

Hydration of silicate phase and mechanical evolution in “alite-tricalcium aluminate-gypsum” complex system.

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Abstract

Using simultaneously calorimetry and dynamic mode rheometry, it has been possible to evidence mechanical consequences of chemical interactions between the components of the “alite-C₃A-gypsum” system.

The concept of “mechanical efficiency of calcium silicate hydrates», R , was introduced to quantify the effect of the mixtures on the cohesive properties of C-S-H. $R = dG' / dQ$, is the increase in the elastic modulus dG' corresponding to the formation of a certain amount of C-S-H, estimated by the released heat dQ .

For the alite-C₃A mixture, aluminate ions decrease both the growth rate of C-S-H and R ; for great quantities of C₃A, there is a positive effect of the surface developed by AFm on R . If gypsum is added, the hydration of alite is not affected a lot by C₃A and R increases with the added gypsum quantity.

In most cases, complex system does not behave like the sum of simple systems.

1 Introduction

The mechanical properties of the hardened Ordinary Portland Cement (OPC) paste are mainly due to calcium silicate hydrate (CaO-SiO₂-H₂O noted C-S-H) [1], which is the hydration product of tricalcium silicate (C₃S), the main phase of OPC. However, it is known that the content of aluminate phase also plays a role on the reactivity and mechanical properties of OPC. It is difficult, studying different OPC to discriminate the effects since a lot of properties such as alite/belite ratio, alite size, calcium sulfate optimum... are modified in the same time. It is possible to quite easily determine the intrinsic mechanical properties of C-S-H during early age hydration of alite. Indeed, setting of cement takes place in two mechanical steps [2,3]:

- the first step, named coagulation, results from attractive forces between non hydrated particles and leads to the formation of a connected system of anhydrous grains.

- the second, named rigidification, is due to the strengthening of the contacts of the connected system by C-S-H precipitating at the surface of anhydrous grains near the contact points.

By following simultaneously the evolution of the mechanical properties of the connected structure, through its storage modulus for example, and the amount of precipitated C-S-H, by calorimetry for example, during hydration at early age, it is possible to calculate $R = dG'/dnC-S-H$ which represents the increase of modulus due to the formation of one mole of C-S-H. In the present work we attempt to evaluate by this way, the effect on the mechanical properties of C-S-H of the presence, on one hand, of the C₃A-gypsum system which is representative of what happens in a cement paste at early age, and on the other hand, in presence of C₃A alone which is representative in a cement paste of what happens after the consumption of all the calcium sulfate.

2 Experimental

The hydration was followed by a high sensitivity (0.1μW) isothermal Tian-Calvet type at 25°C [4].

The evolution of the mechanical properties of the paste has been followed by dynamic mode rheometry [5] with a controlled strain rheometer (RDA II Rheometrics). The sample is submitted to a sinusoidal strain, $\gamma(t) = \gamma_0 \cos(\omega t)$, and the resulting stress is determined : $\tau = \tau_0 \cos(\omega t + \delta)$. The sample is submitted to a strain with constant frequency (1rad/s), and a constant amplitude (0.02%) smaller than the critical strain [6], the material structure is not destroyed. The strain range before this critical value is the linear viscoelastic domain of the material. In this domain, a complex modulus of the material can be defined as $G^* = \tau/\tilde{\gamma}$. This complex number can be written as $G^* = G' + i G''$. G' is the storage modulus, G'' the viscous modulus.

A classic parallel plates geometry was used and maintained at 25°C to be in isotherm conditions. The surface of the plates has been roughened in order to avoid wall slippage. The sample is a disk of paste, with a diameter of 8 mm and a thickness of 2 mm.

C₃A and alite were first gently ground by hand in a mortar in order to get the best homogeneity as possible. The powder was then mixed with water by a strong hand mixing (4 g powder/ 2 mL water). In such conditions we got a good reproducibility. A part of a same mix was used for rheometry and the rest is placed in the calorimeter. A special device was developed to avoid heat emission while introducing the calorimetric cell in the calorimeter and so access as possible to the heat liberated by early hydration.

3 C-S-H formation and Numerical simulations

To quantify, as precisely as possible, the amount of C-S-H precipitated and the characteristics of the precipitation at early age from heat evolution rate curves, they were fitted according to a mesoscopic numerical model of C-S-H growth on the tricalcium silicate surface around primarily heterogeneous nucleation sites [7]. In the model, the evolution of the percentage of hydration is described from the aggregation around initial nuclei of identical particles in an anisotropic way [8]. Ca_3SiO_5 surface is simulated by a matrix A whose elements are 0 or 1. The dimension of the matrix corresponds to the surface area of the grains. A C-S-H nucleus on the surface corresponds to a value of 1. The parallel growth is obtained by successive convolution products of the “surface matrix A” by a “growth matrix $B(x,y)$ ”. Each convolution product is associated with iteration (l). The number of generated elements at each iteration is equal to the dimension of the growth matrix. The greater the dimension of $B(x,y)$, the faster the growth parallel to the surface. The perpendicular growth is obtained by superposing (kl) layers identical to those formed by parallel growth. At each iteration, the number of generated elements is multiplied by k (multiplication factor). The greater k, the faster the growth perpendicular to the surface. The algorithm of the numerical simulation is described elsewhere [Error! Bookmark not defined.7]. The validity of the model stops when most of matrix elements are 1, i.e. when the grain surface is practically completely covered by hydrates. The parameters of the model are:

- the specific surface on which C-S-H grows (dimension of the surface matrix)
- the number of initial nuclei,
- the parallel growth rate (dimension of the convolution matrix),
- the perpendicular growth rate (the value of the multiplication factor).

4 Results and discussion

4.1 “alite- C_3A system”

4.1.1 Hydration of alite- C_3A mixes

The figure 1 presents the heat evolution rate curves observed during hydration of alite- C_3A mixes with different quantities of C_3A . The curves are typical ones of the hydration of tricalcium silicate with a first peak of short duration and a main peak characteristic of the hydration of C_3S . Both first and main peaks are strongly affected by the addition of C_3A .

Fig.2 shows the evolution of the first peak which is, in these conditions, mainly related to the fast hydration of C_3A in AFm [9, 11] as shown by its strong increase with the C_3A percentage in the mix. The linearity between maximum intensity of the first peak and the percentage of C_3A in the mix (Fig.3) indicates that maximum rate of C_3A hydration is

not modified by alite presence during this period. The Figure 3 also presents the cumulated heat flow at 120 minutes (time for which the greatest part of C_3A is consumed), obtained from integration of heat flow curves, versus quantity of C_3A . The proportionality indicates that the hydration of C_3A is not modified by alite anymore.

In agreement with the Tenoutasse's results [10], it can be noticed an influence of the quantity of C_3A on the evolution of the intensity and the time of appearance of the maximum of the second peak corresponding to alite hydration. The evolution of the main peak is non monotonous with increasing amount of C_3A . The maximum of the peak is reached all the later as the quantity of C_3A in the mixture is important, except for the mixture 50% - 50%. The rate of alite hydration which is proportional to the heat flow, is also modified; it decreases when the quantity of C_3A is 5% and, for greater percentages, it becomes greater than for pure alite but continuously decreases. The ratio of the rate of hydration of C_3S in the different mixes on the rate of hydration of pure C_3S can be directly obtained by dividing the maximum heat flow for each mix by the maximum heat flow of the pure C_3S hydration (curve a on Fig.1). Except for the lower percentage of C_3A , the rate is greater for the mixes than for pure C_3S and continuously decreases with increasing amount of C_3A (Fig. 4).

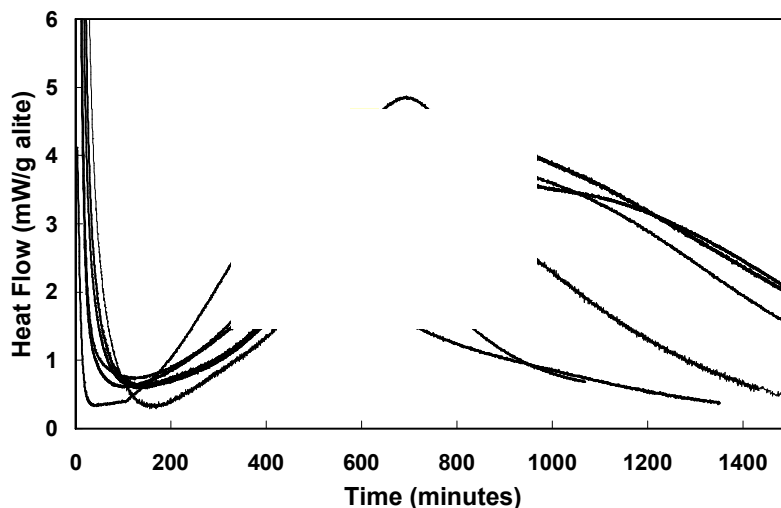


Figure 1: Heat evolution rate curves for hydration, with $W/C=0.5$, of different alite- C_3A mixes, a : 100% alite, b : 95%, c : 90%, d : 80%, e : 75% and f : 50 %. A shoulder appears in curves c, d and e; it can be allotted to heterogeneity of the mixture: the experiments were repeated three or four times and this shoulder does not appear systematically.

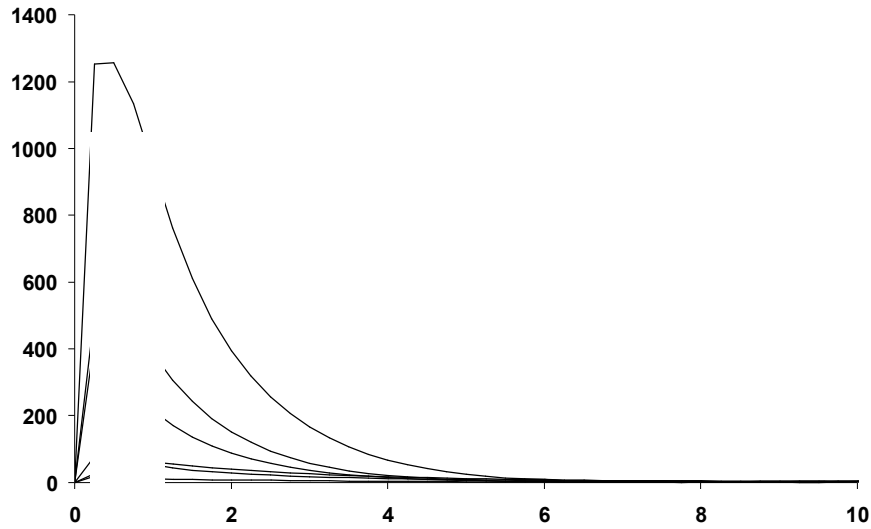


Figure 2: Heat evolution rate curves during the first minutes for hydration, with $W/C=0.5$, of different alite- C_3A mixes, a : 100% alite, b : 95%, c : 90%, d : 80%, e : 75% and f : 50 %.

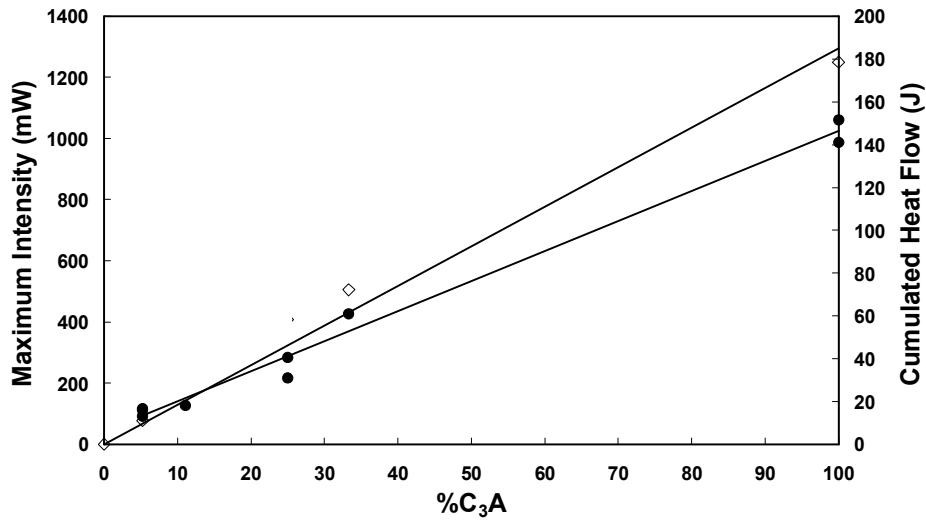


Figure 3: Evolution of maximum intensity of the first peak of Figure 1 and evolution of the cumulated heat flow obtained at 120 minutes versus percentage of C_3A for hydration of different alite- C_3A mixes.

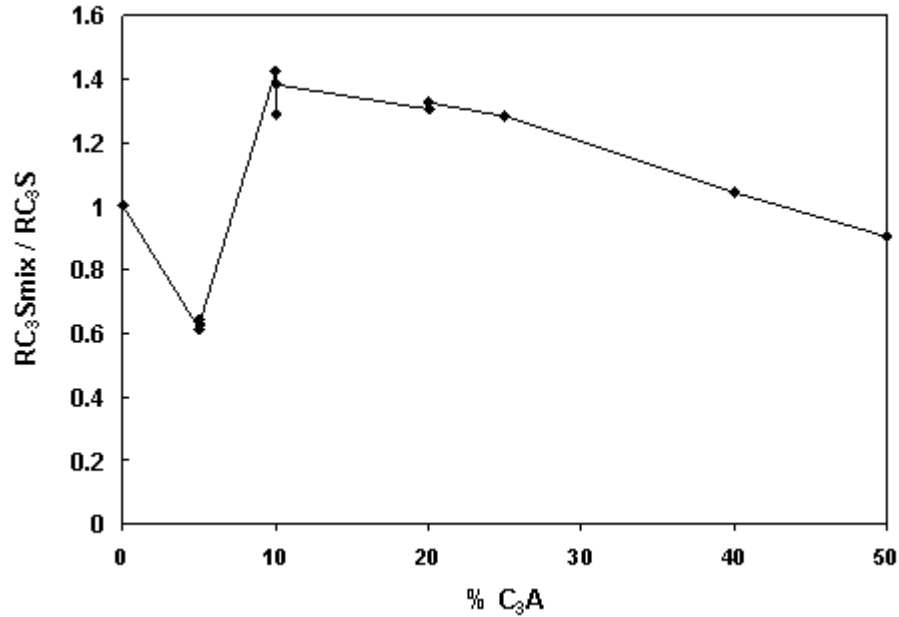


Figure 4: Evolution of the ratio of maximum rate of alite hydration in the mixes/ maximum rate of hydration of pure alite versus percentage of C₃A in the mixes corresponding to Figure 1.

To explain this evolution, the hydration kinetics curves have been simulated using the model presented above. For this purpose, the heat evolution rate curves of Figure 1 have been integrated (cumulated heat) and the quantity of heat attributed to C₃A hydration (before 120 minutes) has been subtracted; the results are reported on the figure 5. To account for the experimental curves, it is necessary to decrease growth rates of C-S-H comparatively to the hydration of alite alone (Fig.6) which can be attributed to the influence of aluminate ions in solution on C-S-H growth. It is also convenient to increase surface matrix (Fig.6) with C₃A quantity. It is due to the C₃A hydrates, AFm, which act as accessible nucleation and growth surfaces for C-S-H. For a small amount of C₃A, this phenomenon is not observed because of the corresponding small quantity of precipitated hydrates. The non monotonous evolution of figure 4 can then be explained by the negative effect of aluminate ions on growth rate of C-S-H joint to the positive effect of added surface given by AFm.

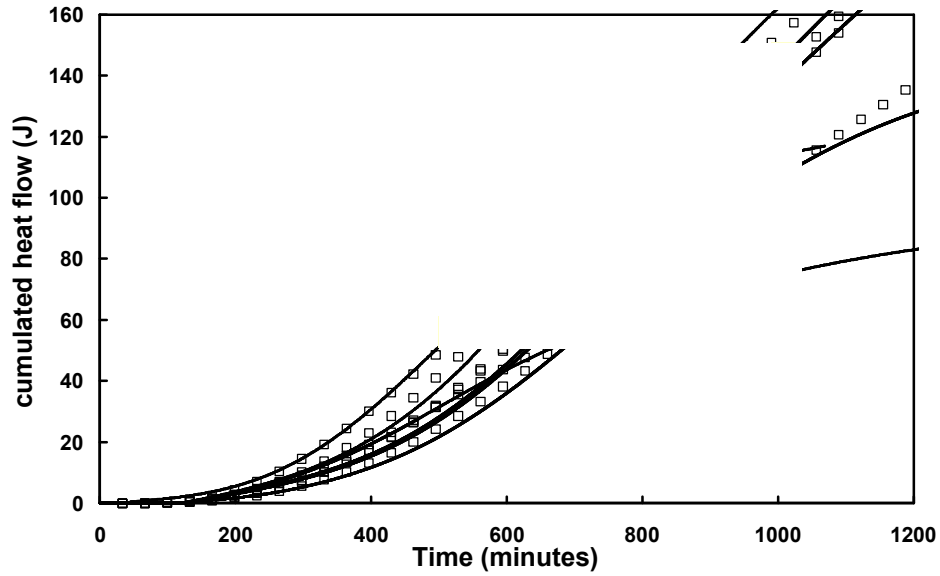


Figure 5: Evolution of cumulated heat flow versus time for hydration, with $W/C=0.5$, of different alite- C_3A mixes, a : 100% alite, b : 95%, c : 90%, d : 80%, e : 75% and f : 50 %. Simulated curves (indicated by square) are obtained with values reported on Figure 6.

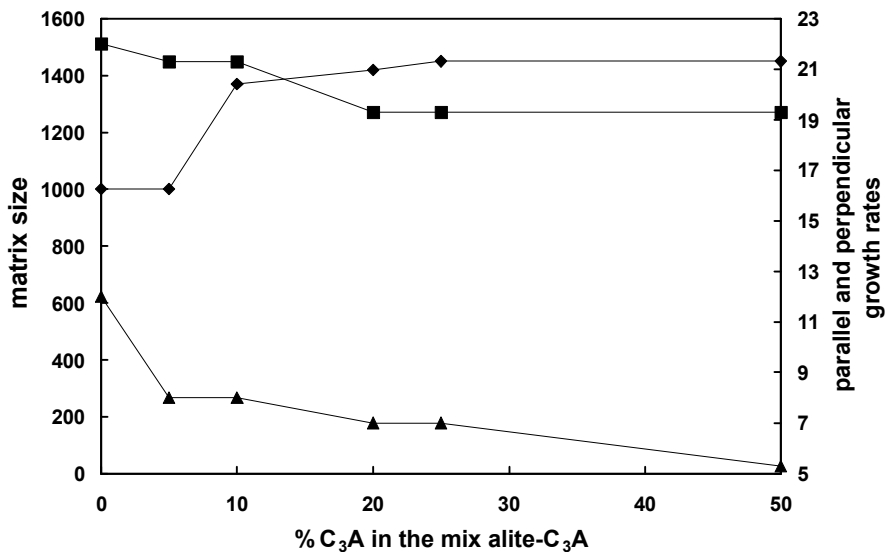


Figure 6: Evolution versus C_3A quantity for studied mixes of surface matrix dimensions i.e. the surface available for C-S-H growth (●) and the parallel (■) and perpendicular (▲) growth rates used to simulate experimental curves of figure 5.

4.1.2 Strength development of alite-C₃A mixes

The results obtained from the rheometry experiments are presented on Figure 7.

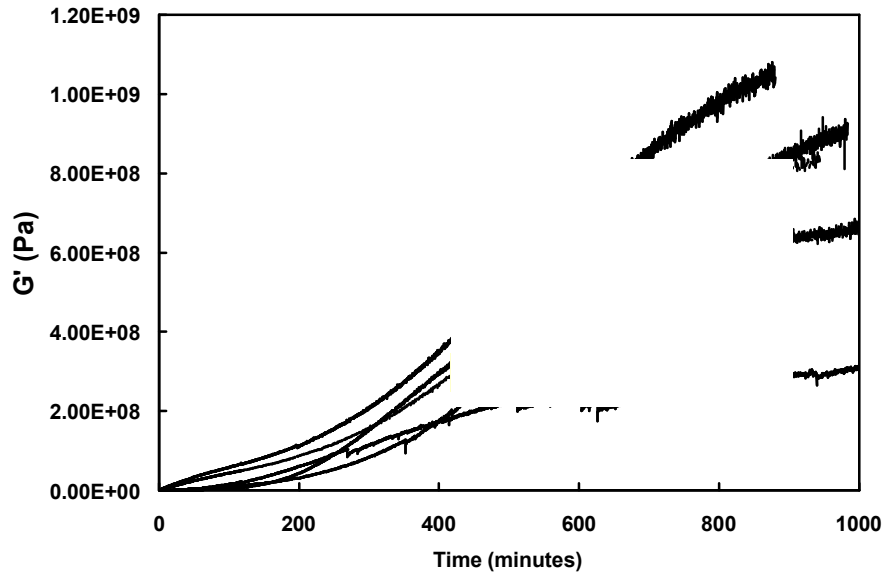


Figure 7: Evolution of storage modulus versus time for hydration, with $W/C=0.5$, of different alite-C₃A mixes, a : 100% alite, b : 95%, c : 90%, d : 80%, e : 75%.

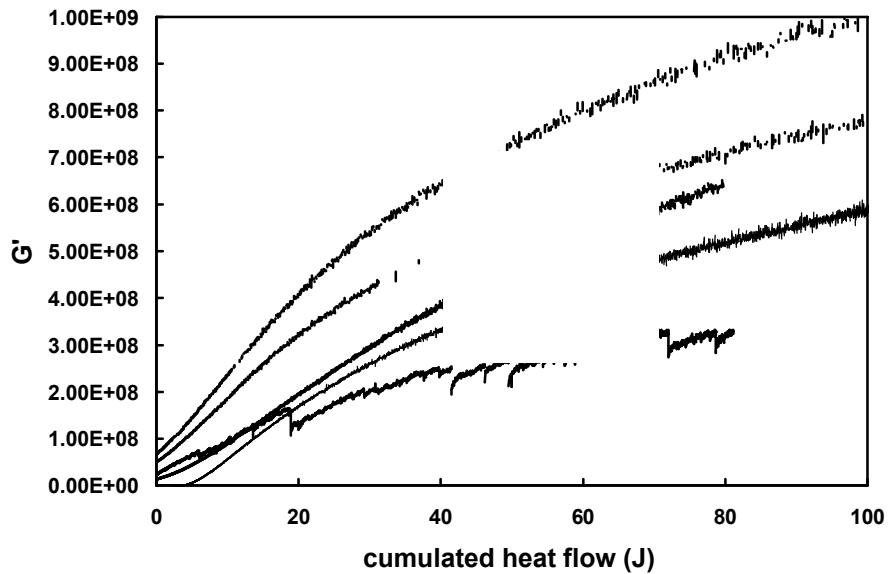


Figure 8: Evolution of storage modulus versus cumulated heat flow for hydration, with $W/C=0.5$, of different alite-C₃A mixes, a : 100% alite, b : 95%, c : 90%, d : 80%, e : 75%.

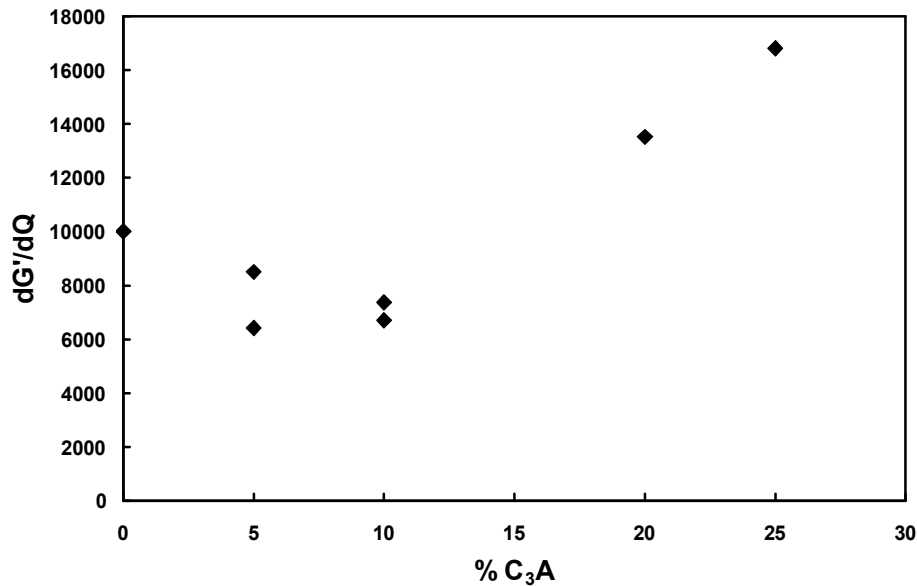


Figure 9: Evolution of mechanical efficiency of C-S-H versus percentage of C₃A in the different mixes.

First, it can be observed that the storage modulus increases with C₃A content in the mix during the first minutes of hydration. It is well known that this effect is due to calcium aluminate hydration in AFm which induces the stiffening of the paste at very early age.

Second, it can be noted that the G' evolution with respect to time is similar to cumulated heat flow evolution (Fig. 1). It seems that the modulus increase follows the degree of alite hydration, the modulus less increase in case of mix disregarding initial increase due to C₃A hydration.

As mechanical strength increases with the quantity of precipitated calcium silicate hydrate, we try to specify if the change of the modulus evolution is only due to the hydration modification or if another influence of C₃A can be pointed out. For that, the evolution of G' has been plotted versus the cumulated heat flow which is proportional to the degree of hydration of alite in this case, for these different experiments. The obtained curves can be divided in two steps: the first one, at low degree of hydration, corresponds to the sticking up of alite grains by C-S-H. The second one is attributed to the precipitated C-S-H which fills in the porosity.

It clearly appears on figure 8 that for a given quantity of hydrate there is change in the modulus when there is C₃A in the mix. Except for the mix 95%alite-5%C₃A, the greater the quantity of C₃A, the greater the modulus is.

The "mechanical efficiency of calcium silicate hydrates", $R = dG' / dQ$, represents the increase in the elastic modulus dG' corresponding to the

formation of a certain amount of C-S-H, estimated by the released heat dQ . It is determined in the first regime of the evolution of G' versus time, corresponding to the precipitation of C-S-H which develop contacts and stick the not yet hydrated cement grains.

When C_3A percentage increases, the evolution of R is not monotonous. It is weaker for quantities less than 10% and higher for others. This initial decrease can be linked to the negative effect of aluminate ions. As a fact, it has been shown by preliminary experiments that the mechanical efficiency decreases when a tricalcium silicate paste is hydrated in a solution containing aluminate ions [11]. The observed increase at high C_3A content is once again linked to the positive effect of C_3A hydrates which act as fine filler in the structure and increase the number of percolation ways.

4.2 "alite- C_3A -sulfate system"

4.2.1 Hydration of the alite- C_3A -sulfate mixes

The figure 10 presents the evolution versus time of heat evolution rate curves obtained during hydration of different alite- C_3A -gypsum mixes. In mixes c and d, the amounts of C_3S and C_3A are kept constant and the amount of gypsum varies. To keep the same water/solid ratio, portlandite is added in mix c. Two or three peaks can be observed: the initial peak, the peak corresponding to alite hydration and sometimes a third peak relative to the end of sulfate consumption by ettringite formation [12]. The intensity of the first peak decreases with gypsum amount when C_3A and alite quantities remain constant; there is slowing down of AFm formation when gypsum and alite are both present. This is not observed with only gypsum or with only alite.

Some remarks can be done first about C_3A hydration. As expected, a third peak can be observed on curves c and e, when all sulfates are consumed and the greater the quantity of gypsum, the later the time of appearance of this third peak. But during the hydration of the same quantity of C_3A with gypsum without alite (curve f, fig. 10), this peak is observed earlier and its intensity is greater, it should take place before the silicate hydration peak. The presence of alite slows down ettringite formation.

Concerning alite hydration, the time of appearance and the maximum of the peak corresponding to its hydration is unchanged in simultaneous presence of C_3A and gypsum. The maximum of heat flow is weaker than those obtained with only C_3A . In presence of gypsum there is formation of ettringite in place of hydroaluminates and ettringite does not seem to act as a precipitation surface for C-S-H.

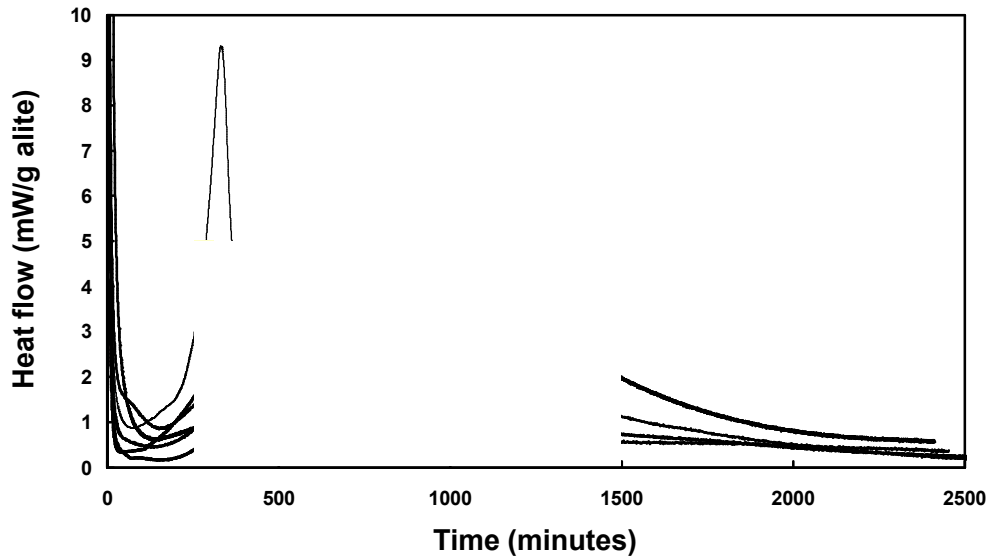


Figure 10 : Heat flow evolutions versus time for hydration, with W/C=0.5, of different alite-C₃A-sulfate mixes, a : 100% alite, b : 80% alite-20%C₃A, c : 76% alite-17%C₃A-3%gypsum-4%portlandite, d : 76% alite-17%C₃A-7%gypsum, e : 75% alite-20%C₃A-5%gypsum and f : 0.24 g of C₃A with 0.045g of gypsum (W/C=0.42).

4.2.2 Mechanical efficiency of C-S-H in the system “alite-C₃A-gypsum”

To obtain the evolution of the storage modulus with respect to the degree of hydration for such a complex system, it has been needed to consider the heat corresponding to the formation of ettringite from C₃A and gypsum dissolution, which continues during the alite hydration. This quantity is subtracted from total heat flow considering ettringite precipitation rate constant, as observed previously [11], with $\Delta H_{\text{ett-formation}} = 480\text{kJ/mol}$.

The figure 11 presents the deduced evolution of mechanical efficiency of C-S-H for the different quantities of gypsum that were added. Results concerning the system “C₃S-gypsum” are reported on the same graph.

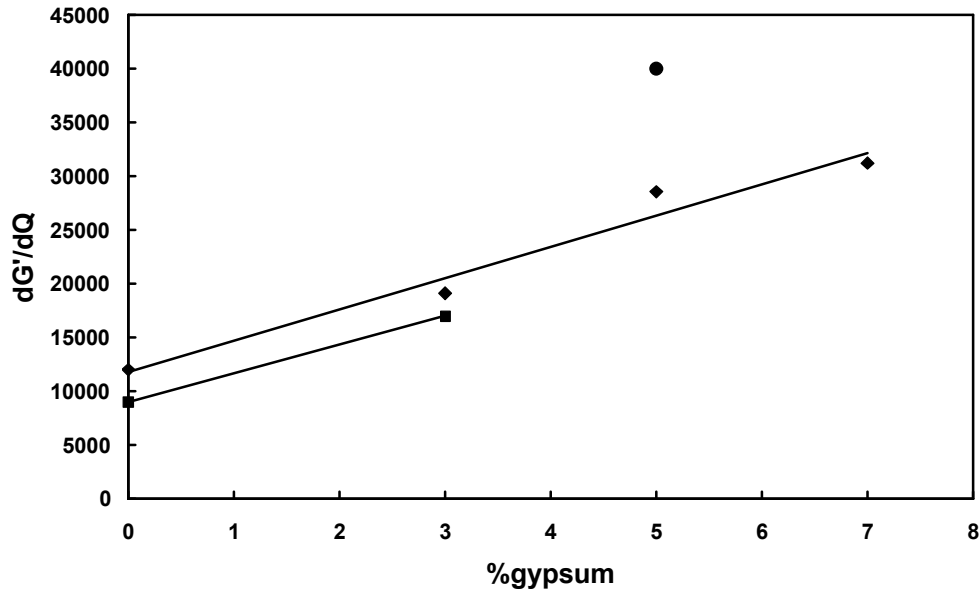


Figure 11: Evolution of mechanical efficiency of C-S-H versus gypsum percentage in the system 76% alite-17%C₃A-gypsum-portlandite (◆), 75% alite-20%C₃A-gypsum (●) C₃S-gypsum (■).

For the mix containing the same quantity of C₃A and alite and for C₃S the mechanical efficiency of C-S-H increases with gypsum quantity. For alite-C₃A-gypsum system this increase seems to be more important when C₃A quantity increases. These observations can not be attributed to ettringite since the amount of precipitated ettringite does not depend on the initial C₃A quantity and this increase is also observed with only C₃S. It has been shown [13] that sulfate ions can modify C-S-H growth but here, sulfate ions are consumed by ettringite formation; the increase of R could be attributed to the presence of solid gypsum which is not consumed when R is determined. As a fact, it has been shown that the rate of ettringite formation is constant and independent of initial gypsum quantity [11], the greater the initial quantity of gypsum the greater the remaining of gypsum when R is calculated. But this does not explain the influence of the amount of C₃A.

Conclusions

Concerning alite hydration, in alite-C₃A system the fast formation of C₃A in AFm stiffens the paste but has not a great influence on the paste cohesion, i.e. storage modulus increase. C₃A has a great influence on hydration and setting of alite. For low C₃A quantity, there is a decrease of the growth rate of C-S-H because of aluminate ions but at high C₃A content, calcium hydroaluminates act as growth surface for C-S-H, that means there is a good affinity between the C-S-H and AFm surfaces. These opposed

effects are back in cohesive properties; aluminate ions decrease the mechanical efficiency of C-S-H but AFm particles increase the number of percolation ways through the connected structure. In alite-C₃A-gypsum system, the silicate hydration seems to be similar to pure alite hydration; there is no affinities between C-S-H and ettringite. An increase of mechanical efficiency of C-S-H with gypsum and C₃A is observed but not explained.

Concerning C₃A hydration, in the system alite-C₃A, it is quickly hydrated in hydroaluminate as it is observed with C₃A alone. But the rates of AFm and ettringite formation are reduced when alite and gypsum are both added.

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