MODE OF OPERATION OF POLYSACCHARIDE STABILISING AGENT IN CEMENT BASED SYSTEMS AND INTERACTIONS WITH SUPERPLASTICISERS

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Abstract

Polysaccharides are incorporated into cement based systems in order to modify the rheological properties. Typically cellulose ethers, sphingan gums or starch ethers are applied. Depending upon their chemistry, molecular architecture, and adsorption tendency, polysaccharides interact differently with the entire cementitious system. Some stabilising agents like diutan gum mainly affect the cementitious paste; other stabilising agents like starch tend to interact with the sand fraction and even with the coarse aggregates. Cellulose shows more divers performances. Often stabilising admixtures like polysaccharides are used, when sophisticated rheological properties are adjusted. Therefore, polysaccharides are often used in combination with superplasticisers. This can cause interactions, particularly when the stabilising agent shows a strong tendency to adsorb on particle surfaces. Adsorptive stabilising agents may reduce the amount of adsorbed superplasticisers, thus affecting both viscosity and yield stress, while non-adsorptive stabilising agents mainly affect the plastic viscosity independently of the superplasticiser. Due to the strong influence of superplasticisers on the yield stress, influences of the stabilising agent on the yield stress retreat into the background, so that their major effect is an increase of the viscosity. The paper provides a comprehensive overview of how different polysaccharide superplasticisers affect cementitious flowable systems and points out the challenges of the combined use of polysaccharides and superplasticisers. Based on rheometric experiments and observations of the hydration process, time dependent effects on the workability as well as of the hydration of cement are presented.

Keywords:

Polysaccharides, Starch, Cellulose, Sphingan, Rheology, Cement, Concrete

1 INTRODUCTION

During the last 15 to 20 years, the use of stabilising admixtures in concrete has increased. In flowable systems they are often added supplementary to superplasticisers with the purpose of increasing the viscosity for better segregation resistance. Sometimes they are referred to as viscosity modifying or viscosity enhancing agents. As they typically affect both yield stress and viscosity, in this paper, they are referred to as stabilising agents (STA).

Polymeric STAs are typically based on polysaccharides (Khayat, 1998). Modified cellulose is often used as a linear polysaccharide. Through etherification, functional groups can be amended, adding anionic charges to the main chain. Other types of stabilising admixtures are sphingans such as welan gum or diutan gum, which are also linear polysaccharides like cellulose ethers. Their side chains consist of one or two monosaccharides and

their backbone contains carboxylate groups providing an anionic charge.

Another important STA type is modified starch. It can be retrieved from potatoes, cassava, maize, or rice and needs to be modified to be cold-water soluble. Starch is similar to cellulose, however the glucose units are arranged pointing in the same direction, while the glucose units of cellulose are arranged alternating to each other at a 180 ° angle. Furthermore, starches consist of two types of macromolecules, the linear amylose (0% - 30%) and the tree-like structured amylopectin (70% – 100%).

The effect of STA on rheological properties of mortar and concrete is extensive, depending on the type and modification of STA. In particular the combination with adsorptive superplasticisers can cause complex interactions. Adsorptive STAs may reduce the amount of adsorbed superplasticisers, thus affecting both viscosity and yield stress, while non-adsorptive STAs mainly affect the plastic viscosity independently of the superplasticiser.(Yammamuro et al., 1997)

For cellulose derivatives and welan gum, Khayat distinguished between different modes of operation, depending on the type and concentration: fixation of water molecules through adsorption, immobilization of water through association, and intertwining of polymers (Khayat, 1998). Due to the similarity between diutan gum and welan gum, these mechanisms should apply for both likewise.

According to Simonides and Terpstra the stabilising mechanism of starches differs. According to the authors, starch molecules, particularly the amylopectin, spreads out between the particles, thus maintain a stable distance (Simonides and Terpstra, 2007). This means, starches affect yield stress, particularly at rest, rather than plastic viscosity. Consequently, the stabilisation mechanism thus involves the whole system, including fines and aggregates.

From these observations, two stabilising modes can be distinguished: stabilisation of the fluid (diutan gum) and stabilisation of the particles in the fluid (starch).

Choosing a type of STA and a specific amount offers the possibility of adjusting the rheology according to specified performance criteria. However, besides rheological effects, STA also affects hydration. Particularly accelerated or retarded setting can be observed (Khayat, 1998, Rajayogan et al., 2003, Izumi et al., 2006, Schmidt and Kuehne, 2007, Schmidt, 2008) These effects are not yet fully understood. It is said that retarded setting may be caused by adsorption of STA on cement particles, modifying the precipitation of minerals (Khayat, 1998). Furthermore, it is reported that the grade of retardation depends upon the C_3A content of the clinker: lower C_3A content causes less retardation (Peschard et al., 2004). The individual composition of stabilisers is reported to be a factor. According to Pourchez et al. the calcium binding capacity, that causes complexation, and a possible chelation due to alkaline instability, might cause set retardation (Pourchez et al., 2006). Results with cellulose ethers, however, only showed a negligible calcium binding capacity and a high stability against high alkaline media. For the sphingan diutan gum it is also reported that the double rhamnose side chains sterically shield the carboxylate backbone, thus avoiding cross-linking by calcium ions (Phyfferoen et al., 2002). The effects of polysaccharides on rheology and setting are not thoroughly understood at this date.

The present paper shows some significant effects that polysaccharide stabilising agents can incorporate into flowable cementitious systems with focus on systems without superplasticiser and with superplasticiser.

Rheometric results of of cement pastes and self-compacting concrete (SCC) are presented. Furthermore the influences of stabilising agents on the early hydration are discussed.

2 DIFFERENT MODES OF OPERATION OF POLYSACCHARIDES

Stabilising agents can affect flowable cement based systems in different ways. Figs. 1 and 2 show experiments where the dosages of starch and diutan gum were chosen in a way that the plastic viscosity

in a Couette type rheometer (Schleibinger Viskomat NT) in a cylindric cell was determined to be 8.0 mPa·s in an aqueous system. For starch and diutan gum the dosages were identified to be 20 g/l and 1.0 g/l.

Fig 1 shows that starch does not have a prominent effect on the increase of the yield stress when added to pure water, but increases the plastic viscosity. Diutan gum increases the yield stress and plastic viscosity directly when added to water. It is also obvious that the diutan gum affects the viscosity much more efficiently than the starch based agent.
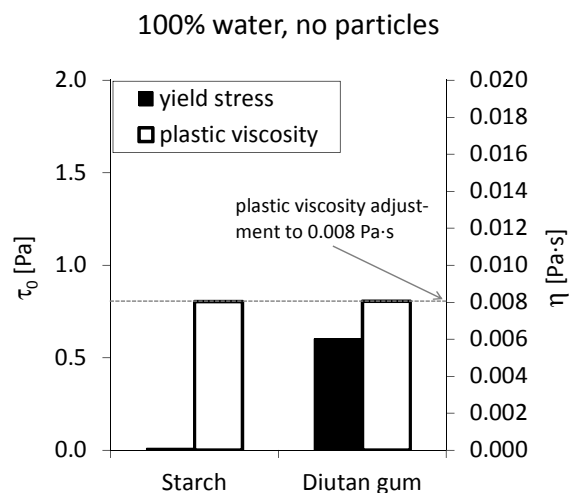
100% water, no particles

Fig. 1: Yield stress and plastic viscosity of aqueous systems with starch and diutan gum at 20 g/l and 1 g/l, respectively. Measurement based on ramp profile in cylindric cell in a Couette type rheometer.
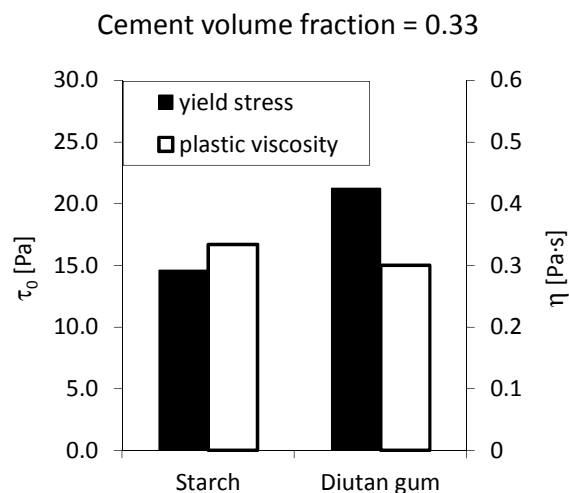
Cement volume fraction = 0.33

Fig. 2: Yield stress and plastic viscosity of water-cement systems at particle volume fraction of 0.33 with starch and diutan gum at 20 g/l and 1 g/l, respectively. Measurement based on ramp profile in cylindric cell in a Couette type rheometer.

Figure 2 shows a dispersed cementitious system at a cement particle volume fraction of 0.33. Here, it can be observed that both starch and diutan gum signficantly affect the yield stress and have different effects on the plastic viscosity. In relation to the aqueous system, the stabilising effect of the starch based agent has significantly increased. The results show that the starch based stabilising agent obviously requires particles in order to become

effective. It could be found that the efficiency of starch increases with higher particle volume fraction (Schmidt et al., 2013a). Hence, the mode of operation for starch and diutan gum can be distinguished between fluid stabilisation and particle stabilisation (Schmidt, 2014).

3 POLYSACCHARIDES IN THE PRESENCE OF POLYCARBOCYLATE ETHERS

Modern flowable concrete and mortar types like self-compacting concrete (SCC), high performance concrete (HPC), ultra-high performance concrete (UHPC) or repair mortar often contain high amounts of superplasticisers (SP). Typical SPs for high performance concrete types are polycarboxylate ethers (PCE). These are comb polymers consisting of a polycarboxylic backbone and ethylene oxide graft chains. Their dispersing mechanism is based on their adsorption on positively charged surfaces and a steric hindrance of the particles upon adsorption (Schmidt et al., 2014, Plank and Hirsch, 2007). Since a cement grain consists of multiple phases exposed to the pore solution exhibiting different zeta potentials in its environment, PCEs adsorb preferably on the aluminous and ferrous phases of the cement clinker. More importantly, they adsorb on newly formed hydration phases upon addition of water such as ettringite and monosulphate, which occur by reaction of water, gypsum and calcium aluminates. Since PCE is added in low amounts, it has a negligible effect on the total solid volume fraction in cement or concrete systems. Thus, the influence on the plastic viscosity is small but there is a very prominent effect on the yield stress

Some polysaccharides such as cellulose, welan and diutan gum are known to provide anionic charges, which makes them adsorb on particles. It is reported that the adsorption of present SPs avoids the adsorption of diutan gum (Phyfferoen et al., 2002). However, there are also studies that indicate that adsorption can still take place to certain amount in presence of superplasticisers (Sonebi, 2006) and that particularly the time dependent rheology of flowable cementitious systems can be affected by competitive adsorption of PCE and STA (Schmidt, 2014).
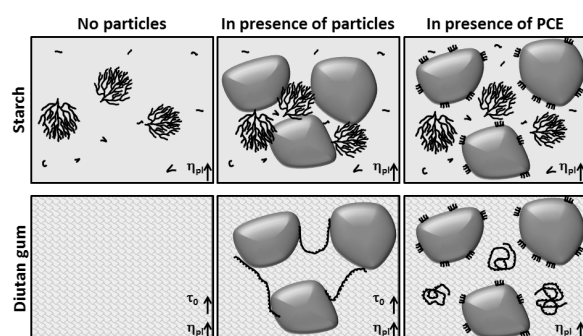

Fig. 3: Suggested stabilising mechanism of starch in different systems of solid particle volume fractions (Schmidt et al., 2013a). In the absence of particles, starches have little effect on the yield stress, while diutan gum forms a network. In the presence of particles starches become effective as spacers, while diutan gum can additionally adsorb. In the presence of PCE, both polymers show a similar effect.

In a study on limestone dispersions and cement dispersions at varied solid particle volume fractions it was shown that starch and diutan gum show similar stabilising mechanisms in the presence of high amounts of PCE despite a prominent difference in their effect on systems without PCE (Schmidt et al., 2013a).

4 POLYSACCHARIDES AND PCE IN FLOWABLE CONCRETE

Concrete systems are complex and contain a high number of mutually interacting constituents. Therefore effects of chemical agents that may occur prominently in cement paste systems do not inevitably have to occur in the same order of magnitude in concrete systems due to the influence of multiple overlapping effects (Schmidt et al., 2007).

Figs. 5 and 6 show the time dependent yield stress and plastic viscosity for SCC with varied STA agent based on either starch or diutan gum.

The analyses were conducted with a mobile concrete rheometer (ConTec Rheometer-4SCC). By measuring the torque in mA at varied rotational speeds and appliance of a Bingham curve, this equipment allows qualitative conclusions on yield stress and viscosity of the mixtures. Since there is no reliable method for the conversion of torque and rotational velocity into shear stresses and shear rates, the results can only provide qualitative information on changes in yield stress and plastic viscosity. Therefore the measurements are referred to as G-Yield for qualitative observations of yield stress changes and H-Viscosity for qualitative changes of the plastic viscosity, respectively.

The rheological properties of the SCC are largely determined by two effects, the growth of hydrates and the respective adsorption of superplasticiser molecules. The yield stress reduction is predominantly influenced by the amount of adsorbed PCEs (Schober and Flatt, 2006). These adsorb competitively with sulphate ions upon occurrence of adsorption sites (Plank and Hirsch, 2007). At low temperatures, the growth of hydrates takes place significantly slower than at higher temperatures.

Due to the lack of sufficient adsorption sites for PCE to become effective, the yield stress at 5 °C is higher than at 20 °C and 30 °C regardless of the STA type (Fig. 5). For each STA a characteristic performance can be observed at a temperature of 5 °C. Starch provides lower yield stress than diutan gum initially but the yield stress of starch increases with time and matches the yield stress of diutan gum after 90 minutes. Due to the low temperature, a yield stress increase due to the formation of significant amounts of hydrates can be excluded. Therefore the fluid phase stabilisation of diutan gum seems to maintain the yield stress in an identical range throughout the observation time. The particle stabilisation of starch, however, does not seem to remain stable over the course of time. The performance loss of the stabilising effect of starch based STA was already reported before (Schmidt et al., 2007).
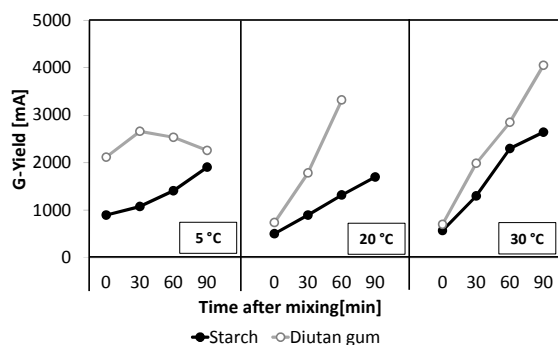
Fig. 5: Influence of polysaccharide type on the yield stress evolution in SCC over the course of time at varied ambient temperatures. Yield stress is expressed qualitatively as G-yield, derived from the electric current at varied rotational velocities in a step profile (5 s pre-shearing at 0.45 s^{-1} followed by a stepwise decrease to 0.05 s^{-1} in 8 steps á 5 s).
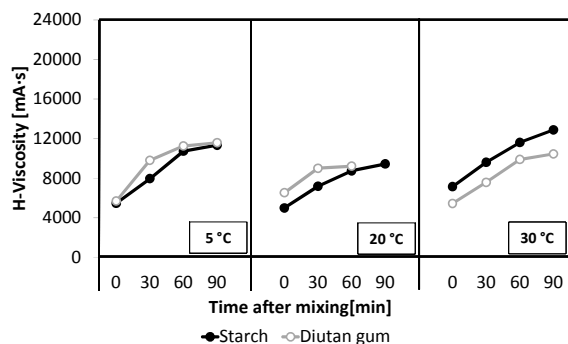

Fig. 6: Influence of polysaccharide type on the plastic viscosity evolution in SCC over the course of time at varied ambient temperatures. Plastic viscosity is expressed qualitatively as H-viscosity, derived from the electric current at varied rotational velocities in a step profile. (5 s pre-shearing at 0.45 s^{-1} followed by a stepwise decrease to 0.05 s^{-1} in 8 steps á 5 s).

At a temperature of 20 °C the time dependent yield stress evolution shows different characteristics. The yield stress increases steadily over the course of time regardless of the used STA. The increase of the yield stress can be explained by ongoing growth of hydration phases in the neighbourhood of adsorbed PCE that consume supplementary non-adsorbed molecules as well reduce their steric effect. The retention of the yield stress is much better with starch. SCC with diutan gum shows a much quicker yield stress increase. At 90 minutes after mixing, the mixtures with diutan gum were too stiff to be measured reliably.

The observations at 30 °C are very similar to those at 20 °C but the increase of the yield stress takes place more rapidly for both stabilising agents. The accelerated hydration reaction causes a quicker consumption of PCE, yielding an even more rapid loss of performance. Similar to the observation at 20 °C, the SCC incorporating diutan gum shows more rapid stiffening than the starch based SCC.

As can be observed in Fig. 6, the time dependent increase of yield stress with diutan gum at 20 °C and 30 °C is not accompanied by a comparable increase in viscosity. This suggests that the quicker yield stress increase of diutan gum systems is not caused by an effect of diutan gum that would accelerate the cement hydration.

The yield stress strongly depends upon the adsorption of PCE, but at high dosages the PCE amount does not significantly influence the plastic viscosity. Therefore it seems to be more likely that the more rapid yield stress increase of SCC with diutan gum is caused by an interaction of the STA with the PCE. Diutan gum contains anionic charges in the backbone, and thus potentially adsorbs on hydration phases or interacts with ions and polymers in the surrounding solution. Possible interactions could be either competitive adsorption between PCE and diutan gum or possible complexation of PCE and diutan gum.

5 POLYSACCHARIDES' EFFECT AFTER PLACING WITHOUT AND WITH PCE

Rheology modifying agents like SP and STA are typically added to a concrete system in order to affect the workability period. However, since the mode of operation of these agents interacts with the hydrating cement system, the polymers continue to have effects on the cementitious system even after placement of the concrete. This can have prominent effects on the entire process until the time of demoulding.

The Figs. 7 and 8 show how differently starch based STA can affect the setting of cementitious systems depending upon the temperature and the presence or not of PCE superplasticiser. The figures show the example of starch STA. However, the same qualitative observations were made for diutan gum based STA.

The histograms show the ratio of the time of the final set with STA vs. the time of the final set without STA. Hence, values higher than unity represent a set retardation due to STA, values lower than unity represent acceleration. The final set defined for the generation of the histograms was specified at a needle penetration depth of 30 mm. This modification was necessary, since due to bleeding and shrinkage, the top layers of the specimens varied greatly, resulting in indistinct curves close to the real final set at 0.5 mm. This effect occurred most prominently at low temperatures, when hydration was strongly retarded.
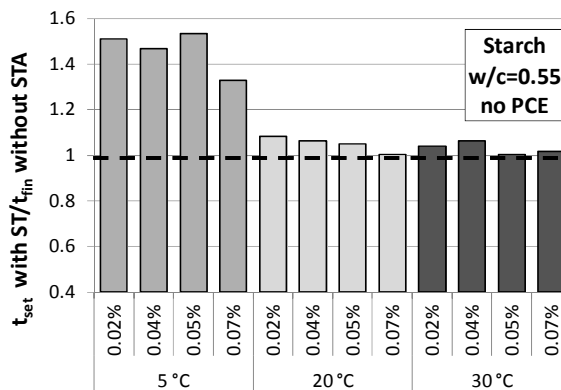

Fig. 7: Influence of starch on the setting time of cementitious systems without superplasticisers at varied temperature (CEM I 32.5; w/c = 0.55).
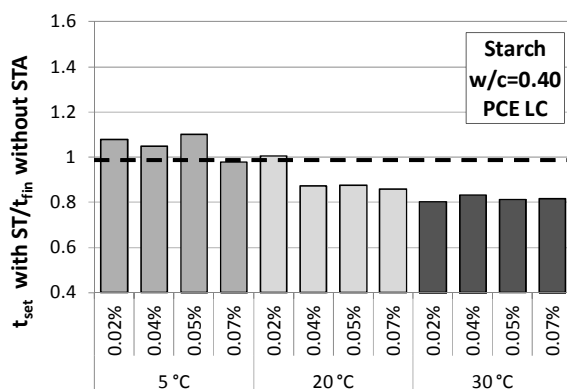
Fig. 8: Influence of starch on the setting time of cementitious systems with PCE superplasticiser (0.6% solids by mass of cement) at varied temperature (CEM I 32.5; w/c = 0.40).

In mixtures without PCE the addition of any amount of STA causes a set retardation (Fig. 7). The retardation is negligible at 20 and 30 °C and rather strong at 5 °C. No clearly identifiable effect of the amount can be observed, indicating that the retardation might not be affected by a particular amount of STA but rather by the fact that STA is part of the mixture at all.

In the presence of PCE, the effect of the STA on the setting varies greatly from the behaviour without PCE (Fig 8). Similar to the case of no presence of PCE, retarded setting can be observed at 5 °C, while at higher temperatures the presence of STA reduced the retarding effect of PCE. No clear influence of the amount of STA can be observed.

However, although the Figs. 7 and 8 indicate that the presence of STA at moderate and high temperature causes a reduction of the retarding effect of PCE, this is not a general conclusion. The effect seems to be strongly dependent on the environmental temperature, the charge density of the PCE, the cement type used as well as the binder setup (Schmidt et al., 2013b, Schmidt, 2014, Schmidt et al., 2012). Nevertheless, in all aforementioned observations it could be observed that regardless of the setup, STA generated accelerated setting or only slightly retarded setting in systems with PCE. In systems without PCE generally retardation by STA could be observed and the retardation was more pronounced than in the presence of PCE. Hence, it can be concluded that the retarding effect of combined PCE and STA, regardless of their modification, seems to be less strong than the sum of their individual retarding effects. This can be only slight retardation caused by the STA or even less retardation than in systems with PCE but without STA.

The discussion of these observations is rather hypothetical. It is known that PCEs have a strong retarding effect on the hydration of cement. In most cases also polysaccharides have a retarding effect, as also in the results presented in Fig. 7.
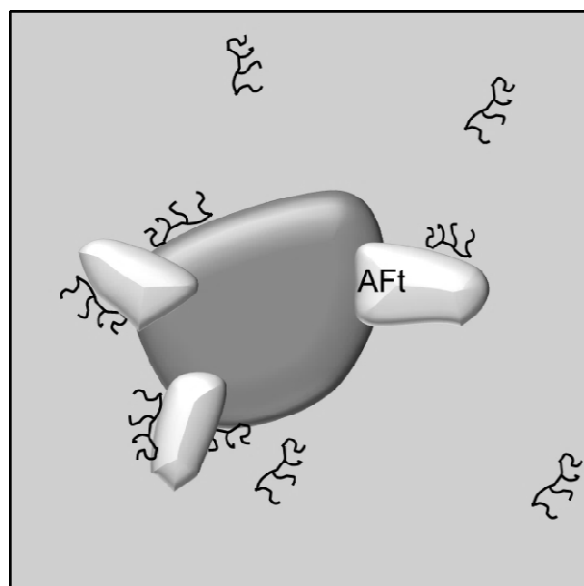

Fig. 7: Ettringite formation and adsorption at the time of accelerated C-S-H formation without STA: PCE and sulphate ions compete for adsorption sites, thus causing lower ettringite formation and hence lower adsorption of PCE.

However, the retarding effect of PCE is typically significantly stronger than the effect of polysaccharides. The fact that PCE in combination with STA shows less retardation than pure PCE therefore indicates that an interaction between STA and PCE takes place that reduces the retarding effect of PCE.

It is known that PCE dosages above the maximum adsorption dosage continue to have a retarding effect on hydration (Sowoidnich and Rößler, 2009, Schmidt et al., 2009). Sowoidnich and Rößler concluded that the retarding effect of superplasticisers can be attributed to the non-adsorbed rather than to the adsorbed PCE polymers (Sowoidnich and Rößler, 2009). If the latter conclusion is taken as a basis and the setting is mainly attributed to the hydration of C-S-H (Scrivener and Nonat, 2011), the reason for the accelerated setting of PCE systems in the presence of STAs, could be explained by a higher adsorption of PCEs on aluminate hydrate phases, so that the adsorbed PCEs do not interfere with the later C-S-H reactions.

PCEs mainly adsorb on aluminate and ferrite clinker phase surfaces (Yoshioka et al., 2002). However, the major adsorption sites for PCE during the first period are ettringite and monosulphate, of which ettringite can attract significantly higher amounts of PCE (Plank and Hirsch, 2007). As a result, a system with high ettringite content would attract more PCEs at early stage and in return leave less PCE molecules to interfere with the later accelerated C-S-H hydration at the setting period.

Assuming that the STAs reduce the mobility of PCEs much more than the mobility of interacting ions such as sulphate ions, it is possible that indeed systems with STAs and PCE generate higher amounts of ettringite than systems with PCE without STA. The lower mobility of PCEs could happen through increased viscosity of the pore solution, a slowed down unfolding of the PCE molecules, or through entanglement of the PCE.
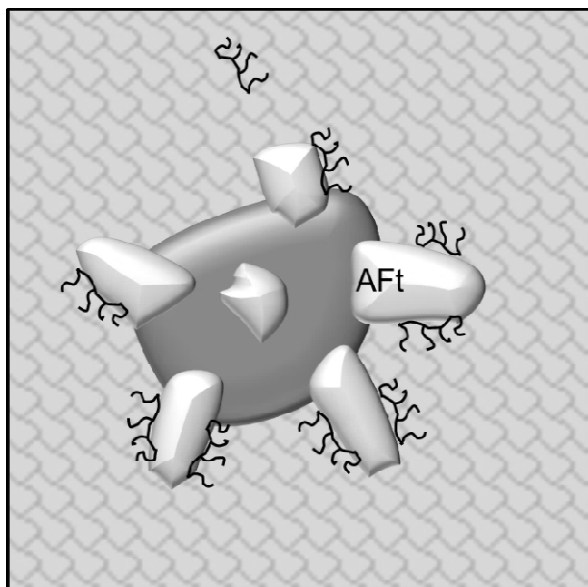
Fig. 8: Ettringite formation and adsorption at the time of accelerated C-S-H formation in the presence of STA: PCE adsorption is reduced by STA to the benefit of sulphate adsorption, thus higher amounts of ettringite are formed that cause more PCE adsorption over the course of time.

Less or no competitive adsorption between PCE and sulphate ions would take place in the presence of STA, since the PCE is slowed down by the STA to the benefit of a better sulphate ion adsorption.

The available aluminates preferably would interact more quickly with sulphates, causing formation of ettringite rather than monosulphate. The increased amount of ettringite would attract higher amounts of PCE over the course of time, yielding earlier setting.

This effect is shown in the Figs. 7 and 8. The higher ettringite formation shown in Fig. 8 causes higher PCE adsorption, thus less free PCE in the pore solution than in Fig. 7.

Such explanation mechanism would also be in line with the observation that at 5 °C the presence of STA causes more retardation, which clearly diverges from the behaviour at higher temperatures. At 5 °C the precipitation and dissolution processes are generally much slower. The mobility reduction of the PCEs by STAs retreats into the background as a withdrawal of PCE from early reactions would not automatically increase the reactivity of aluminate and sulphate due to the slowdown of the hydration. Thus, general retardation can be observed.

The presented hypothesis is only based on observations of macroscopic phenomena. The measurement results do not give conclusive evidence. Alternative interpretations, e.g. based on the crystal structure of ettringite or association or complexation of PCEs with STAs, are thinkable as well. Further studies are in progress.

6 CONCLUSIONS

Polysaccharides as rheology modifying admixtures play an increasingly important role in modern concrete technology.

This paper summarises some important effects of polysaccharides in cement based flowable systems. In general polysaccharides, regardless of the chemical base, increase the plastic viscosity, but their effect on the yield stress can vary.

In dispersed systems sphingan based STAs directly increase the yield stress of the fluid phase, and in return affect the rheology of the dispersion. Starch based STAs only show little influence on the yield stress of the fluid phase, but in the presence of solid particles their effect on the yield stress increases significantly with increasing particle volume fraction.

However, in the presence of adsorbing polymers sphingan and starch based show very similar effect on the rheology, they increase the plastic viscosity without a strong influence on the yield stress of the total system.

For concrete systems sphingan based STA seems to interact stronger with PCE over the course of time. Self-compacting concrete with sphingan based STA showed quicker loss of workability than starch based STA. The reason can be found in the competitive adsorption of the anionic sphingan STA and the anionic PCE.

Polysaccharides also affect the setting of cement based systems. In general they cause a slightly retarding effect on the hydration. However, in the presence of PCE the hydration was less retarded when STA was in the system than in identical systems without STA. This effect may be explained by a mobility reduction of PCE in the presence of STA causing a higher adsorption of sulphate ions and thus a higher ettringite formation. The higher ettringite formation eventually causes a higher PCE adsorption at a point in time when the accelerated C-S-H formation begins.

XRD investigations on STA modified cementitious systems with PCE will show whether the explanation model can hold true.

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