

Parameters Influencing the Microstructural Development of Cementitious Systems. A Model System Approach

E. Gallucci¹, H. Di Murro², D. Sorrentino², K. Scrivener¹, E. Lesniewska³,
C. Vernet²

¹Lafarge Research Center, Saint Quentin Fallavier, France; ²LMC, EPFL, Lausanne, Switzerland; ³LPUB UMR CNRS 5027, University of Bourgogne, Dijon, France

Abstract

Model systems with various contents of alite, C₃A and calcium sulfate were investigated in order to get insight on the parameters which control the diffusion of ions in early age cement pastes and therefore the development of the microstructure of such materials. The microstructural investigation was conducted by mean of SEM-image analysis, EDS chemical analysis, XRD-Rietveld and isothermal calorimetry.

The first results presented in this paper show that the overall development of the microstructure is highly dependent on the availability of calcium sulfate and its chemical interaction with calcium aluminate phases. Comparatively minor changes in the composition of the mixtures could result in large differences in microstructure after few days.

Keywords : alite, C₃A, model systems, calcium sulfate, reactivity, microstructural development

1. Introduction

The hydration of Portland cement is characterized by the dissolution of reacting phases (mainly C_3S and C_3A for clinker' and calcium sulfates) and the precipitation hydrated products, namely calcium silicate hydrates (C-S-H) and Portlandite (CH) for the silicate phases and Aft or AFm phases for the aluminate/ calcium sulfate phases [1]. Independently from each other, the basic reactive mechanisms of each reaction which occur upon hydration are more or less well understood since extensive researches have been carried out over decades.

Concerning the hydration of C_3S (alite), several theories and models have been proposed but have not completely resolved the processes at the nano-level [2,3]. However, all studies agree on a sequence including the initial dissolution, an induction period of a few hours, a fast resumption of the hydration which generates the period of coagulation and the setting of cement with the fast growth of C-S-H and CH [4], and finally a slow reaction governed by diffusion processes. Concerning pure C_3A and gypsum (C\$), the precipitation of hydrates such as ettringite (Aft) and hydroaluminates (Afm) is well understood and documented [5]. When the sulfate source is exhausted, Aft dissolves and reacts with the remaining C_3A to give monosulfoaluminate precipitates [6]. It has been shown [5,7] that increasing the amount of C\$ induces the decrease of C_3AH_6 formed during hydration. A delay of the C_3A hydration was also observed. Several hypotheses were brought to explain this phenomenon. At our knowledge, none of them is completely excluded.

However, real cements are systems much more complex than their individual components and they behave differently: multiple interactions occur between all phases present in the mix, depending on their nature, size, distribution in the microstructure, availability...

These interactions and particularly the dilution and spatial distribution of these individual phases in a complex mixture modify significantly their reactivity so that the link between cementitious systems and their individual components is far from obvious. This motivates the study of mixtures of model phases of C_3S , C_3A and C\$ in order to understand these complex interaction and microstructural development. So far, only a few works concerned model systems of alite- C_3A -C\$. The first studies relating to these systems [8,9] reported that small changes in the C\$ content have a slight effect on alite hydration but a huge influence on C_3A .

The ultimate objective of this study is to characterize the formation and evolution of the hydrates to highlight the possible gradients of diffusion of ions in a cement paste. The present paper focuses on the identification of the parameters influencing the microstructural development of a cement paste through the study of model mixtures made of pure alite, C_3A , and gypsum.

2. Material and methods

2.1. Synthesis of model phases

C₃A Synthesis

The content in C₃A in cement and clinker is generally of 5-10%. Cubic C₃A was prepared by mixing homogeneously 74.6 wt% of CaCO₃ with 25.4 wt% of Al₂O₃ [10]. The mix was ground with water during 1h30 to obtain a homogeneous paste which was heated at 950°C during 1h to de-carbonate CaCO₃. C₃A was then obtained after a firing at 1450°C during 4h. Its purity and crystallinity were checked by chemical dosage and XRD

Alite synthesis

Alite crystallizes in a triclinic T or a monoclinic M1, M2, M3 groups [11] depending on the presence and amount of foreign ions (impurities i.e. Al³⁺, Mg²⁺). In clinker, alite is generally present under the form of a mix of M1 + M3 polymorphs.

81.70 wt% of CaCO₃, 16.40 wt% SiO₂, 1.30 wt% MgO and 0.63 wt% Al₂O₃ [12] were homogeneously mixed, ground with water during 1h30 and heated at 950°C during 1h for de-carbonation. Alite was obtained after a heating at 1600°C during 4h. There again, chemical dosage and XRD were used to check the purity of the phase.

Clinker synthesis

The preparation of a the clinker with 80 wt% of alite and 20 wt% of C₃A was done using the same raw materials, mix designs and procedures as above. The final heating occurred at 1550°C during 4h.

After synthesis, all phases were ground by ball milling until their psd fits with that of ordinary Portland cement.



Figure 1. Schematic representation of monophased (left) and polyphased (right) systems

2.2. Studied mix designs

The studied systems were mixes of clinker or alite and C₃A with gypsum, hydrated at a water to cement ratio of 0.5. Monophased mixes (M) correspond to mixes of pure phases while polyphased mixes (P) relate the use of the clinker. Mix designs (Table 1) were selected to give insight on the influence of the C₃S/C₃A ratio and the fineness of calcium sulfate (two

C\$ psd were used, one centred on 50 μm (labelled GG) and one on 5 μm (GF)).

Table 1- Mixtures of alite-C₃A-gypsum used

The letter P relate to a clinker of alite and C₃A, M to a mix of two powders alite and C₃A, GG = Coarse Gypsum, GF = Fine Gypsum.

System	Alite	C ₃ A	GYPSUM
M90-10-5GG	90	10	5
M80-20-10GG	80	20	10
P80-20-10GG	80	20	10
P80-20-10GF	80	20	10

Hydration of these systems was stopped after 6h, 8h, 12h, 24h, 36h, 72h, 7 days, 14 days and 28 days, either by freeze drying (before 1 day old) or by solvent exchange in isopropanol.

2.3. Characterization methods

BSE imaging and EDS analysis

Through the combination of the information provided by Back Scattering Energy (BSE) imaging and Energy Dispersive Spectroscopy (EDS), a detailed quantification of polished cross sections of the hydrated cementitious matrices was performed. A Philips Quanta 200 microscope and a PGT energy dispersive x-ray analyser were used. The accelerating voltage was set to 15 kV to provide the best compromise between spatial resolution and adequate excitation of all elements involved in these systems.

Isothermal calorimetry

The heat flow generated by the chemical reactions occurring upon hydration of these systems was studied by isothermal calorimetry. Measurements were done using a TAM AIR isothermal calorimeter at a temperature of 25°C. The mix between water and anhydrous raw materials was done in situ, water being injected thanks to a syringe onto the dry powder and mixed mechanically for a minute into the calorimeter itself after temperature equilibrium has been reached.

X ray diffraction

XRD patterns were acquired on cut slices of hydrated pastes using a analytical (Philips) X'pert diffractometer equipped with an X'celerator detector. Phase identification was done by correlation with the JCPDS database. Quantitative analysis was done using the Rietvelt method (X'Pert Highscore Plus software) [13].

3. Results and discussions

3.1. Influence of the C_3S/C_3A ratio in monophased systems

Figure 2 correlates the heat flow measured by isothermal calorimetry with EDS chemical analysis upon hydration.

The first exothermic peak corresponding to the hydration of silicate phases occurs at almost the same time (around 10 hours) for the two systems. On the other hand, the second peak, attributed to the dissolution of C_3A and reaction with ettringite to form Afm phases is highly affected by the chemical nature of the system : it occurs at 20 hours for M90-10-5GG while 40 hours in the case of M80-20-10. This delay in the consumption of sulfate ions is clearly seen through the EDS chemical analysis of the matrix which shows that after 36 hours of hydration, the microstructure of M80-20-10 is still composed of a mix of C-S-H, CH, ettringite and Afm (all measured points lie in between the representative points of these four phases). In the case of M90-10-5, from 1 day of hydration, all points lie in between C-S-H/CH and Afm, showing that all ettringite has been consumed. XRD patterns (figure 3) confirm the above observations with the presence of both ettringite and Afm in M80-20-10 after 72 hours of hydration while at 24 hours, ettringite is no longer identified in M90-10-5.

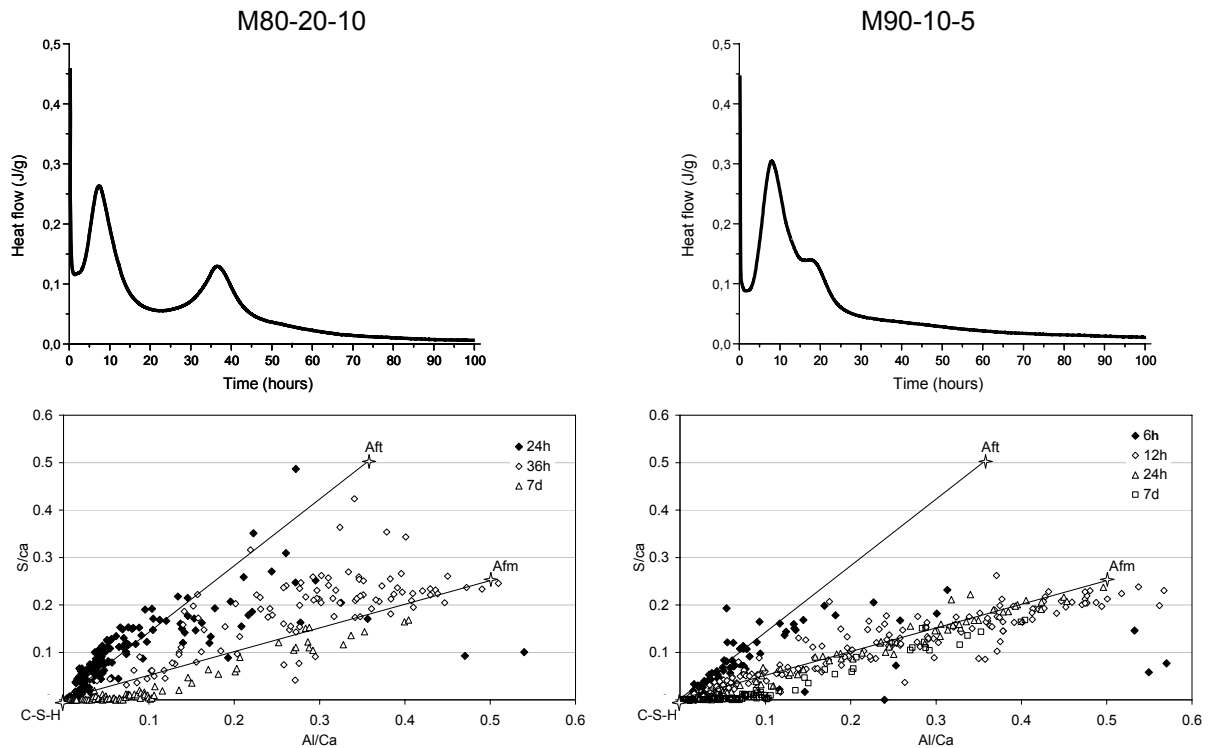


Figure 2. Correlation between hydration heat flow (top) and EDS chemical analysis of the matrix (bottom) upon hydration (colors of calorimetric curves refer to EDS points)

The EDS plots in Figure 2 also show that the level of Al substitution in C-

S-H is the same ($Al/Ca=0.1$) in both mixes meaning that the available content of C_3A has not much influence on C-S-H composition.

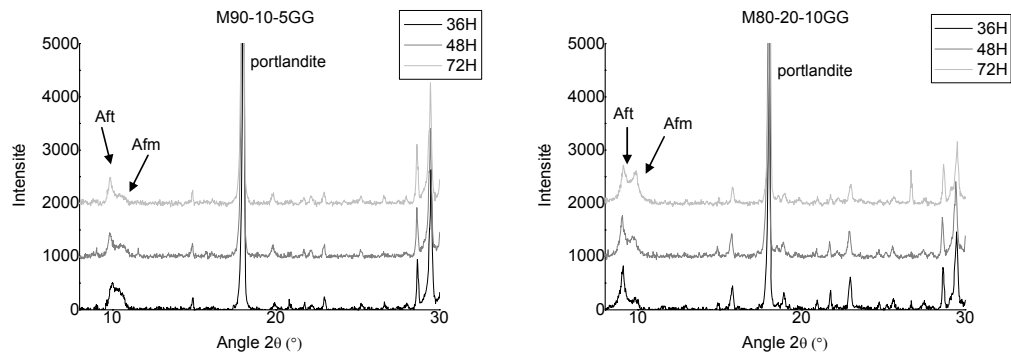


Figure 3 - XRD Analysis of monophased mixes.

From a microstructural point of view, the phase assemblages in these two systems significantly differ from what is usually observed in hydrated Portland systems (Figure 4). The main morphological differences are:

- the absence of shell like structure and gap in between reacting grains and hydration shell as observed in early age Portland pastes,
- the growth of massive Portlandite clusters (instead of platelet's like morphology),
- a coarser capillary porosity and large areas of denser hydrates packing.

These observations are in agreement with previously reported results [14] and mainly relate to the availability of species in solution.

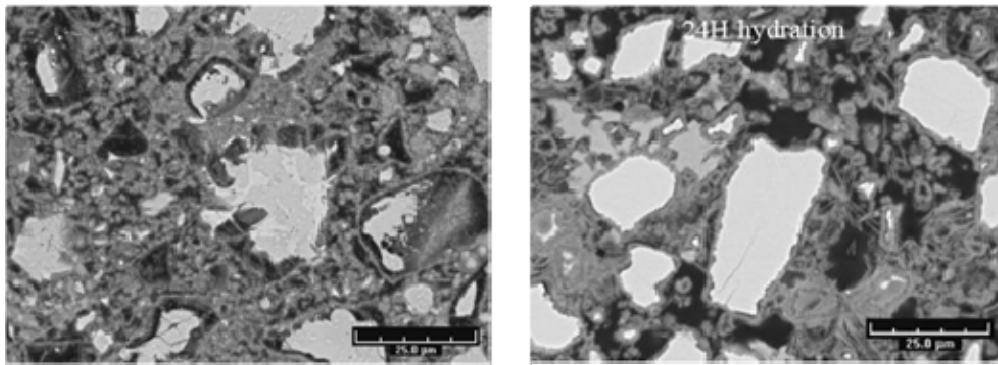


Figure 4. Comparison between Portland cement (left) and M80-20-10GG (right) after 24 hours of hydration (scale : full width=100 μ m).

Therefore, although the C_3A/C_S ratio is the same in the two systems, the higher amount of C_S in M80-20-10 leads to the precipitation of much more ettringite and hydroaluminat (Afm) in the cementitious matrix. This is known to be responsible for a slower reactivity of C_3A and therefore a

slower dissolution of Al^{3+} ions in the system [5]. However, the most probable reason for the faster precipitation of monosulfate in M90-10-5 is certainly related to the lower amount of C\$ and therefore a faster depletion of sulfate ions in this system. As a consequence, C\$ remains longer in the system richer in sulfates and ettringite is stabilised until more than 72 hours, while only for 20 hours in the system with less sulfates and in which they are consumed much more faster.

3.2. Influence of the mono/polyphased nature of the mix

Although they have the same composition, M80-20-10GG and P80-20-10GG differ from each other by the fact that in the polyphased mix, most of the C_3A phase is distributed among all C_3S grains. Its distribution in the cementitious system is therefore more homogeneous. On the other hand, in monophased systems, C_3A is present as a few individual coarse particles while it consists in fine particles evenly distributed in all alite grains in a polyphased clinker.

The EDS spot analysis given in Figure 5 show that in the case of the polyphased system (in which C_3A is less available), the dissolution of Aft associated with the precipitation of monosulfate and a renewed reactivity of C_3A occur between 12 and 24 hours of hydration (confirmed by isothermal calorimetry and XRD measurements which are not reproduced here).

This is much faster than for M80-20-10 (figure 2) and shows that despite being engulfed in alite, its reactivity in a polyphased system is much higher than as an individual grain. This higher reactivity is explained by both the higher homogeneity of the distribution of C_3A in the cementitious matrix and by a shorter mean free distance with sulfate sources (gypsum grains supposedly evenly distributed in the system)

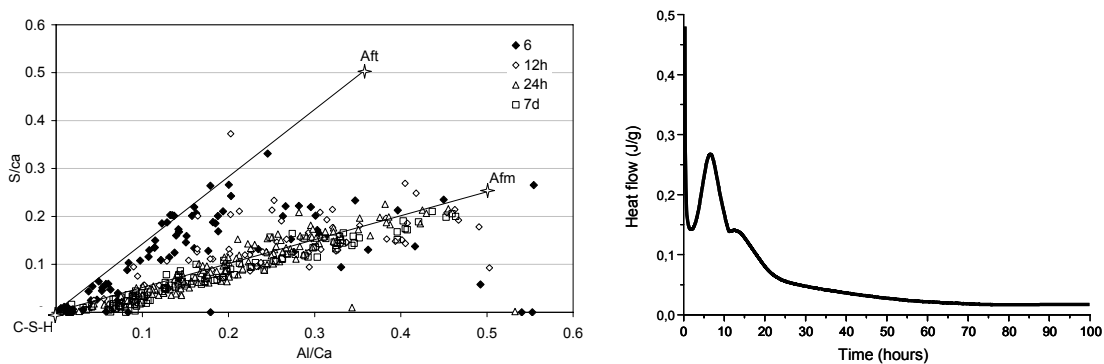


Figure 5. P80-20-10GG : EDS spot analysis over time and heat of reaction.

3.3 Influence of calcium sulfate grain size

The influence of calcium sulfate (C\$) has been investigated on polyphased mixes. EDS chemical analysis (Figure 6) show that with fine gypsum, ettringite remains longer in the matrix while the precipitation of monosulfate is observed very early with coarse gypsum (Figure 5).

Isothermal calorimetry confirms this observation since the peak corresponding to renewed C_3A dissolution occurs much later with fine gypsum than with coarse gypsum. Although the content in gypsum is the same in the two mixes, this result corresponds to a lack of sulfate ions in the coarse gypsum system. Examination of the microstructure (Figure 7) actually shows that the big gypsum particles are often engulfed in large Portlandite clusters which seems to prevent or at least slow down their dissolution. Therefore, both a lower intrinsic reactivity (low specific surface) and a 'pollution' of its surface by calcium hydroxide contribute to the lower dissolution of coarse gypsum and then its lower availability in the mix. Another reason may be, as seen in section 3.2. with C_3A , a more even distribution of sulfate ions in the case of fine gypsum

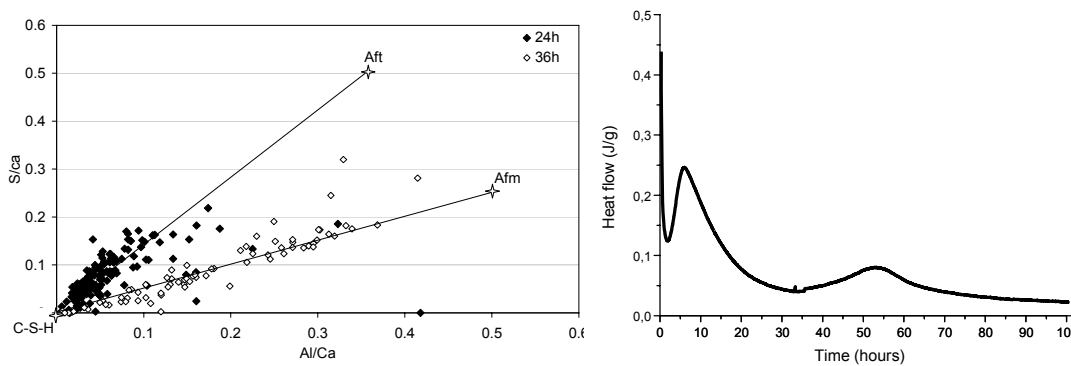


Figure 6. P80-20-10GF : EDS spot analysis over time and heat of reaction

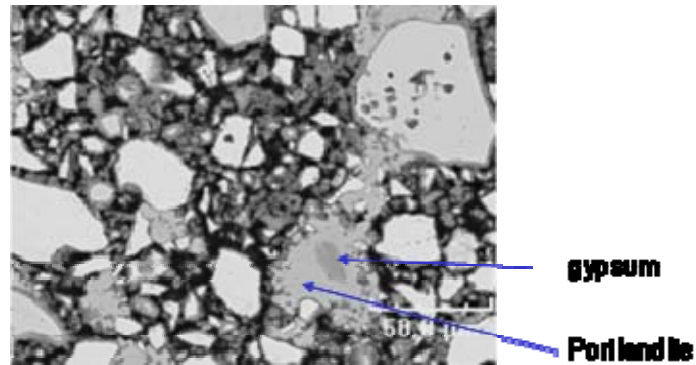


Figure 7. Portlandite crystallization around coarse C\$ grains

The effect of the amount of sulfate ions in the solution induces significant differences in the microstructural development of the two systems. Figure 8 shows the microstructure of P80-20-10GG and P80-20-10GF after 12 and 24 hours of hydration. For comparison, micrographs of an ordinary Portland cement have been added. Coarse gypsum grains leading to a lack of sulfate ions in the solution or at least a delay of their release into the solution, P80-20-10GG behaves almost like a 'flash setting' system :

after 12 hours of hydration, the microstructure is much filled with hydrated products (mainly aluminates) while silicate hydrates are densely packed around alite grains. On the other hand, the system with fine gypsum behaves more or less like Portland pastes: the matrix is less filled with hydrated products and their morphology is similar (distinct thin C-S-H shell around the grain, formation of a characteristic gap in between the grain and the shell, absence of large Afm type products, growth of Portlandite both into big clusters and thin platelets).

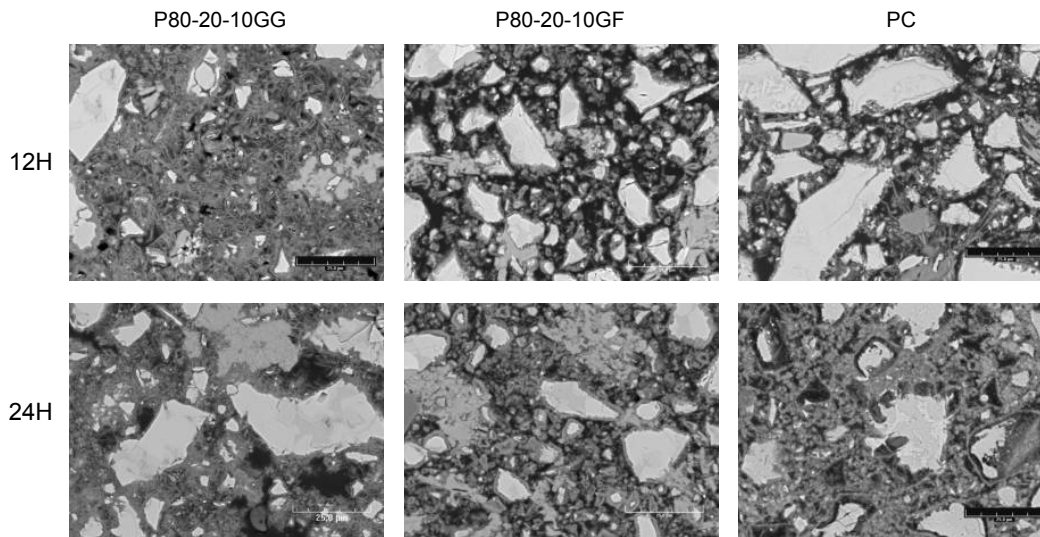


Figure 8. Microstructural development of polyphased systems with different C\$ psd. Comparison with pure OPC. (scale : full width=100 μm)

Conclusion

Model systems made of C_3A , alite and calcium sulfate were studied in order to get insight on the parameters which influence the microstructural development of Portland based systems. This systematic approach helped to identify the effects of the distribution and availability of phases within the cementitious matrix.

Although being minor phases, the hydration of C_3A and C\$ plays a crucial role on the microstructural design which develops at early age. For both of them, grain size is a major issue since it was shown that when their size increases, the reactivity of the system slows down drastically: pollution by Portlandite in the case of C\$, precipitation of large amounts of Afm products for C_3A . Another drawback of dealing with large particles is that even if they are evenly distributed within the matrix, the mean free path

between aluminates and sulfates increases and then also contributes to slow down the reactivity of the whole system.

On the other hand, homogeneous dispersion of fine particles leads to an optimised microstructural design such as expected in Portland based systems.

On the bases of the results obtained here, the diffusion gradients of species (mainly aluminates and sulfates) are under study and will be correlated with the microstructural development observed in the case of OPC systems.

References

[1] S. Diamond, "cement paste microstructure – an overview at several levels", Hydraulic Cement Pastes, 2-30 (1976)

[2] H.M Jennings and P.L Pratt, "On the reactions leading to calcium silicate hydrate, calcium hydroxide and ettringite during the hydration of cement, Proc. 7th Int. Con. of cement chemistry, Paris, II.II, 141-146 (1980)

[3] G.W Groves, "Portland cement clinker viewed by transmission electron microscopy", Journal of Material Science, 16, 1063-1070 (1981)

[4] B.J Daleigh, A. Ghose, H.M. Jennings, P.L. Pratt, "the correlation of microstructure with setting and hardening in cement paste", Congrès de Paris, 1, 137-143 (1982)

[5] H. Minard, 'Etude intégrée des processus d'hydratation, de coagulation, de rigidification et de prise pour un système C₃S-C₃A-sulfates-alcalin', These de l'université de Bourgogne, France, (2003)

[6] H.N. Stein, « Some characteristics of the hydration of 3CaO.Al₂O₃ in the presence of CaSO₄.2H₂O", Silc. Ind., 28, 141-145(1963)

[7] S. Chatterji, Discussion of the hydration reactions in pastes, Cem. Conc. Res. 4, 997-1000 (1974).

[8] W.A. Corstanje, H.N. Stein and J.M. Stevels, Hydration reactions in suspensions of C₃A+C₃S+CaSO₄.2H₂Oaq in water I., Cem. Concr. Res. 3, 791-806 (1973) .

[9] W.A. Corstanje, H.N. Stein and J.M. Stevels, "Hydration reactions in suspensions of C₃A+C₃S+CaSO₄.2H₂Oaq in water II.", Cem Concr Res 4, 193-202 (1974).

[10] M.M. Radwan, M. Heikal, Hydration characteristics of tricalcium aluminate phase in mixes containing β -hemihydrate and phosphogypsum, *Cem. Conc. Res.* 35, 1601-1608 (2005).

[11] M. Regourd, Polymorphisme du silicate tricalcique, *C. R. Acad. Sci., Sci. Paris Terre* 289, 17– 20 (1979).

[12] R. Maggion, Etude de l'évolution microtexturale de pâtes de silicate tricalcique hydraté, PhD thesis, Univ. of Orléans, 1992.

[13] K. L. Scrivener, T. Füllmann, E. Gallucci, G. Walenta and E. Bermejo, 'Quantitative study of Portland cement hydration by X-ray diffraction/Rietveld analysis and independent methods', *Cement and Concrete Research*, 34(9), (2004), pp.1541-1547.

[14] E.Gallucci, K.L.Scrivener, 'crystallisation of calcium hydroxide in early age model and ordinary cementitious systems', *Cement and Concrete Research*, submitted (2006)