Pergamon

Cement and Concrete Research 31 (2001) 1169–1176

CEMENT AND CONCRETE RESEARCH

A simplified view on chemical effects perturbing the action of superplasticizers

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Received 26 July 2000; accepted 30 April 2001

Abstract

Understanding and quantifying effects of superplasticizers in concrete is a complex task. Even for nonreactive systems, such as ceramic suspensions, the stabilizing effects of dispersants are a subject of ongoing research. In cementitious systems, hydration reactions can perturb the behavior of suspensions. In this article, we propose three categories to describe the interactions and state of the superplasticizers with the cement suspensions. The first part would be consumed by intercalation, coprecipitation or micellization, i.e., by the formation of an organo-mineral phase (OMP). A second part of the polymer could be adsorbed onto the surface of particles and help disperse cement agglomerates. The third part consists of the excess superplasticizer neither consumed nor adsorbed and which remains dissolved in the aqueous phase. Thus, at equal dosage, a cement with a larger degree of consumption (Part 1) could have a lower surface coverage and consequently poorer workability (for cements otherwise equal: specific surface, composition, etc.), unless an excess of superplasticizer is added to ensure saturation. Differentiating consumption from adsorption is essential for correct interpretation of experimental data, a fact that is not yet appreciated often enough and to which this paper attempts to draw larger attention.

Keywords: Dispersion; Rheology; Workability; Adsorption; Admixture

1. Introduction

Dispersion of agglomerated cement particles is recognized to constitute the main way by which superplasticizers improve the workability of concrete without increasing the water content [1–5]. Quantifying this mechanism is a difficult task and is further complicated by the ongoing hydration reactions of cement [1]. To overcome this difficulty various authors have chosen to study the effect of superplasticizers on model inert systems [6–12]. It has been possible, using suspensions of magnesium hydroxide, to link the fluidifying effect of superplasticizers exclusively to adsorbed polymers [12]. Such results are necessary, but not sufficient for understanding the behavior of the more complex cementitious suspensions. Indeed, superplasticizers interact with the ongoing chemical reactions [1,13,14]. An organo-mineral phase (OMP) can form around cement particles at the early stages of hydration consuming superplasticizers in an unproductive way. However, the extent to which this alters the workability is still unclear. Understanding these effects is a key aspect for predicting which combinations of cement and superplasticizers will lead to best workability and which ones will not. This clearly represents an objective of great practical importance.

A frequent approach is to compare the effects that various superplasticizers can induce on cements of different compositions. Such results can provide important information. However, they are highly susceptible to misinterpretation because of the large number of differences that can be encountered between the studied cements. The most obvious of these would be specific surface area, particle-size distribution, sulfate type and content, C_3A and alkali content. It has even been shown that a grinding aid can also influence the adsorption of some superplasticizers and cause workability differences between cements produced with the same clinker [15].

Within the ongoing effort towards a better understanding of the perturbation of workability that can arise from chemical reactions, we report a simplified overview. Its

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0008-8846/01/$ – see front matter
PII: S0008-8846(01)00534-8

objective is to describe how some mechanistic misinterpretation of experimental data can arise due to overlooking phenomena such as intercalation, coprecipitation, or micellization of superplasticizers in cement suspensions. The expectations of this simplified presentation are compatible with recent articles, which will be discussed throughout this paper to support the suggested interpretation [3–5,12–23].

Some of the superplasticizer is neither adsorbed nor incorporated into OMP. This part may play a role in dispersion of cement particles [24]. It is well known that suspensions in the presence of polymers display depletion effects that can induce flocculation. It is also argued, though still debated, that depletion may cause stabilization. Because this issue is currently speculative, at least in the case of cement for which no clear experimental evidence of the stabilizing role of nonadsorbed polymers, this question will not be further treated.

In this paper, we first present a series of experimental data that allow us later to develop a simplified but helpful picture of how cement chemistry can perturb the workability of superplasticized concrete.

2. Observations

2.1. Adsorbed layer thickness and interaction distance

The force between a cement compact and a platinum tip was measured by atomic force microscopy (AFM) in the presence of different polymers [4]. Comb copolymers induced the strongest repulsion and the importance of steric effects was emphasized. However, the fact that the interaction began at distances at least 10 times larger than might be expected from the length of the side chains of the studied polymers was not discussed. To obtain an idea of the layer thickness in which polymers could be found at cement particle surfaces, the same group determined by Auger spectrometry the carbon profiles in compacts [16]. In this study, unlike a previous one [17], measurements were performed both in direct and delayed adsorption modes. A striking result was that the depth of the layer in which carbon was found varied by a factor about 10 between both addition modes. In the case of direct addition, the depth they determined is compatible with the polymer size. It also is comparable to the distance at which interaction began in their AFM measurements [4]. However, in the case of delayed addition, both the depth of the carbon containing layer and the distance at which the interaction begins to be observed by AFM are 10 times larger than what might be expected from the length of the side chains of the comb-type copolymers used. In a schematic way, these results can suggest the situation shown in Fig. 1, where a polymer layer at the surface of the compact is 10 times greater when added directly with the mixing water. This apparent discrepancy will be explained later along with the other puzzling observation related below.

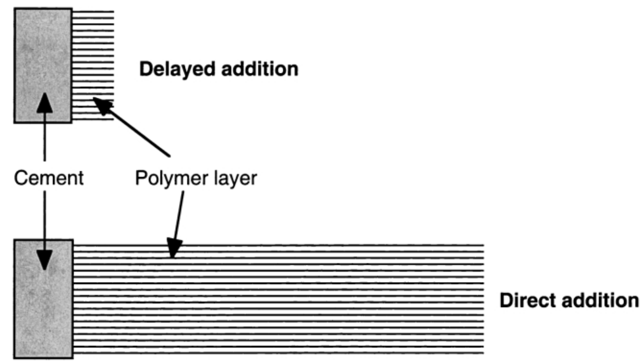

Fig. 1. Schematic representation of adsorbed polymer thickness differences that are suggested by Auger spectroscopy [16] and AFM measurements [4].

2.2. Effect of alkalis

Cements with different levels of alkalis were studied using direct addition of sulfonated naphthalene formaldehyde condensate (SNFC) [18]. It was found that the low-alkali cements tend to adsorb more superplasticizer than high-alkali ones. However, it was also observed that the workability of suspensions prepared with the low-alkali cements was poorer than that of the higher alkali cements. When small amounts (0.2%) of Na_2SO_4 were added to the polymer solution contacted with the low-alkali cement, the consumption of superplasticizers (reported as adsorbed) decreased and the workability improved [19,20]. So, with the addition of sodium sulfate, the low-alkali cements behave more like high-alkali cements.

A very important observation, which we will refer to later, must be made at this point. It is that the workability comparisons in these studies concern equal dosages of superplasticizers.

2.3. Effect of superplasticizer counter-ions

Piotte [25] has studied SNFC with different counter ions. The most striking result of his study was the catastrophic performance of the superplasticizer when the counter ion was magnesium.

It was reported that the precipitation of magnesium hydroxide, which would take place at close to pH 11, consumes much SNFC by coprecipitation or intercalation [26]. It was also reported that this did not appear to occur with a polysulfonate-polycarboxylate polymer referred to as PCA-2 used in other studies by the same group. This correlated well with the fact that the workability obtained with Mg-SNFC was substantially poorer than that with Na-SNFC, while Mg-PCA-2 and Na-PCA-2 led to similar performances.

Addition of $MgCl_2$ to the cement led to a decreased workability of the suspension when SNFC was in the mixing water. When delayed addition was used, no difference was observed between cements with or without added $MgCl_2$. The reduction of workability loss in direct addition mode is however greater if the $MgCl_2$ is dissolved in the mixing water rather than first mixed with the cement [26].

2.4. Effect of a grinding aid (triethanol amine acetate)

Two cements were produced by grinding the same clinker and gypsum in one case with triethanol amine acetate, a common grinding aid, and in the other without this grinding aid. Both were ground sufficient time to obtain the same final fineness. Their BET specific surface areas measured by N_2 adsorption were, respectively, 0.96 and 0.95 m^2/g. Their particle-size distributions were also very similar as shown in Fig. 2 [21].

The adsorption of a polysulfonate-polycarboxylate referred to as PCA-2 was significantly affected by the grinding history of the cement. On the other hand, a similar polymer, PCA-1, was not significantly affected. In addition to altering the adsorption, the use of a grinding aid led to small (about 25%), though statistically meaningful, decrease of the yield stress of cement suspensions [15].

2.5. OMP formation

The behavior of SNFC oligomers in calcium aluminate solutions has been studied and the formation of an OMP identified [13]. A calcium aluminate hydrate with a high degree of SNFC intercalation was detected. A model based on this detailed study was proposed for the intercalation of SNFC into calcium aluminate hydrates (Fig. 3). In cases where sulfate ions are present, ettringite formation is also detected. The amount of ettringite formed increases when the ratio of sulfate to SNFC increases. In addition, the formation of CSH/polymer complexes was recently identified [14]. These OMP were formed during the hydration of β-C_2S in the presence of polymer as well as by precipitation from an aqueous solution. They could be obtained with a wide range of polymers (non-ionic, anionic, cationic, and SNFC), invariably demonstrating that OMP formation occurs.

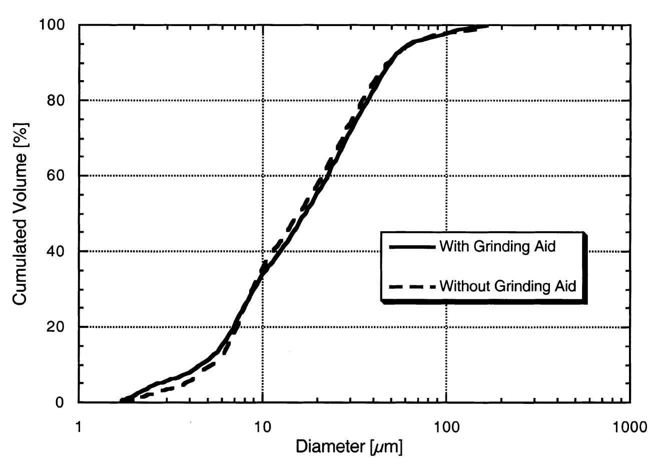

Fig. 2. Cumulated particle size distribution (measured with an X-ray disk centrifuge granulometer) of two OPC from the same clinker ground to the same fineness with and without a grinding aid, respectively.

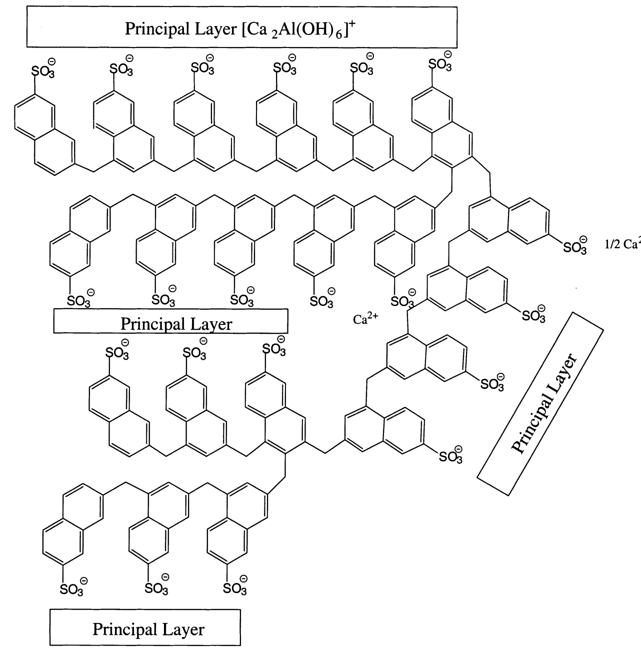

Fig. 3. Calcium aluminate layers intercalated with SNFC [13].

3. Discussion

In this section, we will argue that many of the behaviors reported above can be attributed to differences in the degree to which the polymers form OMP. The nature of this phase may vary depending on the circumstances. It can be formed by coprecipitation, intercalation, or micellization.

3.1. C_3A hydration products as a chemical sink for superplasticizers

The thickness of the organo-mineral layer is compatible with polymer size when polymer is added to a prewetted cement compact [16]. However, this layer is 10 times larger when the cement is not prewetted (direct addition). Therefore, the very fast reaction initiated by the contact between cement and water seems to be significantly perturbed by the presence of a superplasticizer. The morphology of AFt, one of the first phases formed on contact with water, is modified in the presence of superplasticizers. It has been suggested that SNFC acts as an inhibitor of crystal growth. In addition, one also expects intercalation of polymers during the formation of hydrated aluminate phases [13,22]. For this to occur, calcium aluminates and polymer must be simultaneously available in solution (even if it is directly at the particle surface). However, in the case of delayed addition most hydrated aluminates have been consumed in AFt formation at the time the polymer is added. In direct addition, a first layer of highly intercalated AFm is likely to form along with AFt in proportions that depend on the relative availability of polymer and sulfates [13]. If this process takes place, as is suggested, at the surface of the cement particles, then the schematization of dependence of layer thickness on addition mode that is presented in Fig. 1 can be taken one step further in order to explicitly integrate the effect of aluminates (Fig. 4). The last layer in this figure, for the direct addition mode, indicates that once the OMP is completed, the superplasticizer becomes available for adsorption onto the available surfaces. It is this fraction of the polymer that can be expected to contribute most to the dispersion of cement agglomerates as explained in Section 3.3.

3.2. Adsorption measurements

Much discussion on superplasticizer performances is linked to adsorption measurements that are most often performed by solution depletion. This gives adsorption as the difference between the amount of polymer present in the aqueous phase before and after contact with cement. What it really gives is an indication of the amount of polymer consumed both by OMP formation and adsorption. Solution depletion cannot distinguish between consumption and adsorption. Using "consumption" instead of adsorption could help clarify the results from this method.

Solution depletion data (consumption) cannot provide the concentration of superplasticizers adsorbed at the surface of cement particles. Therefore, because this factor is a key element in the correct evaluation of interparticle force changes, only little can be inferred using data from solution depletion results, as long as saturation has not been reached.

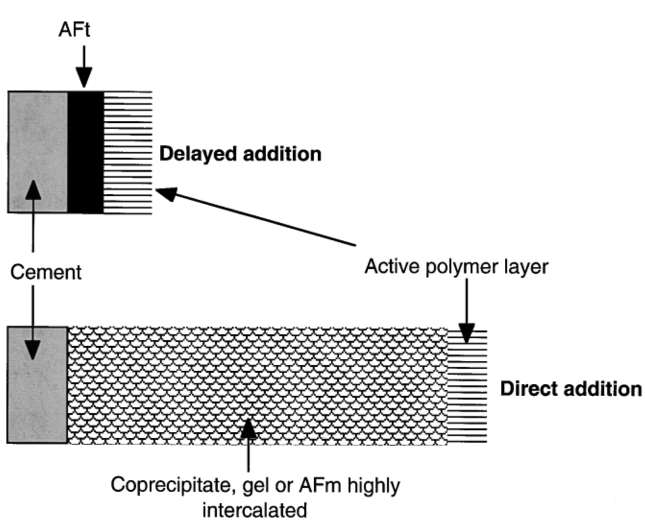

Fig. 4. Schematic illustration of the chemical sink effect of OMP precipitation. In the case of direct addition, many polymers are consumed uselessly. The plane of origin for the van der Waals force would be shifted from the surface towards the base of the polymer layer.

Saturation means that if more polymer is added to the suspension, it will (almost) entirely remain in the aqueous phase. None, or a very small fraction, of this additional polymer will be consumed either by chemical reactions or adsorption.

As far as understanding and quantifying dispersion effects, it therefore appears wiser at first to compare the optimum effects that superplasticizers can induce on cements (at dosages high enough to reach surface saturation), instead of comparing situations at equal dosages.

3.3. Adsorbed layer and dispersion

The effectiveness of dispersion by superplasticizers is believed to increase with the thickness of the adsorbed layer [5]. However, it depends on the hypothesis that the dielectric properties of the adsorbed layer are similar to that of the solution and significantly different from those of the cement particles. As far as the OMP is concerned, the most probable expectation is that its dielectric properties are much closer to those of the mineral phases of the cement than to those of the aqueous phase. Therefore, this layer will also take part in the van der Waals interaction leading to the agglomeration of particles.

So, until enough polymer has been added so that the superplasticizer can really induce a steric layer preventing agglomeration, little or no improvement can be expected in workability. In the case of polymers for which intercalation is very favorable, such as SNFC, this would only occur once the intercalation stops. For polymers containing side chains of ethylene oxide, a dispersion effect almost independent of dosage can be expected because these chains probably stick out during the formation of the OMP. The influence of the length of the side chains on the stabilization of hydrating alite has been shown [23]. Note, however, that the determining layer for reducing the interparticle force is the length of these side chains and not the thickness of the OMP.

This explanation is compatible with a reported interpretation of why the comb-type copolymers are less sensitive to the ongoing hydration reaction of cement than linear polyelectrolytes [27]. Indeed, it was proposed that the side chains (usually polyethylene oxide) maintain workability until the hydration layers growing from the surface have incorporated them (Fig. 5).

3.4. Role of sulfates and alkalis

So far, we have seen that the formation of OMP can reduce the amount of polymer available for modifying interparticle forces. For linear polyelectrolytes, this accounts for the significant differences in rheology that are observed at equal dosages between direct and delayed addition modes. The relative insensitivity of dosage mode for comb-type copolymers can be speculated to be linked to the ability of the polyethylene oxide side chains to extend

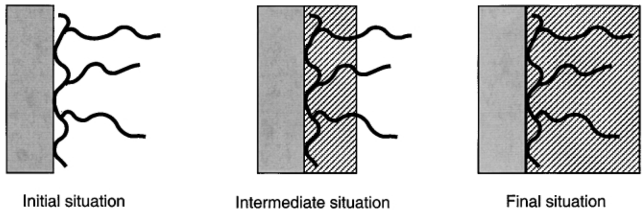

Fig. 5. Illustration of one explanation of the longer induced workability in the presence of comb copolymers, with polyethylene oxide as side chains. Adapted from Sakai and Daimon [27].

into the solution beyond the progressing front of forming OMP. For the linear polyelectrolytes, these reactions therefore represent a major problem for obtaining good workability. Delayed addition is one solution, but is often not considered to be practical.

Let us now consider the conditions that might alter the consumption of polymer through these reactions. In the absence of a superplasticizer the AFt phase is generally first precipitated. It is very unlikely that this phase can take polymers into its structure. However, the polymers can be intercalated into layer phase-like AFm [22] and C-S-H [14], and perhaps also into brucite-like phases in a process similar to coprecipitation.

So, if the objective is to favor a decrease of polymer consumption by such reactions, then AFt precipitation must be favored. This would require making sulfate available enough to be able to substitute for the superplasticizer in the structure detailed in Fig. 3. In other words, an increased sulfate content should enhance the formation of AFt over that of the OMP, as observed [13]. In fact, this expectation fully accounts for previous results [18,20] that showed that low-alkali cements had poorer workability and higher superplasticizer consumption than higher alkali cements.

Precipitation of gypsum and, in some cases syngenite, can occur at very early ages [28] and can limit the formation of AFt. The addition of rapidly soluble sulfates consequently should be adjusted to prevent precipitation of gypsum and syngenite.

There is sometimes confusion concerning the denomination of alkalis in cement. Chemical analysis usually reports them as Na_2O and K_2O. However, most come in the form of Na_2SO_4 and K_2SO_4 [29]. Thus, the so-called low-alkali cements are often in fact low "readily soluble" sulfate cements. For this reason they will have a higher consumption of superplasticizer through coprecipitation. Also because performances are compared at equal dosages, the high-alkali cement, which loses less polymer through coprecipitation, will give better results.

This clearly illustrates how comparing performances at equal superplasticizer dosages is misleading. Indeed, it is the adsorbed fraction and not the coprecipitated fraction of the polymers that causes dispersion and thereby improved workability. Therefore, unless comparisons are made between dosages allowing full surface coverage of both cements, one would effectively be comparing different surface coverages, which by itself can explain most differences in rheological behaviors. This can be misleading for interpreting the mechanism underlying the improvement of workability. Moreover, such misinterpretations could lead to unsound speculations for the development of new superplasticizers or for the solving of practical problems such as cement and superplasticizer incompatibilities.

From these speculations on the role of polymer consumption by intercalation reactions, one would expect the use of delayed addition to decrease differences between suspensions of high- and low-alkali cements. Unfortunately, such data are not currently available. However, it is reported that adding Na_2SO_4 to low-alkali cements enhances workability [19,20], an observation fully compatible with the above expectations, which has been illustrated in Fig. 6.

3.5. Effect of counter ion

We mentioned that if SNFC contains magnesium as a counter ion, very poor workability is obtained. In this case, another type of OMC would form. Indeed, above pH 11 the precipitation of $Mg(OH)_2$ is favored and it is in this product that polymers could be intercalated or trapped. For SNFC, which can contain nonlinear polymers, this probably leads to a gel, which would tend to bridge particles rather than disperse them. The model proposed for illustrating the OMP formed during the coprecipitation of calcium aluminates and SNFC oligomers (Fig. 3) could easily be adapted for this case by replacing a principal layer of $[Ca_2Al(OH)_6]^+$ by $Mg(OH)^+$.

Piotte [25], who had observed this effect of magnesium counter ions, speculated that $Mg(OH)_2$ was not the cause. He argued that this behavior is accompanied by exothermic heat, while as hydroxide precipitation would be endothermic. His argument, however, neglects the fact that consuming hydroxides from the solution will enhance dissolution of other phases, possibly leading to an overall exothermic process.

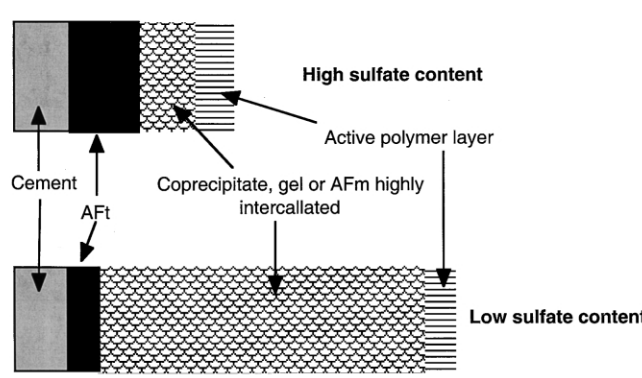

Fig. 6. Schematic representation of the effect of sulfate content in cement. With high amounts of sulfate, less polymer is lost in the chemical sink.

3.6. Effect of triethanol amine acetate grinding aid

We have seen that another factor modifying superplasticizer consumption and effectiveness can be the grinding history, as in the use of a triethanol amine acetate [15]. The ability of triethanol amine to complex ions from C_4AF phase and thereby enhance its dissolution has been reported [30]. This increase of aluminates in solution makes polymer consumption by intercalation into AFm type phases more likely.

Together with results concerning alkali and sulfate contents, this points to defining the reactivity of a cement towards a superplasticizer (Fig. 7). This reactivity can be modified by changing the chemical composition of the cement or with complexing agents such as triethanol amine, a common grinding aid. The more reactive cement would require more polymer to reach total surface coverage and optimal dispersion (except for polymers with nonadsorbing side chains).

The practical value of the effect of a grinding aid as a possible cause of unexpected superplasticizer/cement incompatibility is limited since cement factories do not change frequently their grinding aids. However, it highlights the influence of side factors on the behavior of superplasticizers in concrete. In particular, it indicates that comparative studies that would overlook this effect might well attribute workability differences to another cause that may only be a secondary one.

3.7. Comparison of efficiency between superplasticizers

In practice it is clear that cost plays a role in the selection of a superplasticizer and that comparing effects at equivalent dosages is useful (though comparing dosages at equivalent prices would be even better). However, such an approach cannot lead to a sound understanding of the dispersing power of the adsorbed molecules. It cannot therefore provide adequate information for the design of higher performance superplasticizers as well as a better usage of current ones. Controlling chemistry and interparticle forces are two distinguishable issues. If only efficiencies at equal dosages are compared (usually below saturation), it is not possible to obtain the mechanistic understanding necessary to improve either of these factors.

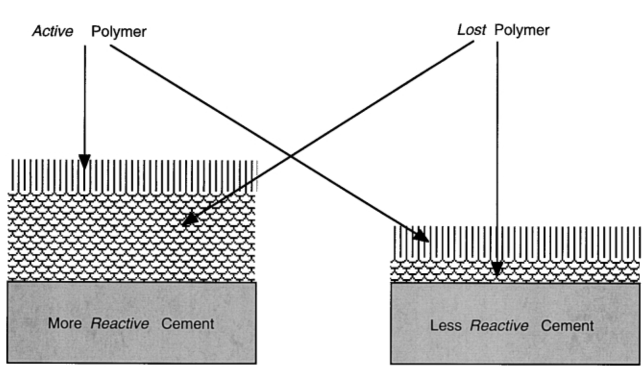

Fig. 7. Schematic representation of the concept of reactivity of a cement towards a polymer. Higher reactivity leads to a higher consumption of polymer in side-reactions and lower availability of the polymer for dispersion. As a result, more polymer is required for equal performance.

If superplasticizer is added in amounts below saturation, then its efficiency at the chosen dosage is intimately linked to the amount consumed by chemical reactions. The higher this consumption, the lower will be the amount of remaining superplasticizer available for inducing dispersion through adsorption. If studies of the superplasticizer performances on different cements overlook this aspect, then profound mechanistic misinterpretations regarding the mode of action of superplasticizers can be expected.

Though chemical consumption of superplasticizers must be further studied, comparing performances at superplasticizer saturation provides a first step for better understanding differences between performances in relation with the chemical structure of superplasticizers.

4. Conclusions

In this paper, we divide the superplasticizer added to a cement suspension into three parts. The first part is consumed by chemical reactions, in particular during the formation of AFt and C-S-H. The second part is adsorbed onto the surface of cement particles and is not integrated into OMP on the time scale required for placing concrete. The third part is the superplasticizer, which remains in the aqueous phase once enough polymers have been added to satisfy the polymer consumption, the system can be said to be saturated with polymer. Here one must bear in mind that depending on the adsorption kinetics polymers may remain in solution before full coverage has been obtained.

Part of the added superplasticizer can be intercalated in diverse hydration products and this fraction is no longer available for dispersing cement agglomerates. This process seems to be most important within the first minutes during which AFt normally has its highest precipitation rate. The sulfate availability is a key factor to allow a rapid AFt formation.

Delayed superplasticizer addition can reduce the polymer consumption especially for linear polyelectrolyte polymers, which are trapped in OMP, and will not contribute to dispersion. For polymers with side chains extending into solution, the addition time should have less influence on workability.

Part two of the adsorbed superplasticizer is the most important for dispersion, but is not easily measured. Analytical methods currently used do not allow distinction of adsorbed polymers from those in OMP, and consequently proper evaluation of the dispersive power of superplasticizers is not possible, unless using model powders or full surface coverage.

The role of the polymers remaining in solution is currently not clearly understood. This debated subject deserves to be considered in further detail because of its potential large implications on rheology of concrete at high superplasticizer dosages.

Finally, it must be emphasized that this paper is deliberately schematic. Its objective has been to bring wider awareness of the danger of misinterpreting data from studies aimed at understanding the mechanism through which superplasticizers allow increased fluidity and that mistakenly discuss adsorption instead of total superplasticizer consumption.

Acknowledgments

This work was made within the framework of the EUREKA Project 1363 ICHRWR and the financial support from the Swiss Commission for Technology and Innovation (CTI) and Sika are gratefully acknowledged. Professor H. Hofmann and Dr. P. Bowen from LTP Lausanne are thanked for their constructive remarks.

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