HYDRATION CHARACTERISTICS OF TETRACALCIUM ALUMINO-FERRITE PHASE IN THE PRESENCE CALCIUM CARBONATE

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Tetracalcium alumino-ferrite phase (C_4AF) prepared from pure starting materials was employed for composing various mixes prepared of C_4AF phase, $CaSO_4 \cdot 2H_2O$, $Ca(OH)_2$ and $CaCO_3$. The effect of replacing calcium sulphate (gypsum) by calcium carbonate as a set retarder on the hydration behaviour of ferrite phase was studied. The mixes were hydrated for various periods and the hydration products were investigated using the appropriate techniques. The kinetics of hydration was studied by measuring the chemically-combined water as well as the combined lime contents. The mineralogical constitution was studied by using XRD, and DTA. The microstructure of some represented hydrated samples was investigated by scanning electron microscopy. Some interesting conclusions have been drawn. It was found that calcium carbonate reacts with tetracalcium alumino-ferrite phase (C_4AF) in the presence of hydrolime [$Ca(OH)_2$] to form carboferrite compounds which may coat the aluminate grains as ettringite does and this may probably regulate the setting time.

INTRODUCTION

The aim of this work is to replace a part of a more valuable ingredient (clinker) by a less valuable substance, e.g. limestone.Therefore, it is planned to investigate the influence of calcium carbonate additions on the hydration characteristics of C_4AF phase found in the portland cement clinker. Although the proportion of C_4AF in portland cement is relatively low, it exerts a significant influence on the heat of hydration and setting property of cement. The flash set property, the formation of various calcium aluminate hydrates, and the formation of calcium carbo- and sulpho-aluminiate (ferrite) hydrates involve the reaction of C_4AF in the absence or in the presence of carbonates and sulphates respectively. It has been reported that there are two series of calcium sulphoferrite, analogous to the sulphoaluminte; these are the high-sulphate sulpho-ferrite $C_3F \cdot 3CaSO_4 \cdot 32H_2O$ and the low sulphate form $C_3F–CaSO_4.aq$. The monosulphoferrite hydrate is fomed in a saturated lime-calcium sulphate solution at room temperature without tendency to give the trisulphoferrite hydrate[1]. It was stated that there is a possibility for different calcium carboferrite hydrate to be formed which are similar to the carboaluminate hydrates. The low carboferrite ($C_3F \cdot 3CaSO_4 \cdot 12H_2O$), that is similar to the low-sulphoaluminate, has been prepared and its X-ray diffraction pattern is similar to that of C_4AH_{13}. Also, there is a possibility for the formation of a hemicarboferrite $C_3F \cdot 1/2CaCO_3 \cdot 12H_2O$ [1]. As mentioned before, the ferrite phase reacts in the same way as C_3A phase but at a slower rate, with calcium carbonate in the presence of calcium hydroxide to form iron (III) substituted derivatives of the aluminum (III) compounds, monocarboaluminate and tricarboaluminate [2]. It was stated that upon the addition of $CaCO_3$ to O.P.C clinker and gypsum, a reaction occurs between $CaCO_3$ and C_4AF present in the clinker to form calcium carboaluminates (ferrite) hydraes [1,2]. It was found that calcium carbonate may partially substitute gypsum in portland cement, this is due to the low cost of the limestone and to the good mechanical porporties of the resulted concrete [3,4]. It has been also reported that the addition of $CaCO_3$ to the hydrating cement affects the physicomechanical proporties due to the reaction between $CaCO_3$ and the C_3A as well as C_4AF phases [5,6] and the hydration kinetics of the C_3S phase remain unaffected. It was stated that the strength of C_3A and C_4AF increased upon the addition of calcareous fillers due to the formation of a low-form of calcium carboaluminate i.e., $C_3A \cdot CaCO_3 \cdot 10-11 H_2O$. [7-9] It was also found that sulphate-resisting properties of portland cement increased by the addition of calcareous fillers which was attributed to the formation of monocalcium carboaluminates [10-12]. The main objectives of the present investigation are to study the

magnitude of influence of varying calcium carbonate additions on the kinetics of hydration, mineralogical and morphological features of hydrating pastes of C_4AF phase in addition to testing the possibility of replacing ($CaSO_4 \cdot 2H_2O$) by $CaCO_3$ as a set regulator for the C_4AF phase.

EXPERIMENTAL

C_4AF had been prepared at the laboratory by firing at 1280ºC the stoichiometric composition of the phase using highly pure limestone (99.0% $CaCO_3$), techanically pure Al_2O_3 (99.0%) and pure Fe_2O_3 in the molar weight ratio of 4:1:1, CaO:Al_2O_3: Fe_2O_3 respectively. Firing of the mix was repeated until nearly complete formation of the phase occurred. This was checked by testing the fired product for its free lime and insoluble residue contents. The final product contained not more than 0.5% any of them. The fired C_4AF product was crushed and finely ground to pass completely through a 90 μm standard sieve and packed in a plastic containers. The XRD of the prepared C_4AF is shown in Figure 1.
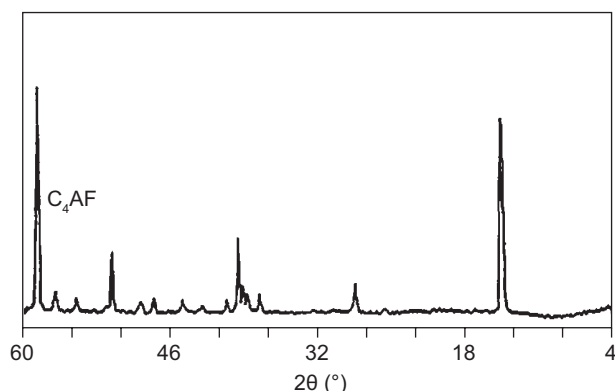

Figure 1. XRD Patterns of the C_4AF Phase.

Preparation of the anhydrous mixes and hydrating pastes

Table 1 shows the prepared mixes of C_4AF phase. 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. It was preground to a Blaine surface area of about 3000 cm²/g. The required amount of mixing water was added to each mix and the ingredients were mixed for three minutes and the pastes then casted into one-inch cube moulds which were compacted to remove air bubbles and then placed in a humidity cabinet having 100% R.H at 23±2 °C for 24 hrs. After demoulding, the cubes were placed under water until time of testing.

Table 1. Mixes Compositions with C_4AF Phases.

Mix No	C_4AF	Limestone	Gypsum	$Ca(OH)_2$
	(wt.%))			
1 Control	85	-	10	5
2	85	2	8	5
3	85	4	6	5
4	85	6	4	5
5	85	8	2	5
6	85	10	–	5

Methods of investigation

In order to analyse the hydration products, suitable samples were ground in acetone-methanol mixture to stop the hydration process and then dried in a CO_2 free atmosphere at 70°C for two hours. The dried samples were employed for the determination of combined water and free lime contents. Approximately 2g of the predried sample were gradually ignited up to 1000°C for 15 min soaking time and then cooled in a desiccator and weighed and the combined water was calculated. The determination of free lime was carried out by using the method described in reference.[13] The values of combined lime were calculated by subtraction of the determined values of free lime from the total percentages added to the original mix compositions. The hydrated cement samples were also investigated by X-ray diffraction with the aid of a Philips PW 1390 under the following settings: Cu Kα radiation (wavelength = 1.542 Å), equipped with Ni filter, 40 KV, 5 mA, counts per second = 1×10^3, t.c = 2, chat speed : 1 cm = 1θ, and differential thermal analysis techniques (type Shimadzu DTA-50 Thermal Analyzer - Japan) as well as by scanning electron microscopy.

RESULTS AND DISCUSSION

Combined Water

The results of combined water obtained for the pastes prepared from the six different C_4AF mix compositions are given in Figure 1 as a function of combinations of $CaCO_3$ and gypsum substitutions. Figure 1 shows a similarity between the behaviour of combined water contents for the samples cured for 1 and 3 days in that they decrease as the percent of $CaCO_3$ substitute for $CaSO_4$ is increased up to mix (3) and then increased again for mix (4) with a tendency of a small decline in the rate of increase for mixes (5) and (6). This behaviour can be attributed to the fact that the reaction between $CaCO_3$ with C_4AF is slower than that with $CaSO_4$. This is up to 40% substitution of $CaCO_3$ for $CaSO_4$. Further substitution of $CaCO_3$ for gypsum is accompanied by a little increase in the amounts of chemically - combined water for mixes(4), (5) and (6).
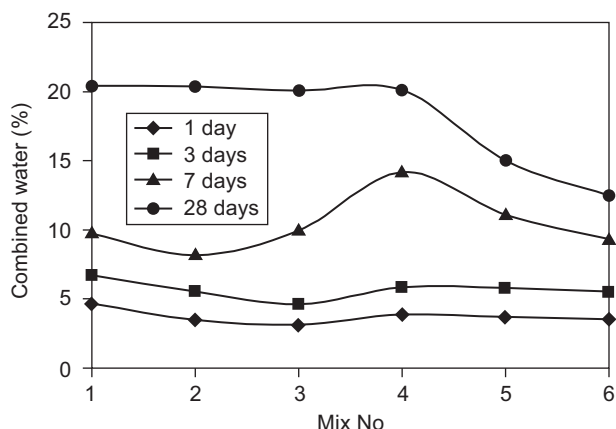
Figure 2. Relationship between combined water and combinations of calcium carbonate and gypsum substitutions to tetracalcium alumino-ferrite pastes cured for various periods.
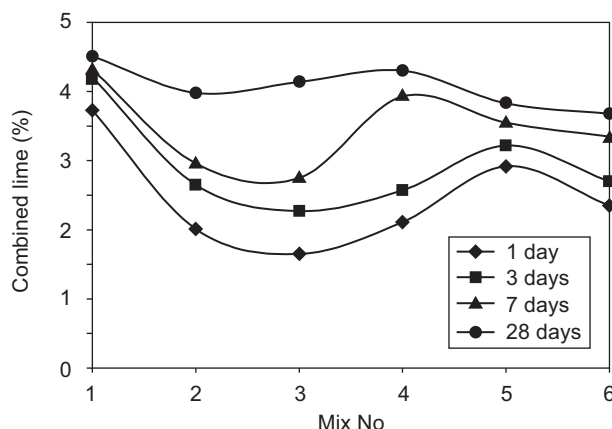

Figure 3. Relationship between combined lime and combinations of calcium carbonate and gypsum substitutions to tetracalcium alumino-ferrite pastes cured for various periods.

This is actually due to that the reaction between $CaCO_3$ and C_4AF leads to the formation of low carbo-ferrite hydrates ($C_3F \cdot CaCO_3 \cdot 12H_2O$) without tendency to form the high carboferrite hydrates. For samples cured for 7 days, the results indicated that there is a big increase in the combined water contents starting again from mix (3) (40% $CaCO_3$ substitution for $CaSO_4$) to mix (4) (60% $CaCO_3$) which is mainly attributed to the formation of the high carboferrite hydrates together with the high sulphoferrite hydrates. For mixes (5) and (6), there is another drop in the amounts of combined water. The latter mixes contained very little or no $CaSO_4$ which leads to a diminishing trend for the formation of the sulphoferrite hydrates. For the pastes cured for 28 days, the influence of the substitution of $CaCO_3$ for $CaSO_4$ is weak up to mix (4) as can be seen from Figure 1 and then it decreases as in the case of 7 days due to the increasing deficiency in $CaSO_4$ content. This behaviour can be attributed to the fact that curing for 28 days is enough for the slower rate of reaction of C_4AF with both $CaCO_3$ and $CaSO_4$ to come to its conclusion with up to 60% $CaCO_3$ substitute for $CaSO_4$. The two forms of sulphoferrite and carboferrite hydrates are almost the same and there is only a little difference in the values of combined water of both compounds.

Combined lime

The results of combined lime obtained for the pastes prepared from the six different C_4AF mix compositions are given in Figure 3 as a function of combinations of $CaCO_3$ and gypsum substitutions. It is to be mentioned that the original dry mix compositions contained 5% $Ca(HO)_2$. The results of Figure 3 show that the values of combined lime decrease sharply for all curing periods up to mix (3) (40% $CaCO_3$:60% $CaSO_4$) except for those of the 28 days in which the initial decrease in the values

of combined lime ended at mix (2) only. This indicate that up to 40% substitution of $CaCO_3$ for $CaSO_4$ the incorporation of $Ca(HO)_2$ in the reaction of C_4AF and $CaCO_3$ is smaller than that with $CaSO_4$ due to the fact that the rate of the reaction of the former is slower than that of the latter.

For the samples cured for one and 3 days, the values of combined lime increase again for mixes (4) and (5) as a result of the formation of carboferrite hydrates, in the presence of increasing of $CaCO_3$ content, together with the sulphoferrite formed due to the presence of $CaSO_4$. For mix (6), which contained zero percent $CaSO_4$, the values of the combined lime for the samples hydrated for one and 3 days decrease again as seen in Figure 3. In the samples cured for 7 days, the extent of the increase in the values of combined lime for mix (4) is higher; this may be due to the possibility of formation of the high carboferrite hydrate. By increasing the carbonate percent to 80% (out of the total $CaCO_3$ and $CaSO_4$), the values of combined lime decrease again sharply due to the deficiency in $CaSO_4$ content and to differences in the rates of reaction as well as to differences in the solubility of $CaCO_3$ and $CaSO_4$. The increase in combined lime content for the 28 days-cured samples in mix (3) is attributed to the fact that the curing period is enough for the substituted amount of $CaCO_3$ to react with C_4AF which compensate for the decrease in the amounts of formed sulphoaluminates. The decrease in the contents of combined lime after 7 and 28 days for mixes (5) and (6) is probably attributed to the deficiency in the formed amounts of sulphoferrite because of the availability of lower amounts (mix (5)) or to the complete absence of $CaSO_4$ (mix (6)). It is obvious from the results of combined water (Figure 2) and those of combined lime (Figure 3) that there is a good evidence for the formation of carboferrite from the reaction of $CaCO_3$ with C_4AF in the presence of $Ca(OH)_2$ either in the presence or in the absence of $CaSO_4$ within the reaction medium.

Differential thermal analysis (DTA)

Figure 4 illustrates the DTA thermograms obtained for the hardened pastes prepared from mix (6) and hydrated for 1, 3, 7 and 28 days. As can be seen from the figure, the endothermic peak at 150-170 °C is due to the dehydration of tricarbonate compound and that at 240 - 270°C to the monocarbonate which appeared after one day hydration time and increased up to 28 days except that for the 7 days. The abnormal decrease in the two endotherms of the high and low carbonate compounds of the sample hydrated for 7 days may be connected with the appearance of another endotherm at 400°C which corresponds to C_3AH_6 probably as a result of partial dissociation of the two carbonate compounds. This compound, C_3AH_6 after enough hydration time (28 days) may react again with the excess CO_3^{2-} ions to form the two carbonate forms. This is confirmed by the disappearance of the C_3AH_6 peak for the curve of 28 days and the increase of the two peaks corresponds to the two carbonate forms. From the above discussion, it is possible to assume that the high and low carboferrites are the main products of the hydration reaction in the system $C_4AF–CaCO_3–Ca(OH)_2$ and those compounds have large crystals analogous to the sulphoferrites which may coat the C_4AF grains leading to a retardation
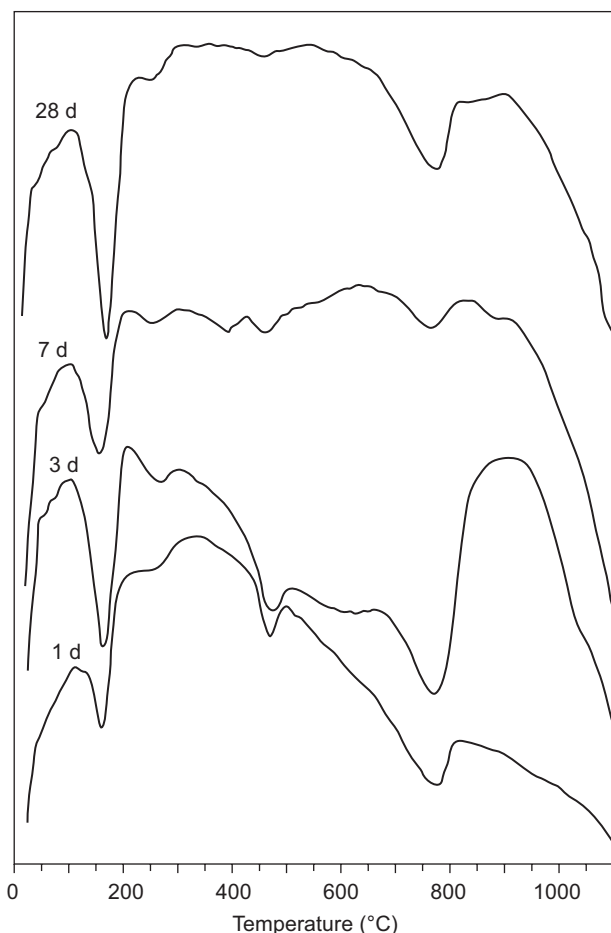

Figure 4. Differential Thermal Analysis Diagrams of Mix (6) Prepared with C_4AF Phase and Cured for Various Periods.

effect of the setting similar to that in the C_3A phase. The decrease in the peak intensity at 470°C, which corresponds to calcium hydroxide is primarily attributed to its incorporation in the reaction between C_4AF and $CaCO_3$. As can be seen from Figure 4, the intensity of the endothermic peak of calcium carbonate at 750-790°C decreases with the prolongation of curing period, which indicates the incorporation of CO_3^{2-} in the hydration reaction of C_4AF phase.

X-Ray diffraction analysis (XRD)

Figures 5 and 6 illustrates the XRD patterns of the hydrated pastes of mixes (1) and (6) [0% Limstone and 0% gypsum, respectively] from 1 day up to 28 days, respectively. The XRD pattern of mix (6) indicates that the peaks of the low and high forms of carboferrite (similar to those of low and high forms of sulphoferrite) are seen in the pattern. The tricarbonate peaks are observed at 8.75, 5.54, 3.83, 2.564 and 2.09 Å and those of the monocarbonate at 7.499, 3.77 and 2.495 Å [1]. As hydration proceeds from one to 28 days, the peaks of the two forms of carboferrite were clearly increased. For the pastes hydrated for one day, the small peaks correspond to $Ca(OH)_2$ began to disappear with curing time which accounts for its participation in the hydration reaction. The peaks of $CaCO_3$ also decreased by increasing the curing time which is attributed to the incorporation of CO_3^{2-} in the reaction between C_4AF and $CaCO_3$ in the presence of $Ca(OH)_2$ to give the low and high carboferrites. The presence of strong peaks for the hydrated C_4AF namely CAH_{8-12} may be attributed to the slow rate of reaction between C_4AF and $CaCO_3$ which furnishes conditions for direct hydration of the ferrite phase at this early curing period [1,2]. After 3 days of hydration, the peaks of carboferrites increase and those of CAH_{8-12} gradually decrease due to their reaction with $CaCO_3$. In the samples hydrated for 7 days, it was observed that there is a gradual decrease in the peaks intensity of carboferrites accompanied by a little increase in that of the CAH_{8-12}. This may be attributed to the partial dissociation of the tricarbonate to give more CAH_{8-12}, that is the same phenomenon observed with the DTA results for mix(6) illustrated in Figure 4. A further increase in the amounts of carboferrites was observed after hydration for 28 days due to the reaction of the CO_3^{2-} with the ferrite phase. Comparison of the X-ray diffraction patterns of mix (1) and (6) illustrated in Figures 5 and 6, respectively by following up the characteristic peaks of sulphoferrites, carboferrites, $Ca(OH)_2$, $CaCO_3$, gypsum and hydrated C_4AF phase (CAH_{8-12}) which reveals that the two patterns are quite similar except for some fine details due to differences in the rate of formation of the hydration products of the two mixes. In spite of the contradictions concerning the hydration products of C_4AF phase in prbable formation of intermediate phases, present available data in this work can not exclude or confirm such results [16,17].
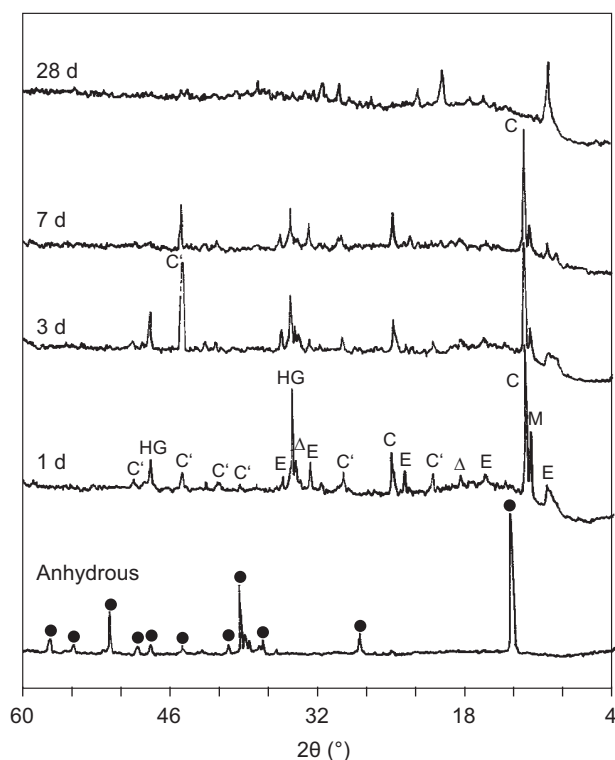
Figure 5. X-Ray diffraction patterns of mix (1) prepared with C_4AF phase and cured for various periods ($\bullet$ - Anhydrous C_4AF phase, E - Ettringite, M - Calcium monosuphoaluminate, Δ - $Ca(OH)_2$, C - CAH_{10}, C' - CAH_{8-12}, HG - Hydrogarnet).
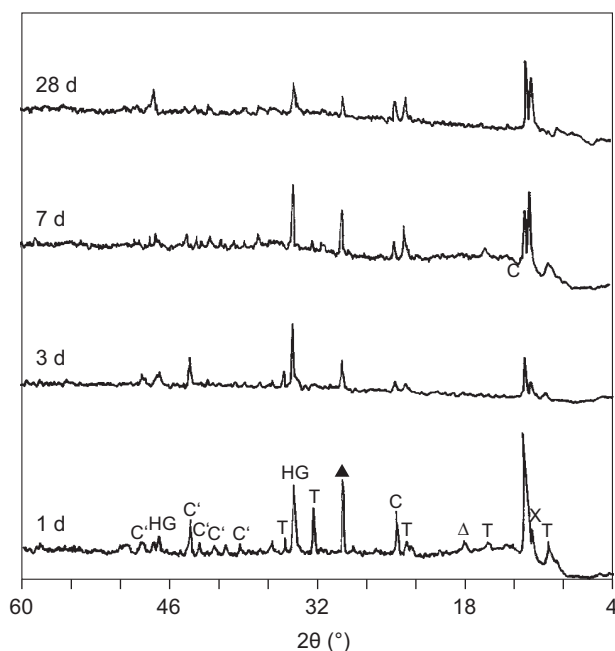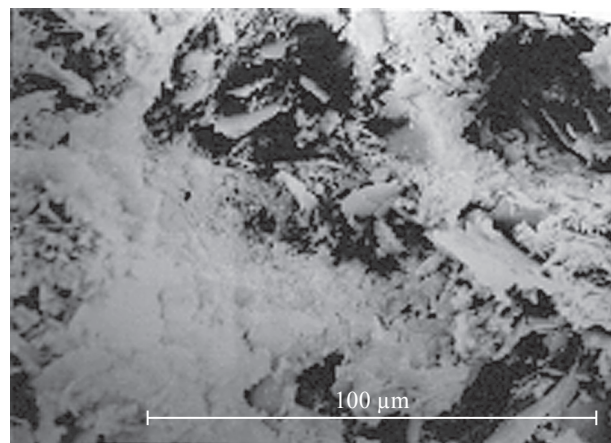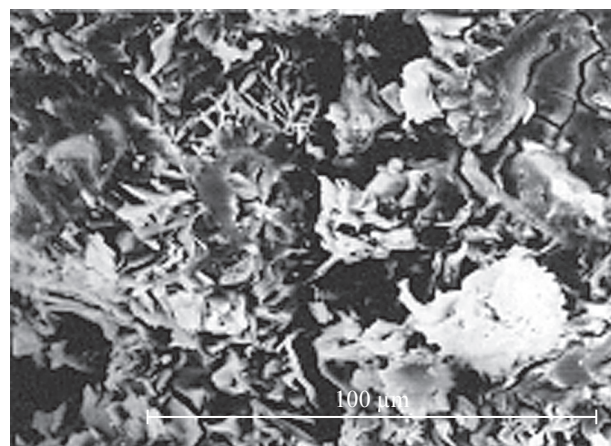

Figure 6. X-Ray diffraction patterns of mix (6) prepared with C_4AF phase and cured for various periods ($\bullet$ - Anhydrous C_4AF phase, T - Calcium tricarboaluminate, X - Calcium monocarboaluminate, Δ - $Ca(OH)_2$, $\blacktriangle$ - $CaCO_3$, C - CAH_{10}, C' - CAH_{8-12}, HG - Hydrogarnet).

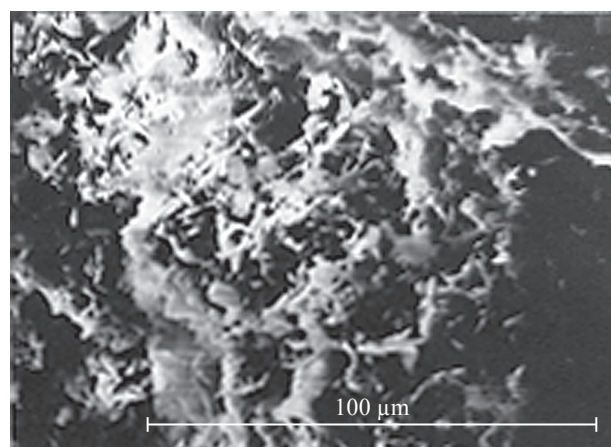### Scanning electron microscopy (SEM)

Some paste samples prepared of mixes (1), (3) and (6) of the ferrite phase and hydrated for 28 days have been investigated by SEM. The plates A, B and C of Figure 7 represent the Micrographs of mixes (1), (3) and (6), respectively. Plate (A) representing mix (1) which

a) plate A (mag. : 1000×)

b) plate B (mag. : 1000×)

c) plate C (mag. : 1000×)

Figure 7. Scanning electron micrographs of the hydrated mixes (1), (3) and (6) prepared with C_4AF phase and cured for various periods.

contained $CaSO_4$ and no $CaCO_3$ shows small particles of micro crystalline ettringite[14,15] together with scattered hexagonal crystals of the C_4AF hydrates. These are coated by agglomerates of ettringite crystallites. The microstructure of the sample representing mix (6) which contained $CaCO_3$ and no $CaSO_4$ and seen in Figure 7c is different from that of mix (1) in that the carboferrites crystals covered the micrograph have no definite shape but appeared as malformed aggregates. The aggregates of carboferrite are seen to coat the hexagonal crystals of C_4AF hydrates. The micrograph, Figure 7b represent the middle composition i.e., contained both $CaSO_4$ and $CaCO_3$. It is seen that it has an intermediate morphological features between those of the other two micrographs of mixes (1) and (6) shown in Figures 7a,c, the samples contained both $CaSO_4$ and $CaCO_3$, microcrystalline sulphoferrite crystals and malformed carboferrites are seen to coat the hexagonal crystals of C_4AF hydrates.

CONCLUSIONS

The results indicate that the reaction between $CaCO_3$ and C_4AF leads to the formation of low carboferrite hydrates ($C_3F \cdot CaCO_3 \cdot 12H_2O$) without a tendency to form the high carboferrite hydrates. However, at later ages of hydration and with a relatively high percent of $CaCO_3$ substitute for $CaSO_4$, there is a possibility for the high carboferrite and sulphoferrite hydrates to be formed. The results of scanning electron microscopy showed that there was a difference in the microstructure of the hydrated samples which contained only gypsum ($CaSO_4 \cdot 2H_2O$) and those contained only $CaCO_3$ in that the particles of the former are microcrystalline (ettringite) and those of the latter which are carboferrite

crystals having no definite shape but appeared as malformed aggregates coating the hexagonal crystals of C_4AF hydrates.

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