Understanding of Reactional Sequences and Limiting Stages during Tricalcium Aluminate Hydration with and without Gypsum.

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Tricalcium aluminate reacts quickly with water to form calcium hydroaluminates while addition of calcium sulphate leads to the formation of ettringite with a slower rate. A lot of hypotheses have been proposed to explain this behaviour without general agreement. This problem is revisited here by a systematic study of the systems "C_3A" and "C_3A-sulphate" in diluted stirred suspensions by isothermal microcalorimetry and the analysis of the solutions. It makes possible to understand the sequence of the reactions and the limiting stages in both systems.
In all cases, as it is in contact with the solution, C_3A starts to dissolve leading to the instantaneous precipitation of a certain amount of calcium hydroaluminate.
Without calcium sulphate, hydration rate which decreases continuously, is controlled by C_3A dissolution.
With gypsum, the rate of hydration is then controlled by the low rate of ettringite formation. After consumption of sulphate, hydration is limited by C_3A dissolution.

1. Introduction

Tricalcium aluminate (C_3A), which can constitute until 15% of the Portland cement, reacts very quickly with water to form calcium hydroaluminates that induces the stiffening of cement paste. To avoid this phenomenon, calcium sulphate is added which leads to the formation of calcium trisulfoaluminate, ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}, 26H_2O$) or $C_6A\$_3H_{32}$ with a slower process. Also, the reactivity of the tricalcium aluminate - calcium sulphate system is of a very high importance since it controls the workability of cement paste. Many hypotheses regarding the action of calcium sulphate have been suggested but the mechanisms by which C_3A reacts slower are not yet fully elucidated [1-6]. Disagreements in the interpretations of the experimental data are probably due to the fact that most of the phenomena occur at very early age, even during mixing. Moreover, results are strongly depending on the experimental conditions which are not always perfectly controlled. In particular, making a paste with very reactive powders and a small amount of water inevitably introduces local heterogeneities.
So, more work is required to understand the reactivity and the kinetics of the C_3A-H_2O and C_3A-$CaSO_4$–H_2O mixes. In the present work, to avoid the heterogeneity problems, we proceeded in stirred diluted suspensions.

Indeed, this procedure has been found very efficient to understand the mechanisms and the parameters controlling the reactivity of tricalcium silicate at early age. In addition, it is easy, in theses conditions, to follow the evolution of the liquid phase which is the way of exchange of matter between solids during the reaction. The overall reaction has been followed by isothermal microcalorimetry according to the procedure developed to study C_3S hydration [7]. In parallel, the same experiments have been performed in conductimetry reactors allowing picking up samples at different hydration times for solid and liquid phase analysis.

This paper reports the study of the hydration of C_3A in water and lime solution without and with addition of gypsum. Different parameters were studied such as the C_3A granularity, because of the importance of fineness grains on reactivity, and the gypsum amount with the objective to identify and quantify the first hydration products in order to evaluate their eventual impact on the kinetics of C_3A hydration.

2. Materials and Methods

2.1 Methods

Hydration of C_3A was followed at 25°C with a high sensitivity (0.1µW) isothermal Tian-Calvet type micro calorimeter (SETARAM ms80) in diluted suspension which is associated with a conductimetric system (radiometer). 50 mL of solution were introduced in the cell with the appropriate amount of solid gypsum if necessary. 2 g of C_3A (7,4mmol) were stored in a special tank.

The calorimetric cell is then introduced in the calorimeter and the stirring of the solution begins; once the thermal equilibrium is reach (about 2hours), C_3A is introduced in the cell. Both heat flow and conductivity evolutions were obtained as a function of time. The thermal inertia of such a calorimeter is relatively high. If the thermal event is shorter than the time constant of the calorimeter, when the total heat is correct, the intensity of the observed signal is smaller and its duration is greater than those of the true event. The true signal corrected from the transfer function of the calorimeter was obtained from a one step Fourier filter.

Same experiments than those performed in the calorimeter were reproduced in a thermo regulated (25°C) reactor (25g of C_3A -250mL of solution) equipped with a conductivity cell (radiometer) . Recording the electrical conductivity of the solutions in both experiments allows synchronising them. The chemical composition of the liquid phase was determined in taking few millilitres of solution at several times; each solution was filtered (0.3µm, Millipores) and a small known quantity of hydrochloric acid was added. Calcium and aluminium concentrations were checked by Spectrometric Atomic Absorption (Perkin-Elmer, model 3030) and sulphate concentrations by ionic chromatography (Dionex).

In the other hand, solid part was washed with pure alcohol in order to analyse solids by X-ray diffraction (Inel CPS 120) and the products was studied by SEM (Jeol, model 6400F).

2.2 Materials

C_3A was synthesized by burning the appropriate amount of calcium carbonate and alumina. Samples L were supplied by Lafarge LCR and sample C was supplied by CTG Italcimenti. Their specific surfaces, determined by Blaine's method, were respectively $3250 cm^2/g$ and $3300 cm^2/g$.
$C_3A(L)$ was also used to prepare samples of different grain size : a mix of 30 grams of C_3A (L) was mixed in an inert solvent, absolute ethanol, submitted to a high dispersive treatment (Ultrasound 30seconds) and poured in a long tube (1 meter long , 2cm in diameter). The suspension was leaved to stand during one month. The solvent was then eliminated and the sediment dried. The sediment was separated to obtain C_3A slices with different diameter from fine particles on the surface to big one in the bottom.

Pure gypsum from Merck was used. Lime was obtained by decarbonation overnight at 1000°C of calcium carbonate provided by Aldrich.

3. Results and discussion

3.1 The C_3A-H_2O system

Figure 1 shows the evolution of the experimental heat flow and conductivity of the solution recorded during the hydration of 7.4mmol of C_3A (C) in 50ml of pure water and a solution saturated with respect to portlandite respectively(L/S=25). When both heat evolution rate curves are very similar, the evolutions of the conductivity are opposite. The heat evolution rate curves consist in a sharp and intense initial exothermic peak, then the heat flow drops rapidly and there is a new small exothermic peak between 400 and 500 minutes. In the same time, in water, the conductivity increases rapidly to reach a plateau when the conductivity decreases in saturated lime solution to reach the same plateau. Then, the conductivity increases again in the case of hydration of C_3A in lime solution and decreases in water when the heat evolution rate curves show the second exothermal peak. XRD analyses of the solid phases during hydration reveal that the first peak corresponds to the disappearance of C_3A to the profit of AFm and the second to the dissolution of AFm to form hydrogarnet.
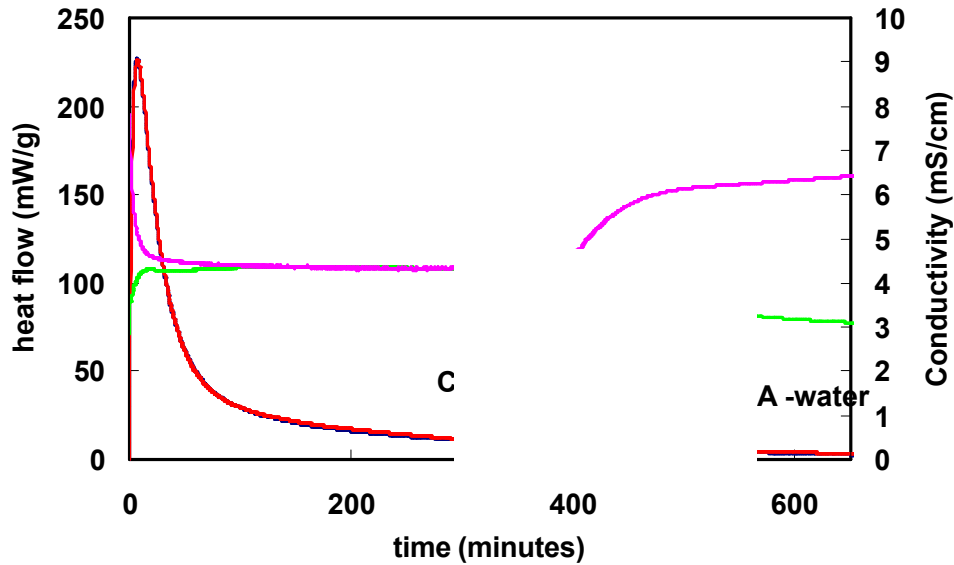
Figure 1 : Heat evolution rate curves and conductivity recorded during the hydration of C_3A (C) in water and a solution saturated with respect to portlandite (L/S=25). The heat flow is corrected from calorimeter inertia by a one step Fourier filter.

Solution analyses performed by sucking a part of the solution during the hydration of C_3A show that the conductivity perfectly reflects the evolution of calcium concentration (Figure 2). In each case, hydration in water or a lime saturated solution, the aluminium concentration evolves in the opposite way than the calcium concentration. The conductivity plateau corresponds to a calcium concentration plateau; that means the hydration product formed during this plateau has a C/A stoichiometric ratio very close to the one of C_3A whatever the hydration solution, i.e. close to 3. If hydration begins in water the stoichiometry is lower than 3 (close to C_2AH_8), and if it begins in a lime saturated solution it is greater than 3 (close to C_4AH_{13}). Analysing simultaneously conductimetric and calorimetric data leads to the conclusion that a solid solution CxAHy probably exists in which C_2AH_8 and C_4AH_{13} are the two limits. The percentage of hydration of C_3A versus time is plotted on Figure 3. It shows that the rate of hydration is mainly controlled by the C_3A dissolution tacking into account the decrease of the reacting surface.
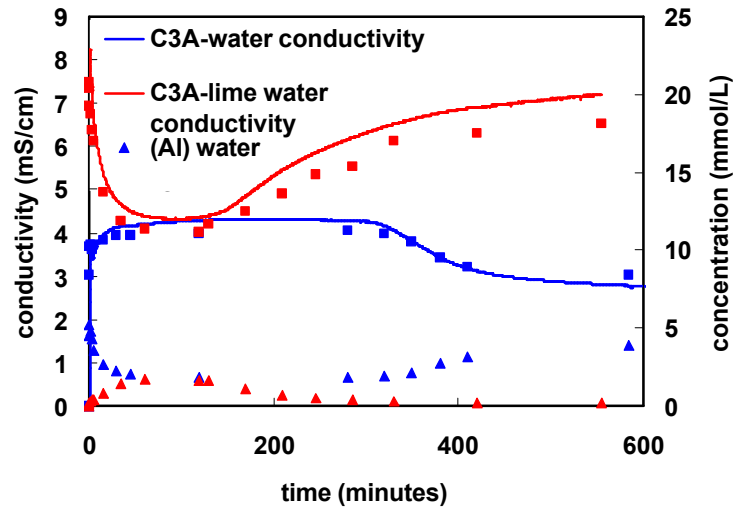
Figure 2 : Ionic concentrations and conductivity evolutions during hydration of C_3A (C) in water and a solution saturated with respect to portlandite (L/S=50).
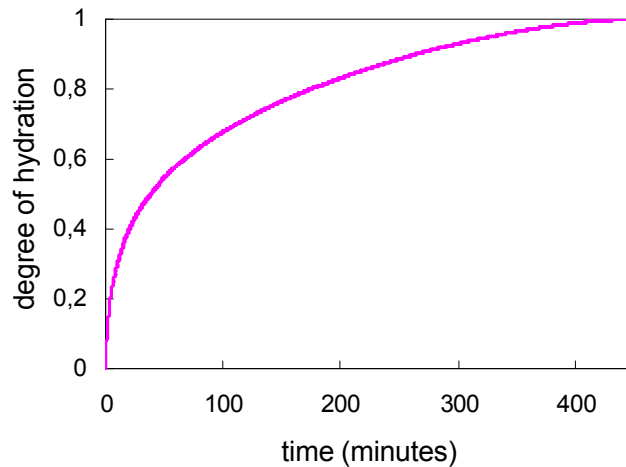

Figure 3 : evolution of the degree of hydration of C_3A (C) versus time in water and a solution saturated with respect to portlandite (L/S=25). It is estimated by integrating the heat evolution curve.

3.2 The C_3A-$CaSO_4$-H_2O system

The influence of the initial amount of gypsum was studied on the different stages of hydration of C_3A(L). In all experiments 1g (3,7mmol) of C_3A was used and the amount of gypsum varied from an experiment to another from 6 to 43% in weight. These experiments take place always with a solid gypsum reservoir. Experimental heat evolution rate curves recording during hydration of C_3A (L) carried out with various amount of gypsum are

reported on Figure 4. They all show the succession of two strong exothermic peaks. The beginning of all heat evolution rate curves are superposed whatever the amount of gypsum. The amount of gypsum does not have any effect on the beginning of the hydration.
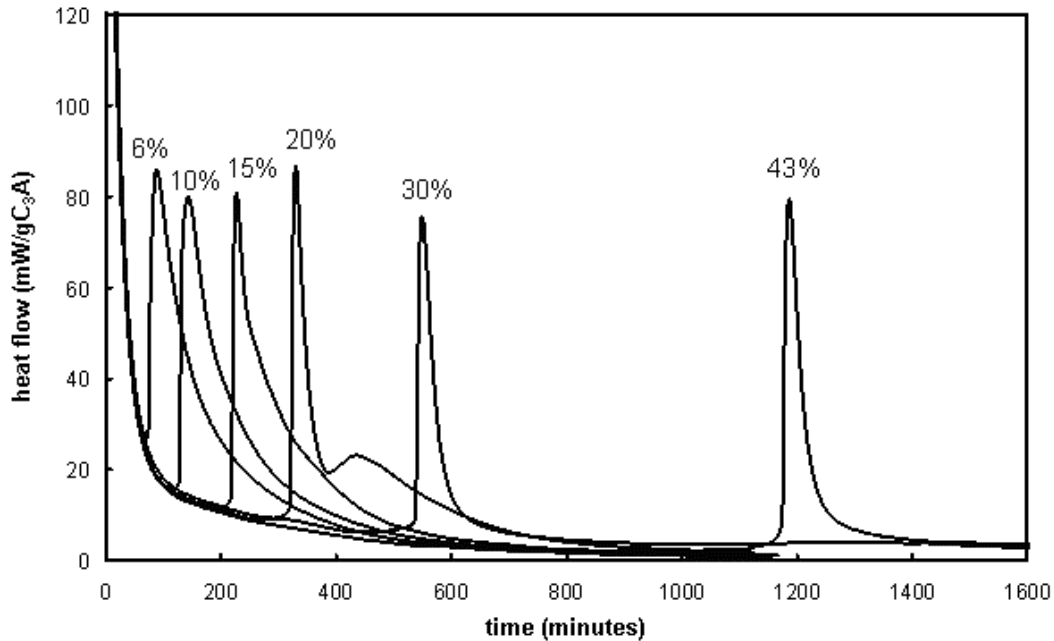

Figure 4 : Heat evolution rate curves during the hydration of C_3A (L) in solutions saturated with respect to portlandite (L/S=25) carried out with various quantities of gypsum.

The time of occurrence of the second exothermic peak, increases with the gypsum quantity. On the contrary, the intensity of the second strong exothermic peak does not seem to be greatly modified by the initial amount of gypsum.

Figure 5 shows the evolution of the experimental heat flow corrected from the inertia of the calorimeter and conductivity of the solution recorded during the hydration of 7,4mmol of C_3A (resulting from a batch C in 50ml of a solution saturated with respect to portlandite (L/S=25). Under these conditions all the gypsum was not initially dissolved, it remains 0.875mmol solid gypsum in the initial suspension before C3A is added. The heat evolution rate curve shows two strong and narrow exothermic peaks due to very fast events. Corresponding ionic concentrations are represented on Figure 6 with conductivity.
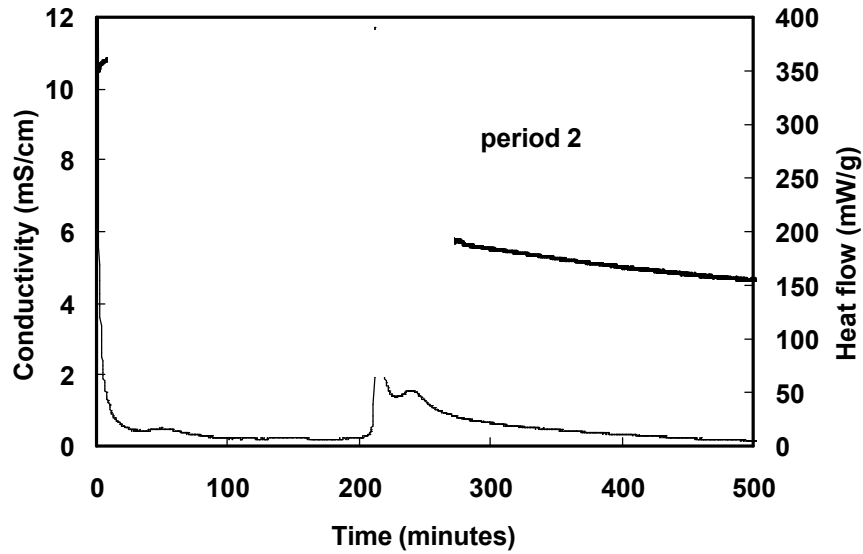
Figure 5 : Heat flow and conductivity evolutions during hydration of 7,4mmol of C_3A (C) and gypsum (1,5mmol) in 50ml of a solution saturated with respect to the portlandite (L/S=25).
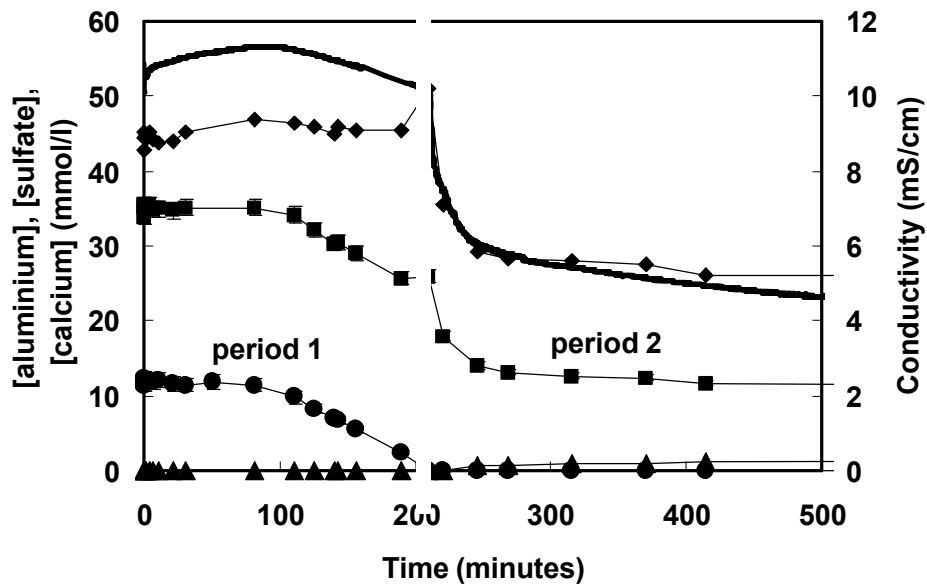

Figure 6:   Ionic concentrations (aluminium : ▲, sulfates: ●, calcium:■ and calculated hydroxide :◆) and conductivity evolutions during hydration of 7,4mmol of C_3A (C) and gypsum (1,5mmol) in 50ml of a solution saturated with respect to the portlandite (L/S=25).
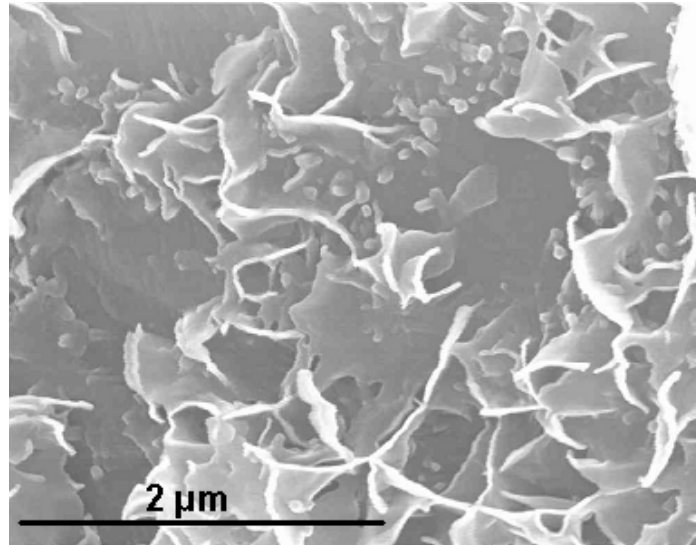
Figure 7 : : Micrography of a grain of C_3A hydrated during 3 minutes in a solution saturated with respect to calcium sulphate and calcium hydroxide

A distinct period was arbitrarily associated to each peak and to the weakest thermal activity which follows it. Period 1 corresponds to the presence of sulphate ions in solution; it refers to the period of calcium sulphate consumption. The initial sulphate concentration corresponds to the solubility of gypsum in a saturated solution with respect to portlandite which is 2,15g/L or 12,5mmol/L. Period 2, begins when all the sulphate ions are entirely consumed, and then the second exothermic peak appears.

Then the sulphate concentration increases slightly although this species is consumed at least for the formation of ettringite. During this stage, it always remains solid gypsum in equilibrium with solution, a quasi stationary state is established, where all ions consumed by ettringite formation are replaced by gypsum dissolution. The value to which is established the "stationary" state is surprisingly very closed to the gypsum solubility. The dissolution of the gypsum is then not a limiting step.

From the kinetic point of view, the heat evolution rate curve (Figure 5) shows, after the decrease of the initial peak, a new exothermic peak followed by a constant flow when the sulphate concentration decreases quasi linearly until the complete disappearance of this ion. The calcium concentration decreases also continuously. The aluminium concentration is practically lower than the limit of detection of the analytical method for all the period except for the first point at 15 seconds when it is about 10 µmoles. At the end of this stage, ettringite is the dominating hydrated phase. The second exothermic peak represents, assuming a constant reaction heat, an increase of the hydration rate; it could be interpreted as

the acceleration of ettringite formation which follows a classic process of germination-growth. it is interesting to notice that the linear decrease of the sulphate concentration corresponds to one period of constant flow, i.e. a constant reaction rate. It is possible to show that, during this period, there is only consumption of sulphates ions from the solution, the reduction in the sulphate concentration in solution is thus due to the fact that all the solid gypsum was consumed in this stage [8, 9].

The beginning of period 2, after the exhaustion of the sulphate ions, coincides with a strong renewal of thermal activity. It shows, at the beginning, a peak with an intense exothermic component whose intensity in the case of this experiment is about 400mW/g C_3A corresponding to a very fast exothermic reaction. The calcium concentration increases simultaneously with the exhaustion of the sulphate ions in solution, then decreases. The aluminium concentration is not zero; it is increasing step by step. One cannot impute the very narrow peak to the fast ettringite-calcium monosulfoaluminate transformation contrary to what is often advanced in the literature [6, 10]. Ettringite remains a longer time. This strong exothermic peak can only be attributed to the continuation of dissolution of C_3A. Indeed the solution is very undersaturated with respect to C_3A which dissolves until the solution becomes supersaturated with respect to AFm which then precipitates. This step of pure dissolution of C_3A is very short; this is why the thermal peak is very narrow. It is also often evidenced, by the transient peak on the conductivity curve corresponding to the hydration of a coarser C_3A (not shown here). But the thermal peak is also very intense, that is to say the dissolution rate of C_3A is very high; that means that ettringite and other hydration products does not limit the dissolution of C_3A. The solution is then free from sulphate ions; it is a solution for which the concentration is close to the solubility of portlandite. Very quickly, the dissolution of C_3A in such a solution leads to the precipitation of calcium hydroaluminates, consuming calcium ions and releasing from the aluminium ions in solution; this is the origin of the strong drop of conductivity (Figure 5) at this moment. Later, an exothermic peak of smalller intensity takes place then followed by a relatively weak thermal activity. The calcium and aluminium concentrations do not evolve a lot. Impoverishment of the calcium ions concentration in solution (due to the precipitation of the calcium hydroaluminates) results in precipitation of calcium monosulfoaluminate which becomes more stable from a thermodynamic point of view than ettringite which dissolves; it is a very slow transformation. After 2 days of hydration of C_3A under the above experimental conditions, ettringite in the form of needles and calcium monosulfoaluminate in the form of hexagonal plates cohabit, ettringite did not completely disappear (Figure 8).
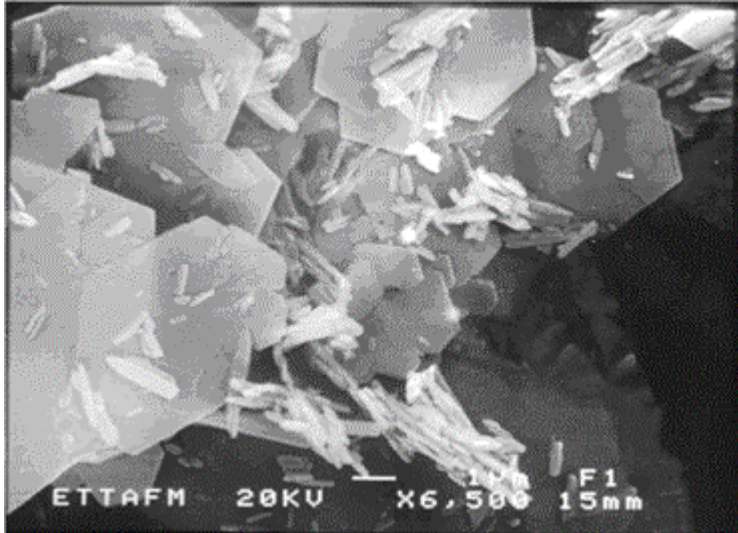
Figure 8: Micrograph of C_3A hydrated during two days in presence of calcium sulphate, L/S = 25.
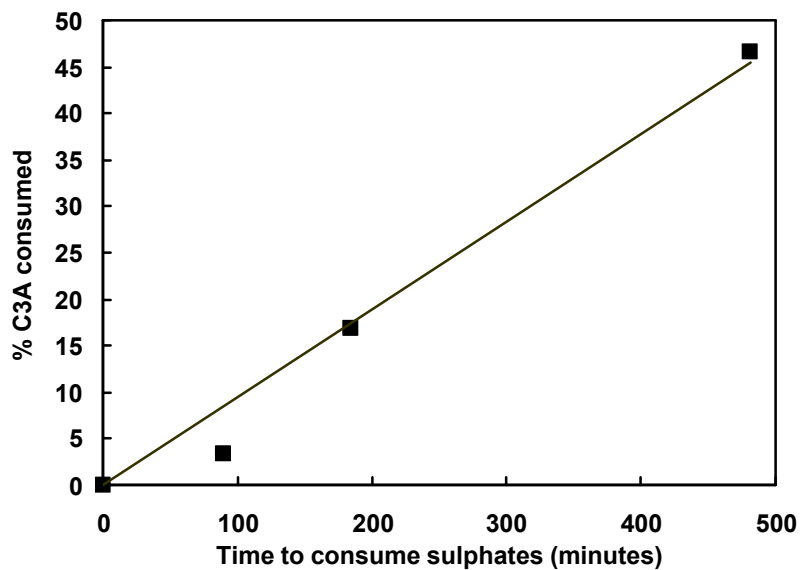

Figure 9 : Evolution of the percentage of consumed C_3A with the time needed to exhaust all the calcium sulphate for different amounts of gypsum in the case of a mono dispersed slice of C_3A (L); D_{50}=3µm.

The formation of ettringite is not at the origin of this slowdown otherwise on the one hand, reaction rate would not be constant according to the quantity of formed ettringite as observed with small homodispersed grains in Figure 9, on the other hand, the rate of dissolution of C_3A should not so high at the end of gypsum consumption. The hypothesis of a formation of ettringite barrier that would limit the reaction rate is not valid.

The initial formation of AFm can not either explain why reaction rate decreases because, without gypsum, in calcium hydroxide solutions, the same product is formed and the C_3A reacts very quickly.

The specific adsorption of the sulphate ions on the surface of the grains of C_3A could explain this slowdown; these would block certain dissolution sites of C_3A.

4. Conclusion

These studies on the hydration of the tricalcium aluminate in the presence of gypsum show the formation of two different hydrates during the period when the gypsum is consumed: ettringite as awaited but also AFm phase at the early beginning. None of these phases plays a barrier role to limit the hydration rate of C_3A. The slow process of ettringite formation could be limited by ettringite growth rate but the dependence on the surface area of C_3A would indicate rather a limitation by its dissolution. The high C_3A dissolution rate which is observed after the disappearance of sulphate ions in solution would credit the assumption with the role of the adsorption of the ions sulphates on the dissolution of C_3A.

5. Acknowledgments

6. References

[1] Collepardi, M., Baldini, G., Panri, M., and Corradi, M., Tricalcium aluminate hydration in the presence of lime,gypsium or sodium sulfate. Cem Conc Res 8 (1978) 571-580.

[2] Bailey, J.E. and Chescoe, D. A progress report on analytical electron microscopy studies of the hydration of tricalcium aluminate. in 7th ICCC. 1980. Paris.

[3] Havlica, J., Roztocka, D., and Sahu, S., Hydration kinetics of calciumaluminate phases in the presence of various ratios of Ca2+ and SO4-- ions in liquid phase. Cem Concr Res **23**(2) (1993) 294-300.

[4] Brown, P.W., Libermann, L.O., and Frohnsdorff, G., Kinetics of the early hydration of tricalcium aluminate in solutions containing calcium sulfate. J Amer Ceram Soc 67 **(**1984) 793-795.

[5] Feldman, R.F. and Ramachandran, V.S., The influence of $CaSO_4.2H2O$ upon the hydration character of 3CaO, Al_2O_3. Mag of concrete research, 18(57) (1966) 185-196.

[6] Skalny , J. and Tadros, M.E., Retardation of tricalcium aluminate hydration by sulfates. J Amer Ceram Soc 60(3-4) (1977) 174-175.

[7] Damidot, D., Nonat, A., and Barret, P., Kinetics of Tricalcium Silicate Hydration in diluted Suspensions by Microcalorimetric Measurements. JAmer Ceram Soc 73(11) (1990) 3319-3322.

[8] Minard, H., Garrault, S. and Nonat A., Tricalcium aluminate-gypsum hydration, Cem and Conc Res (to be published).

[9] Medala, M., Minard, H., Nocun-Wczelik, W., Garrault, S., and Nonat , A., Hydration of C_3A-$CaSO_4$-H_2O system revisited. Ceramics, 92 (2005) 275-281.

[10] Stein, H.N., Some characteristics of the hydration of $3CaO.Al_2O_3$ in the presence of $CaSO_4.2H_2O$. Silicates Industriels, 25(3) (1963) 141-145.