

INTERACTION BETWEEN CEMENTS AND SUPERPLASTICIZERS

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ABSTRACT

The interaction between CEM I type cements and a superplasticizer of polycarboxylate grafted with PEO side chains type was explored. The adsorption of the superplasticizer was examined in relation with the rheological behavior of the cementitious slurries and the composition of the aqueous phase. The particular importance of the alkali sulfates level of the clinker was brought to the fore. The sulfates in solution are not only in competition with the superplasticizer for the adsorption on cement grains surface but they induce a drastic reduction of the number of existing adsorption sites, that it be for sulfates or superplasticizer adsorption. The fluidity of cementitious slurries can thus be inferred from the sulfates concentration, which determines the level of PC-PEO adsorption and, consequently, the deflocculating efficiency.

1 INTRODUCTION

The development of high performance and/or high fluidity concretes (as HPC or SCC for example) is closely linked to the use of superplasticizers of PC-PEO type, that is PolyEthyleneOxide (PEO) side chains grafted on a PolyCarboxylate (PC) backbone. Economically reasonable amounts of such products (from 0.05 to 1% of dry matter with respect to cement) have to induce both, high initial fluidity, and good spread/slump retention of cementitious formulations. In addition, these molecules should be efficient with the largest number of cements. Now, incompatibility issues between cements and PC-PEO are a well-known concern. They recover all the cases in which at least one of the previous requirements is not met. Moreover, incompatibilities increase as W/C ratio decrease [1].

The fundamental dispersing mechanism of PC-PEO is a steric repulsion between the PEO side chains of polymers adsorbed on cement surface [2, 3]. Studies about incompatibility issues with these superplasticizers brought to the fore the role of sulfates: this species is believed to be able to compete with PC-PEO for adsorption at cement surface [4-5]. Thus, the adsorbed amount of PC-PEO, and correlatively, the spread of the cementitious formulation, is all the lower as the amount of sulfates in the aqueous phase is the higher. The implication of sulfates in the aqueous

solution raises the question of solubility rates of sulfate phases. To this respect, the solubility rates of the alkali sulfates from the clinker are much higher than the ones of calcium sulfates from the set regulator [6-9]. Hence, the first ones could be the key parameter of cement's chemistry controlling the compatibility between cement and PC-PEO.

Given this background, this study focuses on the influence of the alkali level of the clinker in CEM I type cements on the interaction with a superplasticizer of PC-PEO type. The consumption isotherms of the superplasticizer and the rheological behavior of the cementitious slurries are successively examined with respect to the composition of the aqueous phase. This study aims at demonstrating the competition between PC-PEO and sulfates in the adsorption on cement grains surface responsible for ill-dispersing efficiency of some incompatible PC-PEO/cement couples.

2 MATERIALS AND METHODS

2.1 Materials

Six CEM I type industrial cements, referenced from C1 to C6, were studied (Table 1). From C1 to C6, the alkali level increases. In comparison, the composition calculated from the Rietveld analysis of the XRD diagrams, the Blaine specific surface area and the median diameter show little variations, apart from the absence of C₄AF in C1 (white cement), from a high C₃A level in C5, and from a lightly higher Blaine surface area for C4. Last, the six cements show a wide diversity of the repartition between different calcium sulfate phases in the set regulator.

| Technique | Quantity | C1 | C2 | C3 | C4 | C5 | C6 |
|---|---|----------|---------|----------|--------|---------|---------|
| XRF | Na ₂ O _{eq} (% w/w) | 0.07 | 0.26 | 0.37 | 0.53 | 0.74 | 1.07 |
| XRD, Rietveld analysis | C ₃ S (% w/w) | 67.7 | 58.7 | 67.4 | 53.3 | 67.6 | 59.0 |
| | C ₂ S (% w/w) | 17.9 | 18.7 | 12.9 | 19.6 | 5.6 | 20.7 |
| | C ₃ A (% w/w) | 2.9 | 3.5 | 1.7 | 1.6 | 13.6 | 4.1 |
| | C ₄ AF (% w/w) | 0 | 13.2 | 12.6 | 14.6 | 2.9 | 11.9 |
| Set regulator composition (DSC/DRX) (gypsum / hemihydrate / anhydrite) (% SO ₃ eq) | | 48/22/30 | 84/0/26 | 34/22/44 | 0/8/92 | 77/23/0 | 79/21/0 |
| Blaine specific surface area (cm ² /g) | | 4300 | 4100 | 4400 | 4800 | 3850 | 3950 |
| Median diameter (µm) | | 10.9 | 10.8 | 9.1 | 10.2 | 13.1 | 12.8 |

Table 1: main characteristics of the six CEM I type industrial cements.

A superplasticizer of PC-PEO type from Axim-Italcementi Group, designed to confer good spread retention for concrete formulations, was used. It will be referred to as PC-PEO in the following. The backbone contains 80% (n/n) of methacrylic monomers and 20% (n/n) of acrylic monomers. About 40 % of these monomers are grafted with PEO side chains, of two different lengths (resp. about 40 and 120 unit monomers). The weight-average molecular weight determined with Steric Exclusion Chromatography is about 100.000 g/mol.

As the fluidizing action of the superplasticizer is supposed to be linked to cement/polymer interaction, we studied cementitious slurries (that is, the paste of a concrete). All these cementitious grouts were of constant water content ($W/C=0.44$), and varying PC-PEO content (SP/C , expressed as the weight percentage of PC-PEO dry matter with regard to cement).

2.2 Experimental techniques

Cement grouts were obtained mixing for 3 min the liquid (water + PC-PEO) with the cement with a helix Bioblock Scientifix mixer. The introduction of the solid in the liquid was taken as time origin. Two time scales were explored: 15 or 90 min. They are respectively representative for initial and final behavior on a typical timescale of grout manipulation. They were chosen to assess initial fluidizing effect and spread retention.

Aqueous solutions were extracted from grouts by a 10 min centrifugation at 4000 rpm with a 5804R centrifuge from Eppendorf (maximum relative centrifugal force: 2050 G).

PC-PEO isotherms were measured at room temperature, after 15 or 90 min, using the Chemical Oxygen Demand technique. The latter measures the concentration of bichromate oxidizable species from the redox titration of excess bichromate. PC-PEO quantification in the aqueous phase requires assessing its "oxidability" by $Cr_2O_7^{2-}$. PC-PEO consumption by cement, Q , is then calculated from the reduction of PC-PEO concentration in aqueous phase induced by contact with cement (PC-PEO concentration is calculated after deduction of the $Cr_2O_7^{2-}$ consumption from the plain slurry aqueous phase). Consumption was interpreted as an adsorption in the following. In other terms, the incorporation of PC-PEO into organo-mineral phases was neglected since it is reported to be much less for PC-PEO's than for polynaphtalene sulfonates [4, 10-12]. Moreover, if J. Plank et al. reported PC-PEO intercalation in aluminate phases in the absence of sulfates (and at very high polymer contents), intercalation was no more observed as the sulfate content was increased [13-14]. Contrary to "usual" adsorption isotherms, measurements are not performed under equilibrium as cement is an evolving system. They are however representative of the system status at a given time. Q is expressed in mg of PC-PEO adsorbed per unit Blaine specific surface area of the anhydrous cements ($mg\ SP/m^2\ C$). Indeed, the adsorption density, rather than the adsorption per unit mass of solid, should rule the deflocculating efficiency of the PC-PEO [15]. However, the evolution of surface area due to cement hydration was not measured* here and so neglected. Q is plotted vs PC-PEO concentration in the aqueous phase, C , expressed in grams of superplasticizer per gram of aqueous solution ($g\ SP/g\ AS$).

* the hydration arrest protocol, as the mode of redispersion of the solid so obtained, necessary to perform this measurement, are under study

Ionic concentrations in the aqueous solution were measured by Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) at 1150 Watts with an Iris Advantage radial from ThermoElectron. Measurements were performed on aqueous solutions extracted from grouts of SP/C=0 and 0.40 %, after 15 and 90 min. Only the major species concentrations, that are calcium, potassium, sodium and sulfur, were measured. In the following, sulfur will be considered as representative of sulfates.

Rheological measurements were performed on an AR 1000 N controlled stress rheometer from TA Instruments, equipped with an anchor type geometry (Couette-equivalent). Every 15 min, the grout is presheared at 50 s^{-1} for 1 min, then allowed to rest for 1 min, followed by a stress sweep from $7.8 \cdot 10^{-4}$ to 768 Pa in 7 min 30 s, measuring 50 logarithmically spaced points per decade. This procedure insures a single measurement kinetic for all grouts. This would not be possible with a stationary state measurement, hence judged ill-adapted for time evolving materials such as cement slurries. In the same time, each 15 min, a spread measurement is also performed with a mini-cone (reduction at scale 1/5 of Abrams cone). To do so, the grout is first remixed 1 min with the helix mixer, then set in the mini-cone and let at rest 20 s before raising the mold.

3 RESULTS AND DISCUSSION

3.1 Superplasticizer adsorption vs sulfates adsorption

As illustrated in Fig. 1, after 15 as after 90 min, all cements exhibit PC-PEO isotherms of Langmuir-type (Eq. 1). In the latter, Q_o is the adsorption capacity of the monolayer and K_{SP} is the affinity constant of the PC-PEO.

$$Q = \frac{Q_o K_{SP} C}{(1 + K_{SP} C)} \quad \text{Eq. 1}$$

The only exception noticed was the case of C6 at 90 min for which the eventuality of a two successive layers constitution could be considered. Nevertheless, this case will be discussed together with the other ones, considering only the first layer. Moreover, as also shown in Fig. 1, PC-PEO consumption decreases from C1 to C6, that it be after 15 or 90 min.

Now, the adsorption sites of the PC-PEO, that are the calcium ions from the double layer of cement grains [12], are also bound to interact with sulfates. Supposing that either carboxylates from PC-PEO or sulfates from the aqueous solution can adsorb in each of these sites in a Langmuir-type process leads to Eq. 2 [15]. This hypothesis implies that no steric hindrance intervenes in the interaction between PC-PEO and adsorption sites, so that the number of possible adsorption sites for carboxylates from PC-PEO is not inferior to the one for sulfates. This should be the case in the scope of Langmuir adsorption, which, among other assumptions, relies

on the hypothesis of equivalent adsorption sites distributed on a uniform surface on a microscopic scale [16]. The introduction of the sulfates/PC-PEO competition for adsorption induces the substitution of K_{SP} in Eq. 1, by an apparent affinity constant, K_{app} (Eq. 2), integrating the adsorption of sulfates with an affinity constant K_{sulf} (Eq. 3).

$$Q = \frac{Q_o K_{app} C}{(1 + K_{app} C)} \quad \text{Eq. 2}$$

$$K_{app} = \frac{K_{SP}}{1 + K_{sulf} [SO_4^{2-}]} \quad \text{Eq. 3}$$

Now, the ICP-AES measurements enabled to assess the sulfate concentration. For the six cements, a very good correlation ($R^2=0.95$) between $[SO_4^{2-}]$ and the alkali concentration, $[Na^+]+[K^+]$, was observed (Fig. 2), confirming H. F. W. Taylor's statement [6] that most of the soluble sulfates stem from the soluble alkali. Nevertheless, part of the dissolved sulfates are bound to reprecipitate since the slope of about 1/3 is inferior to the values of 1/2 and 3/2 expected respectively for the dissolution of arcanite (K_2SO_4), apthitalite ($(K_2SO_4)_3.(Na_2SO_4)$) or thenardite (Na_2SO_4) in the one hand, and calcium langbeinite ($K_2SO_4.2(CaSO_4)$) in the other hand. For all cements, after 15 as after 90 min, $[SO_4^{2-}]$ is not affected by the introduction of 0.40 % of PC-PEO. It was hence assumed that $[SO_4^{2-}]$ is constant on the whole PC-PEO dosages range explored for isotherms measurements. The media of the values measured for 0 and 0.40 % of PC-PEO was thus used for each isotherm.

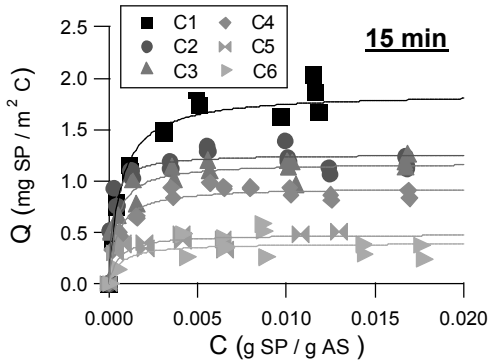


Figure 1: PC-PEO consumption isotherms after 15 min.

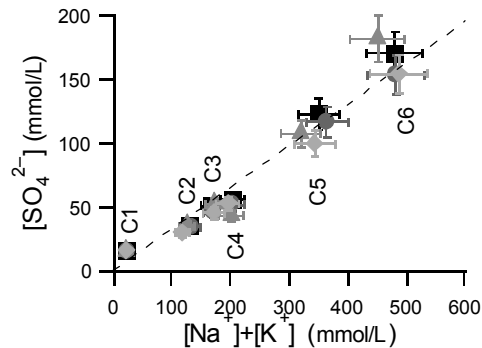


Figure 2: sulfate concentration vs soluble alkali concentration.

Three variables remain unknown in the model of competitive adsorption (Eq. 2 and 3): Q_o , K_{SP} and K_{sulf} . It was chosen to proceed in two steps. First, the two parameters of Eq. 2, Q_o and K_{app} , were identified by fitting adsorption isotherms. Indeed, a two-parameters fit is far more reliable than a 3-parameters one. Moreover, if the model of competitive adsorption is valid, K_{SP} and K_{sulf} can be inferred from the variations of K_{app} with $[SO_4^{2-}]$. So, in a second time, the affinity constants of the two species in

competition, K_{SP} and K_{Sulf} , were determined plotting the inverse of K_{app} as a function of $[SO_4^{2-}]$.

Three fitting techniques of the isotherms were first used: either a direct fit of Eq. 2 (Langmuir fit), or the two linearizations of this model in the form of $C/Q=f(C)$ (classical Langmuir linearization [16]) or $1/Q=f(1/C)$ (Lineweaver-Burke plot). The first (respectively second) linearization technique provides $1/(Q_o K_{app})$ and $1/Q_o$ as the Y-intercept and slope (or resp. slope and Y-intercept) of the line, stressing the influence of the high (resp. low) C values. For the six cements taken after 15 or 90 min, these three fitting methods provide remarkably close values of the adsorption capacity of the monolayer, Q_o (Table 2). So, from now, the average and twice the standard deviation of these three values are used for Q_o and its error bar.

| | 15 min | 90 min |
|-----------|-------------------------------|-------------------------------|
| C1 | 1.88/1.81/1.88 (± 0.07) | 2.26/2.22/2.27 (± 0.10) |
| C2 | 1.29/1.22/1.26 (± 0.05) | 2.05/2.15/2.13 (± 0.14) |
| C3 | 1.18/1.21/1.14 (± 0.04) | 1.56/1.51/1.52 (± 0.07) |
| C4 | 0.89/0.97/0.96 (± 0.02) | 1.70/1.71/1.69 (± 0.08) |
| C5 | 0.51/0.47/0.47 (± 0.02) | 0.99/0.95/0.93 (± 0.04) |
| C6 | 0.39/0.41/0.39 (± 0.07) | 0.59/0.45/0.52 (± 0.13) |

Table 2: Q_o values (mg SP / m² C) obtained with the classical Langmuir linearization / Lineweaver Burke plot / direct Langmuir fit. The maximum error bar of these three determinations is reported into brackets.

Conversely, important variations of the K_{app} values obtained with these three fitting techniques were registered. Indeed, as K_{app} is quite high (> 1000 g AS/g SP), the two linearizations are imprecise because of the very low values of $1/(Q_o K_{app})$. So, together with a direct Langmuir fit, a third linearization was used: $Q/(Q_o-Q)=f(C)$, which gives K_{app} as the slope of the straight line going through zero. Both fits were done using the Q_o value assessed previously. Moreover, they were performed both on raw data (that are the several measurements done for each SP/C value), or on the averaged isotherm (for each SP/C value, the average of the several (C,Q) measures is considered). Among the four $1/K_{app}$ values thus obtained, the three closest are kept. Their average and twice their standard deviation are taken for $1/K_{app}$ value and the associated error bar. K_{app} value is calculated inverting this $1/K_{app}$ value. The Langmuir fit of the raw data in Fig. 1 uses the values of Q_o and K_{app} so determined.

Going from C1 to C6, while the alkali content of the anhydrous cement increases, the adsorption capacity of the first monolayer, Q_o , decreases. The interaction between PC-PEO and aluminates (and especially C₃A) is often believed to play a crucial role in compatibility issues. So Q_o was plotted both vs the content of cubic and total C₃A, respectively named C₃A^{cub} and C₃A^{tot} (Fig. 3 and 4). These two quantities were assessed with Rietveld analysis of DRX diagrams. The curves obtained show no clear

correlation between them and Q_o . These factors should not rule the adsorption capacity of the monolayer. Another possibility to explain the variations of Q_o going from C1 to C6 would have been the increase of surface area due to hydration progress that we did not take into account here. Now, at short times, the two main species of main reactivity are C_3A and, to a minor extent, C_3S . Neither of them shows a monotonic evolution from C1 to C6, so that we do not believe that this parameter could explain Q_o observed variations. Moreover, we wonder to which extent a surface area measurement after hydration arrest could quantify the surface area developed by hydrates. Indeed, if the hydrates recover the anhydrous matter (what is quite likely), the surface area measured will be less than the one of the initial anhydrous cement plus the one of hydrates formed. Now, it is with this latter surface area that the PC-POE (and the sulfates) will interact for adsorption. This said, the only monotonic parameter of anhydrous cements left going from C1 to C6 is the alkali content. As evidenced previously, this induces a correlated increase of sulfates in the aqueous phase, and sulfates are bound to compete with PC-PEO for adsorption at cement's surface. So, Q_o is plotted vs $[SO_4^{2-}]$ (Fig. 5). After 15 as after 90 min, Q_o decreases exponentially while $[SO_4^{2-}]$ increases from C1 to C6. The decrease of the adsorption capacity going from C1 to C6 seems then to be correlated with the sulfate concentration. This means that the role played by sulfates in PC-PEO interaction with cement goes far beyond a competition for the occupation of a given adsorption site. Indeed, an increase of sulfates concentration is, besides, responsible for a reduction of the number of adsorption sites. This would mean that the composition of the aqueous phase influences the composition of the double layer as suggested by [17]. The latter would be responsible for a reduction of the number of adsorption sites.

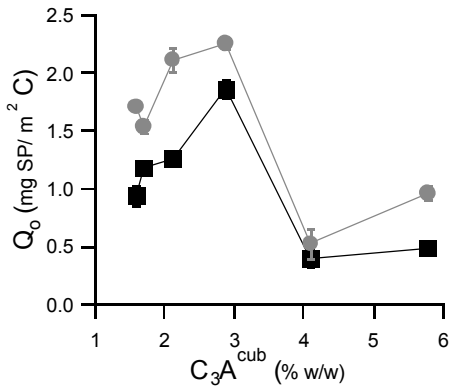


Figure 3: adsorption capacity of the monolayer vs the content of cubic C_3A of anhydrous cements.

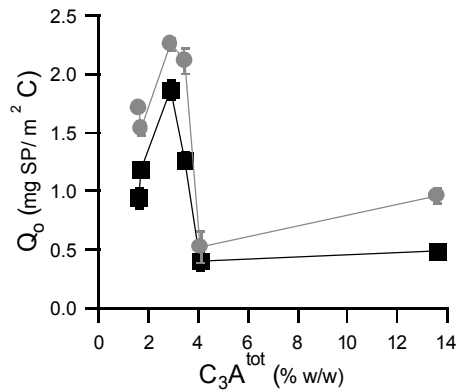


Figure 4: adsorption capacity of the monolayer vs the total content of C_3A of the anhydrous cements.

Another important fact is, for a given value of $[SO_4^{2-}]$, an increase of Q_o between 15 and 90 min. It should be noticed that part of this increase

could result from the ongoing hydration. As a matter of fact, the newly formed hydrates should bear their own adsorption sites. However, it should be considered that the increase of Q_o between 15 and 90 min due to this reason might be overestimated: indeed, our measurements neglect the surface area developed by the hydrates precipitated between these two times while they take into account the adsorption sites that they bear.

The possible competition between sulfates and PC-PEO for the occupation of the remaining adsorption sites is now examined through $1/K_{app}$ values. $1/K_{app}$ is plotted vs $[SO_4^{2-}]$ (Fig. 6). For the 5 grey cements taken after 15 or 90 min, a linear trend is observed with a correlation coefficient R^2 of 0.71. For these cements, the idea of the competition between sulfates and carboxylates for the occupation of adsorption sites is hence validated. Moreover, affinity constants of PC-PEO and sulfates common to the five grey cements at the two times considered are obtained. Hence, the affinity of each species, K_{SP} and K_{sulf} , seems to be independent of grey cement's and of the time considered. On the opposite, the particular behavior of C1 might indicate that the different chemistry of white cements could play a role.

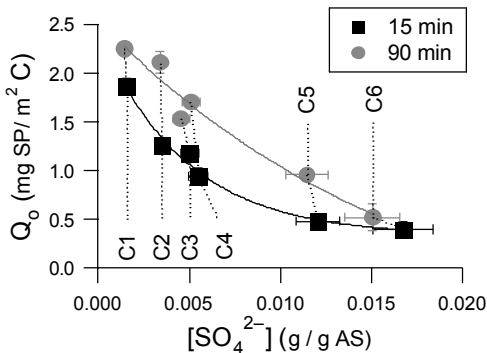


Figure 5: adsorption capacity of the monolayer vs the sulfate concentration in solution.

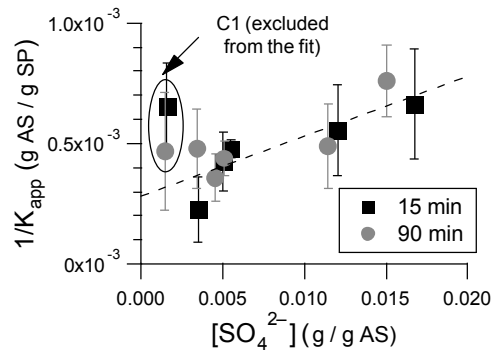


Figure 6: inverse apparent affinity vs the sulfate concentration in the aqueous phase.

The affinity constants, K_{SP} and K_{sulf} , so obtained for the grey cements are expressed in grams of aqueous phase per gram of the considered species. They were converted in liters of aqueous solution per mol of the adsorbing functions units so as to compare the competing functions for adsorption at cement's surface (Table 3). The comparison of K_{SP} and K_{sulf} expressed in these units indicates that the affinity of PC-PEO is far higher than the one of sulfates.

| K_{SP} (g AS/g SP) | K_{sulf} (g AS/g SO_4^{2-}) | K_{SP} (L AS/mol -COOH) | K_{sulf} (L AS/mol SO_4^{2-}) |
|----------------------|----------------------------------|---------------------------|------------------------------------|
| 3550 ± 700 | 90 ± 20 | 6650 ± 1300 | 8.5 ± 1.9 |

Table 3: affinity constants of the PC-PEO and the sulfates assessed with the linear fit of $1/K_{app}$ vs $[SO_4^{2-}]$ in Fig. 3.

3.2 Rheological behavior of the slurries

The value of the yield stress of the slurries was assessed as the intersection of the two power law behaviors observed on both sides of the yield stress (Fig. 7). This value appeared to be in good agreement with the one obtained with a Herschel-Buckley fit in the $\dot{\gamma}$ range between the yield stress and 300 s^{-1} . Last, this yield stress value was also confirmed by the creep measurements performed on some slurries: below t_y , the strain reaches a constant value inferior to unity in 1 min, whereas above t_y , the strain exceeds unity in a few seconds (less than 10 s).

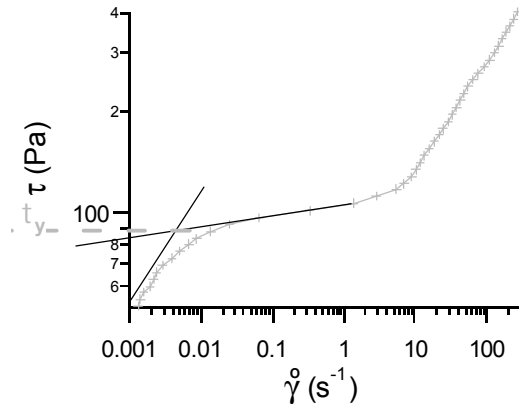


Figure 7: assessment of the yield stress on a typical rheological curve.

Yield stress, t_y , (Fig. 8) and spread radius, R , (Fig. 9) are represented vs PC-PEO consumption, Q . The latter is calculated from PC-PEO content, SP/C , using the values of the parameters Q_o and K_{app} of the PC-PEO adsorption isotherms determined above (section 3.1). This requires the resolution of a second degree equation for the PC-PEO concentration, C .

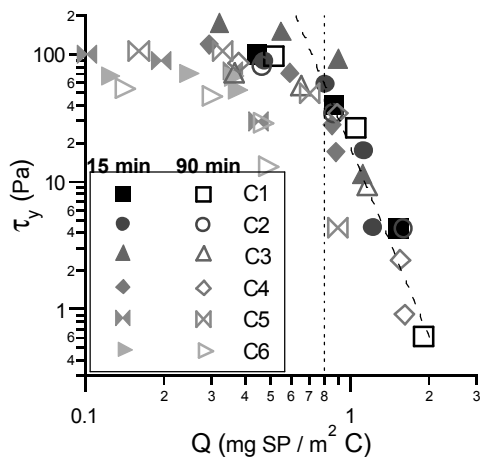


Figure 8: yield stress vs PC-PEO consumption.

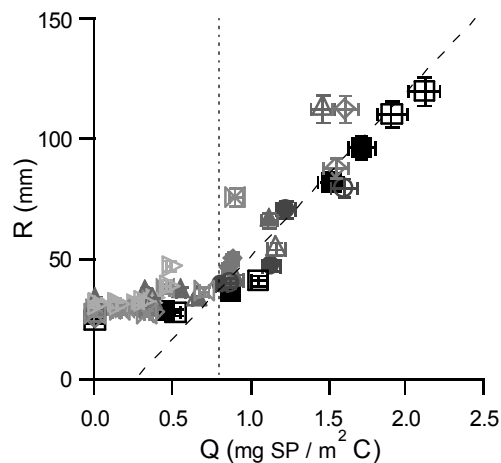


Figure 9: spread radius vs PC-PEO consumption. Legend: see left.

As expected, for all cements, t_y and R resp. decreases or increases while Q increases: the PC-PEO deflocculates cement grains, all the more as the covering of cement particles by adsorbed PC-PEO increases. In addition, for t_y as for R , above a critical adsorption level ($Q=0.80$ mg SP/m² C), a master curve is observed for all cements after the two times considered (15 and 90 min). This curve is respectively a power law of exponent -5 for t_y ($t_y=AQ^{-5}$) and a linear relationship for R ($R=R_o+B(Q-Q_{min})$). Such a linear relationship between spread and superplasticizer adsorption was already reported [18]. In addition, in this range of high Q values conferring important spread, the cement slurries studied obey the model of N. Roussel et al. [19], which predicts that the yields stress varies with the inverse 5 power of spread radius. The conjugation of these two dependencies leads to the master curve observed for yield stress variations above the threshold value of 0.80 mg SP/m² C.

These master laws mean that above this critical value of PC-PEO adsorption, most probably linked to a critical covering of cement grains surface, $[SO_4^{2-}]$ rules the adsorption, which in turn pilots the deflocculation and hence the fluidity of the cement slurries. In other terms, taking into account the influence of sulfates concentration on PC-PEO/cement interaction enables to predict the fluidity of a given cement/PC-PEO couple.

From a theoretical point of view, the yield stress contains both a micro structural contribution and an interparticle force contribution. To get rid of the micro structural variations encountered when going from one cement to another, the yield stress was normalized with respect to the corresponding plain slurry yield stress, $t_y^{0\%}$. This normalization is similar to the one adopted by Z. Zhou et al. [20] for alumina suspensions of varying ζ potential, whose yield stress was normalized by the yield stress at the isoelectric point. Doing so will hence enable to follow the deflocculation rate conferred by the PC-PEO. Nevertheless, the adimensional yield stress so obtained is not only representative of the interparticle force, but also of the connectivity of the particle network, that is the number of junctions between particles owed to flocculation. Indeed, the latter is also affected by the variations of the deflocculating efficiency.

The adimensional yield stress, $t_y/t_y^{0\%}$, is plotted vs PC-PEO consumption in Fig. 10. All the points line up on a master curve of sigmoidal form. This form is characterized by a transition between a high level of 1 at low Q values, representative of the flocculated state, and a low zero-level at high Q values, representative of the deflocculated state in which the yield stress vanishes. The transition intervenes for a critical Q value, equal to 0.70 mg SP/m² C according to the sigmoidal fit. The critical covering necessary to induce deflocculation is hence more or less equal to the critical Q value in Fig. 8 and 9 above which master behaviors are observed. These master behaviors seem hence to be representative of the onset of the deflocculation of

cement. That the points relative to 90 min line up on the same curve as the ones relative to 15 min seems to indicate that the increase of Q_o is well representative of an actual increase of the covering of cement grains by PC-PEO, and not to a calculus artefact*. Indeed, the increase of Q between 15 and 90 min is correlated to an enhancement of the fluidity (that is a decrease of t_y).

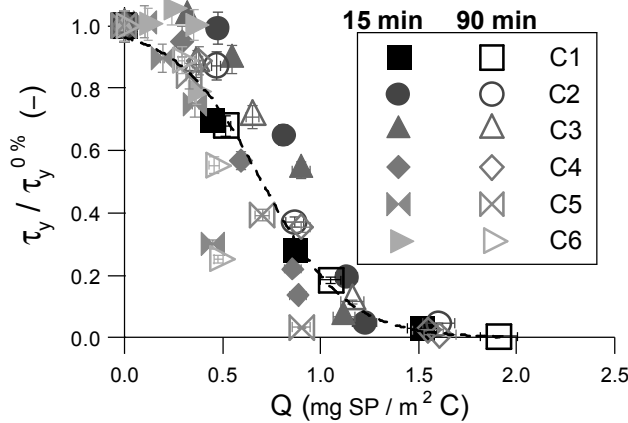


Figure 10: adimensional yield stress vs PC-PEO consumption.

3.3 Discussion on adsorption results

PC-PEO consumption isotherms were considered as representative of adsorption and fitted by a modified Langmuir model, taking into account the competitive adsorption of carboxylates from PC-PEO and sulfates at cement's surface. The two parameters of this model, Q_o and K_{app} , are correlated to the variations of the sulfate concentration, itself ruled by the alkali content of the six anhydrous cements considered. The fact that these cements display important variations of set regulator content and/or composition seems thus to have no more than second order effect.

As the alkali content of the six anhydrous cements increases, the sulfate concentration in the aqueous phase increases with a correlated exponential decrease of Q_o and linear increase of $1/K_{app}$. The decrease of Q_o at increasing $[SO_4^{2-}]$ is relevant of a reduction of the number of adsorption sites as sulfate concentration increases (not reported yet), which could result from a modification of double layer structure under modification of aqueous phase composition as evoked by [17]. Meanwhile, the linear $1/K_{app}$ decrease at increasing $[SO_4^{2-}]$ validates the hypothesis of a carboxylates/sulfates competition for occupation of adsorption sites introduced by [5] and [15]. The relative magnitude of these two effects is discussed hereafter. Even though K_{SP} is far higher than K_{Sulf} , sulfate effect on K_{app} becomes noticeable at high sulfate concentrations. Indeed, for the highest sulfate concentration considered here, the apparent affinity

* this artefact would result from the appearance of new adsorption sites borne by the hydrates precipitated between 15 and 90 min whose surface area was not taken into account into Q calculus.

constant of the PC-PEO, K_{app} , is about one third of K_{SP} . The PC-PEO content needed to reach a given superplasticizer adsorption is hence increased in comparison to what would happen in a "sulfate-free solution". However, this effect is insignificant in comparison to the reduction of existing adsorption sites, Q_o , brought by the double layer reorganization induced by the increase of $[SO_4^{2-}]$. Indeed, for C6 for example, suppression of sulfates/PC-PEO competition would divide by 2.2 the PC-PEO content, SP/C , required to reach $Q=0.9Q_o$. In the meantime, the number of adsorption sites, Q_o , is less than one third of the one of C2, so that even an infinite dosage of PC-PEO would not enable to reach an adsorption equal to the population of 90% of the adsorption sites of C2.

The present study considering the effect of alkali sulfates through six different cements implies variations of clinker's composition, set regulator amount and composition, Blaine surface area and fineness... It could be argued that these facts could impact cement reactivity and the adsorption results observed. To assess the impact of sulfates in the aqueous solution while keeping these parameters constant, a quantity of $Na_2SO_4 \cdot 10 H_2O$ equivalent to 0.50 % w/w of SO_3 with respect to cement was dissolved in the mixing water of C2 slurries. These experiments are referred to as $DSO_3=0.50$ %, and compared with the ones with no sulfate introduction in the mixing water, named hereafter $DSO_3=0$ %. Increasing DSO_3 from 0 to 0.50 % induces an increase of $[Na^+]$ (resp. $[SO_4^{2-}]$) equivalent (resp. inferior) to $Na_2SO_4 \cdot 10 H_2O$ complete dissolution, and no change of $[K^+]$. The $Na_2SO_4 \cdot 10 H_2O$ introduced is then completely dissolved, does not change cement's alkali sulfates dissolution, but part of the sulfates reprecipitates. In agreement with the results of [5], it was observed that the introduction of $DSO_3=0.50$ % of $Na_2SO_4 \cdot 10 H_2O$ decrease the consumption of PC-PEO by the cement, after 15 min (Fig. 11) as after 90 min. Consumption isotherms at $DSO_3=0.50$ % were fitted with the model and methods described in section 3.1. The reduction of Q_o at increasing $[SO_4^{2-}]$ observed when going from C1 to C6 was confirmed, as well as the one of K_{app} (Table 4). The effect of $[SO_4^{2-}]$ increase on the reduction of the number of adsorption sites (that is on Q_o value) is tremendous as compared to the one of the competition between carboxylates and sulfates for the occupation of an existing adsorption site (that is K_{app} value) as shown by Fig. 12. Now, beyond the qualitative agreement between these results and the ones of section 3.1, no quantitative agreement is found. Indeed, the Q_o and K_{app} values are higher than the ones obtained interpolating the results of section 3.1 (that is cements of varying alkali content) for the values of $[SO_4^{2-}]$ measured for $DSO_3=0.50$ % with C2. rather than a possible influence of cement's composition (other than alkali sulfate content), this is understood as the possible result of a difference of supersaturation degree between these two conditions. In other terms, the path used to reach the out of equilibrium state has consequences on the quantitative result, even though the general trend is the same.

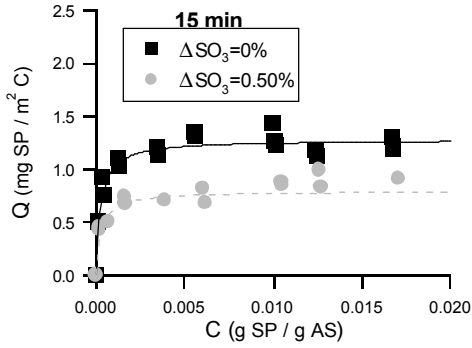


Figure 11: effect of an addition of $\text{DSO}_3=0.50\%$ of $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ on the PC-PEO consumption isotherm of C2 after 15 min.

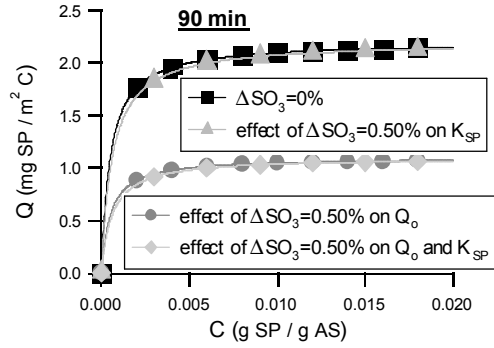


Figure 12: effect of an addition of $\text{DSO}_3=0.50\%$ of $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ on Q_o , K_{app} or both of the PC-PEO consumption isotherm of C2 after 90 min.

| | Q_o (mg SP/m ² C) | | K_{app} (g AS/g SP) | |
|--|--------------------------------|---------------------|-----------------------|--------|
| | 15 min | 90 min | 15 min | 90 min |
| $\text{DSO}_3=0\%$ | 1.26 (± 0.07) | 2.11 (± 0.11) | 4450 | 2100 |
| $\text{DSO}_3=0.50\%$ | 0.79 (± 0.05) | 1.10 (± 0.05) | 3500 | 1700 |
| <i>Interpolation of C1 to C6 laws for $[\text{SO}_4^{2-}]$ equal to the one measured for C2 with $\text{DSO}_3=0.50\%$</i> | 0.46 | 0.88 | 1650 | 1750 |

Table 4: Q_o and K_{app} values for an addition of $\text{DSO}_3=0$ or 0.50% of $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ to the mixing water of C2, or for an interpolation of the laws observed with the six varying cements C1 to C6 (see section 3.1) at the sulfate concentration measured for C2 and $\text{DSO}_3=0.50\%$.

4 CONCLUSION

This study has demonstrated the competition between soluble sulfates (mostly stemming from the dissolution of the alkali sulfates from the clinker) and the polymer in the interaction between CEM I type cements and a PC-PEO superplasticizer. The sulfates are not only implicated in a competition with the PC-PEO for occupying the existing adsorption sites but are also, and above all, responsible for a decrease of the number of existing adsorption sites, all the more important as their concentration in the aqueous phase is higher. As a consequence, the fluidity of the cementitious slurries is decreased because of a less efficient deflocculation, consequence of a reduction of the covering of cement grains by adsorbed PC-PEO.

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