Influence of PC superplasticizers on tricalcium silicate hydration

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The influence of polycarboxylate superplasticizers with variations of content of anionic groups was studied on pure tricalcium silicate hydration. The hydration in diluted suspension has been investigated by conductimetry, calorimetry, and ionic and total organic carbon analysis of the liquid phase. The tricalcium silicate hydration is always delayed in presence of polycarboxylate superplasticizer. Moreover, the delay can be correlated with the number of carboxylate groups which are on the adsorbed superplasticizer molecules. This effect seems to be due to a decrease of the C_3S dissolution rate. Namely the pure C_3S dissolution was studied by ICP with or without a carboxylate functionalized latex. A drastic decrease of the C_3S dissolution rate was observed in presence of the polycarboxylate functionalized latex and this effect increased with higher hydroxyde calcium concentrations.

1 Introduction

A good superplasticizer fits the three following requirements: initial dispersing ability of cement, dispersion retention ability and have no setting retardation effect or the less as possible.. While the use of polycarboxylate based superplasticizers (PCP) continues to grow for superplasticized concrete, many papers and studies still deal with the problem of better understanding the action mode of these polymers and how the different structures influence the performance of these polymers.[1-7]. These previous studies showed a setting retardation due to the presence of PCP superplasticizer and several mechanisms were proposed to explain interactions between cement and SP [8]. Adsorbed SP molecules were thought to hinder the diffusion of water and calcium ions at the cement-solution interface. Because SP molecules form complex with calcium ions, they are also suspected to inhibit nucleation and/or alter growth kinetics and morphology of the hydration products [9-11].
Therefore a mechanism describing the influence of the PC superplasticizers on cement hydration is still not well ellucidated. The cement setting is known to be due to the nucleation-growth of calcium silicate hydrates (C-S-H) resulting from tricalcium silicate (C_3S) hydration [12], so the purpose of this paper is to study the interactions between PCP superplasticizers and pure C_3S during its hydration in

order to bring new insights about the origin of setting retardation in presence of PCP superplasticizer. The present study was led on C_3S suspensions (W/C= 50 to 250), by means of conductivity measurement, flame - atomic absorption spectrometry and ICP- atomic emission spectoscopy. Indeed phenomena relevant to hydration, i.e. C_3S dissolution, nucleation and growth of hydrates, are easier to investigate at higher W/C than at ratio inferior to 1 and previous studies showed that kinetics of C_3S hydration led in diluted suspensions in a saturated lime solution is very close to the paste. [13]

2 Experimentals

Materials

The tricalcium silicate was supplied by Lafarge LCR and ground to a specific area of 400 m^2/kg as determined by Blaine's method. We have already observed that the hydration rate of C_3S strongly depends on its specific surface, and also on its age because of a possible partial hydration over time. So, we decided to perform all the experiments with the same batch of C_3S in order to compare the results.

Three different types of PCP which are water-soluble methacrylic graft polymers were used for this study. They were provided by Chryso. The three polymers had the same main carboxylic and polyoxyethylene side chain lengths.

This polymers structure can be represented as follows:
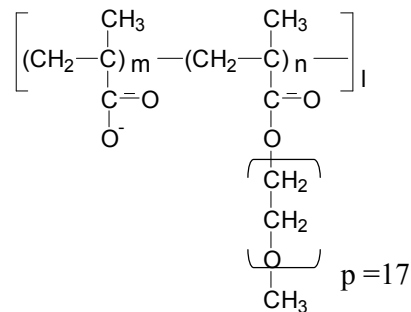
The only difference among these three polymers was the ester rate given by the ratio n / (m+n).
Esterification levels and molar mass of the different PCP used in this study are given in the following table:

Polymer name	Esterification level	polymer Mn (g/mol)
PCP 30	30%	14500
PCP 38	38%	17300
PCP 45	45%	19700

Table 1: main characteristics of PCP

Another "polycarboxylated" additive, supplied by Rhodia, was also used for this study: a latex (POLYAC1) with a soft copolymer core, and surface carboxylic groups. pHmetric titration allowed to determine a density of 284 µeq of carboxylate functions per gramm of latex. The median diameter of the latex determined by light scattering (QELS) is 150 nm.

Methods of investigation:

The C_3S was hydrated at 25°C in diluted suspensions saturated in lime with a liquid/solid ratio equal to 250 under inert atmosphere in order to avoid carbonation. The suspension was continuously subjected to mechanical stirring. The chemical evolution was followed by electric conductivity measured with an XE 150 electrode (Tacussel).
In order to determine concentrations of species in solution ($[Ca_{total}]$, $[SiO_{2total}]$) or the polymer adsorption during the C_3S hydration reactions, small portions of the suspensions were removed, filtered through 0.3 µm millipore filters and acidified to avoid carbonation. A carbon analyser, model TOC 5050 (Shimadzu) was used to follow the evolution of polymer adsorption during the C_3S hydration. Atomic Absorption Spectrometry (Perkin Elmer) was used for the calcium concentrations. As concern pure dissolution experiments, we used a special set-up for determining ions concentrations continuously: this latter allowed us to sample continuously and to filter a very low volume of suspension and transfer it to an ICP-OES directly. (Inductively Coupled Plasma - Optical Emission Spectrophotometer) Vista Pro (Varian) [14]. By this way the L/S ratio is kept constant.

3 Results:

- Hydration of C_3S in presence of PCP:

Hydration of C_3S without additives proceeds by dissolution of anhydrous C_3S and precipitation of hydrates, C-S-H and Portlandite CH, as represented by the three following reactions:
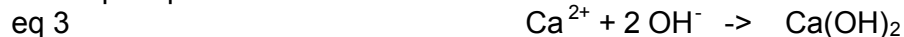dissolution of C_3S :

eq 1 $\qquad Ca_3SiO_5 + 3\ H_2O \rightarrow 3\ Ca^{2+} + 4\ OH^- + H_2SiO_4^{2-}$
C-S-H precipitation:

eq 2 $\qquad x\ Ca^{2+} + 2(x-1)\ OH^- + H_2SiO_4^{2-} \rightarrow (CaO)_x(SiO_2)(H_2O)_y$
portlandite precipitation :

eq 3 $\qquad\qquad\qquad\qquad Ca^{2+} + 2\ OH^- \rightarrow Ca(OH)_2$

The C-S-H precipitation does not consume all the calcium and hydroxide ions released by C_3S dissolution so it is easy to follow the advancement of hydration by monitoring the electric conductivity as long as Portlandite precipitation does not occur. The conductimetric curve corresponding to C_3S hydration in diluted suspension (Figure 1) presents different steps as previously described [15].
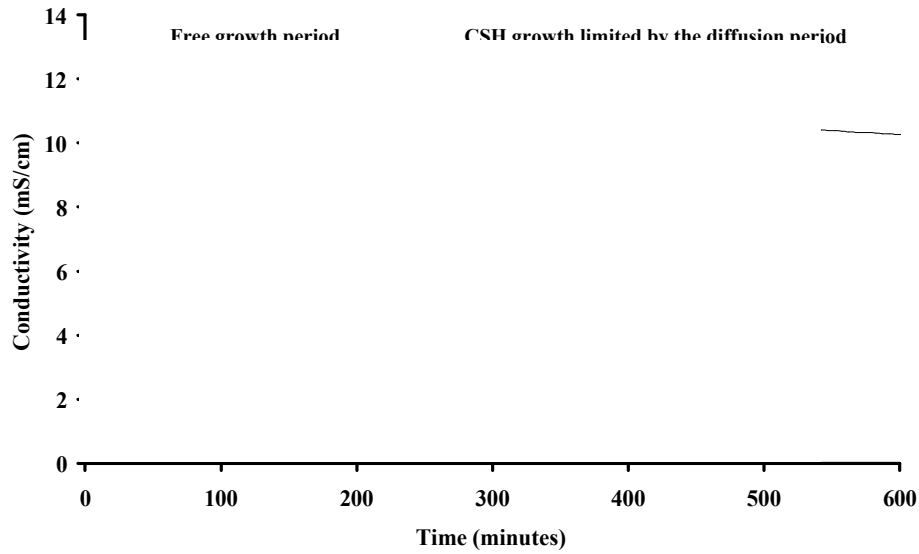
Figure 1 Different steps of a conductimetric curve obtained during the hydration of C3S in diluted suspension (L/S= 50) in a lime solution.

The ability of PCPs to delay hydration of C_3S is correlated to the duration of the conductivity "plateau" (so-called dormant period) observed before the conductivity increasing due to the CSH growth.
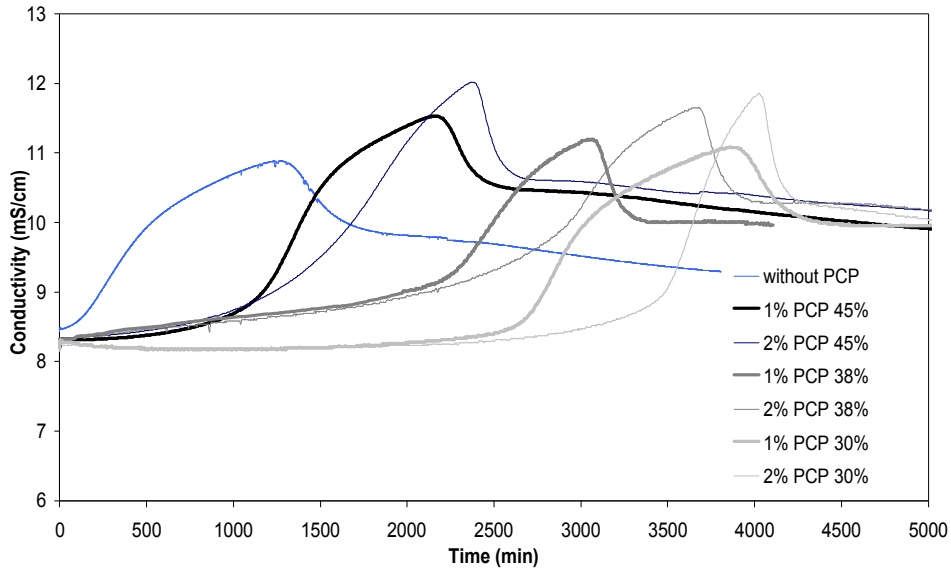

Figure 2: conductivity evolution during C_3S hydration in diluted suspensions (L/S=250) in presence of different amounts of PCP (expressed in dry residue with respect to the mass of solid) and in lime saturated solution.

Figure 2 shows on the one hand that the shortest retardations are observed with PCP having the biggest ester moieties, and on the other

hand the higher is the PCP dosage, the longer is the retardation. In addition, as conductivity slightly increases in presence of PCP 45% and PCP 38% during the initial period, we can conclude that C_3S hydration is not completely impeded. Inversely, under the same conditions PCP containing the most carboxylate functions (PCP 30%) seems to prevent from C_3S hydrating at least 1500 minutes. Namely in this case the conductivity curve does not increase and even worse it seems to decrease. The slight decrease was connected to calcium ions complexation by carboxylate groups. Indeed the same behaviour occured with latex containing only carboxylate functions (Figure 6) proving that the initial decrease of conductivity is not due to an eventual PCP hydrolysis, but rather to a calcium complexation which has been already reported [16]. In addition the first part of the conductimetric curve obtained with PCP 30% can be superimposed on the conductimetric curve obtained by adding the same amount of PCP 30% to a lime saturated solution free of C_3S as shown on the Figure 3.
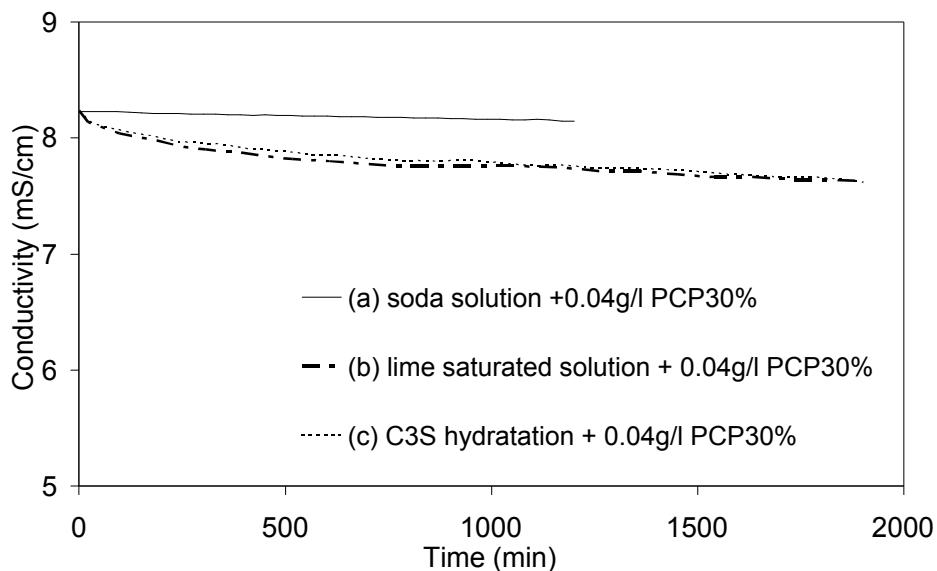

Figure 3 Evolution of the conductivity in the case of (a) a soda solution adjusted to pH 12.6 containing 0.04 g/L of PCP 30% (b) a lime saturated solution containing 0.04 g/L of PCP 30% or (c) C_3S hydration led in a lime saturated solution containing 0.04 g/L of PCP 30% .

Obviously this phenomenon does not occur when PCP is added to a basic soda solution free of calcium ions and adjusted to the same pH as previously.

Hence we conclude PCP 30% consumes a part of calcium ions present in a lime saturated solution by complexing them and moreover this additive impedes C_3S dissolution.

Adsorption of PCP was measured during C_3S hydration carried out in a lime saturated solution and with L/S ratio equal to 50. Under these conditions the amount of PCP adsorbed is high enough to follow PCP

adsorption with good accuracy. Figure 4 clearly shows an initial adsorption which could be attributed to adsorption on C_3S surface maybe partially covered by C-S-H and then the PCP adsorption increasing is certainly connected to adsorption onto C-S-H which are being precipitated. Once again, highest retardations occur with PCPs having the highest esterification rates.

Previous experiments [16] performed in the same conditions displayed that most PCP adsorbs on C-S-H surface rather than onto C_3S, according to the huge difference between both specific surfaces (less than 1 m^2/g for the C_3S compared to more than 200 m^2/g for the C-S-H) [16, 17]. Consequently the adsorption evolution allows to follow C-S-H surface which is appearing. In addition as the conductivity begins to increase, the adsorption also raises. The final plateau value of PCP adsorption corresponds to the total adsorption, meaning after this point there is no more "free" PCP inthe solution which would be able to adsorb. Hence we deduce from the adsorption curves that PCP 30% and PCP 38% certainly prevent C-S-H from precipitating as long as PCP adsorption is plateau (respectively during about 300 and 700 minutes).
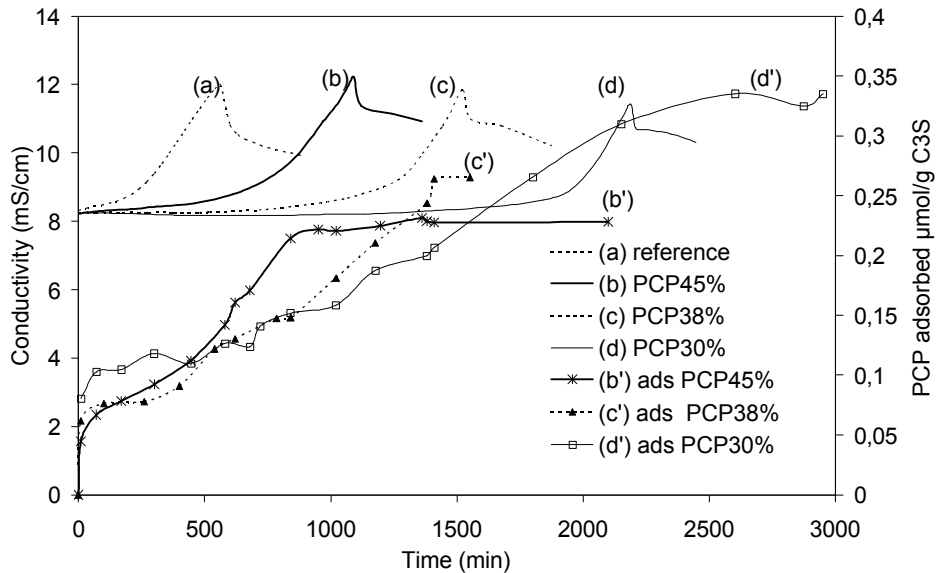

Figure 4: Effect of the ester ratio of PCP on C_3S hydration in a lime saturated solution (L/S = 50). Adsorption is expressed in µmol per g of C_3S introduced. The final adsorption plateau corresponds to 100% of PCP adsorbed.

From the three previous experiments, the number of carboxylate functions initially in the vicinity of C_3S surface can be calculated from the adsorption level and from chemical structure of the PCP. Thus, as a rough approximation the retarding effect is linearly related to the number of COO^- functions likely to interact with C_3S surface (figure 5).
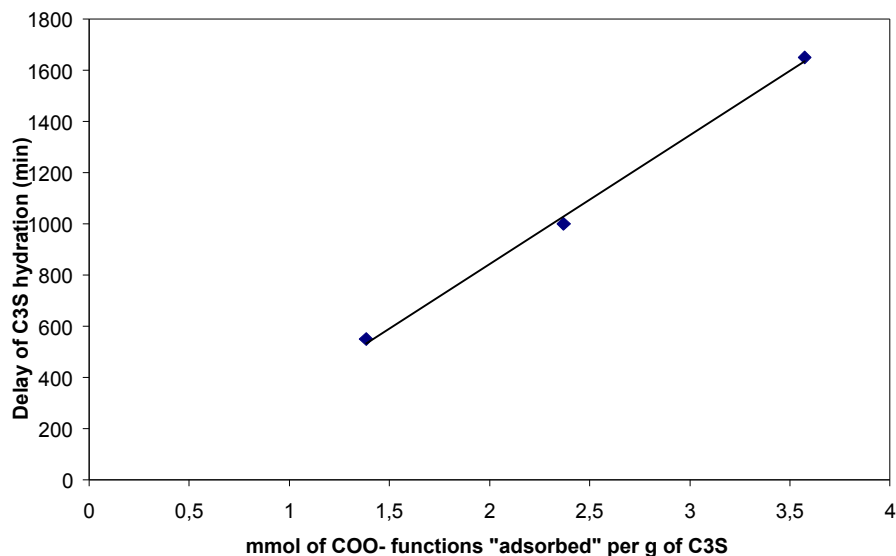
Figure 5. Duration of the low conductivity increasing period in function of the mean number of carboxylate functions initially in the vicinity of C3S surface.

From these results we deduced PCP superplasticizers act on C_3S hydration by retarding it and the delay seems to be connected to the number of carboxylate functions able to interact with the C_3S surface. Moreover, from these results we suspect PCPs with lower esterification ratios impede C_3S dissolution for a long time, and by this way they prevent C_3S from hydrating. A study on pure C_3S dissolution in presence of a carboxylate additive was led in order to confirm the veracity of this hypothesis.

- Effect of the carboxylate functions on pure dissolution of C_3S

The conductimetric curve obtained during the C_3S hydration carried out in a lime saturated solution shows that the "carboxylated" latex behaves in the same way as PCPs. From the data we can calculate that 5% of latex contains approximately the same number of carboxylate functions as 0.7 % of PCP 30%. As represented on the figure 6, under these experimental conditions, the presence of 5% of latex prevents C_3S from hydrating during more than 30 hours. Such a duration is of the same order of magnitude as that obtained under the same conditions in the presence of 1% of PCP 30%.
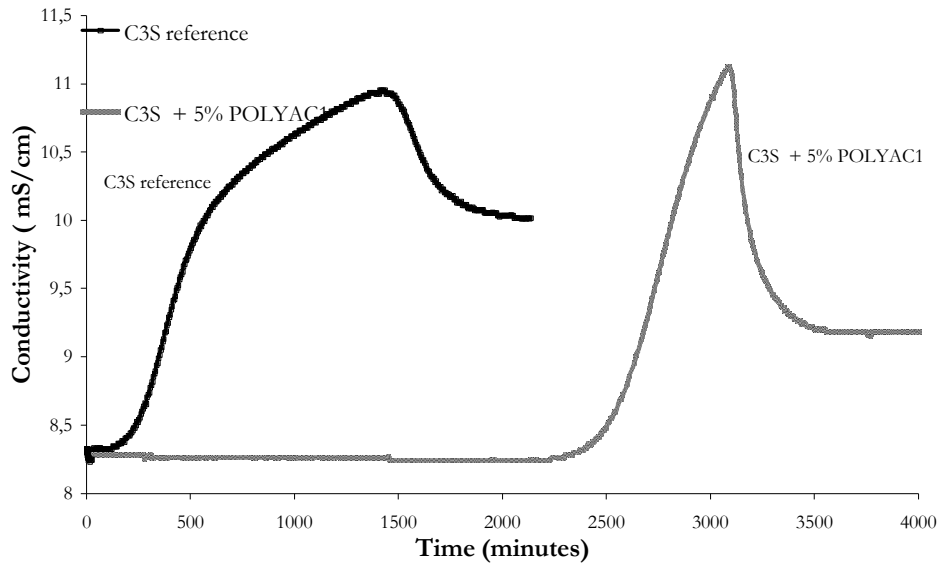
Figure 6: conductivity evolution during C_3S hydration in a lime saturated solution (L/S=250) without latex and in presence of 5% of latex (expressed in dry residue with respect to the mass of solid).

In order to highlight a possible effect of carboxylated additive on the C_3S dissolution rate, pure C_3S dissolution was studied by ICP-OES in presence and without it. The amount of C_3S added to the lime solution was calculated so as to avoid the C-S-H precipitation. Because of the very low solubility of the C-S-H in a lime saturated solution, experiments were carried out in a 11mmol/L lime solution. The silica concentration was continuously determined by using the special set-up previously described. By this way the degree of the C_3S dissolution can be calculated. Figure 7 clearly shows that carboxylated additive strongly decreases the C_3S dissolution rate. This experiment was again undertaken in various lime concentration solutions and the latex again inhibited the C_3S dissolution [14]. Moreover its effect on the C_3S dissolution rate depends on the lime concentration: the more concentrated in lime the solution is, the stronger the latex effect is and so the lower the dissolution rate becomes.
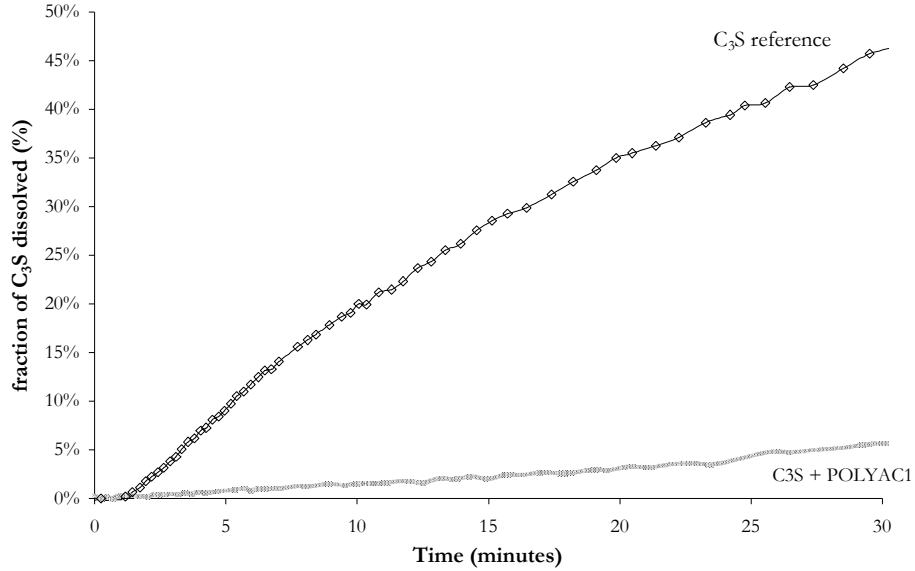
Figure 7: dissolution of 1.5 mg of C_3S in 200mL of a 11 mmol/L lime solution in presence of 0.4g of latex. In order to emphasize the effect of the additive on the dissolution and to take the very high W/C into count, the latex dosage was accordingly adjusted to a volume fraction of 0.2% with respect to the liquid (260% with respect to the C_3S mass).

However, silicate titrations carried out during the C_3S hydration at W/C=250, revealed that C_3S dissolution is not slowed down at the very beginning. Namely, the initial silicate concentration increase that we can see on the Figure 7, mainly accounts for C_3S dissolution, the C-S-H precipitation being negligible at the very beginning. Afterwards the silicate concentration is plateau and higher than without additive.
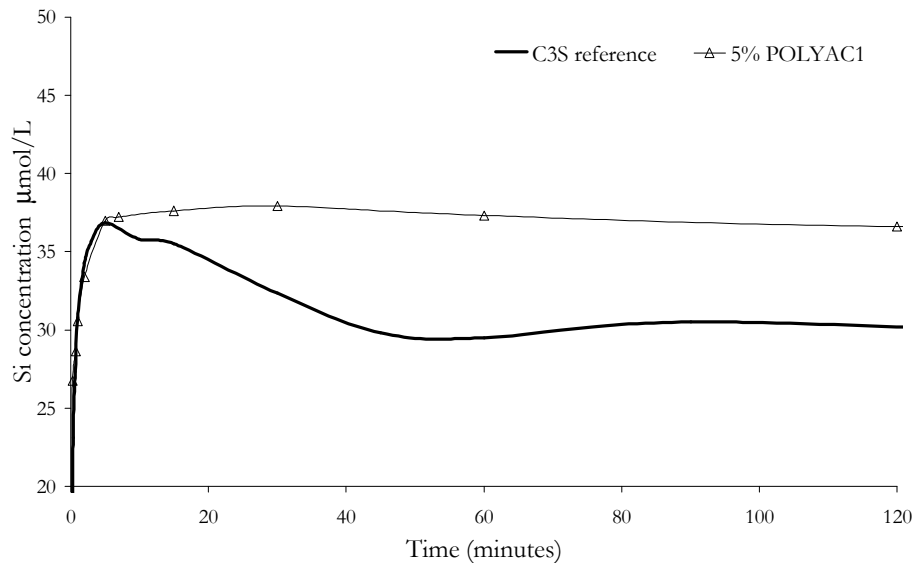

Figure 7: Silica concentration evolution during C_3S hydration in a lime saturated solution (L/S=250) without latex and in presence of 5% of latex with respect to the C_3S mass.

This result seems to be inconsistent if we consider the previous experiments performed at very high W/C. Adsorption kinetics are thought to explain the non-inhibition effect in the very first minutes. This latter is quite favoured in the case of highest W/C ratios, so in the case where there is few C_3S for a huge quantity of latex.

Then, without additive, the silica concentration decreases a few minutes later in connection with the primary C-S-H nucleation whereas dissolution is going on [18] Nevertheless unlike the reference, the primary C-S-H nucleation is not observed within the first hundred minutes in presence of latex (Figure 7). Hence, although the solution is supersaturated with respect to C-S-H, the presence of the latex delays the primary C-S-H nucleation. In addition because both the silica concentration and the conductivity are almost constant during the first hundred minutes, we can conclude that C_3S dissolution and also C-S-H precipitation are very slow under these conditions. Therefore the carboxylate additive again impedes C_3S dissolution although the solution is undersaturated with respect to the C_3S solubility.

Furthermore calcium and silica titrations were carried out during the C3S hydration and are reported on the Figure 8.
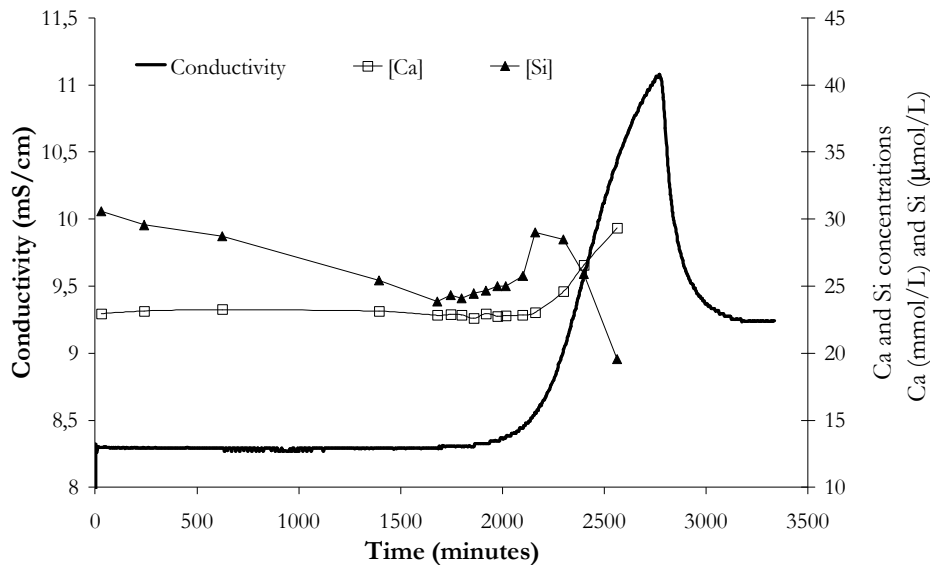

Figure 8: Silica and calcium concentrations evolution and conductimetric curve obtained during C_3S hydration in a lime saturated solution (L/S=250) in presence of 5% of latex with respect to the C_3S.

According to C_3S dissolution and C-S-H precipitation reactions (eq 1 and eq 2) and as long as the calcium concentration remains constant, the silica concentration evolution allows to determine which of both reactions is the fastest. Obviously, as long as Portlandite does not precipitate, calcium concentration evolution gives information on global C_3S hydration rate, the higher the concentration raises, the faster the C_3S hydrates. Therefore the slight decrease of the silicate

concentration observed during the first 1700 minutes indicates that the C-S-H precipitation is faster than the C_3S dissolution. Moreover because the calcium concentration seems to be constant, we can conclude that, the C_3S hydration rate is very low during this period.

After this point and up to 2200 minutes, the silica concentration increases, meaning that the dissolution rate becomes higher than the CSH growth rate. This phenomenon never occurred without carboxylate additive. It could be connected with a resuming of C_3S dissolution indicating that the carboxylate additive does not prevent anymoreC_3S from the dissolution. This behaviour is still not well understood. We can imagine that at this moment, the amount of CSH precipitated might be sufficient to make the additive not enough effective to impede the C_3S dissolution anymore. However this hypothesis has to be verified.

Finally, the silica concentration decreases as the reference whereas calcium concentration raises: C-S-H growth consumes more silicate ions than provided by C_3S dissolution and both reactions accelerate. From this point, C_3S hydration takes place in the same way as without carboxylate additives.

Conclusion

The retarding effect is linearly related to the number of COO^- functions likely to interact with C_3S surface.

Pure C_3S dissolution experiments led in presence of carboxylate additives showed that they strongly decrease its rate.

In presence of carboxylate additives, C_3S dissolution can be negligible for a long time and C-S-H precipitation rate is strongly decreased during this period.

C_3S hydration acceleration occurs when C_3S dissolution rate raises. It means that by delaying C_3S dissolution, these carboxylated additives prevent C_3S from hydrating. The reason why the effect of carboxylate additives on C_3S dissolution stops at this moment is still not clear.

Moreover we have to keep in mind that whereas C_3S is the most abundant phase in cement, the effect of PCP superplasticizers on C_3S hydration in the cement might be affected according to the cement composition. Indeed, sulphate ions concentration strongly depends on the cement mineralogy and on the hydration time and these ions are known to adsorb in a competitive way with PCP [17], and therefore alter the ability of the PCP to delay C_3S hydration.

Furthermore aluminate phases hydration will modify interactions between PCP and the C_3S hydration by disturbing it and also by creating new surfaces able to "consume" a part of PCP by adsorption.

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