The effect of three types of Superplasticizer on tricalcium aluminate hydration

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Summary

Various types of Superplasticizer have been widely used over the past few decades to produce very high strength and durable concrete. These chemicals interfere with the different physical and chemical processes that occur in primary cement paste. This paper presents the results of investigating the effect of superplasticizers on hydration of pure tricalcium aluminate in the presence of gypsum. Suspension hydration has been investigated using conductivity, isothermal calorimetry and total liquid phase organic carbon analysis. The time required for the formation of ettringite without superplasticizer in the presence of three different types of superplasticizer is specified: Polyphenyl sulfonates (PNSs), polycarboxylate-polyoxide (PCP) and polydethylene diphosphonate. Since polyethylene diphosphonate does not appear to modify the hydration of tricalcium aluminate in the presence of gypsum, PCP and even more PNS slow down the formation of ettringitis. This effect appears to be largely due to increased C3A dissolution and may be linked to PCP. Or PNS observed from the initial hydration of C3A. In addition, the presence of PCP superplasticizer reduces the size of the ettringite crystals.

.**Keywords:** Hydration, Ultrafiltration, Tricalcium aluminate

1.Introduction

Super-lubricants are polymers that are added to the concrete, increasing fluidity at an early age without affecting the concrete's resistance and behavior. Different polymers are used for this purpose. Whereas poly naphthalene sulfonates (PNS) have often been reported to act in the dispersion of cement particles Electrostatically repulsive, polycarboxylate with polyoxyethylene bonding chain (PCP) or ethylene mono diphosphonate polymer due to the spatial inhibition effect caused by the extension of their bond chains around the cement particles causes the cement particles to disperse. In addition, it has been reported that the type of super plasticizer (SP) and mixing method as preparation conditions can significantly affect the fluidity of Paste of cement.

2. Experimental Methods

Materials

For this study, three types of lubricants were investigated. The chemical structures and their molecular weights are listed in Table 1 The pH of these additives was adjusted to 9.60 by adding 1 M NaOH to neutralize all acidic functions in the additive. Because the adsorption mechanisms are controlled by the additive concentration in the solution, the lubricating doses were calculated to have the same concentration in the solution. Hydrophilic doses were calculated to have the same concentration in the solution. The polycarboxylate superplasticizer with polyoxyethylene bonding chain (PCP) produced by Chryso is reported as the length of the main polycarboxylic and bonded chain in Table 1. A polyethylene sulfonate polymer (PNS) produced by Handy Chemical (Dysal) was also used by Chryso's mono poly polyoxyethylene diphosphonate polymer. C3A was synthesized by stoichiometric mixing and powdering using calcium carbonate and alumina, and its calcination process was performed at 1400 ° C for 3 h in an electric furnace. C3A was analyzed by XRD. Calcium sulfate, pure gypsum was used. The mole ratio of gypsum to C3A was adjusted to 0.2 by mixing 7.3 mmol pure gypsum (1.25 g) with 37 mmol C3A (10 g).

Laboratory methods

C3A-gypsum mixture was hydrated in a suspension of diluted lime diluted at 25 ° C with a liquid to solid ratio of 25 Immobilized atmosphere (closed environment) to prevent carbonization. The system was constantly exposed to mechanical stirring. Chemical evolution was measured using isothermal thermometry and electrical conductivity with XE 150 electrode. To determine species concentrations in Ca + 2], [SO42 -] [Al3 +] [or polymer adsorption during C3A hydration reactions, small portions of the suspension system were removed through 0.3 mm pore filters and filtered. Acidified to prevent .carbonization

2.Results and Discussion

In order to investigate the effect of different lubricants on C3A hydration in the presence of gypsum, C3A gypsum mixture hydration was first performed without lubricant in lime saturated solution.

Hydration of C3A-gypsum without super-lubricant

The reference experiment was performed by adding 37 mM C3A and 7.25 ml gypsum to 250 ml lime saturation. The evolution of the concentration of sulfate, calcium and aluminum ions and the heat flux induced by isothermal thermometry is reported in Figure 1. Figure 1 shows two parts. During the first part, sulfate ions are still present in the solution and used to precipitate hydrates. That's the situation during the performance period. Part II begins when the sulfate concentration is zero.

Part I - When the C3A gypsum mixture is immersed in a lime-saturated solution with no additives, these dissolution reactions produce calcium, hydroxide, aluminate and sulfate ions in the intermediate solution due to the dissolution reactions. Give:

$$Ca_3Al_2O_6+6H_2O\rightarrow 3Ca^{2+}+2Al^{3+}+12OH^- \quad (1)$$

$$CaSO_4,2H_2O\rightarrow Ca^{2+}+SO_4^{2-}+2H_2O \quad (2)$$

The suspension very quickly becomes supersaturated with respect to ettringite and AFm. Previous studies have clearly showvn that although ettringite is the more stable hydrate, AFm phase precipitates at the very beginning of the C3A hydration and the early AFm precipitation depends on different factors as for example the sulfate type used, C3A granularity or superplasticizer presence Consequently the exothermic peak obtained at the beginning of the first part expressed the very high reactivity of the system and this peak results from the exothermic C3A dissolution and AFm and/or ettringite precipitation.

This peak is followed by a period of a low thermic activity. Under the experimental conditions, there is still solid gypsum at the beginning of the C3A hydration giving rise to the sulfate concentration plateau, because of the limited solubility of gypsum in lime saturated solution which is equal to 12.5mmol/L.

Since aluminium concentration remains constant and very low so that it is not detectable, we can deduce all the aluminium ions liberated by the dissolution are consumed by ettringite precipitation. Namely, under these conditions, the supersaturation level is the highest for ettringite which is then the more stable phase. Ettringite precipitates according to the reaction :

$$3Ca^{2+}+2Al^{3+}+12OH^{-}+3Ca^{2+}+3SO_4^{2-}+26H_2O \rightarrow Ca_6Al_2(SO_4)(OH)_{12},26H_2O \qquad (3)$$

Ettringite precipitation consumes calcium, aluminium and sulfate ions which causes further C3A and gypsum dissolution. A stationary state is then established resulting from dissolution reactions and from ettringite precipitation reaction. When gypsum is totally dissolved, ettringite precipitation rate can be deduced from the decrease of sulfate ions concentration. As usually reported and observed in these systems, the average rate of ettringite precipitation from C3A and gypsum, is decreasing according to time. For instance Fig.1 shows that 70 minutes (duration of the “sulfate plateau”) are needed to precipitate 1.4 mmol of ettringite from 4.2 mmol of gypsum and 1.4 mmol of C3A (according to reactions I, II and III), while 140 minutes are needed to “convert” the last 3 mmol of sulfate into 1 mmol of ettringite. Moreover, because sulfate concentration decrease is linear, we assume ettringite precipitation is quite constant during this period. Such an evolution on the rate of ettringite precipitation from C3A and gypsum has already been reported [18]. The average rate of ettringite precipitation clearly depends on the C3A granularity but also on other parameters as sulfate concentration.

Second Part.--This part begins when sulfate concentration becomes equal to zero. C3A hydration without sulfate leads to a metastable calcium hydroaluminate precipitation according to the reaction:

$$4Ca^{2+}+2Al^{3+}+14OH^{-}+6H_2O \rightarrow Ca_4Al_2\,(OH)_{14},\ 6H_2O \qquad (4)$$

The exothermic peak appearing at the beginning of this period is attributed to C3A dissolution which is going on faster and C4AH13 precipitation. Due to C3A dissolution (I) and C4AH13 precipitation (IV), calcium ions concentration decreases and consequently conductivity too, whereas aluminium ions concentration increases. In the same time monosulfoaluminate (3CaO Al2O3.CaSO4,12H2O) becomes more stable than ettringite and consequently precipitates by using sulfate ions liberated by ettringite dissolution. This last reaction is very slow and ettringite is still present two days later. Finally, all these reactions give rise to a stationnary state.

Consequently, the conductivity curve allows us to determine the duration of the first step which corresponds to the precipitation of 2.4 mmol of ettringite under our conditions from C3A and gypsum. Moreover, the evolution of sulfate ions concentration allows us to determine the time needed to precipitate total ettringite and also the first 1.4 mmol.

Effect of the superplasticizers on the reactivity of the C3A-gypsum system in a lime saturated solution

The evolution of the electric conductivity during the hydration of a C3Agypsum system in a lime saturated solution and in presence of 0.5g of superplasticizer that is to say 5% with respect to the C3A weight is represented in Fig.2. From these curves it appears that the diphosphonate doesn't modify the duration of ettringite precipitation whereas both PNS and PCP decrease the rate of ettringite formation. Next Figures (Fig.3,4,6) represent the evolution of the ionic concentrations during the C3A-gypsum system hydration in presence of the different superplasticizers.

Diphosphonate.--The C3A-gypsum mixture was introduced in a lime saturated solution containing 5% of diphosphonate with respect to the C3A weight.The results are presented in Fig.3. The reference experiment was carried out with the same C3A sample. As we can see In fig.2 the diphosphonate doesn't modify the duration needed to precipitate ettringite from gypsum and C3A. The same experiment was also carried out with higher levels of gypsum (2 and 2.5g of gypsum) and again, the time needed to precipitate the ettringite is the same with or without the diphosphonate, as reported in Fig.3. The only noticeable difference is relative to the initial conductivity. The slight increase observed in presence of the diphosphonate can be attributed to the ability of the diphosphonate to form a complex with calcium ions and consequently increases the solubility of lime

PNS.--The average rate of ettringite precipitation is drastically decreased in the presence of PNS; the time needed is approximately multiplied by four in the experimental conditions (Fig.2). The decrease of the rate depends on the PNS dosage as shown in the Fig.4. Moreover Fig.4 shows the decrease of the precipitation rate when the sulfate concentration is at the plateau level and also when it decreases. Figure 5 suggestes that the time needed to precipitate ettringite in the presence of PNS could be correlated with the initial adsorption level of PNS. The slowing down of the ettringite precipitation is maybe linked to a decrease of C3A dissolution rate

PCP.--Figure 2 shows a slowing down of ettringite precipitation as a result of the PCP presence. Under the experiment conditions the time needed to precipitate the ettringite is multiplied by 1.5 in presence of 5% of PCP. Moreover an increase of the PCP amount (5 to 6 %) leads to higher duration (Fig.7). As the slope of the sulfate concentration decrease is linked to the rate of ettringite precipitation we conclude that PCP slows down the rate of ettringite precipitation. Nevertheless it appears that the rate of ettringite precipitation is not affected when the sulfate concentration is high enough and at the "plateau" value (Fig.7). In the same time, the size of ettringite crystals precipitated in the presence of PCP during this period, is smaller than usually. Indeed in order to determine concentrations of species in solution during the C3A hydration reactions, small portions of the suspensions were removed, and as usually filtered through 0.3 µm millipore filters. However in the presence of PCP, aluminium, calcium and sulfate concentrations proved that ettringite crystals were present in the filtered solution (Fig.8). In this case a new filtration was done using 0.1µm filters in order to prevent ettringite from going through. SEM images of the solid collected on the 0.1µm filter one hour after the beginning of the C3A-gypsum hydration in saturated lime solution in the presence of PCP are presented in Fig.9. PCP clearly decreases the size of the ettringite crystals formed.

Consequently, the presence of PCP induced a slowing down of the rate of ettringite precipitation and a decrease of the size of ettringite crystals. The PCP may act on ettringite precipitation by decreasing its growth rate. Previous studies already showed such a decrease of the growth rate or a modification of the ettringite morphology as a result of a polymer adsorption However the average rate of ettringite precipitation is not affected when the sulfate concentration is high enough and at the “plateau” level Namely when the sulfate concentration is high enough and at the plateau level, ettringite nucleation might take place and by this way the rate of ettringite precipitation would not be decreased during this period.

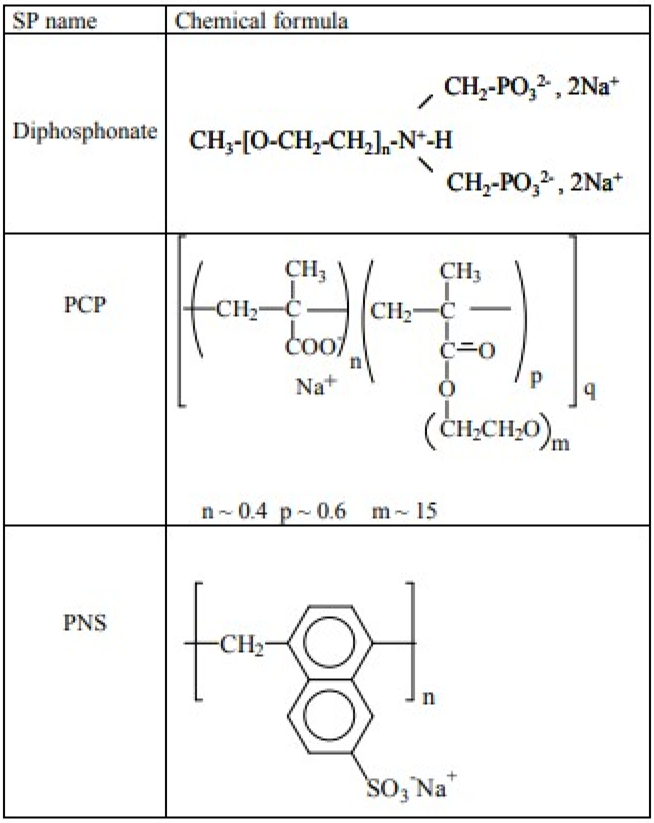
Study of the adsorption

Preliminary adsorption isotherms were established on pure ettringite, mosulfoaluminate and C3AH6 for each superplasticizer in saturated lime solution and with a liquid to solid ratio adjusted to 25. They are reported in Fig.10. The specific surface area determined by B.E.T. using nitrogen are reported in Table 2. As expected, the adsorption level mainly depends on the specific area of the hydrate and consequently the adsorption level on monosulfoaluminate and ettringite is similar and larger than that on C3AH6 phase. Therefore the adsorption should be larger again on platey hexagonal C4AH13 crystals. Moreover PNS and PCP show larger ability to adsorb than the diphosphonate. By using these informations we are able to approximately determine the amount of each superplasticizer likely to be adsorbed on 2.4 mmol of ettringite that is to say on ettringite which will precipitate during C3A hydration under our conditions. By this way about 9mg of diphosphonate and 30 mg of PNS or PCP should adsorb on ettringite as represented in the Fig.12. The evolution of the superplasticizer adsorption during the C3A-gypsum hydration is reported in Fig.11. An initial adsorption is only observed for both PCP and PNS. In the case of the PNS, a large part of the superplasticizer, about 150mg (30%), is adsorbed during the first minutes. The initial adsorption could happen on the anhydrous phases but also on the AFm formed at the very begining of the C3A hydration, because of its important specific surface area. In a second time, a quite linear increase of adsorption is observed during the ettringite precipitation with all superplasticizers. Nevertheless, whereas about 100mg of PCP or PNS are adsorbed on ettringite, only 10mg of diphosphonate seems to be adsorbed on ettringite. These amounts are larger than the values previously calculated for the PCP and PNS (~30mg for PNS and PCP). These values are reported inf Fig.12. These differences can result from the adsorption of other phases which could also be formed (AFm for example). Furthermore, we also can suspect a modification of ettringite morphology due to the adsorption of superpasticizer on ettringite giving rise to an increase of ettringite specific surface area. Namely, the previous observations made on the effect of PCP on the size of ettringite crystals lead us to conclude that the superplasticizer adsorption should be higher because of the increase of the specific area of the ettringite formed in this case. At least, when there is no more sulfate ions in solution, hydroaluminate begins to precipitate, giving rise to a large adsorption of the superplasticizers. The adsorption level gets fastly maximum, all the superplasticizer able to be adsorbed are adsorbed.

CONCLUSIONS

The interaction of superplasticizers with C3A when hydration occurs in presence of gypsum was studied with three types of superplasticizers. Diphosphonate does not modify the average rate of ettringite precipitation. No adsorption happens during the first minutes and the adsorption level of the polymer on ettringite is low. The PNS slows down the ettringite precipitation. The decrease of the average rate of ettringite precipitation is higher with higher PNS dosages. Moreover, the time needed to precipitate ettringite varies as a function of the initial PNS adsorption level. PNS may act on C3A hydration by decreasing its dissolution rate, in consequence of its strong initial adsorption. By using PNS delayed addition, the strong initial adsorption on the aluminate phases can be avoided and consequently more PNS can act efficiently on silicate phases in slowing down its hydration and delaying setting. PCP also slows down ettringite precipitation, but the decrease of ettringite precipitation is less strong than with PNS. Whereas PCP may decrease the C3A dissolution rate, it mainly acts on ettringite growth giving rise to smaller size of ettringite crystals.

Table 1--Chemical structures of te different Superplasticizers



SP name	Chemical formula
Diphosphonate	$CH_3\text{-}[O\text{-}CH_2\text{-}CH_2]_n\text{-}N^+\text{-}H$ with $CH_2\text{-}PO_3^{2-}, 2Na^+$ and $CH_2\text{-}PO_3^{2-}, 2Na^+$
PCP	n ~ 0.4 p ~ 0.6 m ~ 15
PNS	

Table 2--Specific area of different hydrates formed during C_3A-Gypsum hydration

Compound	Hydrogarnet C_3AH_6	ettringite	Monosulfo aluminate
BET Specific surface area (m^2/g)	3.5	1.1	1.2

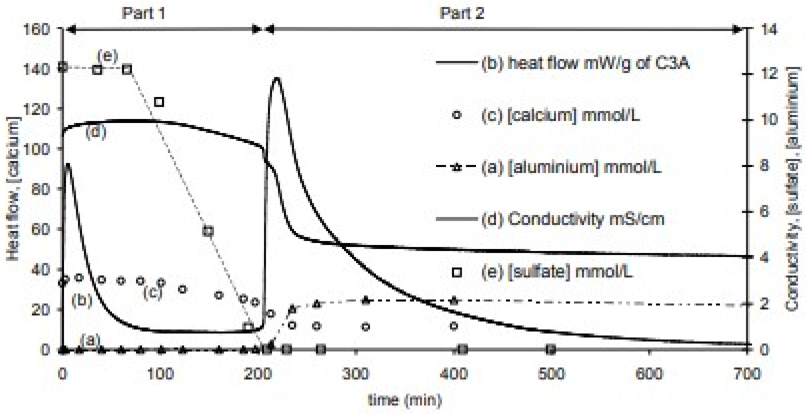


Fig.1--Evolution of heat flow, electric conductivity and ions concentration during C_3A hydration (10g) in saturated lime solution in presence of 1.25g of gypsum. The liquid to solid ratio was adjusted to 25

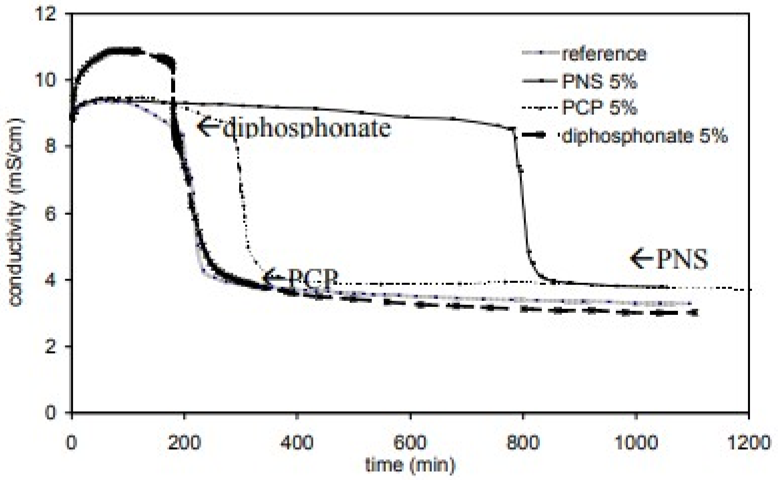


Fig 2--Evolution of the electric conductivity during C_3A hydration (10g) in a lime saturated solution in presence of 1.25g of gypsum and in presence of 0.5g of superplasticizer. The liquid to solid ratio was adjusted to 25.

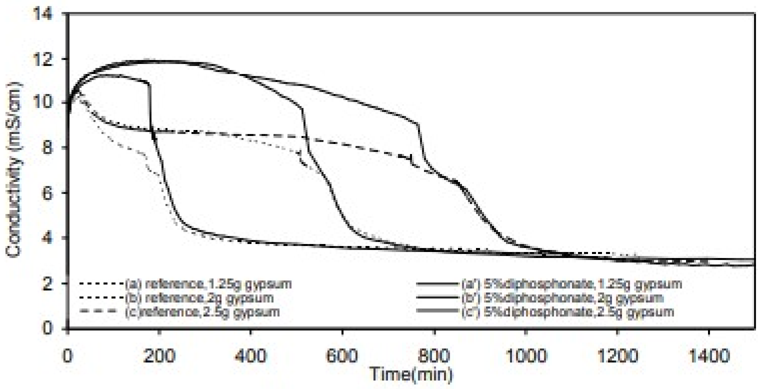
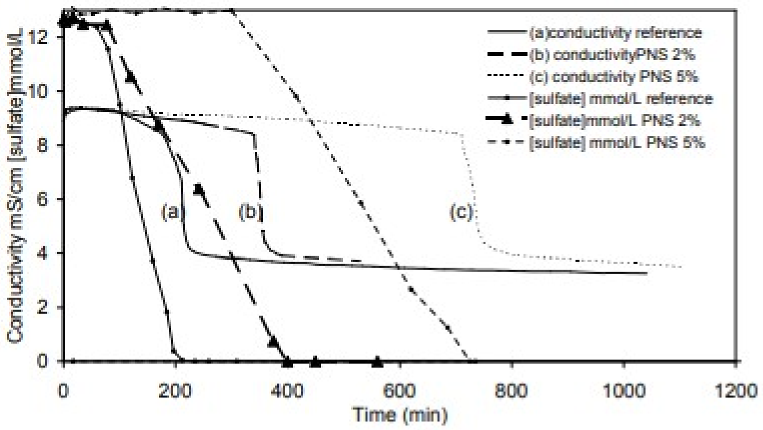


Figure 3
Evolution of the electric conductivity during C3A hydration (10g) in a lime saturated solution with or without 0.5g of diphosphonate and in presence of different quantities of gypsum. liquid/solid =



25.

figure 4
Evolution of the electric conductivity during C3A hydration (10g) in a lime saturated solution in presence of 1.25g of gypsum and in presence of different amounts of PNS. The liquid to solid ratio was adjusted to 25.

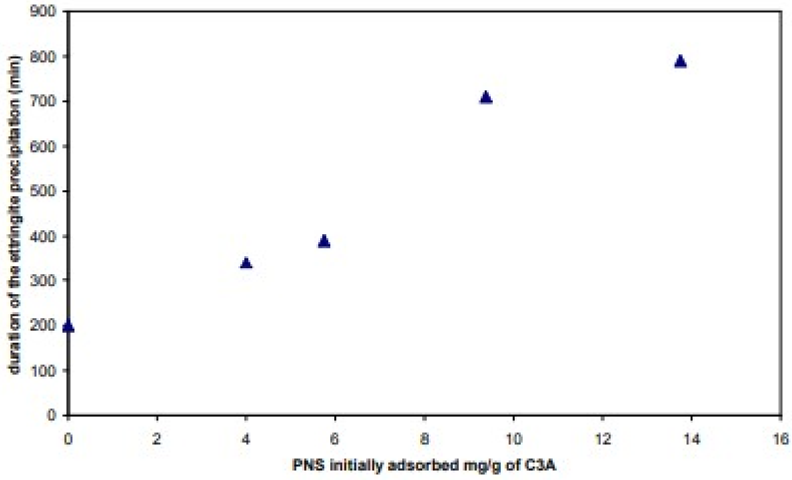


figure 5
Evolution of the duration of the ettringite precipitation versus the initial adsorption level of the PNS. 10g of C_3A were hydrated in 250ml of a lime saturated solution and in presence of 1.25g of gypsum.

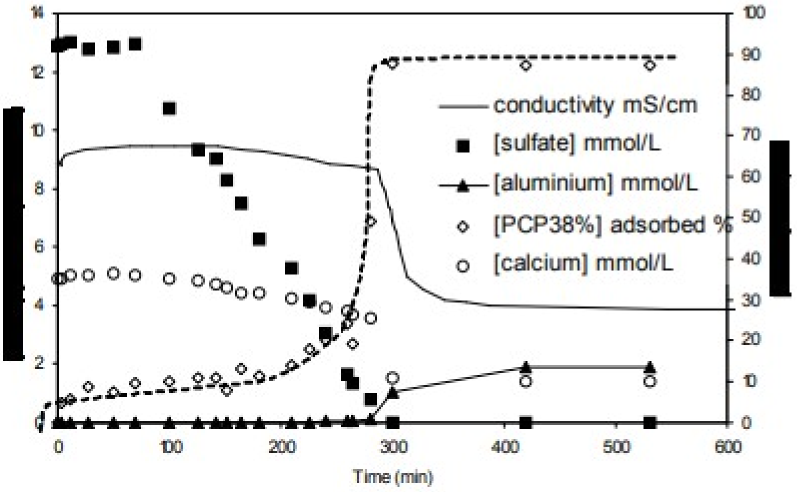


Figure 6
Evolution of the electric conductivity and ions concentration during C3A hydration (10g) in a lime saturated solution in presence of 1.25g of gypsum and 0.5g of PCP. The liquid to solid ratio was adjusted to

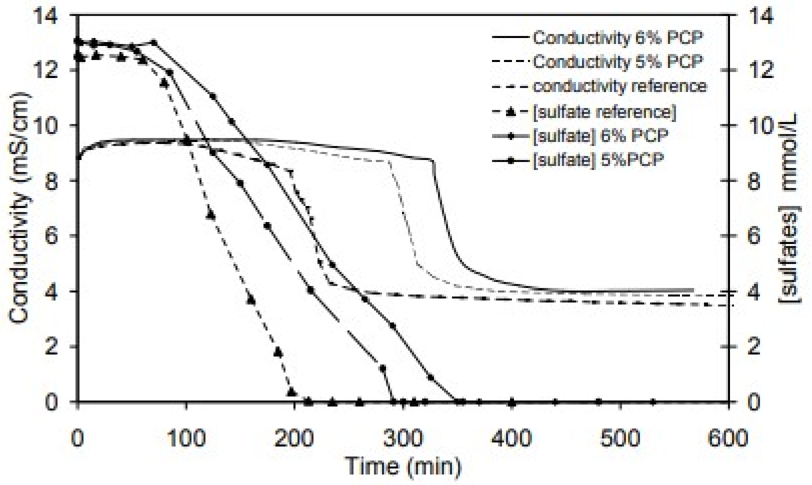


Figure 7 :
Evolution of the electric conductivity and the sulphate concentration during C3A hydration (10g) in a lime saturated solution in presence of 1.25g of gypsum and in presence of different amounts of PCP

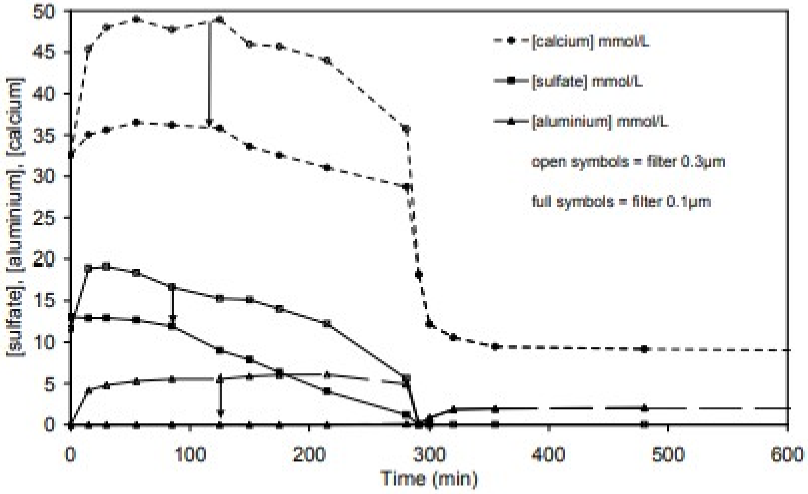


Figure 8
Evolution of the aluminium, calcium and sulfate concentrations of the solution filtered through 0.3 µm or 0.1 µm millipore filters during the C3A-Gypsum hydration in presence of 5%PCP.

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