JOURNAL OF MATERIALS SCIENCE 38 (2003) 4499–4505

Hydration characteristics of tetracalcium aluminoferrite phase in mixes containing β-hemihydate and phosphogypsum

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Tetracalcium aluminoferrite phase was prepared from pure chemicals on a laboratory scale. Five mixes were prepared from the prepared C_4AF phase, β-hemihydate, phosphogypsum and calcium hydroxide. The mixes were hydrated at various intervals namely, 24, 72, 168 and 336 h. The kinetics of hydration was mentioned by measuring the chemically combined water and combined lime contents. The phase composition and microstructure were studied by FT-IR Spectroscopy, XRD, DTA and SEM techniques. This work aimed to study the effect of partial to fully substitution of β-hemihydrate for phosphogypsum on the hydration characteristics and microstructures of tetracalcium aluminoferrite phase. The mechanism of the hydration of tetracalcium aluminoferrite phase in the presence of phosphogypsum proceeds through a similar manner as in the case of β-hemihydrate and affects to a slight extent the rate of hydration reaction. © *2003 Kluwer Academic Publishers*

1. Introduction

Phosphogypsum is an important industrial by-product of phosphoric acid manufacture by dihydrate process in Egypt. It consists of $CaSO_4 \cdot 2H_2O$ and some impurities such as P_2O_5, F^- and organic substances ... in its structure. Almost 90% of the phosphogypsum produced through this manufacturing process is not economically utilized causing an environmental problem and creating a need for large area for disposal. Therefore, many attempts are being undertaken to use phosphogypsum in building industry, road, rail works fill and stabilization of base course. Phosphogypsum is used as setting controller in Portland, trass and supersulphated cement [1, 2].

The effect of phosphogypsum and refined phosphogypsum on the hydration of Portland and trass cements was studied by chemical analysis, setting behaviour, flexural and compressive strength, volume expansion, and heat of hydration and scanning electron microscopy. It was concluded that untreated phosphogypsum can be used as a controller only in the hydration of trass cement and refined phosphogypsum obtained by various methods is equivalent to the natural gypsum and can be evaluated as the retarder of the hydration of both cements [3].

Hydration products of aluminoferrite phase are proved to be similar to those of tricalcium aluminate: In the presence of gypsum, AFm and/or AFt phases (monosulfate and ettringite, respectively) are formed, with the difference that in tricalcium aluminate, the calcium to sesquioxide ratio is 3, while in the aluminoferrites this ratio is 2; this means that besides AFm and AFt, aluminium and/or iron hydroxides are formed, too. As most of these hydroxides are amorphous, X-ray diffraction (XRD) cannot be used for identification; alternative methods, e.g., Mössbauer spectroscopy are preferably used instead. Reaction rates are, however, different; hydration of aluminoferrites is slower, and this rate is further decreased by the presence of calcium hydroxide, gypsum or both. The first hydration product is ettringite, but this is later transformed to monosulfate, after the consumption of available gypsum [4–6].

Ramachandran and Beaudoin [7] reported that during hydration of C_3A and C_4AF separately, formation of the hexagonal phase and its conversion to the cubic phase proceeded much faster in the C_3A-H_2O system than in the C_4AF-H_2O system. Whereas C_3A forms hexagonal plates within a few minutes of contact with H_2O, the C_4AF phase hydrated to the same extent did not develop a well-defined morphology. In case of C_4AF phase a higher surface area product enveloping the unhydrated C_4AF grains, impeded the diffusion of water molecules more efficiently than the crystalline product formed on the C_3A grains.

Collepardi *et al.* [8] studied the influence of gypsum on C_4AF hydration and compared with those obtained for the C_3A hydration. It was concluded that, gypsum is effective in retarding the hydration of C_4AF and the mechanism of retardation could be assumed to be due to ettringite coating C_4AF grains. Ettringite produced during the C_4AF hydration in the presence of gypsum, seemed to be more stable than that produced in the case of $C_3A{\cdot}\overline{CS}{\cdot}H_2{\cdot}H_2O$ system. The consumption of gypsum, the transformation of ettringite into monosulphate and the hydration of C_4AF in the $C_4AF{\cdot}\overline{CS}{\cdot}H_2{\cdot}H_2O$ systems were much slower than those in the $C_3A{\cdot}\overline{CS}{\cdot}H_2{\cdot}H_2O$ system. This means that $\overline{CS}{\cdot}H_2$ retards the hydration of C_4AF more effectively than that of C_3A.

Jawed *et al.* [9] studied the effect of lime and/or gypsum on the hydration of C_4AF. It was concluded that lime acted as an accelerator while gypsum or gypsum and lime solutions retarded the hydration very strongly. With lime solution, SEM depicts hexagonal hydrates on the surface of C_4AF. After 5 min, the surface got entirely covered with hexagonal hydrates. The hydrated surface on the C_4AF crystals was rather loosely packed and had rather larger pores which could account for the less retarding effect of lime on the hydration of C_4AF as compared to C_3A which has densely covered surface with very small hexagonal hydrates. Also, it was concluded that, in the presence of sufficient amount of SO_4^{2-} ions in solution, ettringite was first formed on the C_4AF surface; the hydration process was very slow due to the quite rapid formation of ettringite. But in the presence of low concentration of SO_4^{2-}, monosulphate was produced resulting in breaking the ettringite layer and accelerating the hydration of C_4AF.

Bensted [10] reported that during the hydration of C_4AF in presence of lime and gypsum, the formation of the AFt phase and the molar ratio of calcium to sulphate consumed should be 1:3.3. The formation of an iron rich phase associated with AFt formation regardless of the presence of $Ca(OH)_2$ was also suggested. In according with these findings, Scrivener [11] observed, by electron optical methods, the formation of iron rich C_4AF pseudomorphs in Portland cement after 7 days of hydration. Thus, an iron rich phase appeared to form both during the hydration of C_4AF with gypsum and in cement. The formation of this phase did not appear to be related to the availability of $Ca(OH)_2$ in the system.

Brown [12] studied the early hydration of C_4AF in gypsum and lime-gypsum solutions. He concluded that the products first formed via the hydration of C_4AF in gypsum were rich in iron and alumina, low in calcium, and almost free of sulphate. Analysis of the stoichiometry of the solution phase suggested that these products were an iron rich gel and either alumina gel or C_2AH_8. The early formation of AFt was observed to occur by a dissolution-precipitation (through-solution) mechanism. X-ray and chemical analysis of AFt precipitates indicated the formation of a product free of iron and compositionally identical with ettringite. However, this observation did not preclude the subsequent formation of an iron containing AFt phase. An amorphous, iron rich phase appeared to form simultaneously with the AFt phase. Although, the evidence was indirect, a material balance suggested that the iron rich phase also contains calcium. The presence of calcium hydroxide, while significantly slowing the rate of C_4AF hydration, did not appear to affect the composition of AFt phase.

This work aimed to study the effect of partial to fully substitution of β-hemihydrate by phosphogypsum on the hydration characteristics and microstructures of tetracalcium aluminoferrite phase.

2. Materials and experimental work

2.1. Preparation of tetracalcium alumino-ferrite (C_4AF)

Tetracalcium Alumino-ferrite had been prepared at the laboratory by firing at appropriate temperatures the stoichiometric composition using pure limestone ($CaCO_3$), techanically pure Al_2O_3 and pure Fe_2O_3 in the molar weight ratio of 4:1:1, $CaO:Al_2O_3:Fe_2O_3$ respectively. 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 1280°C for 2 h, repeated the firing until complete formation of the phase was occurred. The prepared specimens were checked for their free lime and insoluble residue contents; the final product contained not more than 0.5% any of them. The fired C_4AF stored was crushed and finely ground to pass completely through a 90 μm sieve and packed in a plastic container. The XRD of the prepared C_4AF is shown in Fig. 1.

2.2. Preparation of the anhydrous mixes and hydrating pastes

Table I shows the prepared mixes of C_4AF phase, β-hemihydrate, phosphogypsum and $Ca(OH)_2$. The chemical composition of the utilized phosphogypsum was shown in Table II. For each mix the ingredients were thoroughly mixed in a porcelain ball mill to ensure complete homogeneity. For the preparation of C_4AF mixes, nearly pure alabaster gypsum sample (99% $CaSO_4{\cdot}2H_2O$) was employed for preparation of β-hemihydrate. It was preground to a Blaine surface

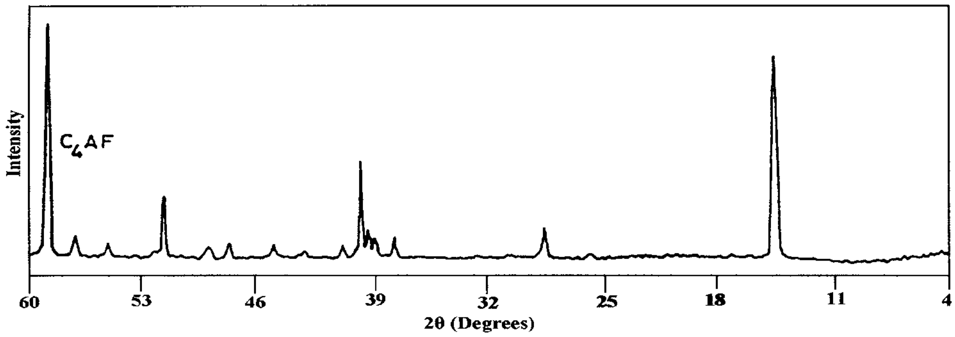

Figure 1 XRD patterns of the prepared anhydrous C_4AF phase.

TABLE I Mix design of the investigated mixes

	Mass%			
Mix. no.	C_3A	β-hemihydrate	Phosphogypsum	$Ca(OH)_2$
M.0	70	20	0	10
M.5	70	15	5	10
M.10	70	10	10	10
M.15	70	5	15	10
M.20	70	0	20	10

area of about 3000 cm^2/g. The required amount of mixing water was added to each mix and the ingredients were mixed for three minutes then moulded into 1/2 inch cubic moulds and compacted to remove air bubbles then placed in a humidity cabinet 100% R.H. at 25 ± 2°C for 24 h. After demoulding, the cubes were placed under water until time of testing.

2.3. Methods of investigation

A set of at least three 1/2 inch cubes of the hardened pastes representing each mix at a given curing period was used for the compressive strength determination. The rate of loading was fixed at a thrust of 500–600 kg/min, and the mean value was considered. In order to analyze the hydration products, suitable parts of the crushed samples after the strength determination were ground in acetone-methanol mixture to stopping the hydration process and then dried in a CO_2 free atmosphere at 70°C for 1/2 h. The dried samples were utilized for the determination of combined water and free lime contents. Approximately 1 g of the predried sample was gradually ignited up to 1000°C for one hour and then cooled in a desiccator, weighed, and the combined water was then calculated. The determination of free lime content was carried out as described elsewhere [13]. The combined lime was calculated from the difference between lime added at the zero time, (10 mass%), and the residual free lime at any prescribed time. The hydrated pastes were also investigated by X-ray diffraction, FT-IR spectroscopy and differential thermal analysis as well as by scanning electron microscopy to reveal their mineralogical and microstructural features.

3. Results and discussion

3.1. Chemically combined water contents

The results of combined water contents of pastes of different mixes were graphically illustrated as a function of curing time in Fig. 2. M.0 (20 mass% β-hemihydrate) shows the highest values of chemically combined water, which sharply increase with curing time. It is well known that the rate of hydration of C_4AF phase is slower than that of C_3A phase [14]. The substitution of 5 mass% of phosphogypsum instead of β-hemihydrate (Mix M.5) decreases the values of combined water contents. This result indicates that addition of phosphogypsum retards the hydration reaction of C_4AF phase at all curing ages.

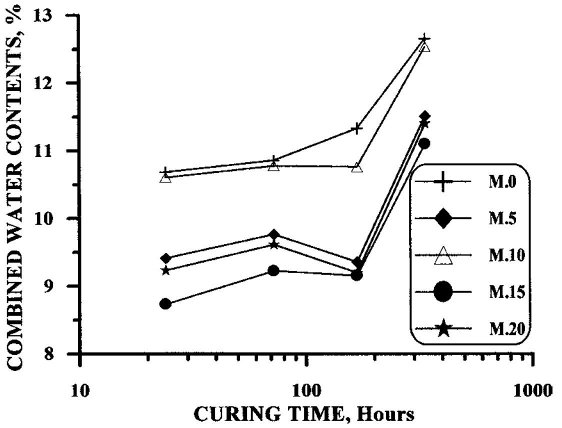

Figure 2 Chemically combined water contents of C_4AF hydrated as a function of curing time and phosphogypsum contents up to 20 mass%.

Phosphogypsum consists of $CaSO_4 \cdot 2H_2O$ and some impurities such as P_2O_5, F^- and organic substances in its structure. The compounds: $Ca(H_2PO_4)_2 \cdot 2H_2O$ and H_3PO_4 as $CaHPO_4$ are considered as impurities, not main constituents. The impurities (P_2O_5 and F^-) adsorbed on the surface of the phosphogypsum. Accordingly, they may form a solid solution of $Ca_3(PO_4)_2$ and CaF_2 compounds which may react with the hydration products of ferrite phase forming a protective film on the surface of the anhydrous particles which will cause the retardation effect [2]. Fluoride is sometimes present as NaF and Na_2SiF_6 [15]. The decrease of chemically combined water values for mixes containing phosphogypsum between 72 and 168 h curing time may be due to the tendency of the formed ettringite to transform into monosulpho-aluminateferrite [16].

In a previous work [16] it was found that there is an acceleration effect on the rate of hydration of C_3A phase between 24 and 72 h in the presence of phosphogypsum as a substitute of β-hemihydate, which may be due to the presence of impurities such as F^- and/or P_2O_5, which may enhance the formation of ettringite. The hydration behaviour of C_4AF phase is somewhat different from that of C_3A phase in that the hydration rate of C_4AF phase is much slower. However, the presence of 5 mass% phosphogypsum at the expense of β-hemihydate results in a decrease in the rate of formation of sulphoaluminate compounds rather than the acceleration effect due to the presence of minor constituents in phosphogypsum, which may be responsible for this acceleration as mentioned above [16].

On increasing of the amount of phosphogypsum up to 10% mass (M.10), give higher combined water contents than those of the other mixes compositions containing phosphogypsum, but it is still lower than that of M.0

TABLE II 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

(20 mass% β-hemihydate). It is interesting to note that the rate of hydration of M.10 was not effected by the impurities, hence phosphogypsum does not so markedly retard the hydration of mix M.10 [17]. The mix composition M.10 that shows the higher values of combined water could be considered the optimum mix composition. This may be attributed to the presence of an equal amounts of both β-hemihydrate and phosphogypsum (10 mass%), the first enhances the formation of calcium sulphoaluminate compounds and the second has an acceleration effect on the hydration reaction of C_4AF phase which results in the formation of more hydrated compounds of the phase and consequently results in an increase in the combined water values for this mix composition M.10. Also, Fig. 2 shows that the values of the chemically combined water of hydrated pastes of M.20 (0 mass% β-hemihydrate and 20 mass% phosphogypsum) are higher than those of M.15 (5 mass% β-hemihydate and 15 mass% phosphogypsum), this indicates that there is little acceleration effect. This effect may enhance the hydration process of C_4AF phase and as a result of that a large amounts of aluminate hydrate phases as well as the sulphoaluminate compounds will be formed. These findings will be confirmed by XRD, DTA and FT-IR spectroscopy.

3.2. Combined lime contents

The variation of combined lime contents in the hydrated specimens are graphically represented in Fig. 3. Fig. 3 shows that the values of combined lime increase with phosphogypsum contents for all curing periods. At 24 h M.5 has the higher combined lime contents. Accordingly, both of C_3A and C_4AF consume $Ca(OH)_2$ during the hydration reaction forming calcium aluminate hydrates (C_4AH_{13}, CAH_{10} and C_3AH_6). However it is well known that the hydration reaction of C_4AF is very similar to that of C_3A as well as the great similarity of the hydration products except that the hydration rate of C_4AF is much slower. Brown [18] concluded that the rate of hydration of C_4AF with calcium sulphate is dependent on whether the source of calcium sulphate is hemihyrdate or gypsum and whether hydration is carried out under water or in saturated lime solution. Addition of phosphogypsum consumes more lime due to formation of calcium aluminoferrite hydrate compounds rather than the formation of sulphoaluminate compounds, which indicate that the reaction rate of $CaSO_4$ containing phosphogypsum with C_4AF shows slower rate than in the case of hemihyrdate especially at small addition of phosphogypsum. At early ages, (24–72 h), according to Figs 2 and 3 the combined lime and combined water increase, whereas the free SO_4^{2-} decreases. This could be attributed to the formation of ettringite. After this period comes to an end, large increase in the amount of combined water content was detected. The decrease in the detection of combined lime in some mixes, which may be suggested by an accompanied free SO_4^{2-} into the solution that the first formed ettringite, which started to decompose partially with the release of SO_4^{2-}. On the other hand, the increase of combined lime and combined water content indicates the formation of monosulphate hydrate phase, which consumed SO_4^{2-} than those released during the decomposition of ettringite.

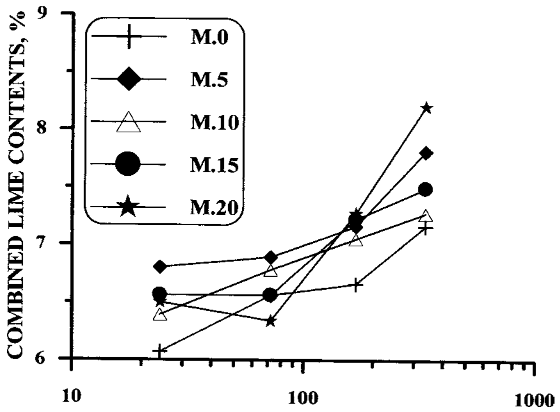

Figure 3 Combined lime content of C_4AF hydrated as a function of curing time and phosphogypsum contents.

The values of combined lime of M.10 decrease are lower than M.5 during all curing periods, which is considered the optimum mix composition. The decrease in the values of combined lime may be accompanied by an increase in the formation of sulphoaluminate compounds, which contain higher amounts of combined water as shown in Fig. 2. The replacement of 50% β-hemihydate with phosphogypsum enhances the replacement of $Ca(OH)_2$ in calcium aluminoferrite hydrate by SO_4^{2-} to form the sulphoaluminoferrite hydrate as well as accelerates to some extent the hydration reaction rate which results in the formation of more calcium aluminate hydrate compounds and consequently the combined lime and combined water contents, but still in a lower rank than M.0. The increase of combined lime extended with phosphogypsum content to cover the later hydration periods (168–336 h).

3.3. X-ray diffraction

Fig. 4 represents the XRD diffraction patterns of different hydrated pastes cured at 3 days. As shown in Fig. 4,

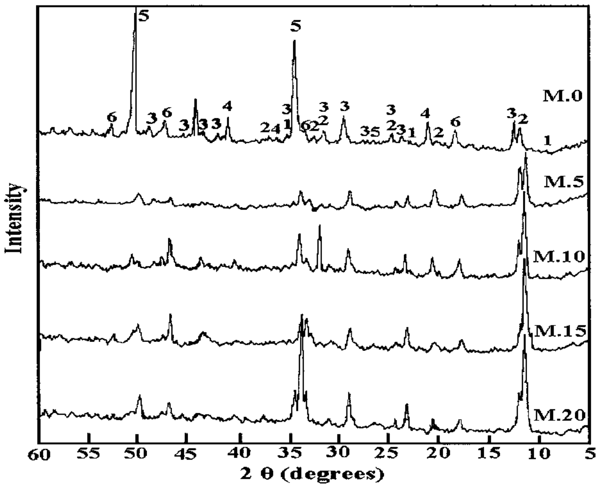

Figure 4 XRD patterns of mixes M.0, M.5, M.10, M.15 and M.20 cured at 24 h; 1, ettringite; 2, Monosulphate; 3, CAH_{10}; 4, CAH_{8-12}; 5, C_3AH_6; 6, $Ca(OH)_2$.

ettringite is not clearly observed especially for mixes with high percentages of phosphogypsum. This is due to the tendency for transformation to monosulphate. It is very clear from Fig. 4 that all the peaks characterizing the hydration products of M.5 were diminished due to the retardation as discussed later. The increase of main peaks of monosulphate, which is found at 7.499, 3.77 and 2.495 Å, may be attributed to the overlapping with that of $CaSO_4 \cdot 2H_2O$, which are located at almost the same d-spacing ranges. On the other hand, the rest of hydration products such as CAH_{10}, CAH_{8-12}, C_3AH_6 hydro-garnat were also diminished for Mix M.5. With the increase of the amount of phosphogypsum up to 10 mass% (M.10), the characteristic peaks height of hydration products were increased especially those for monosulphoaluminoferrite. However, when the phosphogypsum increases, the retardation effect is compensated to produce an acceleration effect. The large increase in the peaks height of monosulphoaluminoferrite with phosphogypsum content can be attributed to the tendency for formation of more stable monosulphoaluminoferrite. Monosulphoaluminoferrite can be formed also from the replacement of OH^- group by SO_4^{2-} group in the compound $C_3A \cdot Ca(OH)_2 \cdot 12H_2O$ [14]. As a result of this the peaks height of CAH_{10} decreases with phosphogypsum. Fig. 4 shows that M.10 represent the optimum mix composition, which gives the maximum hydration products close to M.0. On the increase of phosphogypsum percentages (M.15 and M.20) the characteristic peak of monosulphate at about 7.499 Å increases. The increase of the characteristic peaks of almost all hydrated compounds of M.20 more than those of M.15 can be attributed to the accelerated effect for the hydration reaction of C_4AF phase due to the presence of the impurities (P_2O_5 & F^-) present in the structure of phosphogypsum, which was confirmed by the results of combined water and lime.

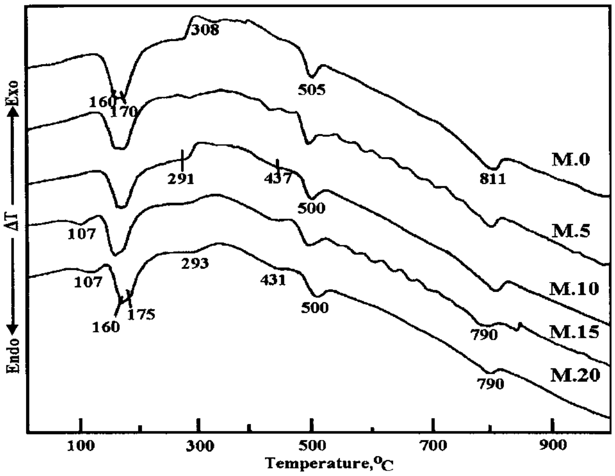

Figure 5 DTA of C_4AF hydrated at 168 h in presence or absence phosphogypsum.

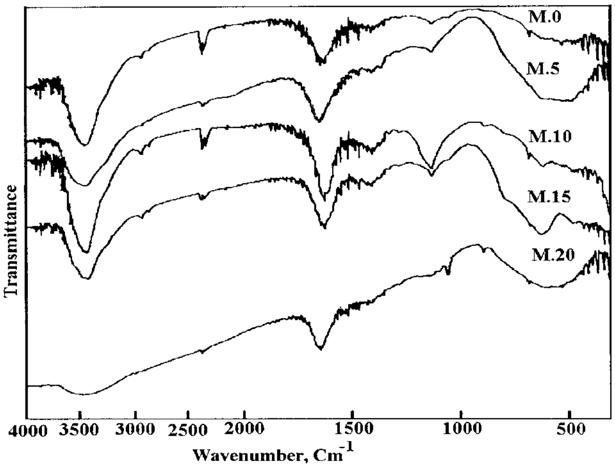

Figure 6 FT-IR spectroscopy of hydrated C_4AF phase at 24 h in the presence or absence of phosphogypsum.

3.4. Differential thermal analysis

Differential thermal analysis technique was employed to follow up the products, which formed during the hydration reaction of C_4AF in the presence of both phosphogypsum and β-hemihydate. Fig. 5 illustrates the DTA curves of the hydrated pastes of all mix compositions cured for 168 h. The following phases detected in Fig. 5 are hexagonal hydrate (C_2AFH_8 or C_4AFH_{13}), cubic hydrate (C_3AFH_6), ettringite ($C_4AF\bar{S}_3H_{32}$) and monosulphate ($C_4AF\bar{S}H_{12}$) as well as carbonate at about 780–835°C. The peak at 107°C is due to the decomposition of ettringite. The two endothermic peaks at 160°C and 175°C is due to the decomposition of calcium aluminoferrite and monosulphate hydrates, which represent a little change with the increase of phosphogypsum content. This may be due to the expected overlapping of the characteristic endothermic peak of the decomposition of the residual gypsum ($\overline{CS}\,H_2$) present in each mix composition, which is found the same temperature range. Examination of curves showed that an endothermic shoulder in the range of 290°C corresponds to the monosulphoaluminoferrite compounds. The shoulder appears for mix M.0, and highly diminished for M.5 as a result of the retardation effect due to presence of small amounts of phosphogypsum (5 mass%) which confirm the results of combined water and combined lime. This peak characteristic to the monosulphoaluminoferrite increases with phosphogypsum. The endotherm found at the temperature range of 400–430°C characterizing the hydrogarnat (C_3AH_6), increases with phosphogypsum. The peak located at 500°C is attributed to the dehydration of residual hydrolime. It shows a very slight variation with phosphogypsum percentages because of the lime was added in order to furnish a suitable condition for the crystallization of sulphoaluminoferrite compounds and it partially incorporates in the calcium aluminate hydrated products. The endothermic peak located at about 780–835°C is attributed to the decomposition of $CaCO_3$ as well as due to the presence of some carbonated compounds contaminated with phosphogypsum.

3.5. FT-IR spectroscopy

FT-IR spectroscopy can be used to give important information about the hydroxyl bonds and monitoring the dynamic changes in the sulphate region during the hydration reactions. The spectral are shown in three

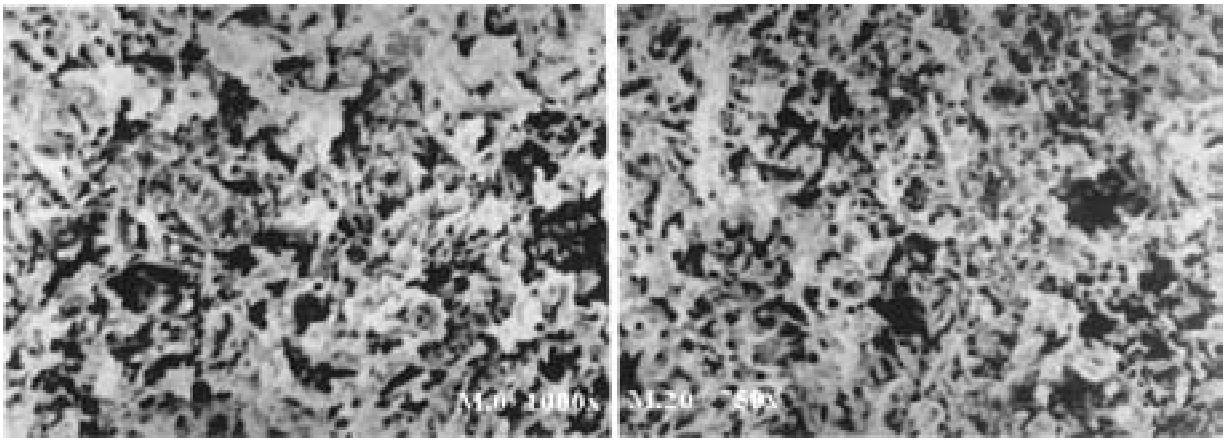

Figure 7 SEM of C_4AF hydrated at 168 h of mix M.0 and M.20.

regions: the water region, sulphate region and aluminate (AlO_6) region. The broad bands centered at 3400 cm^{-1} are due to stretching vibration of O—H water molecule. The bending vibration of water molecule located at 1640 cm^{-1}. The presence of doublet bands at 1120 and 1180 cm^{-1} is due to ettringite and monosulphate hydrates, which are the main hydration products in this system. These can be confirmed by the deformation of water molecule at 1640 and 1680 cm^{-1}. The bands at 500–600 cm^{-1} are due to vibration of aluminate phase.

Replacement of 5 mass% of β-hemihydate by phosphogypsum (M.5) shows a slight increase in the band at 540–590 cm^{-1}, which is due to aluminate phase and decrease in the υ_2-H_2O at about 1635 cm^{-1} as well as 3400 cm^{-1}, which indicates a decrease in the combined water due to the decrease of sulphoaluminate compounds. Increase of the amount of phosphogypsum up to 10 mass% (M.10) showed a large decrease in area of bands at 540–590 cm^{-1}, whereas the bands due to stretching and bending vibration of water molecules were broaden. This indicates an enhancement of tri and monosulphate compounds. M.15 and M.20 patterns show increase in the aluminate bands and decrease in the bands due to stretching and bending vibration of water molecules indicating that the aluminate phases formed before the sulphoaluminate phases. The IR findings confirm again the previous results of the combined water.

3.6. Scanning electron microscopy

Fig. 7 shows SEM of Mixes M.0 and M.20, which contained 0 and 20 mass% phosphogypsum respectively cured for 168 h. The micrograph of mix M.0 shows an accumulation of small particles of microcrystalline ettringite and scattered hexagonal crystals of C_4AF hydrate, which are coated by agglomerates of ettringite crystals [19, 20].

The micrograph of mix M.20 shows somewhat different structure in which the monosulpho-aluminoferrite crystals covered the micrograph, but appeared as malformed aggregates. These aggregates of monosulpho-aluminoferrite are seen to coat the hexagonal crystals [19, 20].

4. Conclusions

The results of the chemically combined water and combined lime showed that the addition of small amounts of phosphogypsum (5%) at the expense of ß-hemihydrate to the C_4AF phase in the presence of hydrolime has a retardation effect on the rate of the reaction of the ferrite phase with the calcium sulphate to give the calcium sulphoaluminate compounds. On increasing the amounts of phosphogypsum up to 10 mass% (M.10) which was considered the optimum mix composition that gives the higher combined water values which is due to the acceleration effect due to the presence of the impurities contaminated with the chemical structure of phosphogypsum (P_2O_5 & F^-). The XRD analysis showed that an increase in the intensities of the characteristic peaks of the hydrated compounds of C_4AF phase in the mix compositions containing higher amounts of phosphogypsum (M.15 & M.20) which indicates the acceleration of the hydration reaction of these two mixes. Also, the XRD and DTA reveal that there is a great tendency for the decomposition of ettringite to give the more stable monosulphoaluminate compounds with the presence of more phosphogypsum. The study of FT-IR spectroscopy confirm the above mentioned findings and the SEM showed that there are some differences in the crystal shape of the sulphoaluminate compounds but that formed in the presence of phosphogypsum were seem to coat the C_4AF particles and may regulate its hydration reaction.

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Received 21 February
and accepted 5 August 2003