

Influence of Aluminate Hydrate and Iron Hydroxide Precipitation on Early-Age C₃S Hydration Kinetics.

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1: Introduction

During these last decades, the hydration kinetics of the tricalcium silicate (C₃S or Alite), major component of Portland cement, has been extensively investigated [1,2,3,4,5,6]. It is generally held that the hydration of Alite mostly controls the setting and early strength of mortar and concrete due to the formation of C-S-H following a dissolution-precipitation mechanism. However, cement is a complex mixture of numerous compounds including mainly silicate phases (C₃S, C₂S), aluminate phases (C₃A and C₄AF) and calcium sulphate. Due to the polyphasic form of cement grains, the hydration of a Portland cement is much more complicated than the hydration of the individual clinker phases. In fact the reactions of the different compounds proceed simultaneously at differing rates and thus can influence each other. In this way, many studies have been devoted to the mutual interaction between C₃S and C₃A or CA without calcium sulphate [7,8,9,10,11]. It has been shown that the high reactivity of the tricalcium aluminate C₃A without calcium sulphate gives a flush of calcium and aluminate ions in solution and leads to the precipitation of aluminate hydrates to a significant extent onto any exposed Alite (C₃S) surfaces implying both a delay of silicate phases hydration and a poor strength development. A "surface poisoning" effect induced by aluminate ions in solution has been proposed in this specific case of free calcium sulphate cements [7,8]. In his work, De Jong proposed that the incorporation of aluminate ions into calcium hydrosilicate formed or that the variation of calcium or hydroxyl ions due to the reactivity of the C₃A could delay the C₃S hydration [9]. Similarly and according to the hydration of the aluminoferrite phase in a cement, surface iron compounds such as iron hydroxide could also form a shield around silicates grains. This shield presents a protective layer of water and ionic species reducing the silicate phase hydration and thereby hindering mechanical strength development [12,13]. Despite these different studies, only a few ones have considered the interaction between the major phase C₃S and aluminate phase (C₃A or C₄AF) in presence of calcium sulphate. In this way, we simulated the Portland cement by adding aluminium and/or iron sulphate solutions to C₃S hydrating in the presence of gypsum and excess calcium hydroxide in order to have access to the underlying chemistry and explain the main hydration processes that occur at early age in a Portland cement.

2: Experimental procedure

2.1: Materials

Pure C₃S was laboratory made and ground to a fineness of about 350 m²/kg.(BSA) The purity of the final product was checked by X-Rays and the free lime content (0.8%) determined by a complexometric method.

Pure aluminium sulphate Al₂(SO₄)₃.18H₂O and iron III sulphate Fe₂(SO₄)₃.xH₂O with (8<x<9) were used.

All experiments was performed with deionised water.

2.2: Methods

Hydration kinetics was followed by isothermal calorimetry on paste and by electrical conductivity in suspension at a temperature equal to 20°C.

Using calorimetry, the heat flow Q is connected to both the enthalpy ΔH and the rate V of all reactions that occur simultaneously in a cement paste.

$$Q = \sum_i V_i * \Delta H_i \quad (\text{Eq.1})$$

Conductivity values depend on both the ionic species and their activities in solution following this equation:

$$S = \sum_i \lambda_i * a_i \quad (\text{Eq.2})$$

where λ_i is the equivalent ionic conductivity and a_i = γ_i*C_i the activity of ion i. For calorimetric trials, in order to simulate the interstitial solution during the initial hydration stage of a cement paste, 3g of C₃S have been hydrated in both lime and gypsum saturated solution with an excess of Portlandite (0.05g) using a 0.46 liquid to C₃S ratio.

Electrical conductimetry measurements were then performed on stirred suspensions using a chemical reactor (liquid/C₃S = 50). 1.6g of C₃S has been hydrated in both lime and gypsum saturated solutions without an excess of solid. From theses stirred suspensions, aqueous phases were extracted after varying periods of hydration and analysed for dissolved species (ionic concentrations measured) using an ICP apparatus.

Moreover and in particular cases, characterization of hydrates formed was conducted by SEM observations.

For all experiments, sulphate salts (aluminium and iron or a mixture of both) have been used in order to have the same molar concentration in solution.

3: Results

3.1: Isothermal calorimetry

First of all and before discussing results obtained in presence of additives, the mechanism of hydration of the pure C₃S has to be briefly described. The fig 1 shows the variation of both the heat liberated and the percentage

of hydration (cumulative curve of the heat liberated) measured during the hydration of a C_3S paste in a lime saturated solution. The hydration kinetics follows a sigmoid curve characterized by two stages. In the first one, after the C_3S dissolution and due to the fact that the solution becomes supersaturated with respect to the hydrosilicate of calcium, C-S-H nuclei precipitate during the induction period. The higher the number of nuclei formed, the shorter the induction period^[5,6]. Then, the accelerated period is mainly controlled by the growth of C-S-H clusters. The growth mode proceeds by a three-dimensionnal agglomeration of nanoparticles onto the Alite grains. C-S-H nuclei grow according to two directions, the first one parallel to the Alite surface (axes a and b) and the second one (axis c) perpendicular to the same surface (fig 2). The mode of growth, which is affected by the lime concentration, proceeds until the point I (second stage) where the hydration rate decreases due to the existence of a continuous layer of hydrates around the anhydrous grains implying so an hydration kinetics controlled by a diffusion process [6]. Obtaining the point I enables us to estimate the percentage of hydration at which the rate becomes controlled by a diffusion process.

Based on these key points of the mechanism for the C_3S hydration, the influence of aluminium and iron sulphate salts has been studied and results are presented in figs 3 and 4.

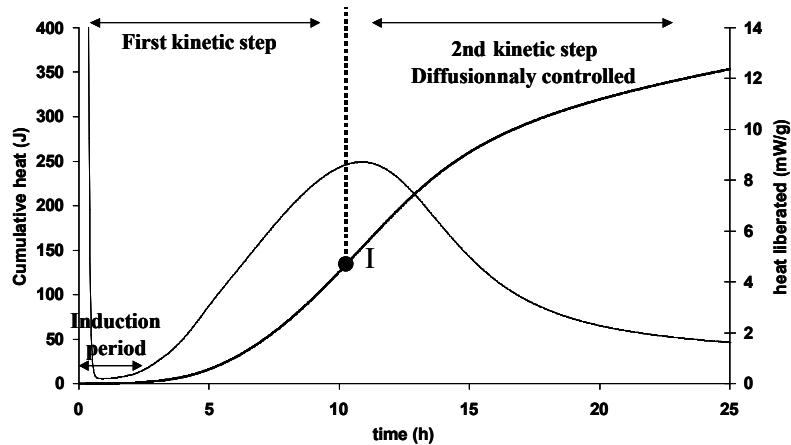


Figure 1: Variation of the hydration kinetics of tricalcium silicate in a lime saturated solution versus time. $l/s = 0.46$. $T = 20^{\circ}C$.

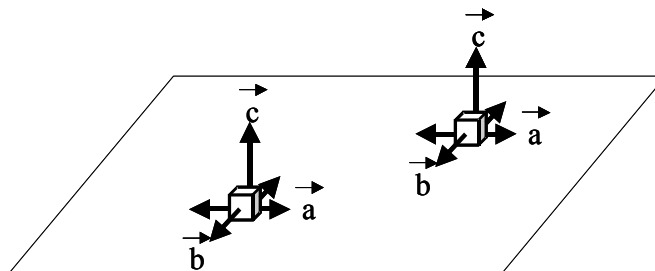


Figure 2: Representation of the mode of growth of C-S-H onto Alite surface. Axes a and b represents the parallel growth while the c axis characterizes the normal one.

3.2.1: Influence of aluminium sulphate.

In fig 3a, it appears that the C_3S hydration is accelerated in presence of aluminium salt compared to the reference one performed without additive. The induction period appears to be reduced meaning that the number of C-S-H nuclei should be higher in presence of aluminium sulphate. Moreover, the I2 transition point is reached for a lower value of cumulative heat than I1. According to previous considerations, the percentage of hydration at which the kinetics becomes controlled by diffusion is thus lower in presence of aluminate sulphate,. This observation implies that the C-S-H mode growth has been modified in presence of aluminium sulphate. Finally, the rate of hydration when it is controlled by a diffusion process, is lower than in the reference.

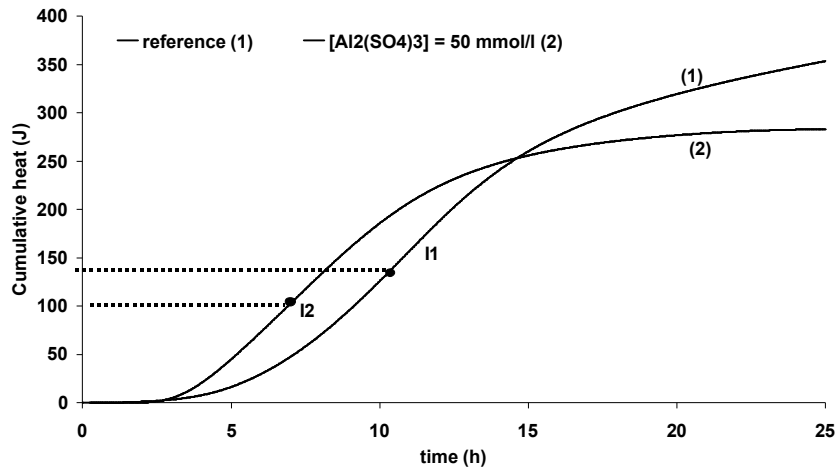


Figure 3a: Heat liberated during a tricalcium silicate hydration with and without aluminium sulphate. Experiments performed on paste in both lime and gypsum saturated solutions with an excess of Portlandite (0.05g). $l/s = 0.46$ $T = 20^{\circ}C$.

3.2.2: Influence of iron sulphate.

The hydration kinetics of the C_3S is also modified in presence of iron sulphate. In figure 3b, it can be clearly seen that the induction period is slightly extended involving so a weak decrease of the number of C-S-H nuclei. Moreover, the percentage of reaction for which the C_3S surface is completely covered by C-S-H appears to be quite similar to the reference one. However, the hydration rate when it is controlled by diffusion is higher in presence of iron sulphate compared to the reference one.

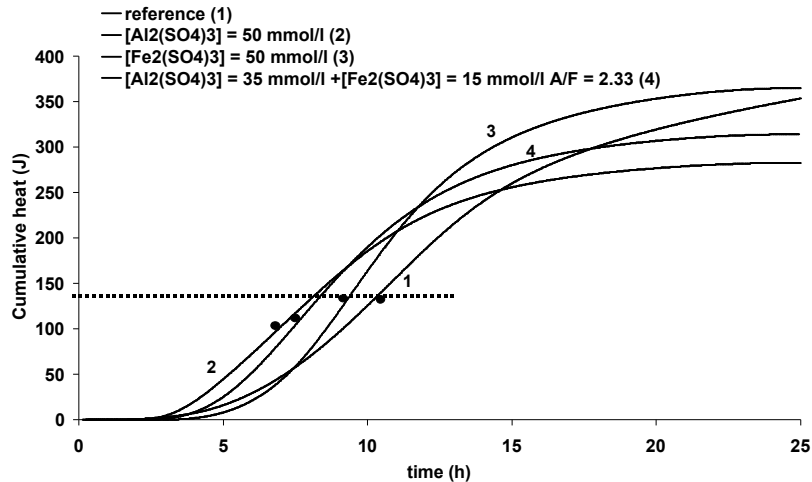


Figure 3b: Percentage of hydration during a tricalcium silicate hydration in presence of different sulphate salts. Experiments performed on paste in both lime and gypsum saturated solutions with an excess of Portlandite (0.05g). $l/s = 0.46$ $T = 20^{\circ}\text{C}$.

3.2.3: Influence of a mix of aluminium and iron sulphate salts.

An intermediate behaviour between pure aluminium and iron sulphate is obtained in presence of a mix of salts. As shown in fig 3b, the induction period is reduced with respect to the reference but lesser than that obtained with pure aluminium and the percentage of hydration useful for a complete covering of C-S-H is bounded by the reference and pure aluminium salt. In the same way, the mode of growth is affected and bounded by the iron sulphate and the reference one. From these results, it can be considered that both aluminium sulphate and iron sulphate systems correspond to the boundaries of this study.

As a first conclusion, both salts altered the course of the C_3S hydration but in a different way. The remainder of the work described herein was aimed at answering the origin of the change of the C_3S hydration kinetics in presence of sulphate salts which occurs at early age.. Thus, while being ensured as a preliminary to observe the same trends as in paste, a study was carried out using conductimetry following by aqueous phases extraction from these diluted suspensions.

3.2: Electrical conductivity

The influence of sulphate salt on the hydration of the C_3S was plotted in fig 4. Similarly to the calorimetric results, both ferric sulphate or aluminium sulphate salts affect the C_3S hydration kinetics. In addition, the evolution of conductimetric measurements in the first hour of hydration lets suppose that the changes of hydration kinetics can find an origin in the reactions which occur initially. Indeed, in the case of iron as for aluminium, a reduction in electric conductivity is recorded whereas the soluble salt addition should naturally generate a significant increase in this one. This

reduction can be attributed only to the initial precipitation of hydrates then consuming the various ionic entities present in solution, Ca^{2+} , SO_4^{2-} , OH^- , $\text{Al}(\text{OH})_4^-$ and $\text{Fe}(\text{OH})_4^-$. It also appears that the decrease of the conductivity seems more important in the case of the aluminium than of iron as testifies the two kinetics carried out in the presence of 5 mmol/l, meaning so that the nature of the formed hydrates in the two systems would be different. With an aim of progressing on the nature of the hydrates precipitated initially, aqueous phases were extracted after varying periods.

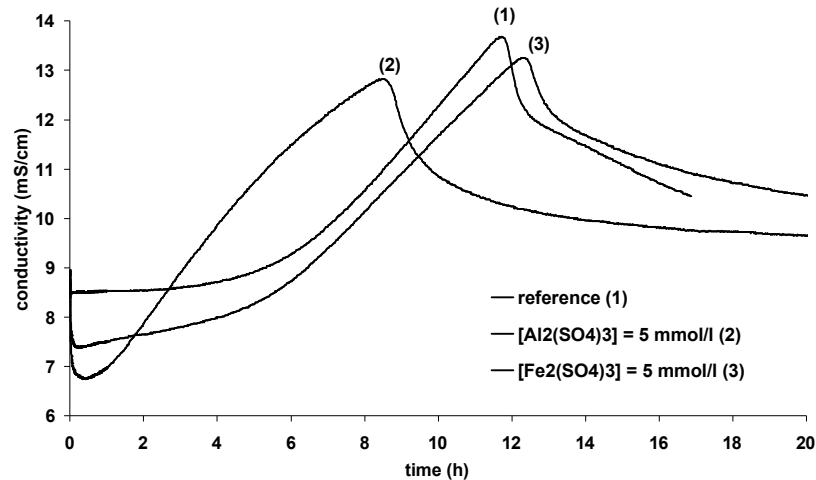


Figure 4: Evolution of the electrical conductivity during a tricalcium silicate hydration without salt and in presence of different sulphate salts. Experiments performed on stirred suspensions in both lime and gypsum saturated solutions. $l/s = 50$ $T = 20^\circ\text{C}$.

3.3: Aqueous phases analysis

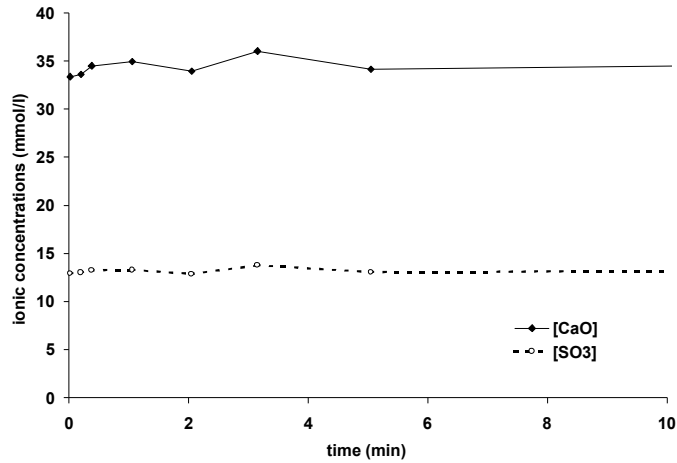
To clarify the interpretation of the previous results, the analysis of the ions concentrations in solution will be discussed at very early age of the hydration ($t < 10$ minutes). The results of the evolution of the ionic concentrations (CaO , SO_3 , Al_2O_3 and Fe_2O_3) versus time are plotted in fig 5.

First of all without salt (fig 5 (a)), we can note that both the calcium and sulphate concentrations remain quasi constant versus time and correspond to the solubility of gypsum in a lime saturated solution. The evolution of the concentration in silicates ions during the hydration is not presented here because it remains constant and close to the solubility of the C-S-H, i.e $30 \mu\text{mol/l}$.

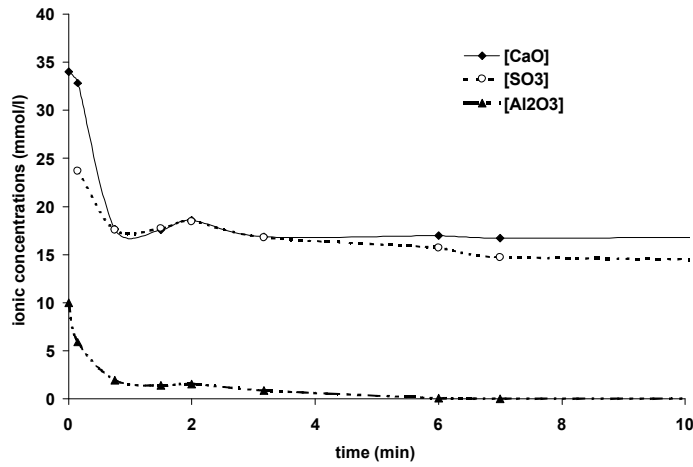
In presence of salts (fig 5 (b) and 5(c)), the evolutions of the ionic entities become more complex. We can note that the changes of the concentrations of calcium, sulphate, aluminium and iron versus time are not similar when the C_3S hydration is carried out in the presence of aluminium or iron.

The presence of aluminium sulphate leads to an instantaneous reduction in the three ionic concentrations i.e calcium, sulphate and aluminium (fig 5(b)). These decreases can be justified by a precipitation of solid(s) phase(s). Among those we can quote ettringite $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot x\text{H}_2\text{O}$, monosulfoaluminate $\text{Ca}_4\text{Al}_2(\text{SO}_4)(\text{OH})_{12}\cdot x\text{H}_2\text{O}$ or calcium hydroaluminates $\text{Ca}_x\text{Al}_2(\text{OH})_{6+2x}\cdot y\text{H}_2\text{O}$. From the assessment of the decrease of the three concentrations in solutions, an attempt at determination of the precipitated hydrates can be considered. However to carry out these calculations, it is also necessary that an additional condition is met based on the quasi instantaneous kinetics of dissolution of aluminium sulphate. This last one is appeared to be fast and shorter than 3 minutes. Moreover, it is nevertheless remarkable that neither increase in the aluminium nor in sulphate concentrations related to the progressive dissolution of salt in the three minutes is observed what means that the precipitation of hydrate(s) starts immediately after the release of ions from the sulphate phases. After 3 minutes and if only one hydrate precipitated, the assessment of the consumed ions, calcium, aluminates and sulphates, should lead us to consider a solid of stoichiometry: $\text{Ca}_6\text{Al}_3(\text{SO}_4)_{3.7}(\text{OH})_{12}\cdot x\text{H}_2\text{O}$. The different ratios Ca/Al , Al/SO_4 or Ca/SO_4 do not correspond to the stoichiometry of one of the hydrates previously quoted and more particularly the ettringite. In addition, if only ettringite had precipitated, we should not have measured any aluminium concentration in the solution because the solubility of ettringite is about $[\text{Al}(\text{OH})_4^-] = 20 \mu\text{mol/l}$ in the range of calcium concentration found in this study. This last condition is joined later beyond 6 minutes of hydration. In conclusion and at very early ages, it thus seems that a mixture of hydrates, ettringite and calcium hydroaluminate of uncertain composition precipitates initially.

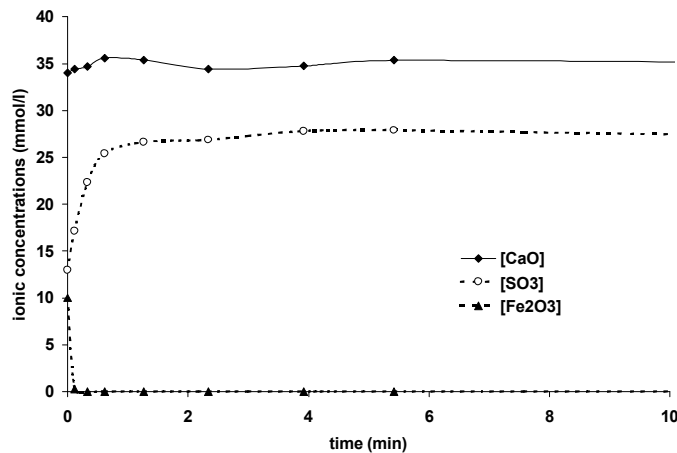
About iron sulphate (fig 5 (c)), results are different from the aluminium ones since the calcium concentration remains constant while the iron concentration decreases instantaneously and the sulphate one grows. In this case, the interpretation is much simpler than previously. Indeed, for sulphate ions, the increase of the concentration up to 3 minutes is related to the dissolution of ferric sulphate which is also reached after approximately 3 minutes. The solution reaches a sulphate concentration of 28 mmol/l corresponding to the contribution of both the 15 mmol/l of ions sulphates initially introduced as salt and the 13 mmol/l corresponding to the solubility of gypsum into a lime saturated solution. Neither sulphates nor calcium ions are thus consumed to form calcium aluminate hydrate at early age. It follows that the reduction of the iron concentration is connected to the only precipitation of the ferric hydroxide $\text{Fe}(\text{OH})_3$ which is very fast. This precipitation is very well characterized in experiments because the opalescent solution of the C_3S quickly takes a rusty color.



(a): without salt



(b): aluminium sulphate



(c): Iron sulphate

Figure 5: Evolution of calcium and sulphate concentration versus time. Aqueous phases extracted from stirred suspensions corresponding to a tricalcium silicate hydration in presence of: (a) no salt, (b) aluminium sulphate (5 mmol/l) and (c) $\text{Fe}_2(\text{SO}_4)_3$ (5 mmol/l). Experiments performed on diluted suspensions in both lime and gypsum saturated solutions. $l/s = 50$ $T = 20^\circ\text{C}$.

3.4: Hydrates characterization

The small quantity of hydrates precipitated initially as their small degree of crystallization makes their characterization using X-Rays Diffraction very difficult. This is why, only a qualitative microscopic analysis was performed by SEM. Micrographs obtained after 3 minutes of hydration, from experiments carried out in diluted suspensions, are presented in the fig 6. The first micrograph in top on the left represents anhydrous grains of C_3S . Then, on the three following images which well illustrate the discussion relating to the ionic analysis, one can observe the differences of hydrates formed according to the nature of sulphated salts used. Without salt, few hydrates corresponding to C-S-H hydrates seem to partially cover the surface of anhydrous grains. In the presence of aluminium sulphate, ettringite is easily identifiable by the shape of the small needles which precipitated on the C_3S grains. Additionally denser zones of hydrates are observed, which possibly could correspond to the calcium hydroaluminate. In the presence of ferric sulphate, no needles of ettringite are observed at early age, then consolidating the assumption according to which only the ferric hydroxide initially precipitates .Ettringite is then identified after approximately 1 hour of hydration.

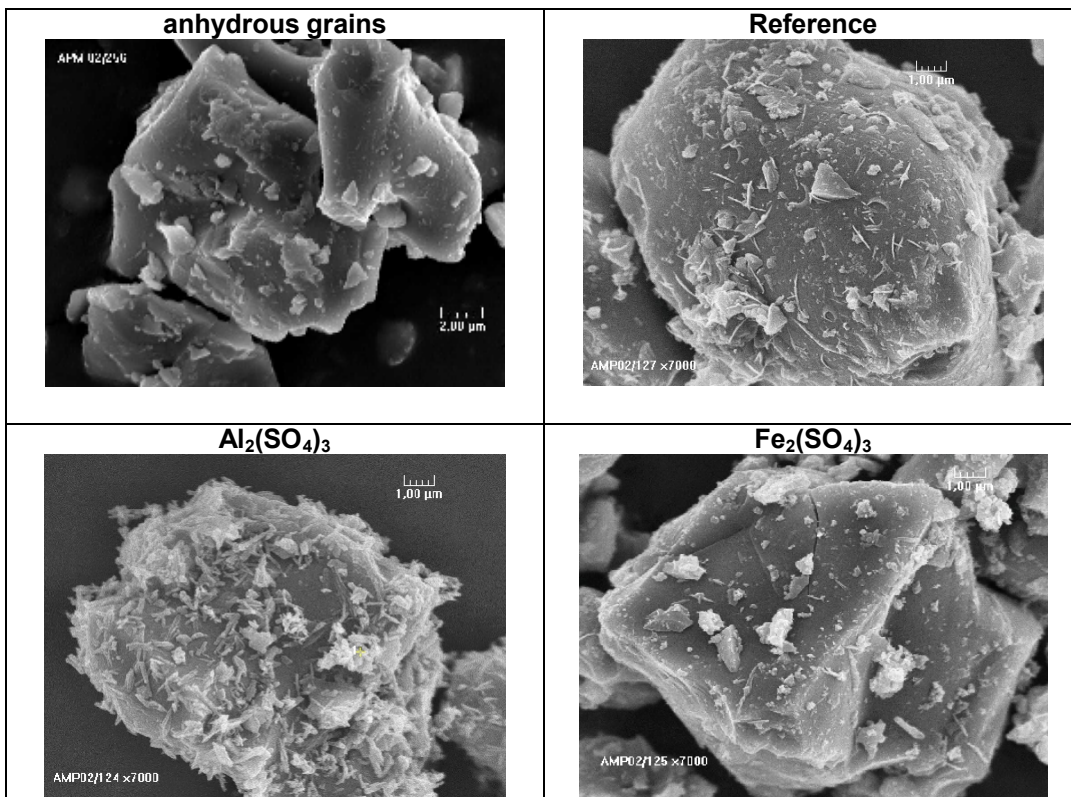


Figure 6: SEM micrographs of anhydrous C_3S grains (in top on the left) and surfaces hydrated 3 minutes. Hydrated phases extracted from stirred suspensions corresponding to a tricalcium silicate hydration without salt and in presence of $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ (5 mmol/l). Hydration kinetics performed on suspensions in both lime and gypsum saturated solutions. $l/s = 50$ $T = 20^\circ C$.

4: Discussion

Two sulphated salts were used to artificially reproduce the interstitial solution of the cement paste. Their influence on the C_3S hydration kinetics at very early age was evaluated by a coupling of various techniques. The reported experimental results clearly show the following:

1) In presence of ferric sulphate and from stirred suspensions (fig 5(c)), we have shown that only the ferric hydroxide $Fe(OH)_3$ precipitates instantaneously. In parallel and using isothermal calorimetry on paste, a slight delay of the initial C_3S hydration kinetics has been characterized by a longer induction period. According to Damidot or Garrault, the number of C-S-H nuclei formed initially should be smaller compared to the reference. But when the rate of C_3S reaction is accelerated, an hydration degree of the C_3S higher than that without salt is obtained (fig 3). This lead us to conclude that the initial $Fe(OH)_3$ precipitation on the anhydrous C_3S grains does not form a protective layer that impedes the C_3S hydration kinetics, according to the view also expressed in particular by Chiesi [13].

2) In presence of aluminium sulphate, from the assessment of the ionic species in solution (fig 5(b)), it has been pointed out that ettringite and calcium hydroaluminate precipitate initially. Knowing that ettringite is the less soluble hydrate, it should have been the only one phase to precipitate according to the thermodynamic data [14]. This result is comparable with those obtained by Minard since it has also been shown that calcium hydroaluminate precipitates instantaneously and before the ettringite during the initial hydration of the C_3A in presence of gypsum [15]. Moreover, this double hydrate precipitation is distinguished in the first minutes of hydration by a decrease of both calcium and hydroxyl concentrations in solution (fig 5(b)). However, it is well known that the lime concentration in solution alters the course of the C_3S hydration in the sense that the weaker the lime concentration the higher the initial C_3S hydration kinetics [5,6]. But from pastes experiments, an excess of Portlandite ($Ca(OH)_2$) has been used in order to perform measurements at a constant lime concentration. So, the assumption of a variation of the $Ca(OH)_2$ concentration can be excluded to explain the modification of the C_3S hydration kinetics that occur in presence of aluminium sulphate.

Then after 6 minutes of hydration and due to the ettringite precipitation, the aluminate concentration in the interstitial solution becomes very weak: $[Al_2O_3] \approx 20 \mu mol/l$. So the poison effect of the aluminate ions on the C_3S hydration kinetics observed in free calcium sulphate systems is removed [7,8]. That also explains why we do not observe a delay of the C_3S hydration kinetics when a sulphate source is used. It has even been highlighted using calorimetric measurements that an acceleration of the C_3S hydration kinetics happens. In particular, the induction period is clearly shorter meaning that the number of C-S-H nuclei formed initially should be higher compared to the reference one. In relation to the nature

of hydrates discussed previously, one can assume that the new surfaces developed by the calcium hydroaluminates and/or ettringite could be used as nucleation support for new C-S-H clusters and could then generate a higher initial degree of the C_3S hydration.

Consequently in presence of aluminium sulphate, even if calcium hydroaluminate or ettringite precipitate initially on the anhydrous C_3S grains, the C_3S hydration kinetics is not delayed and an acceleration of its hydration rate is underlined.

3) In addition, it was shown thanks to calorimetric measurements (fig 2 and 3) that results obtained for experiments carried out with a variable ratio A/F are bounded by both pure aluminium and ferric sulphate salts. The C_3S hydration kinetics at early age depends on the initial ratio A/F. The higher the Al content the higher the number of C-S-H nuclei precipitated initially. This could be connected to the nature and the relative proportion of hydrates which precipitate initially in presence of aluminium or iron in the sense that the higher the calcium hydroaluminate content, the higher the number of C-S-H clusters.

4) Finally, it has been proved that, during the C_3S hydration the C-S-H growth proceeds in a parallel mode and a perpendicular mode on the surface of anhydrous calcium silicates particles [6]. We have shown in presence of aluminium sulphate that the percentage of hydration to reach a complete covering of Alite grains is lower than the reference one while the number of nuclei formed initially was higher with respect to system hydrated without salt. These results can be linked to those obtained by Garrault when lime concentration varies [6]. Indeed, the lower the lime concentration the higher the number of nuclei formed initially and the lower the percentage of hydration for which the rate of hydration becomes controlled by diffusion. In order to account for these experimental results, Garrault proposed that the parallel growth mode would be favoured [6]. Based on this, the mode of C-S-H growth is therefore modified in presence of aluminium sulphate and also characterized by a favoured parallel growth mode. Only the origin of the higher number of the nuclei formed is different since in this study the lime concentration in paste is buffered by $Ca(OH)_2$. As discussed above in point 2, the new surfaces developed by aluminate hydrates would be at the origin of the higher number of nuclei formed initially.

Moreover, both aluminium and iron sulphate corresponded to the boundaries of the study and intermediate behaviour has obtained in presence of mix of salts. That implies that the modification of the C-S-H growth depends on the initial ratio A/F. The A/F ratio affects also the rate of hydration when it is controlled by a diffusion process. In presence of aluminium sulphate, the hydration kinetics is slower than the reference what can be connected to a higher density of the product layer. Conversely, the higher the iron content the more porous the C-S-H layer around the C_3S grains. However, the mechanism by which the

permeability of the C-S-H layer is increased is not yet well known even if it has been proposed that the higher the C/S ratio the higher the C-S-H layer permeability [16,17]. Although the C-S-H structure modification remains qualitative in this study, it will be sure that a change of the C-S-H permeability could have an influence on the ions diffusion through the C-S-H layer formed and so could have a real impact on the durability of mortar or concrete.

5: Conclusions.

Both aluminium and iron sulphate salts were respectively used to simulate the composition of the interstitial phase of cement in the first moments of the C_3S hydration kinetics.

According to the nature of salt used, hydrates of different nature precipitate initially. Ettringite and calcium hydroaluminates were identified in the presence of aluminium sulphate whereas only the ferric hydroxide is formed instantaneously in the presence of ferric sulphate salt.

No significant retardation of C_3S hydration is observed in either case; in fact, acceleration is more often observed. These results imply that aluminate and ferrite hydrates precipitating at early ages in Portland cement hydration under typical conditions of use do not form a protective layer that impedes silicate phase hydration.

The number of the C-S-H nuclei formed initially as well the porous structure of the C-S-H layer appear to be modified according to the initial ratio A/F. The first one could be correlated to the relative proportion of calcium hydroaluminate precipitated initially which should increase with the aluminium content while the higher the iron content the more porous the C-S-H layer would be. However, this last modification remains unexplained and further work is necessary.

References

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- [1] Taylor H.F.W and al. " The hydration of tricalcium silicate" RILEM Comittee-68-M.M.H task group 3, Mater Constr., 102, (1984), pp 457-468.
 - [2] Brown P.W. and al. " Analysis of the aqueous phase during early C_3S hydration." Cem. Concr. Res.,14, (1984), pp 257-264.
 - [3] Gartner E.M., Gaidis J.M., "Hydration Mechanisms I", Materials science of Concrete, (1989), pp 95-125.
 - [4] Barret P., Bertrandie D. " Fundamental Hydration Kinetic features of the major cement constituents Ca_3SiO_5 and Ca_2SiO_4 " J.Chim.Phys. 83, (1986) pp765-775.

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- [5] Damidot D. and al. " Kinetics of tricalcium silicate hydration in diluted suspensions by microcalorimetric measurements" *J.Am.Ceram.Soc.* 73, (1990), pp 3319-3322.
- [6] Garrault S., Nonat A., "Hydrated layer formation on tricalcium and dicalcium silicates surfaces: Experimental study and numerical simulations", *Langmuir*, 17, (2001) pp 8131-8138.
- [7] Cottin B.F. "Some interactions between C₃A and C₃S during cement portland hydration". 7th Int. Congr. Chem. Cement, Paris, vol 4, (1980) pp 504-509.
- [8] Damidot D., Rettel A. , Study of the interaction between the hydration of CA and of C₃S at room temperature, 11th Int. Congr. Chem. Cement, Durban, vol. 4, (2003), pp 1845-1854, .
- [9] De Jong J.G.M, Stein H.M., Stevels J.M. " Mutual interaction of C₃A and C₃S during hydration" Supplementary paper II-35, 5th Int. Congr. Chem. Cement Tokyo (1968), pp 311-320.
- [10] Gaidis J.M., Gartner E.M. "Hydration Mechanism II" *Materials Science of Concrete II*, (1991), 2, pp 9-39.
- [11] Tenoutasse N. "The hydration mechanism of C₃A and C₃S in the presence of calcium chloride and calcium sulphate" Supplementary paper II-118, 5th Int. Congr. Chem. Cement Tokyo (1968), pp 372-378.
- [12] Gartner E.M., Myers D. "Influence of tertiary alkanolamines on Portland cement hydration" *J.Am.Ceram.Soc.*, 76 (6) (1993), pp 1521-1530.
- [13] Chiesi C.W., Myers D., Gartner E.M., "Relationship between clinker properties and strength development in the presence of additives" *Proceedings of 14th Int'l Conference on cement microscopy.* (1992), pp 388-401.
- [14] Damidot D., Glasser F.P. "Thermodynamic investigation of the CaO-Al₂O₃-CaSO₄-H₂O system at 25°C and the influence of Na₂O". *CCR*, 23, 1, (1993), pp 221-238.
- [15] Minard. H. " Integrated study of the processes of hydration, coagulation, rigidification and set for a system C₃S-C₃A- sulphate – alkali" PhD Thesis University of Burgundy. (2003)
- [16] Taylor H.F.W. " Hydrated calcium silicates. Part I. Compounds formation at ordinary temperature" *J.Chem.Soc.*, (1950), pp 3682-3690.
- [17] Greenberg S.A., Chang T.N. "Investigation of the colloid hydrated calcium silicates. II, Solubility relationships in the calcium-oxide-silica-water system at 25°C." *J.Phys.Chem.*, 69, (1965), pp 182-188.