Rheological and physico-chemical study of cement mortars with superplasticizers of polycarboxylate-type

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Abstract

Most modern concrete structures for coastal and marine environment integrate superplasticizers. The polycarboxylate-type products present a great efficiency at short interval. But sometimes the plasticity is not maintained with the time due to an incompatibility between aggregates, binder and superplasticizer.

Various workability tests were performed using different combinations of cement paste and superplasticizers. The stiffening is assessed on paste by the Tousshenbroeck's test and on mortar by the Haegermann's spreading. These tests allow showing that the premature rigidity of a mix was linked with the W/C ratio.

The calcium sulphate added to the clinker has an impact on the stability of cement paste. Pure gypsum is mixed with superplasticizers. The set results clearly indicate solubility increases in presence of superplasticizer. This phenomenon could be due to the formation of chelate complexes of Ca^{2+} by polycarboxylates.

The mineralogical composition of cement can also influence the stability of mixes. The study of various systems by analytical techniques (XRD, TGA, DSC…) was performed. Chemically, consistency of a cement paste can be related to the formation of ettringite. The test results show that the crystallographic variety (cubic or orthorhombic) of the aluminate phase is the cause for an excessive production of ettringite.

Keywords: aluminate, cement, incompatibility, polycarboxylate, rheology, superplasticizer

1. Introduction

The degradation of concrete structures in marine and coastal environment is a world-wide problem with potentially large economic impacts. The concrete works in this kind of environment are in contact with some aggressive agents. Indeed the see water is at the origin of some concrete pathologies. For instance, the sulphate ions are able to react with the components of the hardened cement paste creating inflations then cracks in the material. The steel structures present in the reinforced concrete are very vulnerable to corrosion caused by the chlorides. The physical and chemical properties of concrete must be adapted to these conditions in order to ensure a good durability of materials. The formulations of mixtures should produce a hardened cement paste slightly porous and permeable to protect the material from the outside environment. These characteristics can be obtained by lowering the water on cement (W/C) ratio. That's why most modern concrete incorporate superplasticizers.

Superplasticizer is part of admixtures which are able to modify the rheological properties of fresh concrete. This product improves the fluidity of concrete by dispersing cement particles in paste. High-performance that includes high-strength concrete can be produced with superplasticizer by reducing W/C ratio while keeping a satisfactory workability. The last generation polycarboxylate-type products present a great efficiency at short interval. But, in few cases, the plasticity is not maintained with the time due to incompatibility reasons between aggregates, binder and superplasticizer.

The cement – superplasticizer interactions are complex processes. Actually Portland cements are multi-phasic inorganic materials, comprising major components (C_3S, C_2S, C_3A, C_4AF) and minor phases ($CaSO_4.xH_2O$, CaO, $(Na,K)_2SO_4$, etc.). It is the same for the organic admixtures, which often contain several components owing to the nature of the product or to the result of their manufacturing process (Jolicoeur *et al.* 1998). A literature review has permitted to choose for these study only three parameters among the numerous playing a part in cement – superplasticizer interactions.

Firstly the W/C ratio seemed an obvious factor in incompatibility cases between binder and superplasticizer. It pointed out that, at lower W/C, a slight fluctuation of water content in superplasticized cement paste can cause large variations of the fluidity. On the other hand, at higher W/C, a small fluctuation of water content can be negligible (Yamada *et al.* 2000). In this present work, a similar trend has been researched on superplasticized mortars.

Secondly the impact of polycarboxylate molecules on the solubility of calcium sulphates proved to be interesting. Indeed, the importance of sulphate ions on the initial consistency of cement paste was described by many authors (Locher *et al.* 1977, Bonin A. 1980, Regourd M. 1982). Previous studies were led on polynaphtalene sulfonate showed that this kind of superplasticizer could interfere with the solubility of the different calcium sulphates. They may adsorb on calcium sulphates, which retards the dissolution rate (Aïtcin *et al.* 1987, Dodson *et al.* 1989). The influence of two polycarboxylate-based superplasticizers on the solubility of pure gypsum has been measured here so as to point out an effect on the dissolution rate of this specie.

Finally the aluminate phase C_3A is known to have the higher reactivity during the first hours of cement hydration. Its hydration product in presence of a sulphate source, so-called ettringite ($Ca_6Al_2O_6(SO_4)_3.32H_2O$), regulates the hydration reaction of the cement by forming a protective barrier at the anhydrous grains surface. However in commercial available cements the aluminate phase could be found in two crystallographic varieties: cubic and orthorhombic (Taylor 1990). These crystal modifications depend on the amount of entrapped alkali ions (Older et al. 1983), and also on the burning and cooling history during the cement manufacture process (Locher *et al.*1982*).* But it was proved that the orthorhombic C_3A reactivity is greater than the cubic C_3A one (Bilanda *et al.* 1980, Plank *et al.* 2006). Two superplasticized cement pastes presenting different stiffening are examined in this paper. The influence of the crystallographic varieties of C_3A on the ettringite formation is discussed.

2. Experimental Program

2.1 Materials

Ordinary Portland cements CEM I 42.5 R, produced at different time, have been used for all the tests on pastes and mortars. These cements present the particularity to have a low C_3A content (less than 5%). Their average composition, determined by Rietveld analysis, is shown in Table1.

Table 1: Average mineralogical composition (%) of Ordinary Portland Cements CEM I 42.5 R

C_3S	C_2S	C_3A	C_4AF	free CaO	$C\bar{S}$	$C\bar{S}H_2$	$C\bar{S}H_{0,5}$	K_2SO_4
54.0 – 59.3	20.5 – 24.9	2.4 -3.1	11.9 – 12.9	0.2 – 0.3	2.5 – 3.1	0.1 – 0.4	0.6 – 1.0	0.2 – 0.7

For the investigations on mortars, aggregates consist of standard sand CEN EN 196-1 (Beckum, Germany).

Admixtures chosen are two commercial products based on aqueous solutions of polycarboxylate-type superplasticizers usually used by the concrete producers.

The solubility measurements have been performed on calcium sulphate dihydrate (Riedel-de-Haën, 99%).

2.2. Workability characterization

The intensity of stiffening cement pastes is evaluated by the Van Tousshenbroeck's test adapted to the EN 196-2 standard. This measurement is carried out on mixtures whose W/C ratio is 0.35 and superplasticizer content is 0.3% compared to the cement mass. The cement paste is mixed for 15 seconds at low speed and for 45 seconds at high speed. The penetration of the Vicat's consistency probe is measured at 3, 5, 7, 10 and 15 minutes after the start mixing.

The evolution of plasticity mortars as a function of time is monitored by measuring the Haegermann's spread according to EN 1015-3. Mixtures have an initial spread of 200 mm which corresponds to a normal consistency. Preparations are placed in a transport simulator between two consecutive measurements.

2.3. Chemical analysis

The determination of the sulphate concentration is produced by gravimetry. The sulphate ions SO_4^{2-} were precipitated by the barium Ba^{2+}. When the precipitate is formed in the presence of superplasticizer, the powder is calcined at 800°C in order to eliminate organic polymers adsorbed onto the grains.

The hydration of cement paste is stopped by immersion of the suspensions in acetone. The solid phases collected were subjected to several tests of solid state chemistry. The anhydrous or hydrated crystallized phases are characterized by X-ray diffraction (XRD). Thermogravimetric and thermodifferential analyses (TGA and TDA) were conducted to identify and quantify hydrates formed. Also the thermal decomposition of the superplasticizer adsorbed can be viewed by this technique. The microstructure of hydrated pastes was observed by scanning electron microscopy (SEM).

3. Results and Discussion

3.1. Time evolution of normal consistency mortars using superplasticizer

The Haegermann's spread of mortars of different compositions is followed over time. A mortar containing no admixture and with an initial spread of 200 mm is taken as reference. Two contents in superplasticizer are selected and amounted to 0.3% and 0.6% compared to the cement mass. The water content in the preparations is assessed to ensure an initial consistency similar to all mortars. The results for both superplasticizers of this study are reported in Fig. 1 and Fig. 2.

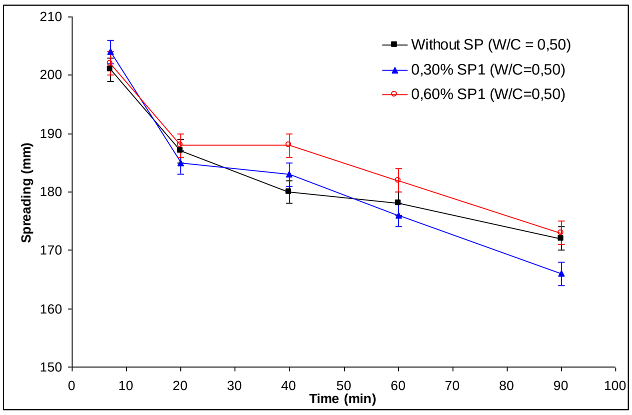


Fig. 1 : Time evolution of reference cement mortars using superplasticizer 1

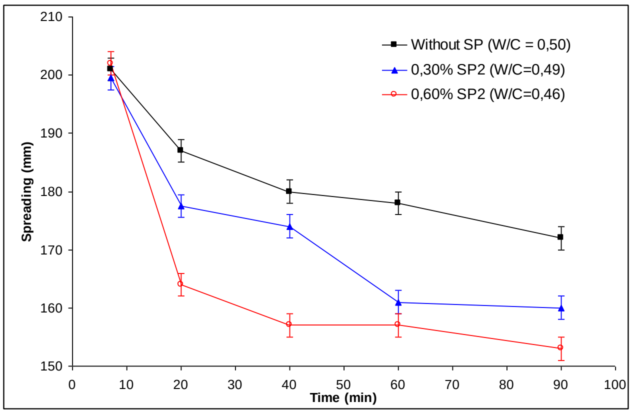


Fig. 2 : Time evolution of reference cement mortars using superplasticizer 2

It appears differences in behaviour depending on the origin of the admixture used. The superplasticizer 1 does not confer any reduction of the water content even for a dosage of 0.6%, while the superplasticizer 2 used in the same proportions allows reducing the W/C ratio of 8%. Additional tests carried out on the superplasticizer 1 reveal that the reduction of water quantity is only effective in an admixture dose of 0.9%. The action of superplasticizer on plasticity mixtures is therefore dependant on the origin of the products and hence on the chemical structure of polymers: length of the side chains, anionic group density (Yamada *et al.* 2000).

Mixtures performed using the superplasticizer 2 show a loss of workability as a function of time even stronger than the W/C ratio is low. The spread of reference mortar decreases of 29 mm after 90 minutes of hydration. In presence of 0.3% of admixture (W/C=0.49), loss of spread is 40 mm. It amounts to 49 mm for 0.6% of superplasticizer (W/C=0.46). The loss of spread increases with the W/C ratio lowering. We observed a similar trend on mortars made from cement of different compositions (reduced dosage in $CaSO_4$ or content reduced C_3A).

These results highlight the importance of the W/C ratio to maintain the workability of a mortar in time and therefore in the phenomena of incompatibility. This influence can be linked to the decrease of the distance between the grains of cement in suspension when the W/C ratio is lowered. The moving closer of the grains relative to each other create an increase in frictional forces, and therefore contribute to develop stronger shear stresses. That's why the events of incompatibility are less frequent for mortars with a high W/C ratio (Yamada *et al.2000)*.

These classical rheological tests were conducted in preparation for rheometric measurements of yield stress and viscosity of mixes. A more fundamental description of mortars flowing properties could then be made.

3.2. Action of polycarboxylate-type superplasticizer on the solubility of gypsum

The rate of gypsum dissolution is followed in distilled water and in two polycarboxylate solutions. The values measured as a function of time are shown in Fig. 3. It is cleared that the solubility of gypsum is increased by the presence of polycarboxylate and that for the both studied superplasticizers.

The total solubilities of gypsum after 60 minutes in the various solutions are grouped in Fig. 4. Solubility increases of 88% and 49% respectively in superplasticizer 1 and 2 solutions compared with distilled water. This increase is probably due to the complexation of the Ca^{2+} ions by anionic polymers (Uchikawa *et al.* 1995). A schematic representation of a polycarboxylate-Ca^{2+} complex is shown Fig. 5. The anionic charges of carboxylate groups have the ability to form a coordination liaison with the Ca^{2+} ion and thus to stabilize this specy in the aqueous phase. The Ca^{2+} ion no longer availed to precipitate in the form of gypsum, the solubility is increased.

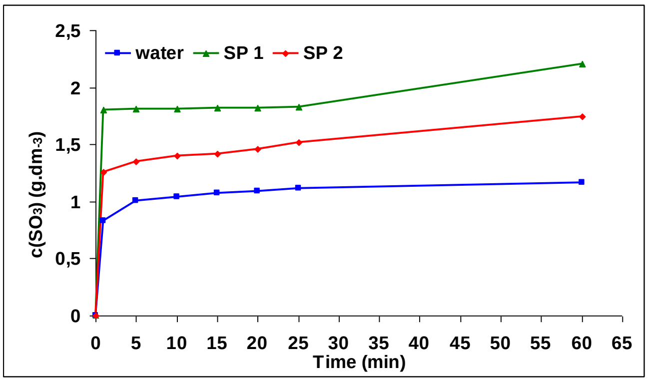


Fig. 3: Dissolution rates of gypsum in water and in solutions of polycarboxylate

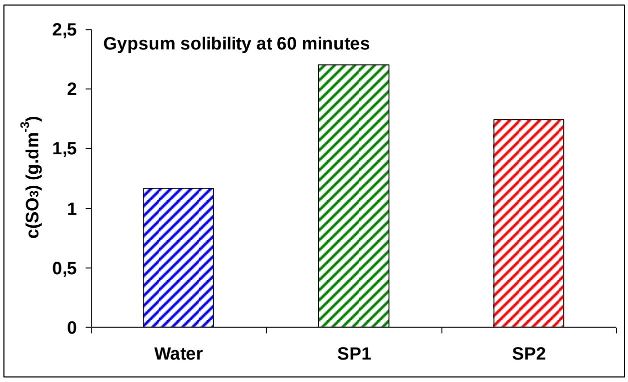


Fig. 4 : Gypsum solubilities in water and in solutions of polycarboxylate

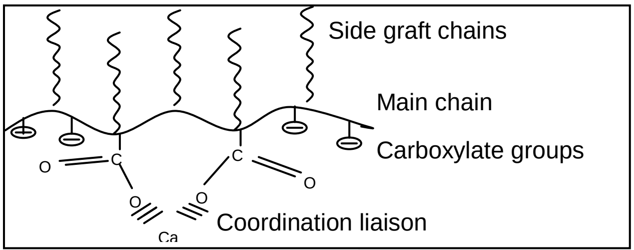


Fig. 5 : Polycarboxylate-Ca^{2+} complex

The passage of the sulphate ions in solution is a quick process. Indeed more than an half of the total solubility is reached after three minutes (Fig. 3). This trend is maintained in presence of superplasticizer but does not seem really accentuated.

It should be noted that the conclusions stem from these results are simplified. Indeed, the measurement conditions (neutral pH) are quite different from those encountered in a cement paste (basic pH). In addition, several authors have shown that there is a competitive adsorption on the active sites of aluminate phase between sulphate ions and polycarboxylate molecules (Yamada *et al.* 2001). This phenomenon is not taken into account while its influence on the solubility of calcium sulphates in a cement paste is certainly important. Anyway the complex characterization could be done only in simplify conditions like a neutral diluted solution.

3.3. Stiffening of cement pastes due to the crystallographic variety of aluminate phase

Two samples of cement CEM I 42,5 R, namely cement A and cement B, have been tested by the Van Tousshenbroeck's method in presence of superplasticizer 2.

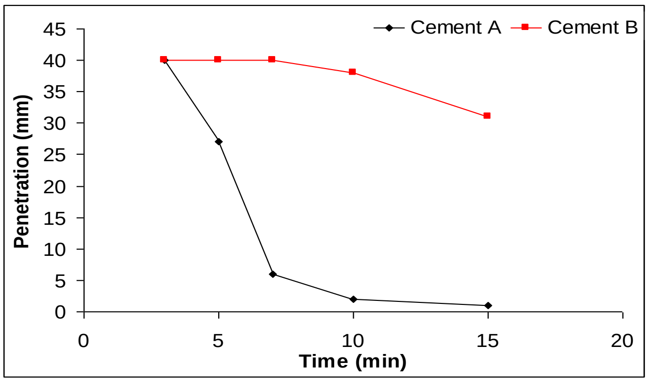
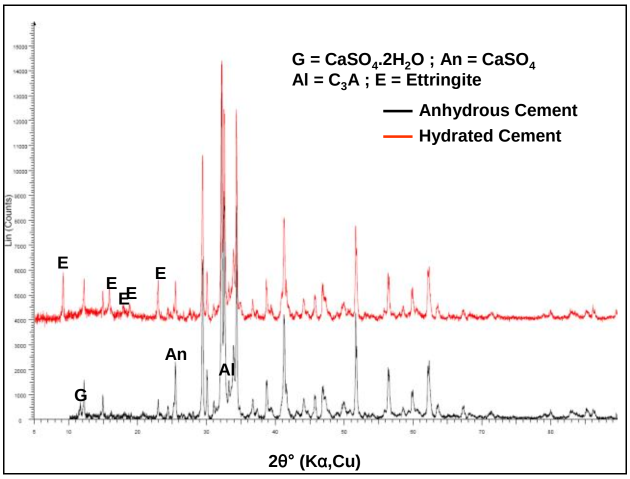


Fig.6:Tousshenbroeck's stiffening of cement pastes using superplasticizer 1

Measurements are presented Fig. 6. It appeared that cement A showed very strong stiffening at 15 minutes of hydration while cement B does not present a very small one at the same time.

The analyses by X-ray diffraction of anhydrous and hydrated (15 minutes) cements are shown in Fig. 7 and Fig. 8. The anhydrous cement diffractogramms not reveal any qualitative differences regarding to the mineralogical composition. Specially, the calcium sulphates are present in both case in the form of gypsum and anhydrite. Therefore the observed stiffening difference is not due to the presence of $CaSO_4.0,5H_2O$ which would be converted into secondary gypsum and would have led to a well-known phenomenon of false set. However significant differences were revealed on hydrated cements diffractogramms.



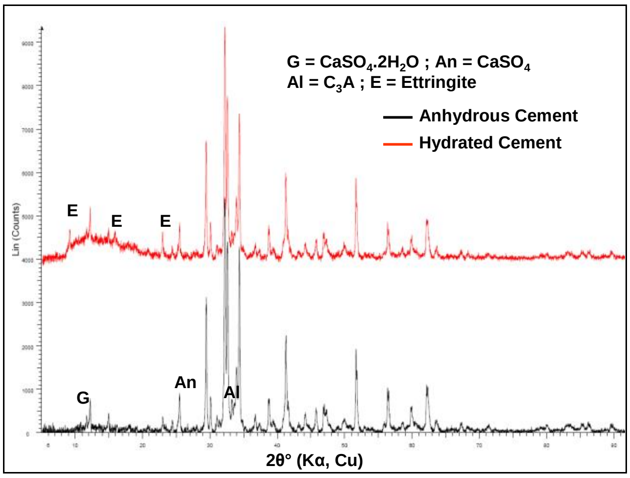


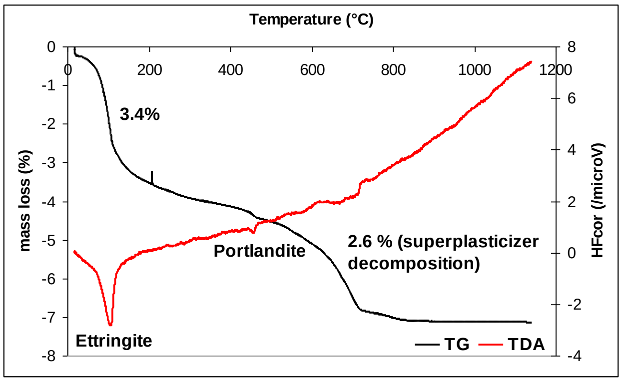
Fig. 7 : X-Ray Diffractogramms obtained from Cement A

Fig. 8 : X-Ray Diffractogramms obtained from Cement B

In case of cement A, the ettringite - hydration product of the C_3A - appears sharply with the distinction of several diffraction peaks. The gypsum has disappeared, so it can be assumed that this reagent has been entirely consumed for the formation of ettringite.

In the case of cement B, the ettringite is also present but in a less pronounced way. The amount of gypsum appears to have decreased significantly without having completely disappeared.

Fig. 9 and Fig. 10 represent the thermogravimetric and thermodifferential analysis carried out on the solid phases of hydrated (15 minutes) cement pastes. The measurement confirms the complete disappearance of the gypsum in the cement A as compared to cement B. The proportion of ettringite is more important in the cement paste which presented high stiffening, even if it contains a higher quantity of superplasticizer.
These results clearly indicate that the high formation of ettringite is at the root of the plasticity loss of the cement A paste.



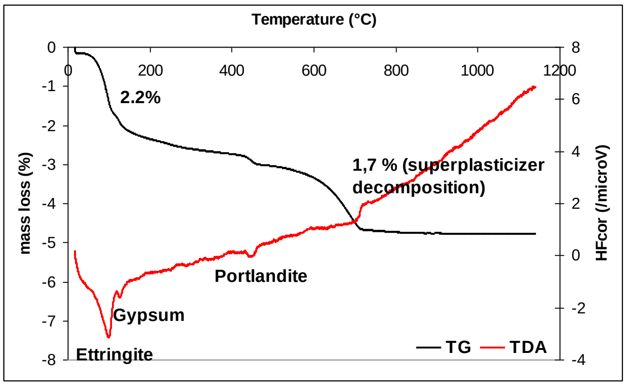


Fig.9 : TG and TD analyses from cement A paste

Fig.10 : TG and TD analyses from cement B paste

Both cement pastes also show different microstructures revealed by scanning electron microscopy. The micrographs are shown Fig. 9 and Fig. 10. It appears that the surface density of cement A hydrates is greater than the cement B one. Therefore, the grains in suspension have a high roughness when the number of hydrates formed on the surface increases. The frictions generated thus decrease the plasticity of the suspension.

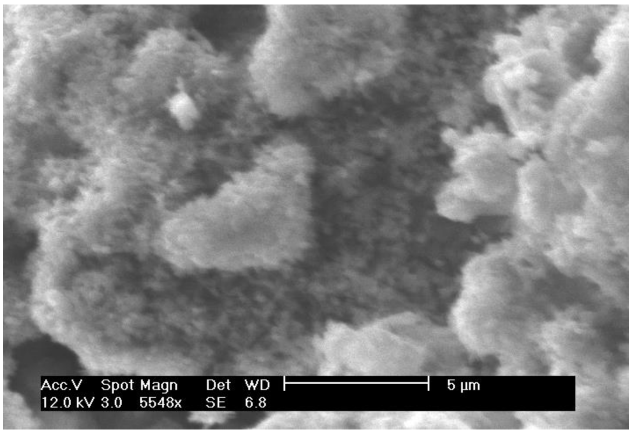


Fig. 9 :Scanning electron micrograph from cement A paste

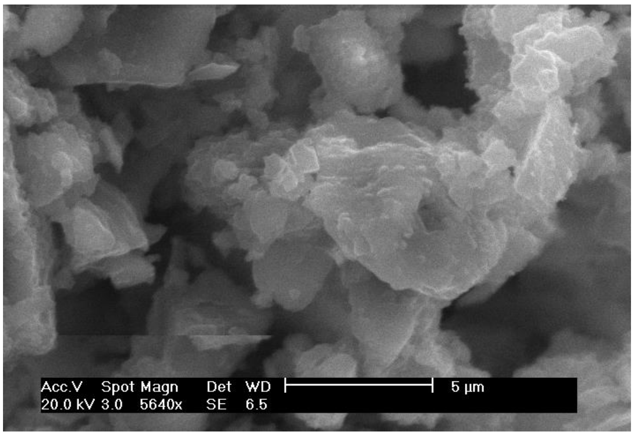


Fig. 10 : Scanning electron micrograph from cement B paste

Rietveld analysis was performed on these two cements in order to quantify the mineralogical phases and most specially the two crystallographic varieties of aluminate phase: cubic and orthorhombic C_3A. The mineralogical compositions of the two cements are gathered in Table 2.

Table 2: Mineralogical composition (%) of cement A and cement B
(C_3Ac = C_3A cubic ; C_3Ao = C_3A orthorhombic)

Cement	C_3S	C_2S	C_3Ac	C_3Ao	C_4AF	free CaO	$C\bar{S}$	$C\bar{S}H_2$	$C\bar{S}H_{0,5}$	K_2SO_4
A	57.5	21.5	1.79	1.26	12.0	0.30	2.85	0.36	1.00	0.57
B	59.3	21.7	1.78	0.90	11.9	0.17	2.45	0.13	0.84	0.24

Cement A has an orthorhombic C_3A content higher than cement B. But it was shown that orthorhombic variety of aluminate phase was more reactive than cubic one (Plank *et al.* 2006).
The strong stiffening of the cement A paste can thus be attributed to a high formation of ettringite caused by an excessive orthorhombic C_3A content.

4. Conclusion

In this paper, three factors efficient on the cement - superplasticizer interactions have been examined and clarified:

- The W/C ratio proved to be important for the mortars stability with time in a similar way as cement pastes. Indeed a slightly variation of the W/C ratio can led to a great consistency change.
- Gypsum solubility increased in diluted polycarboxylate solutions. The Ca^{2+} ions are certainly stabilized in the aqueous phase by formation of chelate complexes with anionic polymers.
- The orthorhombic C_3A proportion in anhydrous cement could be at the origin of an excessive reactivity and of an important ettringite formation leading to a premature stiffening of the paste.

However these set results are not completely explained and must be the subject of a thorough investigation on the notions of distance between cement particles, solubility in basic medium or reactivity of pure cubic and orthorhombic aluminate phases The plasticity loss in these mixes could be linked with the distance between the grains in suspension. Rheometric measurements could classify the mixes more noticeably as a function of yield stress and viscosity.
in the vicinity of superplasticizer.

Thanks to superplasticizers a slightly porous and permeable cement paste can be produced in high-strength concretes. So the materials durability is improved and the application in marine and coastal environment is conceivable. The problems which can occur during the placement must be yet solved. That is why the mechanisms involved in the incompatibility phenomenon must be deeply understood.

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