Hydration of C₄AF in the presence of artificial CaSO₄ and lime

S El-Alfi, S Abd-Aleem & H El-Damony

Refactories, Ceramics and Building Materials Department, National Research Center, Dokki, Cairo, Egypt
Faculty of Science, Cairo University, Fayoum, Egypt
Faculty of Science, Zagazig University, Zagazig, Egypt

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The ferrite phase consists of about 8-13 wt% portland cement. This phase has received little attention with regard to its hydration. The aim of present investigation is to synthesize the ferrite phase and study the rate of hydration in the presence of CaSO₄ and CaO up to 28-days in suspension. This study is followed by the determination of the free lime as well as combined water contents and the hydration products by the XRD analysis. The results revealed that whatever the amount of CaSO₄ the monosulphate AF₃ was the only phase formed from 6 h up to 28-days and the ettringite AF₅ was not formed. In the presence of 1 mol CaSO₄ and 2 mol CaO, the monosulphate AF₅ with carboaluminate was the dominant phase at 28-days. When the amount of CaSO₄ was increased to 3 mol with the same amount of lime the hydration was retarded in comparison with that containing 1 mol of CaSO₄. Very small amount of sulphoaluminate ferrite hydrate was formed with residual reagents such as C₃AF, CaSO₄ and Ca(OH)₂.

The ferrite phase comprises about 8-13 wt.% of portland cement, and is generally represented by the formula 4CaO.A1₂O₃.Fe₂O₃. It is solid solution series in which the ratio of Al₂O₃/Fe₂O₃ varies in a large range. A typical composition in cement clinker is C₃AF and in some cases it may be C₆AF₂ or C₆A₂F. The ferrite phase may have a variable composition that can be expressed as C₃(AlₙFₐ)₂₃where 0<n<0.7.

It is well known that the first crystalline product of ferrite phase hydration in the presence of CaSO₄ is AF₃ containing Fe³⁺ and later is replaced by AF₅. The rate of hydration reaction of the ferrite phase decreases with Fe/Al ratios and is retarded by Ca(OH)₂. Mehta attributed the retardation to forming a ferrite crystal covering on the hydrated particles. Fukuhara et al. concluded that the AF₅ phase formed from C₄AF in pastes at 20 °C had an Al/Fe ratios of about 3 and postulated that FH₃ was also formed. Brown indicated that the initial AF₅ phase made from C₄AF contains little or no Fe³⁺ and an iron oxide gel containing some Ca²⁺ is formed in the presence of gypsum.

Chen and Shi concluded that the products of C₄AF hydration in the presence of gypsum include AF₅ containing Fe³⁺ and Fe³⁺ with Ca²⁺. After gypsum is consumed, AF₅ will be gradually replaced by AF₆.

Many investigations have shown that the hydration products of C₄AF are essentially similar to those formed from C₃A under comparable conditions. The first crystalline products to form in the absence and presence of CaSO₄ are AF₅ and AF₃ phases, respectively, the AF₅ phase being later replaced by AF₃ phase as in the case of C₃A. Both types of product phase contain Fe³⁺ as well as Al³⁺, and tend to undergo further change to give hydrogarnet phases.

Some of the earlier studies indicates that reaction of C₄AF is accelerated in the presence of CH, but later work showed that, as with C₃A reaction is retarded by CH, more strongly by gypsum and still more strongly by the two together. Under comparable conditions, C₄AF appears normally to react more slowly than the C₃A. Generally, it appears that the rate of reaction of the ferrite phase decreases with the Fe/Al ratios.

The aim of the present work is to synthesize C₄AF phase from the stoichiometric composition of reagent grade CaCO₃, Al₂O₃ and Fe₂O₃. Also, the kinetics of hydration in the presence of CaSO₄ and CaO were studied.

Experimental Procedure

C₄AF was synthesized from reagent grade CaCO₃, Al₂O₃ and Fe₂O₃. The materials were mechanically mixed together in the proper mole ratios in a ball mill for one hour. The mixture was calcined at 1000°C for 2 h. Pellets were made from the calcined materials, dried and ignited up to 1300°C for 2 h, sudden cooled...
in the air, then ground, pelletized and fired at the same temperature 1300°C for 2 h. The phase is completely formed as seen from the XRD pattern in Fig. 1. It illustrates only the lines of the C₄AF phase.

The C₄AF was ground to surface area of about 3000 cm²/g, dry mixed with the appropriate amounts of CaSO₄ calcined at 750°C as well as CaO fired at 1050°C, then suspended hydrated by using 10 w/s ratio of distilled water in closed tube. The hydration was stopped at any time of hydration up to 28-days. The combined water, the free lime and the XRD of the hydrated samples were determined.

Results and Discussion

Hydration of C₄AF in the presence of CaSO₄

It was found that the use of artificial as well as natural calcium sulphate, has best effect on the early and final strength of supersulphate cement paste. Schwiete and Dobler found that artificial anhydrite CaSO₄ improves the early strength at three and seven days to the formation of the hydrated calcium sulphi-alumina-nates such as monosulphate and ettringite which are responsible for the early strength. Therefore, artificial anhydrite burned at 750°C was used in the hydration of C₄AF with CaSO₄ and CaO. This temperature is the most suitable firing temperature of anhydrite.14

The XRD patterns of the hydrated C₄AF with one mole of CaSO₄ (M₁) as a function of curing time up to 28-days are seen in Fig.2. Sample with one mole CaSO₄ and hydrated for 6 h illustrates the presence of monosulphate aluminate ferrite hydrate (AFₐm) as the predominant phase and monocarboaluminate hydrate with residual anhydrite and ferrite phase. After one day of hydration, the intensity of monosulphate hydrate (AFₐm) increases with the presence of monocarboaluminate hydrate due to the carbonation

with carbon dioxide as well as residual CaSO₄. As the hydration proceeds up to 28-days, the hydration products are the same such as monosulphate and some monocarboaluminate hydrates. These findings are in contradiction with those of other investigators8,9. Ettringite (AF₁) may be formed at very ages of hydration before 6 h. The hydration was strongly retarded by the presence of CaSO₄(ref.15).

C₄AF with 3 mol CaSO₄ (M₂) and hydrated up to 28-days are seen in the XRD patterns in Fig.3. Sample of C₄AF with 3 CaSO₄ shows the presence of poorly crystalline ettringite ferrite phase (AF₁) and monocarboaluminates hydrate after 6 h of hydration. The anhydrite and ferrite phase are also present. At one day of hydration, the anhydrite decreases with the increase of ettringite. As the hydration proceeds, monosulphate (AFₐm) and ettringite (AF₁) as well as unreacted CaSO₄ and C₄AF are present at three days. Sample hydrated for 7-days gives monosulphate hydrate with unhydrated CaSO₄ and anhydrorous calcium aluminoferrite. On the side, at 28-days the monosulphate hydrate (AFₐm) is sharply increased with the appearance of monocarbonate hydrate and the disappearance of anhydrite and calcium aluminoferrite. It can be seen that the ettringite is not
formed whatever the ratio of CaSO₄ in respect to one mole of C₄AF. Very small amount of ettringite was formed at early ages and transformed to monosulphate.

The chemically combined water contents can be taken as a degree of the hydration of the hydrated suspension. Fig.4 shows the chemically combined water contents of the hydrated C₄AF with one mole (M₁) and three moles (M₂) of anhydrite in relation with curing time. It is clear that the degree of hydration occurs in two steps. In the first step, the hydration increases strongly up to one day. In the second step the rate of hydration increases at higher rate up to 28-days than the first step. This may be due to the retardation of hydration at early ages.

On the other side, the degree of hydration of the ferrite phase with one mole (M₁) of CaSO₄ is higher than that containing three moles (M₂) of CaSO₄ at all ages of hydration. This may be due to the presence of excess amount of CaSO₄ which acts as a retarder for the hydration of C₄AF. It was concluded that gypsum retards the hydration reaction of C₄AF and decreases with the content of gypsum. This is also seen from the formation of monosulphate hydrate in the case of one mole at early ages (one day) as seen from the XRD patterns. Therfore, the results of the X-ray analysis are in a good agreement with the values of the chemical analysis. Also, it can be concluded that the consumption of C₄AF is delayed by the presence of CaSO₄ and this retardation is elongated with the increase of CaSO₄ content.

In a previous work the hydration of C₄AF with 0.6, 1.0 and 1.5 mole ratio of gypsum was studied. The characteristic X-ray diffraction patterns of C₄AF were disappeared after one day in the mixture with mole ratio of gypsum to C₄AF = 0.6. In the mixtures with 1.0 and 1.5 mole ratio, the anhydrous phase is well recognized in the one day sample but it is consumed after three days. On the other hand, gypsum is instantaneously consumed in the mixture with lower sulphate concentration 0.6 and within 30 min in the other mixtures. At 0.6 mol ratio, the ettringite is recognized in one hour then is converted to the monosulphate hydrate after one day. In mixture with higher gypsum content as 1.0 mol the ettringite is already formed after 30 min and increases with time and converts to monosulphate hydrate after three days. The ettringite phase is appeared instantaneously in the mixture of 1.5 mol ratio and was not converted to monosulphate.
Hydration of C₄AF in presence of CaSO₄ and CaO

Fig. 5 shows the XRD patterns of the hydrated C₄AF + CaSO₄ + 2CaO (M₁) as a function of curing time up to 28-days. The anhydrous mix illustrates the peaks of C₄AF, anhydrite CaSO₄, and Ca(OH)₂ as well as CaO. Sample hydrated for 6 h recognizes the same phases in addition to small amount of calcium sulfoaluminate hydrates and the disappearance of CaO due to its hydration with the increase of the hydrated lime. The peaks of Ca(OH)₂ is increased in comparison with its content at zero time of hydration. The same phases were also detected up to 7-days of hydration. Sample hydrated for 28-days shows the presence of tetracalcium aluminoferrite hydrate C₄(AlF)H₁₃ with some essential carbonate as the predominant phase with monosulphate hydrate AFm, small amount of unhydrated C₄AF and may be also traces of Ca(OH)₂. It can be concluded that the presence of 2CaO with CaSO₄ retards the hydration of C₄AF. Also, the presence of lime with CaSO₄ tends to increase the formation as well as retard the hydration of C₄AF. Therefore, the C₄AF is also detected in the presence of CaO and is completely disappeared with only CaSO₄ in the absence of CaO.

The combined water and free lime contents of the hydration of C₄AF with CaSO₄ and CaO (M₃) as well as without CaO (M₁) shown in Fig. 7. The free lime of the hydrated mix containing lime decreases sharply in the first 7-days then slowly up to 28-days. This in a good agreement with the results of XRD analysis. On the other side, sample without lime shows no lime at all ages of hydration.

The combined water contents of the CaSO₄ + 2 CaO are lower than those containing only CaSO₄ at all ages of hydration due to the retardation effect of lime. The increase of combined water of samples without lime is occurred in the first three days, at later ages (3-28days) the combined water is slightly increased.

Conclusion

From this study the following conclusions can be made: C₄AF was completely synthesized after two firing at 1300°C for 2 h of the pelletized of a reagent
grade chemicals. The monosulphate hydrate (AFm) was the predominant hydrated phase in mixes containing one or 3 mol of anhydrite.

The presence of 2CaO with one or 3 mol CaSO₄ retards the hydration of C₄AF. The anhydrite cannot be consumed at 3 mol CaSO₄. Poorly crystalline sulphaoluminate hydrates were formed at one and 3 mol CaSO₄ with 2CaO. The presence of CaO with CaSO₄, the hydration was strongly retarded than only CaSO₄.

References