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Interactions of polysaccharide stabilising agents with early cement hydration without and in the presence of superplasticizers

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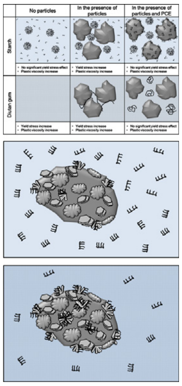
HIGHLIGHTS

- The effect of polysaccharide stabilising agents on rheology and setting was studied.
- Diutan gum affects yield stress in the liquid efficiently, while starch requires particles.
- In the presence of superplasticizers, starch and diutan gum have similar effects.
- Stabilising agents can reduce retarding effects of superplasticizer.

GRAPHICAL ABSTRACT



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ABSTRACT

Polysaccharides are incorporated into cement based systems in order to modify the rheological properties. Typically, cellulose ethers, sphingan gums, guar gum 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 and guar gum shows more diverse performances.

Typically stabilising admixtures like polysaccharides are used, when sophisticated rheological properties are adjusted. Therefore, polysaccharides are often used in combination with superplasticisers, which are added to reduce the yield stress of concrete. 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 plastic 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 and discussed.

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1. Introduction

During the last 15–20 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 plastic viscosity, here, they are referred to as stabilising agents (STA).

Polymeric STAs are typically based on polysaccharides [1,2]. Modified cellulose is often used as a linear polysaccharide. Through etherification, functional groups can be amended and charges can be incorporated. 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 [3–8]. Also guar gum STA has been matter of recent research [9,10]. Guar gum consists of a mannose backbone with randomly arranged branchpoints of galactose. For construction materials, it is typically hydoxy propylated. Another important STA type is modified starch. It can be retrieved from potatoes, cassava, maize, or rice [11,12] and needs to be modified to be cold-water soluble [13–15]. Starch is chemically 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%). Starch based stabilising agents typically require higher dosages than sphingans to become effective [14,16,17]. However, they are much cheaper in price, which makes them attractive for the concrete market [18].

Typically, the mode of operation of STAs is explained by their capability to absorb water. The absorption capacity is assumed to increase with increasing molecular mass [19]. However, there is no linear correlation between molecular mass and water retention effect [20]. It is often assumed that most polysaccharides may be incompatible with the hydration of cement due to degrading in the high alkaline environment in the cement paste or loss of effectiveness due to shrinkage in the presence of metal ions [4,20,21], but there are also studies that show a high stability in alkaline environment for a variety of STAs [22]. Hence, the effect on yield stress and plastic viscosity can also depend strongly upon the degree of modification of the STA [9,10], which affects the alkaline stability.

The effect of STA on rheological properties of mortar and concrete is extensive, depending on the type and modification of STA. Major influences are linked to the molecular weight, the molecular architecture, and the dosage [23,24] as well as to mixture parameters such as the water cement ratio and the pore solution chemistry. For cellulose derivatives and sphingans, 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 [1,25]. The influences therefore mainly take place in the liquid phase. Due to the nature of the STA effect, the effectivity of the stabilising agent is dependent upon the shear rate, and thus the shear regime can have a strong effect on the observations [26]. 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 [27]. 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 (sphingans) and stabilisation of the particles in the fluid (starch). Therefore, this study focuses on diutan gum and starch based STA. Cellulose and HPG are likely to act in between these mechanisms depending upon the structure and modification.

Furthermore, supplementary admixtures can interfere with STAs. In particular, the combination with adsorptive superplasticisers can cause complex interactions. Flowable concrete systems with complex rheological behaviour typically contain high amounts of SPs, typically PCE. STAs and PCEs distinguish strongly from each other in their nature. PCEs may have molar masses between 10,000 and 200,000 g/mol and typically radii of gyration between a few and 150 nm [28–33], while for different polysaccharide STAs molar masses between 300,000 and 5,000,000 g/mol and radii of gyration between several tenth and 500 nm are reported [4,12,21,34]. Admixtures such as cellulose, welan and diutan gum are known to adsorb on particles [1,4,34–37]. Also adsorption of starch was reported by Palacios et al. [38], however, in comparison to welan gum, the adsorption was low. 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 [19]. However, it is also reported that the adsorption of present superplasticisers prevents the adsorption of diutan gum on particles [4]. Since adsorption is not the sole stabilising mechanism of diutan gum, this lack of adsorption in the presence of PCE does not inhibit a stabilising effect, but it assures no negative influence on the efficiency of PCE. The tendency for STA to adsorb competitively with PCE also strongly depends on the order at which PCE and STA are added. However, there are results that suggest that adsorption always takes place to a certain amount also in the presence of superplasticisers [3]. A delayed addition of STA was found to cause less STA adsorption, since adsorption sites were already blocked by PCE [38].

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 [1,16,21,39,40]. 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 [1]. 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 [24]. 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 [22]. 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 [4] so that calcium binding is supposedly not the only effect for retardation. 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 based on starch and sphingan can incorporate into flowable cementitious systems with focus on systems without superplasticiser and with superplasticiser. Starch and sphingan were chosen because of their characteristic difference of their stabilising effect. Rheometric results of cement and limestone filler pastes and self-compacting concrete (SCC) are presented. Furthermore, the influences of stabilising agents on the early hydration are discussed without and in the presence of polycarboxylate ether based superplasticizer.

2. Experimental setup

The rheometric investigations on starch in water and cement pastes were investigated using a Couette type rheometer (Schleibinger Viskomat NT) and a cylinder cell. Plastic viscosity and yield stress were determined at varied dosages of STA in deionised water and in cement pastes with OPC (CEM I 42.5 R) at a solid volume fraction of 0.33. For the experiments a ramp profile was used with an upward ramp, plateau and downward ramp, each lasting 1 min. Each experiment was repeated two times.

Rheometric investigations on cement paste and limestone filler paste in the presence of superplasticizer were conducted with pastes at a solid volume fraction of 0.50 and 0.40 for limestone filler and OPC (CEM I 42.5 R), respectively. Low charge polycarboxylate ether superplasticizer was used with a solid content of 30%. The same rheometer as mentioned before was used, but a double gap cylinder cell was used for the experiments. A ramp profile was set up with an upward ramp, a plateau and a downward ramp for 30 s, 30 s, and 180 s, respectively. Each experiment was repeated twice.

Concrete investigations were conducted with a concrete rheometer type CONTEC Rheometer-4-SCC. By measuring the torque in mA at varied rotational speeds and under the assumption of a Bingham behaviour, this equipment allows qualitative conclusions on yield stress and viscosity of the mixtures. Since the conversion of the measurement data to fundamental physical values is debatable and not required for the interpretation of the observed effects, no conversion was made. Therefore, the results are expressed as G-Yield for qualitative observation of yield stress changes and H-Viscosity for qualitative changes of the plastic viscosity, respectively.

After 10 s pre-shearing at 0.45 s^{-1} the torque was reduced in eight steps by 5 s^{-1}. Each step was held for 5 s. The concrete was composed of 350 kg/m^3 of OPC (CEM I 42.5 R), 130 kg/m^3 of limestone filler, 175 kg/m^3 of water, and 838 kg/m^3 sand (quartz sand from 0.1–4 mm), and 831 kg/m^3 of coarse aggregates (quartz aggregates from 4 to 16 mm). High charge density polycarboxylate ether superplasticizer was used with a solid content of 20%. The solid PCE dosage in the concrete was 0.44% by mass of cement.

The setting experiments were conducted in an automatic Vicat testing machine (ToniSET) with 11 slots. OPC (CEM I 32.5 R) was used for the experiments at a solid volume fraction of 0.55 and 0.40 for pastes without and with PCE superplasticizer, respectively. Due to the high experimental effort only one measurement was conducted for each variation. The PCE used for the experiments was a low charge density PCE with a solid content of 30%. The solid PCE content in the cement pastes modified with PCE was 0.6% by mass of cement.

3. Different modes of operation of polysaccharides

Fig. 1 shows the influence of the dosage of starch and diutan gum on yield stress and plastic viscosity of water and STA mixtures under the simplified assumption of Bingham behaviour. Particularly at high dosages, the Bingham model cannot fully describe the material properties of STA modified fluids, but for easier comparison it was considered as sufficiently precise. While there is a nearly linear increase of the yield stress with increased dosage of diutan gum, the effect of starch on the yield stress is negligible. At the same time, both stabilising agents cause a distinct increase of the plastic viscosity with increased dosage.

Fig. 2 shows the same observation for cement pastes at a solid volume fraction of 0.33. In the presence of cement particles, both diutan gum and the starch have similar effects as in the water systems. The increase of the yield stress with increased dosage of diutan gum is very pronounced, while the effect of the starch dosage on the yield stress is negligible. Nevertheless, it has to be noted that unlike in the water system, the presence of starch incorporates a distinct yield stress. With regard to the plastic viscosity, it can be observed for both STAs that a dramatic increase takes place at low dosages of both agents, and that increasing dosage also increases the plastic viscosity, however with increased dosage the effect is also reduced.

Figs. 3 and 4 summarises the results at a dosage of 1 g/l diutan gum and 20 g/l starch with respect to water. At these respective dosages, the plastic viscosity was determined to be 8.0 mPa·s in the aqueous system (Fig. 1). Fig. 3 shows that at the respective dosages of stabilising agents, the plastic viscosities in water are identical. Upon addition of cement at a particle solid volume fraction of 0.33, the plastic viscosity increases, due to the particles as well as due to the presence of STA. In the presence of starch, the plastic viscosity is higher than with diutan gum.

Fig. 4 shows the yield stress values determined in this experiment. Despite the identical plastic viscosity in the aqueous system, starch and diutan gum show different behaviours when mixed only with water. Diutan gum creates a clearly identifiable yield stress, while the starch has negligible effect on yield stress. However, upon addition of cement particles, both STAs clearly increase the yield stress at the fixed dosages. The yield stress increase in the presence of particles with diutan gum is higher than with starch. Nevertheless, in the aqueous system, the starch has no clear effect on yield stress while in the presence of cement the yield stress becomes significantly higher than in the reference system with particles but without STA. This observation clearly indicates that the starch requires particles in its vicinity to become effective in terms of yield stress increase. It could be found that the efficiency of starch increases with higher particle volume fraction [13,41], so that at very densely packed particle systems the efficiency of starch increases much more than that of diutan gum.

The results clearly show that the mode of operation for starch and diutan gum can be distinguished between fluid stabilisation for diutan gum and particle stabilisation for starch [14].

4. Polysaccharides in the presence of polycarboxylate 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 type polymers consisting of a polycarboxylic backbone and ethylene oxide graft chains. Their dispersing mechanism is based on their adsorption on surfaces of clinker and hydration phases and a steric hindrance of the particles upon adsorption [30,42–50]. 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. However, since the zeta potentials of cement and filler particles become extremely low in the highly ionic pore solution, the real adsorption mechanism can be more complex [33]. More important than the adsorption on clinker surfaces is the adsorption 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, guar gum, welan and diutan gum are known to provide anionic charges, which makes

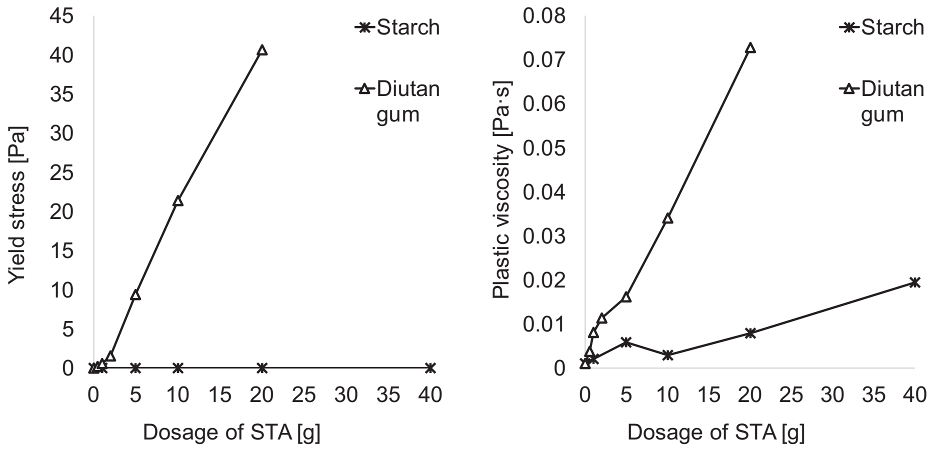


Fig. 1. Yield stress and plastic viscosity changes of water systems with varied amount of STA.

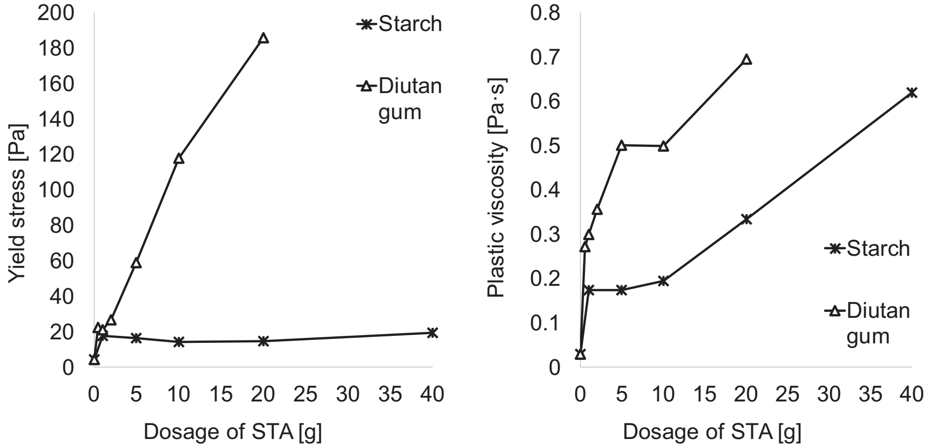


Fig. 2. Yield stress and plastic viscosity changes of cement pastes with a solid volume fraction of 0.33 with varied amount of STA.

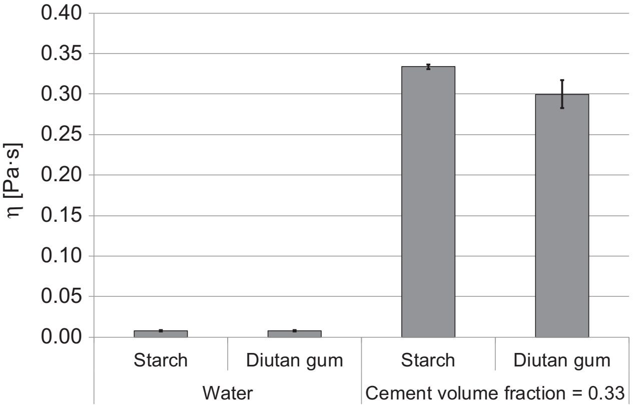


Fig. 3. Plastic viscosity of aqueous systems and of water-cement systems at particle volume fraction of 0.33 with starch and diutan gum at 20 g/l and 1 g/l, respectively. The dosages create equal plastic viscosity for both agents in the aqueous system. Measurement based on ramp profile in cylindric cell in a Couette type rheometer.

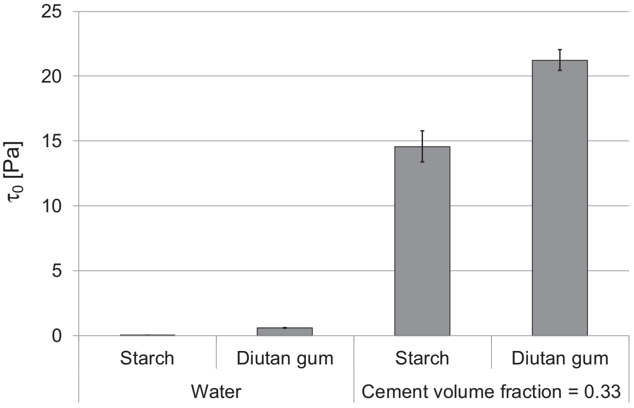


Fig. 4. Yield stress of aqueous systems and of water-cement systems at particle volume fraction of 0.33 with starch and diutan gum at 20 g/l and 1 g/l, respectively. The dosages create equal plastic viscosity for both agents in the aqueous system. Measurement based on ramp profile in cylindric cell in a Couette type rheometer.

them adsorb on particles. It is reported that the adsorption of present SPs avoids the adsorption of diutan gum [4]. However, there are also studies that indicate that adsorption can still take place to certain amount in the presence of superplasticisers [3] and that particularly the time dependent rheology of flowable cementitious systems can be affected by competitive adsorption of PCE and STA [14]. 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 [13].

The effects of PCE on limestone filler and cement dispersions are demonstrated in Figs. 5 and 6. In limestone filler systems, it can be observed that despite a prominent effect of the STAs on the yield stress in the reference without PCE, the yield stress approximates the reference at higher PCE dosages (Fig. 5). At the same time, the plastic viscosity of both STA modified systems maintains significantly higher than the reference without STA, even at high PCE dosage. For the cementitious systems similar observations can be made, however, since much higher amounts of PCE can be adsorbed on cement, the effects appear only at higher dosages of PCE. Like in the limestone filler system, the yield stress reduces dramatically with the addition of PCE, at 1.2% the STA modified systems and the reference system show identical yield stresses. Unlike in the limestone filler system, the plastic viscosity also drops significantly with the addition PCE for both STAs. However, like in the limestone filler system, the plastic viscosity remains significantly higher than in the reference system, which indicates that Diutan gum and starch behave very similar in the presence of high amounts of PCE, although without PCE they show differing performances.

This is summarised in Fig. 7. Without particles and in the presence of particles the different rheological effects demonstrated in Figs. 3 and 4 apply. In the presence of superplasticizer, the PCE adsorption and the thus reduced attractive forces between the particles dominate the yield stress effect. However, a viscosity increase can be observed for both stabilising agents due to the presence of polymers in the fluid. In this context starch and diutan gum perform in a similar way.

5. polysaccharides and PCE in flowable concrete

Concrete systems are more complex than pastes, since there is an even higher 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 [51], other effects may be triggered by the presence of higher solid volume fractions and coarser particles [41,52].

In general, the rheological properties of the SCC are largely determined by the cement and the superplasticizer, and hence the growth of hydrates and the respective adsorption of superplasticiser molecules. The yield stress reduction is predominantly influenced by the amount of adsorbed PCEs [53]. These adsorb competitively with sulphate ions upon occurrence of adsorption sites [30]. However, as can be found in Figs. 8 and 9, the STA can have supplementary influence on the time dependent changes of yield stress and plastic viscosity.

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. 8). 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 based on rapid 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 [51].

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 type. 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 min 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 loss of performance 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. 8, 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 con-

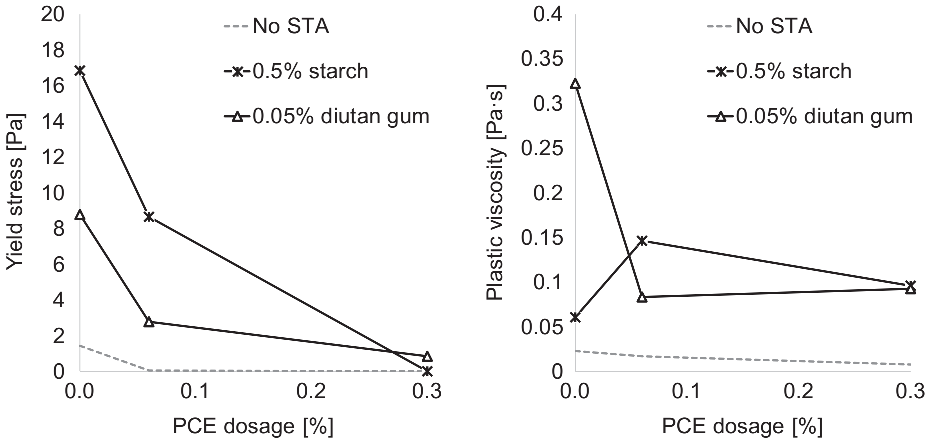


Fig. 5. Influence of PCE dosage on yield stress and plastic viscosity of limestone filler dispersions at a solid volume fraction of 0.50 after [13].

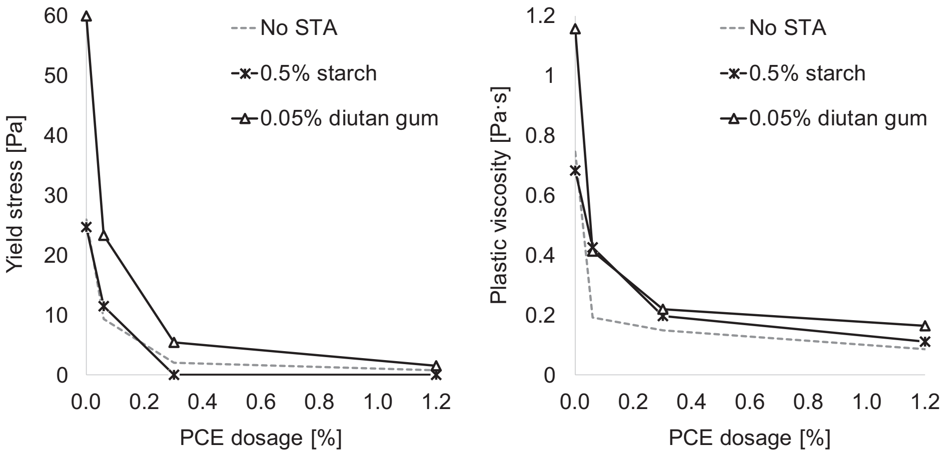
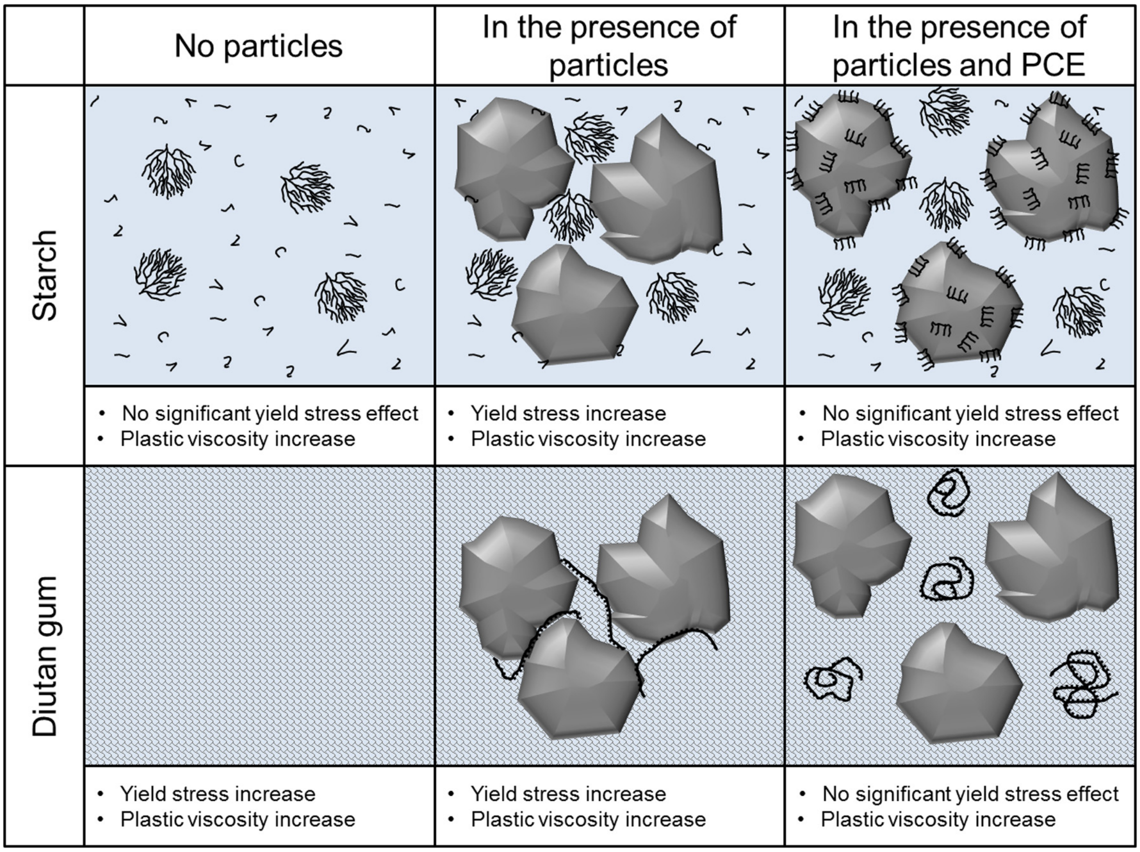


Fig. 6. Influence of PCE dosage on yield stress and plastic viscosity of cement pastes at a solid volume fraction of 0.40 after [13].



	No particles	In the presence of particles	In the presence of particles and PCE
Starch	• No significant yield stress effect • Plastic viscosity increase	• Yield stress increase • Plastic viscosity increase	• No significant yield stress effect • Plastic viscosity increase
Diutan gum	• Yield stress increase • Plastic viscosity increase	• Yield stress increase • Plastic viscosity increase	• No significant yield stress effect • Plastic viscosity increase

Fig. 7. Suggested stabilising mechanism of starch in different systems of solid particle volume fractions [13]. 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 be found adsorbed. In the presence of PCE, both polymers show a similar effect.

tains 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 through calcium ions.

6. 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 performance during the placement 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. 10–12 show how differently STA can affect the Vicat setting of cementitious systems depending upon the temperature and the presence or not of PCE superplasticiser. Regardless of the STA similar observations were made, which were strongly depending upon the surrounding temperature. The histograms show the

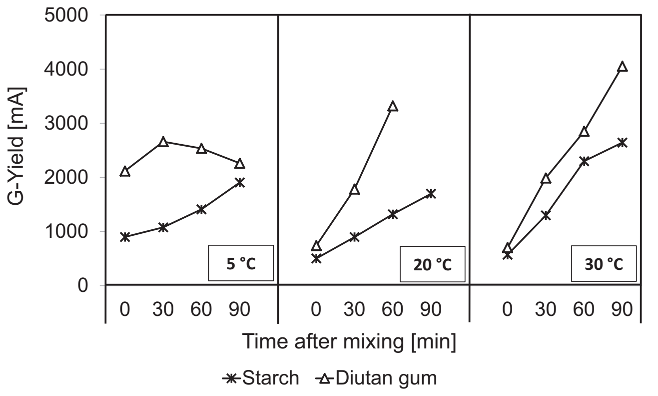


Fig. 8. Influence of polysaccharide type on the yield stress evolution in SCC over the course of time at varied ambient temperatures. Yield stress is expressed qualitatively as G-yield, derived from the electric current at varied rotational velocities in a step profile (10 s pre-shearing at 0.45 s^{-1} followed by a stepwise decrease to 0.05 s^{-1} in 8 steps á 5 s).

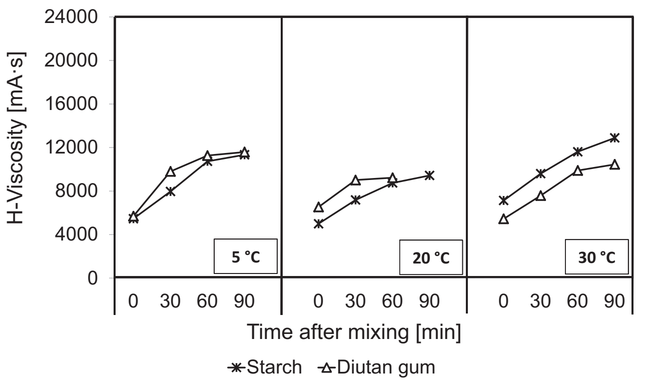


Fig. 9. Influence of polysaccharide type on the plastic viscosity evolution in SCC over the course of time at varied ambient temperatures. Plastic viscosity is expressed qualitatively as H-viscosity, derived from the electric current at varied rotational velocities in a step profile. (10 s pre-shearing at 0.45 s^{-1} followed by a stepwise decrease to 0.05 s^{-1} in 8 steps á 5 s).

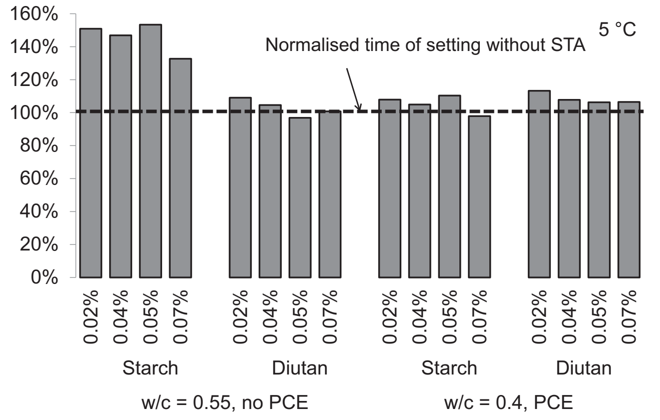


Fig. 10. Influence of starch and diutan gum on the setting time of cementitious systems without and with PCE superplasticisers at 5 °C.

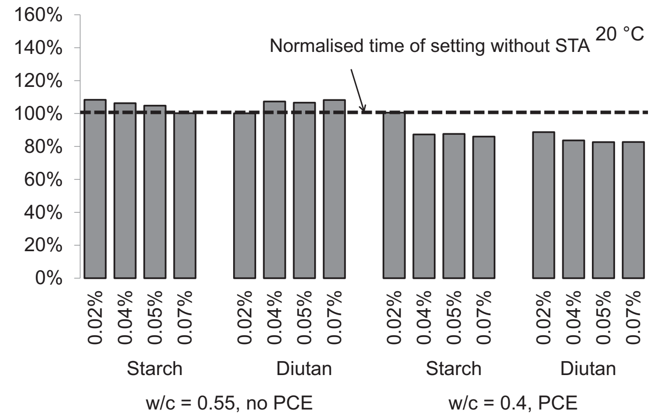


Fig. 11. Influence of starch and diutan gum on the setting time of cementitious systems without and with PCE superplasticisers at 20 °C.

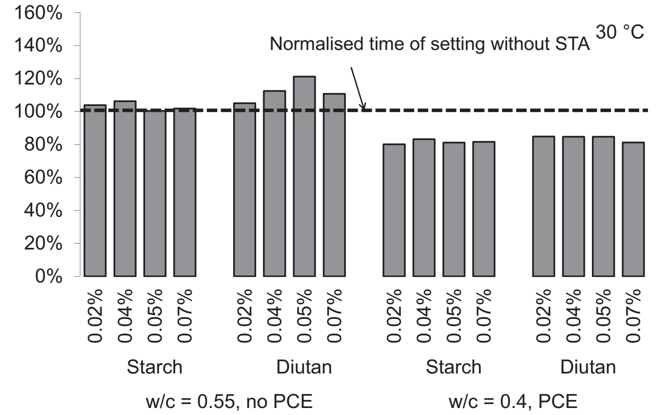


Fig. 12. Influence of starch and diutan gum on the setting time of cementitious systems without and with PCE superplasticisers at 30 °C.

increase or reduction of the setting time of systems with different STA and at different dosages in comparison to a reference without any STA. Due to the strong influence of the temperatures as well as the presence of PCE on the setting the values are normalised. Each values shows the percentage compared to a mixture without STA (100%) but apart from that under identical boundary conditions. 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.

At 5 °C (Fig. 10) it can be observed that all STAs show a slightly retarding effect. Only the mixture with starch without PCE shows a significant retarding effect. At 20 °C and at 30 °C both STAs incorporate a slight retardation of the setting in the pastes without PCE. However, the systems with STA including PCE show a less retarding effect than the reference without STA. In all cases the time effects on the setting do not seem to depend upon the dosage of STA but rather the effects seem to be incorporated by the presence of STA in general.

However, although the Figs. 9–12 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 additionally strongly dependent on the charge density of the PCE, the cement type used as well as the binder setup [6,14,54]. 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 effect that the combination of PCE and STA seems to cause less retardation or only slightly more retardation than only PCE despite the fact that both agents solely cause retardation is interesting and needs further discussion based on mechanisms during the early hydration of cement. 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. 10.

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 [55,56]. Sowoidnich and Rößler concluded that the retarding effect of superplasticisers can be attributed to the non-adsorbed rather than to the adsorbed PCE polymers [55]. If the latter conclusion is taken as a basis and the setting is mainly attributed to the hydration of C-S-H [57], 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 [50]. However, the major adsorption sites for PCE during the placement period are ettringite and monosulphate, of which ettringite can attract significantly higher amounts of PCE [30]. 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 huge 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 due to pure kinetic effects. 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.

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. Whether the hydration takes place at the particle surfaces or in the pore solution is not of importance in this case.

This effect is shown in the Figs. 13 and 14. The higher ettringite formation shown in Fig. 14 causes higher PCE adsorption after a while, thus less free PCE in the pore solution to interfere with the C-S-H hydration during the setting than in Fig. 13.

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.

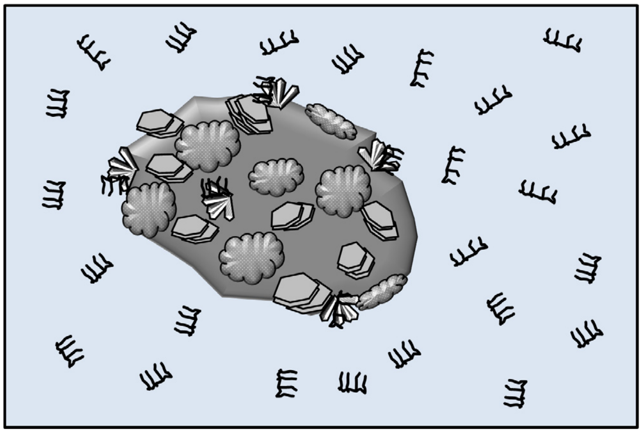


Fig. 13. Ettringite formation and adsorption at the time of accelerated C-S-H formation without STA. PCE and sulphate ions compete for adsorption sites, thus causing lower ettringite formation and hence lower adsorption of PCE.

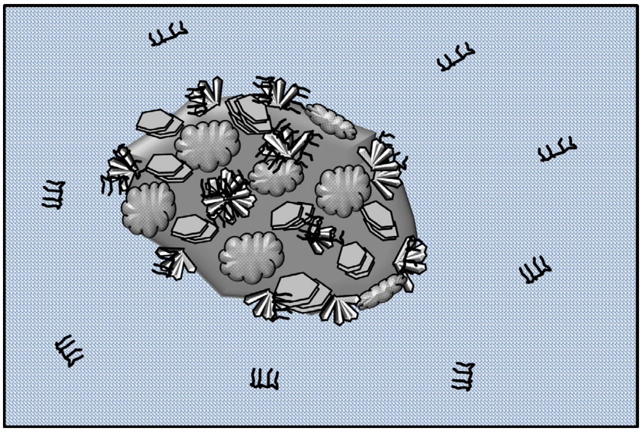


Fig. 14. Ettringite formation and adsorption at the time of accelerated C-S-H formation in the presence of STA. PCE adsorption is reduced by STA to the benefit of sulphate adsorption, thus higher amounts of ettringite are formed that cause more PCE adsorption over the course of time.

The presented hypothesis is only based on observations of macroscopic phenomena. The measurement results do not give conclusive evidence. Nevertheless, the hypothesis is supported by results from a recent study using synchrotron XRD to observe the formation of ettringite without and in the presence of starch based STA [58]. Without and in the presence of PCE, starch increased the amount of ettringite formed during the first hour after water contact. In the presence of PCE and starch, the highest ettringite formation was found. However, alternative interpretations, e.g. based on the crystal structure of ettringite or association or complexation of PCEs with STAs, are thinkable as well.

7. 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 their 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.

In the presence of polycarboxylate ether polymers sphingan and starch show very similar effect on the rheology: they maintain a higher plastic viscosity compared to systems without STA even at high PCE dosages, without a strong influence on the yield stress of the total system. Further research will focus on the shear rate dependency of the STA effect as well as the influences of the ionic composition of the pore solution on water retention properties and rheology modification.

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 small 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. Further in-situ XRD and ESEM investigations on STA modified cementitious systems with PCE will show whether the explanation model can hold true.

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