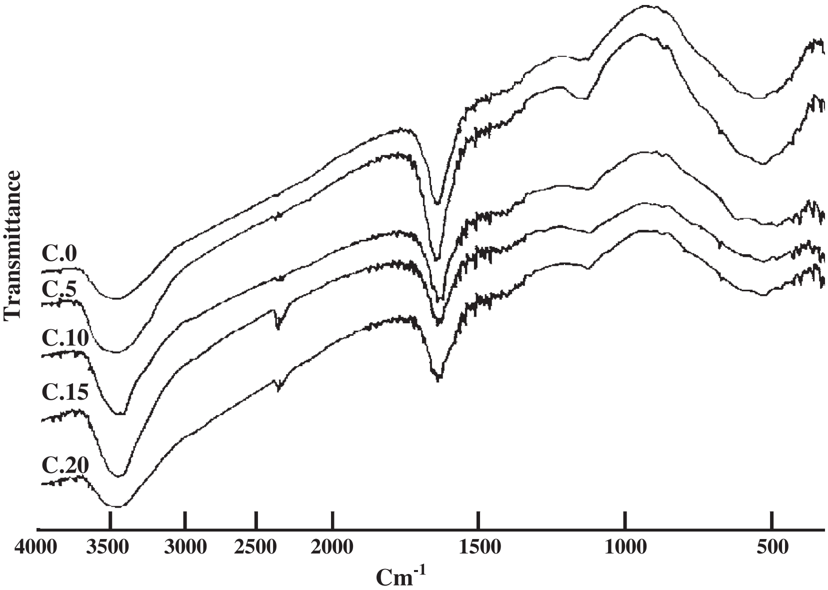

Fig. 7. FT-IR spectroscopy of hydrated C_3A phase at 6 h in the presence or absence of phosphogypsum.

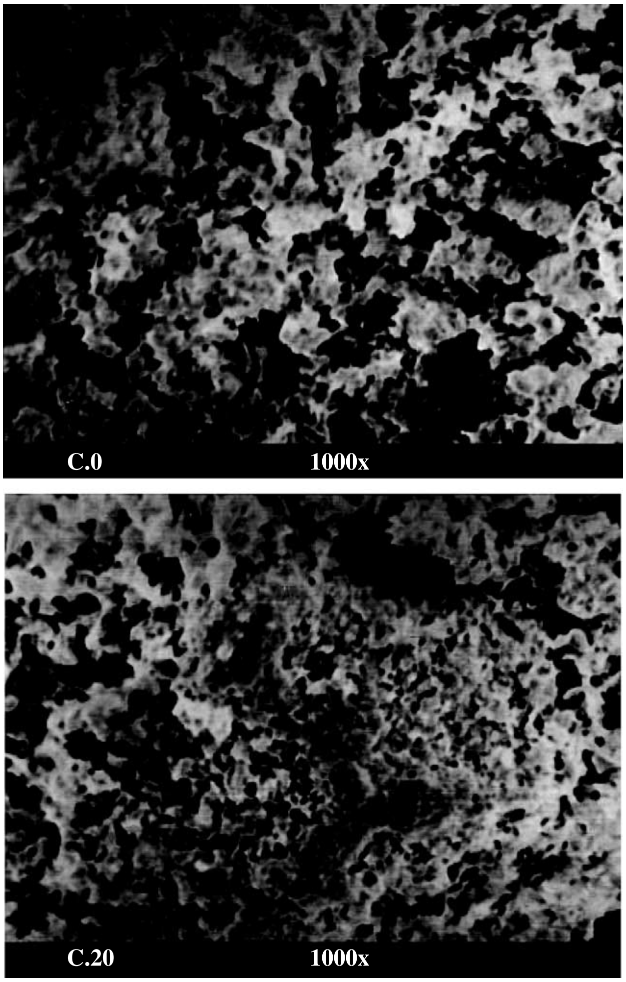

Fig. 8. SEM of tricalcium aluminate hydrated at 7 days of Mixes C.0 and C.20.

stretching region ($\approx$3460–3440 cm^{-1}) becomes broader with the reaction time; this is due to the molecular water. In addition, it was found that the bending vibration of water can be seen at 1640 cm^{-1}. The ettringite phase is the main hydration product in this study at early ages. Upon hydration time, there is a change in sulphate absorption to a singlet, and the subsequent replacement of ettringite to monosulphate by a further return to doublet [13]. The peaks located at 1120 and 1180 cm^{-1}, which is due to υ_3–SO_4^{2-}, supported the presence of ettringite and monosulphate. The peaks located at 1640 and 1680 cm^{-1} were assigned to the deformation of water mode in these phases [20]. The carbonate bands at 1420–1480 cm^{-1} arise from the atmospheric CO_2 with the residual $Ca(OH)_2$ [21]. The hexagonal hydrate and monocarbonate were detected in spectra with split bands υ_3–CO_3^{2-} (1416–1370 cm^{-1}) together with υ_2–CO_3^{2-} (875 cm^{-1}) and υ_3–CO_3^{2-} (712 cm^{-1}).

The FT-IR spectra of C_2AH_8 and C_4AH_{13} showed similarities, as hexagonal plate-type structure, usually overlapped if more than one hexagonal aluminate coexist [22], but these were significantly different from the spectra of cubic hydrate (C_3AH_6).

3.6. Scanning electron microscopy

Fig. 8 shows SEM of Mixes C.0 and C.20, which contained 0 and 20 mass% phosphogypsum, respectively. The micrograph of Mix C.0 shows very small amount of ill-crystallized fibrous-shaped ettringite in addition to hexagonal crystals of monosulphate and C_4AH_{13}.

The micrograph of Mix C.20 shows a closer texture of hexagonal crystals. This is due to the presence of phosphogypsum impurities [23].

4. Conclusions

From the above findings, it can be concluded that:

(1) At early hydration period (6 h), the chemically combined water contents decrease with the proportion of phosphogypsum. With the increase of the amount of phosphogypsum (15 and 20 mass% phosphogypsum), the values of chemically combined water contents decrease at 6 h.
(2) The combined lime slightly increases with the increase of amounts of phosphogypsum in the mix.
(3) DTA shows that the endothermic peak at about 130–140 °C, which characterizes the dehydration of ettringite, is sharply diminished with the increase of the amount of phosphogypsum; that is, ettringite transformed to monosulphoaluminate. It has been mentioned that the trisulphoaluminate (ettringite) in this system is less stable than monosulphoaluminate; thus, it is transformed into monosulphoaluminate after 24 h and persisted up to 168 h.
(4) The XRD patterns showed the increase in the intensities of monosulphate and different forms of calcium aluminate (C_4AH_{13}, C_4AH_{19} and C_3AH_6 with phosphogypsum content).
(5) Phosphogypsum reacts with C_3A in the presence of $Ca(OH)_2$ forming sulphoaluminate hydrates, which are responsible for setting regulation in cementitious system. The mechanism of the hydration process of C_3A phase in the presence of phosphogypsum proceeds in a similar manner to that with β-hemihydate.

References

[1] P. Yan, W. Yang, X. Qin, Y. You, Microstructure and properties of the binder of fly ash–fluorogypsum–Portland cement, Cem. Concr. Res. 29 (3) (1999) 349–354.
[2] P. Yan, Y. You, Studies on the binder of fly ash–fluorgypsum–cement, Cem. Concr. Res. 28 (1) (1998) 135–140.
[3] M. Singh, M. Garg, Cementitious binder from fly ash and other industrial wastes, Cem. Concr. Res. 29 (3) (1999) 309–314.
[4] N. Bhanumatidas, N. Kalidas, NCB International seminar on cement and building materials. Science and Technology, New Delhi, India. (1996) 3, 55.

[5] M. Singh, M. Garg, Relationship between mechanical properties and porosity of water-resistant gypsum binder, Cem. Concr. Res. 26 (3) (1996) 449–455.

[6] M. Singh, M. Garg, S.S. Rehsi, Purifying phosphogypsum for cement manufacture, Constr. Build. Mater. 7 (1) (1993) 3–7.

[7] H. Olmez, F. Frdem, The effect of phosphogypsum on the setting and mechanical properties of Portland cement and trass cement, Cem. Concr. Res. 19 (1989) 337–384.

[8] A. Tabhikh, F.M. Miller, The nature of phosphogypsum impurities and their influence on cement hydration, Cem. Concr. Res. 1 (1971) 663–678.

[9] M. Singh, Utilization of by-product phosphogypsum for building materials, Building Research Note, vol. 9, CBRI Publication, Roorkee, India, 1988 (March).

[10] M. Singh, Influence of phosphogypsum impurities on two properties of Portland cement, Indian Concr. J. 61 (1987) 186–190.

[11] H. El-Didamony, S.A. El-Alfi, M.M. Elwan, Influence of substitution of nature gypsum by phosphogypsum on the properties Portland cement, Sil. Ind. 67 (1–2) (2002) 9–14.

[12] V.S. Ramachandran, Application of Differential Thermal Analysis in Cement Chemistry, Chemical Publishing, New York, 1969.

[13] H.F.W. Taylor, Cement Chemistry, Academic Press, New York, 1990.

[14] P.C. Hewlett, Lea's Chemistry of Cement and Concrete, 4th ed., Edward Arnold, London, 1998.

[15] J. Havlica, D. Roztocka, Hydration kinetics of calciumaluminate phases in the presence of various ratios of Ca^{2+} and SO_4^{2-} ions in liquid phase, Cem. Concr. Res. 23 (2) (1993) 294–300.

[16] C.L.M. Holten, H.N. Stein, Influence of quartz surface on the reaction $C_3A+CaSO_4 \cdot 2H_2O$+water, Cem. Concr. Res. 7 (3) (1977) 291–296.

[17] Egyptian Specification, The Standard Methods for the Chemical Analysis, Egyptian Standard, National Research Center, Cairo, Egypt, 1994, p. 474.

[18] J. Bensted, Early hydration behaviour of Portland cement containing bro-, citro-, desulphogypsum, Cem. Concr. Res. 10 (2) (1980) 165–171.

[19] S.A. Abo-El-Enein, K.Kh. Al-Nuaimi, S.L. Marusin, S.A.S. El-Hemaly, Hydration kinetics and microstructure of ettringite, TIZ-Fachber. 109 (2) (1985) 116–118.

[20] J. Bensted, S.P. Varma, Some application of infrared and roman spectroscopy in cement chemistry: Part 2, Cem. Technol. 5 (4) (1974) 378–382.

[21] R.F. Feldman, V.S. Ramachandran, P.J. Sereda, Influence of $CaCO_3$ on hydration of $3CaO \cdot Al_2O_3$, J. Am. Ceram. Soc. 48 (1) (1965) 25–30.

[22] J. Bensted, An investigation of the conversion of high alumina cement by infrared spectroscopy, World Cem. 13 (1982) 117–119.

[23] A. Roy, R. Kalvakaalava, R.K. Seals, Microstructure and phase characteristics of phosphogypsum–cement mixtures, J. Mater. Civ. Eng. 8 (1) (1996) 11–18.