Influence of Superplasticizer Adsorption on the Rheology of Cement Paste

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Abstract
The production of high performance concrete requires the development of new superplasticizers with increased efficiencies. The knowledge of the mechanisms by which these admixtures act is of primary importance for the design of new polymers. They are believed to be linked to the dispersion cement agglomerates by electrostatic, steric or entropic repulsion, or improved wetting (capillary effect). The two first are directly linked to adsorbed polymers. The third is linked to both adsorbed and solvated polymers, while the last is mainly linked to polymers remaining in solution.

To elucidate the effects of the superplasticizers, two approaches were used. On one hand, adsorption isotherms of polymers were measured by solution depletion. On the other hand, rheological testing leading to the determination of the amount of superplasticizer needed to reach a minimum yield stress. A comparison of both results reveals the relative importance of the possible mechanisms contributing to superplasticizer efficiency.

It is shown that molecular mass distribution effects polymer adsorption. It is also shown how a cement obtained by grinding with and without a grinding aid has different adsorption properties and different polymer requirements. Results are discussed in the light of understanding by which mechanisms polymers are acting.

1.   Introduction

Superplasticizers are today a valuable help in the production of high performance concrete, which exhibits high flow and workability. Such concrete develops high density and durability on setting. However, despite world-wide usage of superplasticizers understanding the mechanisms through which they act is still an object of much study [1-10].

Much has been learned from the field of colloidal science, where surface forces a,nd their role on interparticle interactions has been a subject of ongoing research for many years. Evans and Wennerström [11] and Israelachvili [12] present clear treatments of colloidal, surface and interparticle forces. Horn [13] shows how these concepts can be applied to ceramic processing. Russel *et al* [14] give an extensive treatment of these effects, illustrating how these effects are the regulating factors of the rheology of colloidal dispersions.

In cementitious materials, the time dependence due to on-going chemical reactions complicates the understanding [1]. Nevertheless, intensive work over the past years has brought significant progress in the understanding of this field. In particular, the design of polymers having a backbone containing carboxylic groups and onto which side chains are grafted has allowed much better performances than with the conventional polymers, such as SNFC (sulfonated naphtalene formaldehyde condensate). Uchikawa et al [2] showed by Atomic Force Microscopy (AFM) that polymers with long side chains can be much more efficient than the ones with shorter or no side chains. Yoshioka *et al* [3] and Sakai and Daimon [5] calculated the importance of steric contribution to the stabilization of alite by such polymers. The effect of such polymers on the rheology of cement suspensions was studied by Matsuyama *et al* [6]. Because, straight forward application DLVO[1] theory to monosized spheres indicates that electrostatic repulsion is weak, and because the more recent polymers, which are more efficient, clearly have a major steric effect, the temptation is great to consider all polymers act through steric repulsion.

Understanding which mechanism is dominant and what factors effect it has major implications for the design of polymers with increased performances. It should also allow a better use of current polymers. An interesting interpretation of a case of cement/SNFC incompatibility was presented by Fernon et al [8]. They showed an example in which one particular cement had significantly faster slump loss than a set of cements from an other origin.

Such comparative studies can also provide valuable information to elucidate questions relative to dispersion mechanisms. Nevertheless, in such comparative studies, a couple parameters can easily be overlooked and data thereby misinterpreted. One of these parameters is whether the cement was ground with a grinding aid, and if so which one.

The first objective of this paper is to show a grinding aid can alter the behavior of a superplasticizer/cement combination. The second is to highlight how such differences can lead to misinterpretation of comparative studies intended to solve the mechanistic question regarding the action of superplasticizers in concrete. We also show how neglecting the polydispersity of a superplasticizer can lead to misinterpretation. This does not only have an academic interest. It also means that a manufacturer should be able to control and reproduce molecular mass distributions in order for his product to have a reliable quality.

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[1] From the name of the authors of the theory: Derejaguin, Landau, Verwey, Overbeck.

2. Experimental

2.1 Cements

Two Ordinary Portland Cements (OPC) obtained from the same clinker (Olten, Switzerland), were used. The first was ground without any grinding aid. The second was ground in presence of a couple ppm of an acetate of triethanol amine, a common grinding aid. Grinding times were adjusted so as to obtain two OPC with the same specific surfaces.

The BET specific surface area of both powders was determined by N_2 adsorption (Micromeritics Gemini III 2375). Three samples were measured for each cement. Bulk chemical compositions and specific surfaces (0.95 m^2 g^{-1}) of both cements were similar [15].

2.2 Polymers

Two polycarboxylate-polysulfonates produced as laboratory test products by Sika A.G. (Zurich, Switzerland) were used for this study. Information on their composition is given in Table 1. Both are detectable by UV, which allows their adsorption to be measured as described below. Chromatograms of these polymers show that PCA-2 has a significantly lower polydispersity than PCA-1. The polymeric fraction of the PCA-1 clearly contains different components [15]. They are supplied as concentrated aqueous solutions, with a solid content of about 30-40% by mass.

Table 1 - Characteristics of the polymers used.

Name	Chemical Type	Number Average Molecular Mass, Mn [g mol-$^{-1}$]	Mass Average Molecular Mass, Mw [g mol^{-1}]	Polydispersity Coefficient Mw / Mn [-]
PCA-1	Na-polycarboxylate-polysulfonate	15'600 ± 2'000	40'500 ± 5'000	2.6
PCA-2	Na-polycarboxylate-polysulfonate	11'500 ± 2'000	24'500 ± 5'000	2.1

2.3 Adsorption

Adsorption was determined by solution depletion, using reverse phase HPLC to quantify polymer concentrations, as described in [15]. Polymers were included in mixing water and adsorption times were 5 and 30 min.
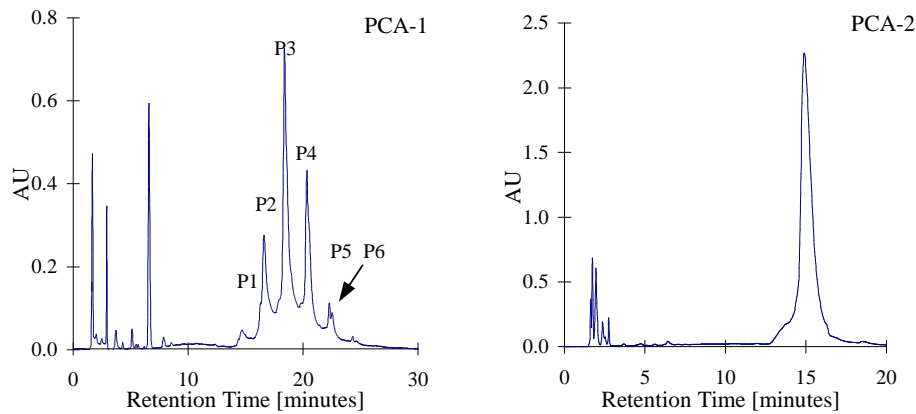
Figure 1 -   HPLC chromatogramms of polymers PCA-1 and PCA-2 obtained with the same elution method.

2.4   Rheology

Rheolgy measurements were all performed at 0.35 W/C. Solutions of known superplasticizer (7 ml) composition were weighed into 50 ml PE flasks. Cements (20 g) were weighed separately into sample holders and then added into the PE flasks.

Samples were then mixed by hand with a spatula from 1-3 minutes depending on the polymer dosage (lower dosages required more mixing). They were then inserted into the sample holder of a coaxial cylinder device (Z20 DIN) mounted on a rheometer (Haake mod. RS100; Karlsruhe, Germany), thermostated at 25°C. The gap between both cylinders is 0.85 mm. Over this gap, the velocity gradient is assumed to be constant.

One commonly mentioned condition for cement rheology measurements to be reproducible is to complete irreversible breakdown of a critical fraction of the agglomerates. High mixing achieves this purpose and one can consider that when a paste is submitted to constant high shear rate, the breakdown is complete at the latest once the viscosity reaches a constant value. For all our samples, 160 s at the maximum shear rate of the instrument ($640\ s^{-1}$) satisfied this condition.

During this initial mixing (160s; $640\ s^{-1}$), 5 points are taken at equal intervals. Then, the samples were left to rest 5 min. After that, the stress was ramped up from 1 Pa to 100 Pa in 8 minutes, taking 20 points logarithmically spaced. Stress ramps are most adequate for directly yield stress [16, pp. 195-196]. If the shear rate reached $640\ s^{-1}$, before 100 Pa, the step was interrupted. After that, the samples were held 3 min at $640\ s^{-1}$, taking one point each minute. Finally, the shear rate was reduced to the minimum value available.

3.   Results and discussion
3.1   Adsorption

Adsorption general trends

Below a specific superplasticizer dosage, the peaks corresponding to the polymeric fractions of the superplasticizer do not appear in the chromatogram of the supernatent. Therefore, below this dosage, all the polymer is adsorbed. Above this dosage, the polymer peaks appear. In addition, their surfaces increase linearly with dosage (Figures 1-3). The slope of the lines on these graphs have been shown to correspond to those of calibration curves, prepared in solutions having the same ionic composition as the cement suspensions [15]. In such cases, adsorption data corresponds to isotherms with step like functions. The plateau corresponds to the ordinate at the origin on these plots. For the polydispersed PCA–1, the same type of linear relation is obtained for each polymeric fraction.

Adsorption plateau values

Adsorption data for each adsorption time / polymer type combination was always acquired at the same time for both cements. Results are plotted in Figures 2-5. They suggest that the slope does not depend on the cement type. This is confirmed by a statistical test (Table 2), which indicates that the confidence allowing to consider that slopes differences are small. For PCA-2 at 30 minutes adsorption, the test is biased by insufficient data. Nevertheless it leads to the same conclusions as the other combinations: the slope is independent of grinding history.

Table 2 -   Confidence intervals to reject the hypothesis that the slopes are equal. For PCA-1 which is not monomodal as PCA–2, the values given are derived from overall polymer response.

	PCA-1	PCA-2
5 min	17%	74%
30 min	28%	6%

By using this information, use data of both cements to calculate one slope and two ordinates at the origin (plateaus), for each polymer type / adsorption time combination. More precise plateaus are thereby obtained. However they are no more independent one of another and this has to be taken into account when testing whether or not adsorption depends on the cement. Results from Table 3 indicate that adsorption of PCA-1 is not affected by the grinding history of this cement, while adsorption of PCA-2 is.
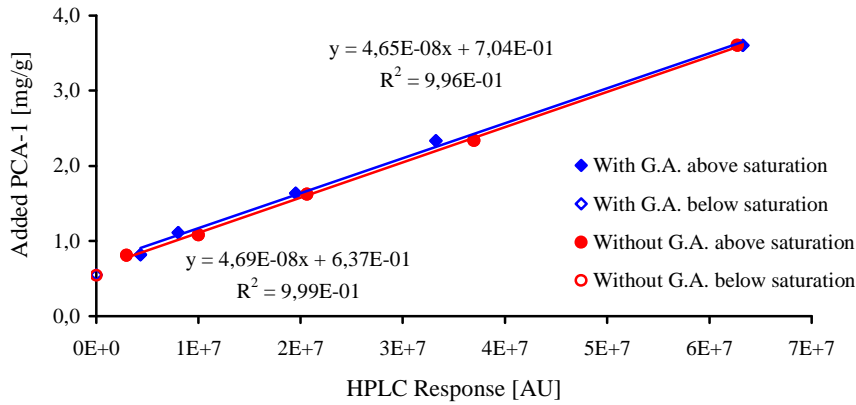
Figure 2 -   Adsorption data for PCA-1 in suspensions of cement with or without grinding aid (G.A.). Adsorption time is 5 min.
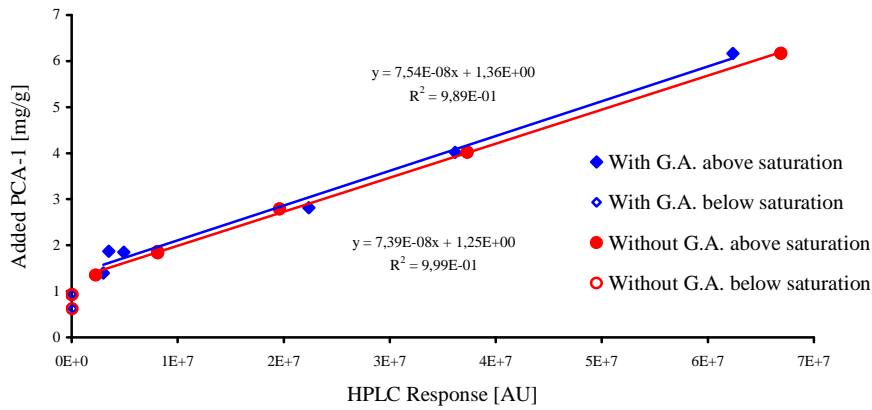

Figure 3 -   Adsorption data for PCA-1 in a suspension of cement with or without grinding aid (G.A.). Adsorption time is 30 minutes adsorption.

Table 3 -   Confidence for rejecting the hypothesis that polymer adsorption is not affected by the type of cement (w/wo grinding aid).

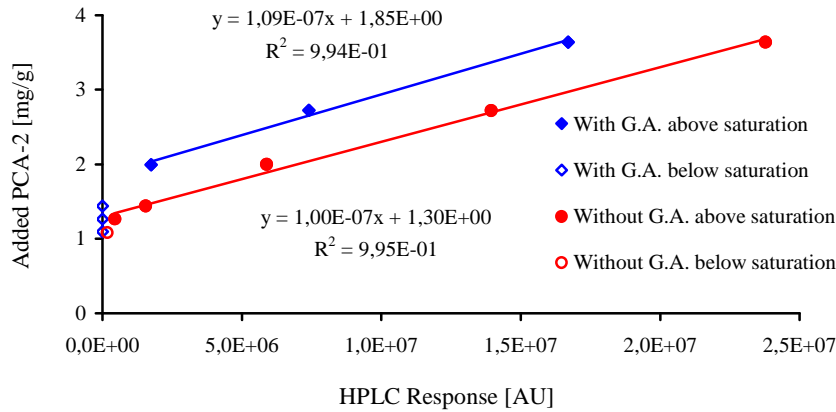| Adsorption Time	PCA-1	PCA-2
5 min	84%	100%
30 min	87%	95%

Figure 4 -   Adsorption data for PCA-2 in suspension of cement with or without grinding aid (G.A.). Adsorption time is 5 minutes.

The amounts of polymers adsorbed are given in Table 4. The errors given correspond to 95% confidence intervals. They should be used with caution since, as mentioned above, they are not all independent one of another.

Table 4 -   Amount of superplasticizer adsorbed given in mg/g.

Adsorption Time	Cement	PCA-1 $[mg_{PCA-1}/g_{cement}]$	PCA-2 $[mg_{PCA-1}/g_{cement}]$
5 min	With G. A.	0.67 ± 0.07	1.9 ± 0.1
	Without G. A.	0.67 ± 0.07	1.3 ± 0.2
30 min	With G. A.	1.31 ± 0.14	2.2 ± 0.5
	Without G. A.	1.31 ± 0.14	1.7 ± 0.3

Adsorption kinetics

Adsorption is increased between 5 and 30 minutes. This increase is much larger for polymer PCA-1 than for PCA-2. On the other hand, it has been shown previously, that if PCA-1 is added as a concentrated solution to a cement suspension after 30 minutes hydration, the amount adsorbed is then smaller than if the polymer is added immediately [15]. This effect is even more pronounced for PCA-2, probably indicating that PCA-2, which adsorbs faster than PCA-1 is included at a higher degree into early products of hydration. Another factor, which can influence adsorption data measured by HPLC, is polymer hydrolysis.
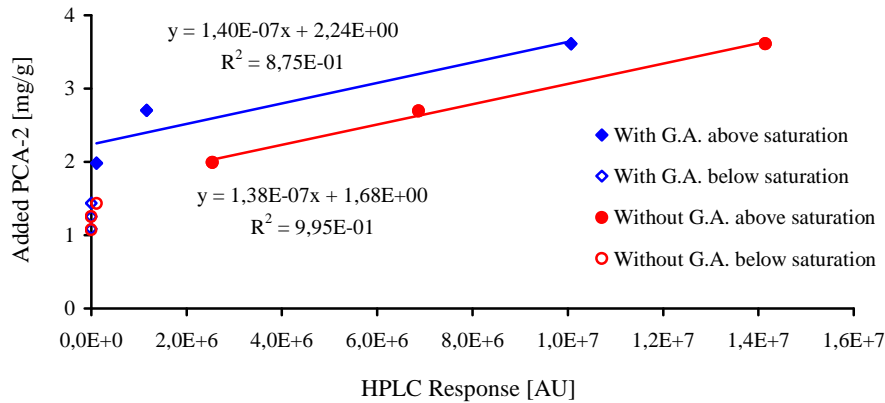
Figure 5 -   Adsorption data for PCA-2 in suspensions of cement with or without grinding aid (G.A.). Adsorption time is 30 minutes.

Polymer hydrolysis

The slopes of the regression curves increase between 5 and 30 minutes of adsorption time. This has also been observed with other cements and does not depend on the order in which the measurements are carried out. In addition, the confidence intervals to reject equality of slopes at both times are of 100% for each polymer.

A given amount of excess polymer in the aqueous phase will therefore give a smaller surface peak for the longer residence times. This response decrease can be linked to adsorption and/or hydrolysis of the polymer in solution. Adsorption should depend mainly on the particle surface area available for adsorption, while hydrolysis will increase regularly with the amount of added polymer.

The hydrolysis can take place in the bulk solution or at the surface of the cement particles. For the second process to have a significant effect on the bulk polymer content in the aqueous phase, the hydrolysis products should be efficiently desorbed. It is assumed that this process is not dominant because desorption rates are expected to be small and because the high liquid to solid ratio used should favor the solution process.

Consider a fast adsorbing polymer such as PCA-2. Very soon, the surface will reach saturation. During the remaining time of the experiment, the excess polymer, which remains in solution, can undergo hydrolysis. Longer residence times will lead to larger hydrolysis, less response and steeper slopes of the linear regression, while the ordinate at the origin will not change significantly.

For a slower adsorbing polymer, the situation is more complicated. Indeed, not only the initial polymeric fractions, but also the hydrolysis products can adsorb. This can shift to

lower values the average molecular mass of the adsorbing polymer. If polymeric fractions do not all adsorb in the same way adsorption data will then be harder to interpret.
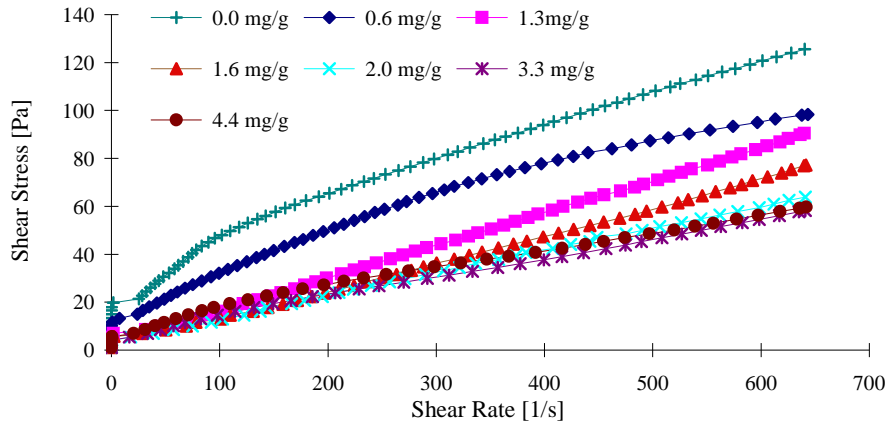

Figure 6 -   Flow curves for increased stress measurements with cement containing grinding aid. The different curves correspond to different dosages of PCA-1.

Polydispersity in adsorption

The polymeric part of PCA-2 is found by HPLC to be relatively monomodal. On the other hand, using the same gradient, the polymeric part of PCA-1 can be separated into six different fractions (Figure 1). Each of these is better quantified using peak highs rather than peak areas [15]. It was found that there is a dosage range in which, only some fractions adsorb. Below this range, all fractions adsorb. Above it, none of these fractions adsorb. To prove this effect, the dependence of peak retention time (fraction) on the dosage above which this fraction does not adsorb was tested. Results from [15] show that for 30 minutes of adsorption time, the absence of a dependence can be rejected for cement without grinding aid with a confidence level of 99%. For the other cement the degree of confidence is also large (92%) and it can be assumed that a similar effect is present. It is assumed that the larger molecular mass polymers can no longer find sufficient space on the powder surface to adsorb above a certain surface coverage.

3.2   Rheology

General trends

Figures 6-9 show the flow curves obtained for cements with and without grinding aid. Each curve corresponds to a different dosage of superplasticizer, while increasing shear stress.

The first observation is that the functionality of the flow curves changes significantly with superplasticizer dosage. A simple model such as the two parameter Bingham model is insufficient to account for these curves. One can also see that above a certain dosage all curves indicate very similar flow behaviors.
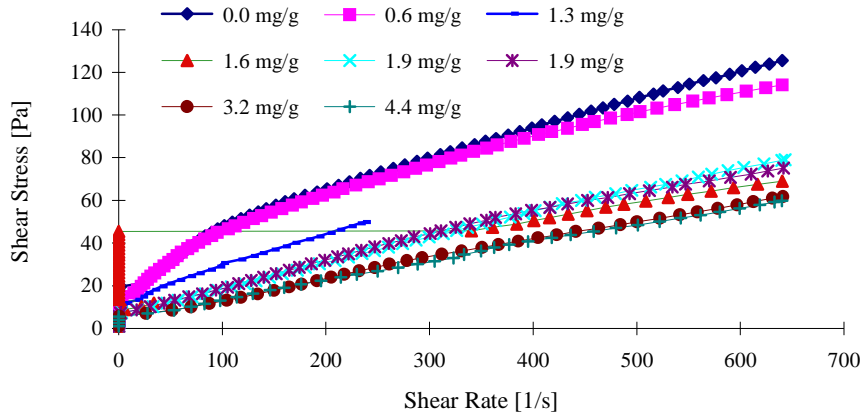

Figure 7 - Flow curves for increased stress measurements with cement containing grinding aid. The different curves correspond to different dosages of PCA-2.
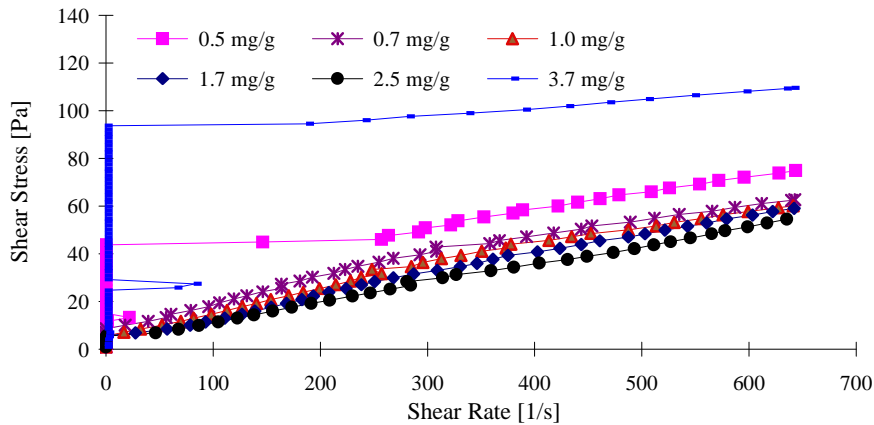

Figure 8 - Flow curves for increased stress measurements with cement not containing grinding aid. The different curves correspond to different dosages of PCA-1. The high yield stress for 3.7 mg is certainly linked to sedimentation.

Up to a certain value of shear stress, the shear rate is equal to zero. Then, there is a sudden increase in shear rate. This limiting stress value can be identified as the yield stress. The amplitude of the sudden shear rate increase rises with yield stress magnitude. In some cases, there are a couple of these steps, indicating that a large particle concentration in one part of the gap causes the rheometer to block. This is due to an inhomogeneous distribution of the particles. Nevertheless, it appears that the first yield point can be considered for discussing yield stress.

Most likely, these shear rate discontinuities indicate that hydration causes a bonded network to form between both walls of the cell. The measured yield stress is dependent on the gap size and the time for which the cement is left to hydrate. Nevertheless, this parameter seems to give valuable information on superplasticizer efficiency. It will therefore be extensively used for discussion of the rheology of these suspensions.

At high superplasticizer dosages, some sedimentation took place. Unreliable data was thereby produced.
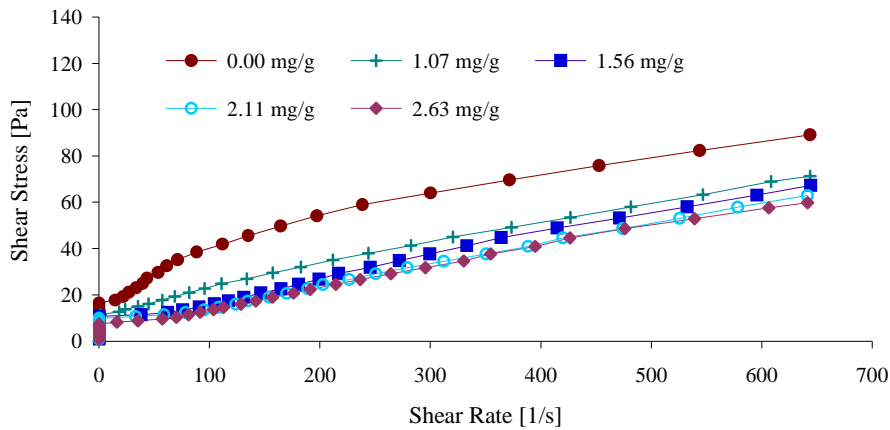

Figure 9 -   Flow curves for increased stress measurements with cement not containing grinding aid. The different curves correspond to different dosages of PCA-2.

Yield Stress

Yield stress is determined by taking the first stress value above which shear rate increases suddenly. In figure 10, values obtained for PCA-1 containing suspensions are plotted against PCA-1 dosage. The vertical lines show the amounts of PCA-1 adsorbed after 5 and 30 minutes. An interesting feature is the steeper decrease of yield stress as PCA-1 is added to the cement without the grinding aid. The plateau value of yield stress is reached earlier for this cement.

For suspensions containing PCA-2, the minimal yield stress is reached for dosages slightly lower than the amount adsorbed at 5 minutes for the cement with grinding aid. For the cement without grinding aid, the situation seems to change around the dosage adsorbed after 5 min (figure 12). In the first case at least, it seems that it is not even necessary to cover the cement particles with polymer to obtain a good dispersion. A similar result was obtained for this polymer and model suspensions of $Mg(OH)_2$ [9]. In that case, it was shown that as solid loading was increased, the polymer requirement increased. The liquid limit was reached more or less once all the powder surface was covered.
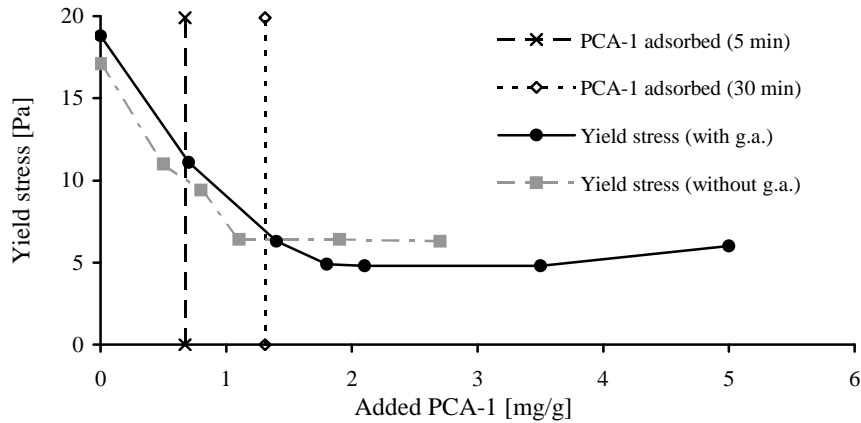

Figure 10 - Measured yield stress of cement suspensions as a function of PCA-1 dosage. The vertical lines indicate the amounts of PCA-1 adsorbed after 5 and 30 minutes.

3.3 General discussion

If adsorption data for cement without grinding aid had been used to discuss rheology of the cement with grinding aid, one would have concluded that more polymer was needed than was adsorbed. This conclusion would have been incorrect.

For polymer PCA-1, we had found that the confidence level for considering adsorption to change between both cements was lower. If such a difference exists, it is too small to be identified within experimental error. Nevertheless, values are systematically higher for cement with grinding aid, as in rheology results. This could explain the higher polymer requirement of the cement with grinding aid.

Another explanation more likely to account for the large differences found in rheology is kinetics of adsorption. Indeed, PCA-1 does not adsorb rapidly. Therefore an excess amount might be required to cover the surface. On adsorption isotherms, this would have translated by non step-like functions. This effect could not be identified in the

experimental conditions used. Nevertheless, regression errors were systematically larger for the cement with grinding aid, mainly due to small deviations at low dosages. There might therefore be a subtle kinetic effect at low dosages coupled with a competition between the polymer and the grinding aid.
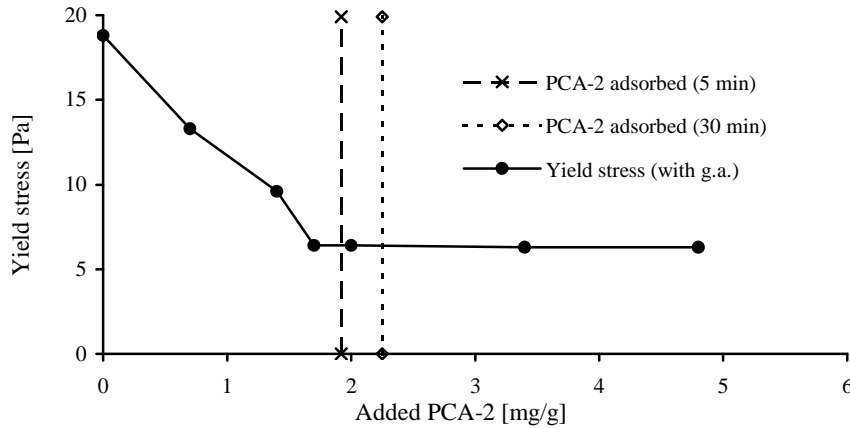

Figure 11 -   Yield stress in suspensions with cement ground with grinding aid. Values are given as a function of PCA-2 dosage. The vertical lines indicated adsorbed amounts.

The error margin of adsorption misinterpretation, which can be linked to polydispersity seems too small to explain the observed differences. Having to use more polymer than can be adsorbed onto the surface is an indication that there is either a kinetic limitation in adsorption, or an equilibrium.

For both cements, the minimum yield stress is systematically lower with polymer PCA-1 than with PCA-2. This difference cannot be accounted for by kinetics since PCA-2 is the faster adsorbing.

Since in model suspensions both PCA-1 and PCA-2 were both found to induce the same zeta potential, this factor cannot account for observed rheology differences. PCA-1 is larger, which can mean that it induces a larger steric repulsion or that the charge that it induces onto the cement particles is farther away from the plane of origin for calculating van der Waals forces. This effect which was found to be responsible for deviations from theory of surface forces measurements in silica based systems. Which of these two effects is dominant remains to be determined.

Finally, one sees that the cement with grinding aid is characterized in its dispersed state by lower yield stresses than the polymer ground without grinding aid. Both cements were ground to obtain the same specific surface area. Therefore, more energy (longer time)

had to be put into the grinding of the cement without grinding aid, probably causing surfaces to be more reactive. On the other hand, one of the designed effects of this grinding aid is to complex the ions from the C_4AF phase, which is often found around the C_3S. This complexation increases dissolution thereby the setting rate. On smaller time scales, it is possible that this dissolution might help to dissolve some interparticle bridging bonds.
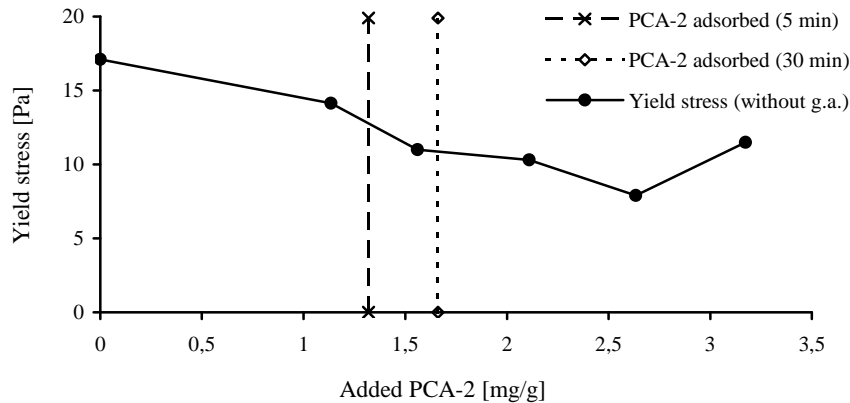

Figure 12 - Yield stress in suspensions without cement ground with grinding aid. Values are given as a function of PCA-2 dosage. The vertical lines indicated adsorbed amounts.

4. Conclusions

Dispersion mechanisms are mainly linked to adsorbed polymers. This conclusion has been reached from polymer PCA-2, which is found to adsorb rapidly. In addition its adsorption exhibits a step like function. This means that until the surface is covered, almost all the polymer added is adsorbed.

In this case, it is easy to see whether optimum dispersion is reached with or without needing to over-dose the superplasticizer with respect to the adsorption capacity of the cement in suspension. It was found for PCA-2, that optimum dispersion was reached before plateau in adsorption isotherm. This is in agreement with similar studies with model systems [9].

On the other hand, PCA-1, a polymer of the same type as PCA-2 but with a larger molecular mass and molecular mass distribution, had slower adsorption kinetics. This probably explains why the amount needed to achieve optimum dispersion exceeds the

amount adsorbed at the time of measuring. This over-dosage exceeds the errors that the polymer polydispersity can lead to.

PCA-1 produces suspensions with lower yield stresses than PCA-2. This must be a result of its larger molecular mass, leading to increased steric hindrance, or increased electrostatic repulsion due to a plane of origin for the electrostatic forces further away from the plane of origin of the Van der Waals forces. The relative importance of these effects remains to be clarified.

Finally, it is important to remark a couple differences between both cements. The minimum yield stress of the cements without grinding aid are slightly higher, but the amount of polymer required is smaller with respect to adsorbable amounts. It is important to draw attention to such differences. Indeed, the grinding history of cements is usually totally neglected in comparative studies on cement and superplasticizer interactions.

Minimal achievable yield stresses are slightly lower for the cement ground in presence of a grinding aid. On the other hand, the cement ground without grinding aid requires significantly less polymer to reach its plateau value of yield stress. This information has definite practical and economical implications.

With other grinding aids, the observed effects will have other magnitudes. It is suggested that a deeper knowledge of interactions between grinding aids and superplasticiers could lead to avoiding some cases of so-called cement/superplasticizer incompatibilities.

The yield stress criterion used here to analyze flow seems a good parameter for looking at supersplasticizer dosage effects on cement paste rheology. Other changes in flow behavior seem to occur around the same dosage as those noted for yield stress. Further analysis of the flow curves should provide more information about cement/superplasticizer interactions and will be carried out in future work.

5. Acknowledgements

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