THE WORKING MECHANISM OF STARCH AND DIUTAN GUM IN CEMENTITIOUS AND LIMESTONE DISPERSIONS IN PRESENCE OF POLYCARBOXYLATE ETHER SUPERPLASTICIZERS

WOLFRAM SCHMIDT*[1], H.J.H. BROUWERS[2],
HANS-CARSTEN KÜHNE[1], BIRGIT MENG[1]

[1] Division 7.4 Technology of Construction Materials, BAM Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany
[2] Eindhoven University of Technology, Eindhoven, Netherlands

* Corresponding author: wolfram.schmidt@bam.de
Fax: x49.30.81041717

Received: 29.3.2013, Final version: 25.6.2013

ABSTRACT:
Polysaccharides provide high potential to be used as rheology modifying admixtures in mineral binder systems for the construction industry such as concrete or mortar. Since superplasticizers have become state of technology, today, concrete is more and more adjusted to flowable consistencies. This often goes along with the risk of segregation, which can be effectively avoided by adding stabilising agents supplementary to superplasticizers. Stabilising agents are typically based on polysaccharides such as cellulose, sphingan gum, or starch. Starch clearly distinguishes in its effect on rheology from other polysaccharides, mainly due to the strong influence of amylopectin on the dispersion and stabilisation of particles. Based on rheometric investigations on cementitious and limestone based dispersions with different volumetric water to solid ratios, the mode of operation of modified potato starch is explained in comparison to a sphingan gum. It is shown that the stabilising effect of starch in a coarsely dispersed system is mainly depending upon the water to solid ratio and that above a certain particle volume threshold starch mainly affects the dynamic yield stress of dispersions, while plastic viscosity is affected only to a minor degree. Sphingans operate more independent of the particle volume in a coarsely dispersed system and show significantly higher effect on the plastic viscosity than on the yield stress. In systems incorporating superplasticizers, influences of both stabilising agents on yield stress retreat into the background, while both observed polysaccharides maintain their effect on the plastic viscosity.

ZUSAMMENFASSUNG:
Polysaccharide weisen als Rheologiemodifizierer für in der Baustoffindustrie verwendete mineralische Bindemittelsysteme wie Beton oder Mörtel ein hohes Anwendungspotential auf. Seit Fließmittel gängige Zusatzmittel in der Baupraxis geworden sind, kann Beton heutzutage verstärkt hinsichtlich seiner Fließfähigkeit spezifiziert werden. Erhöhte Fließfähigkeit geht allerdings häufig mit einer erhöhten Entmischungsneigung einher, der durch zusätzliche Zugabe von stabilisierenden Zusatzmitteln effektiv entgegengewirkt werden kann. Stabilisierer haben üblicherweise Polysaccharide als Grundstoff, z. B. Zellulose, Sphingan oder Stärke. Hierbei unterscheidet sich Stärke in ihrem Einfluss auf die Rheologie deutlich von anderen Polysacchariden, was durch den starken Einfluss ihres Amylopektinmoleküls auf die Dispersion und Stabilisierung von Partikeln begründet werden kann. Anhand rheometrischer Untersuchungen an Zement- und Kalksteinmehlsuspensionen mit unterschiedlichen volumetrischen Wasser-Feststoffverhältnissen werden die unterschiedlichen Wirkungsweisen von modifizierter Stärke im Vergleich zu Sphingan erklärt. Es kann gezeigt werden, dass der stabilisierende Effekt der Stärke in grobdispersen Systemen im Wesentlichen vom Wasser-Feststoffverhältnis abhängt und dass oberhalb eines Partikelvolumengrenzwertes vor allem die dynamische Fließgrenze und weniger stark die plastische Viskosität beeinflusst. Der Wirkungsmechanismus von Sphinganen in grobdispersen Systemen ist deutlich weniger abhängig vom Partikelvolumen. Hier kann ein deutlich größerer Einfluss auf die plastische Viskosität ausgemacht werden. In Systemen, die Fließmittel enthalten, treten Einflüsse der Stabilisierer auf die Fließgrenze in den Hintergrund, während ein deutlicher Effekt hinsichtlich einer höheren plastischen Viskosität ausgemacht werden kann.

RÉSUMÉ:
Les polysaccharides présentent un grand potentiel dans des applications de mixtures modifiant les propriétés rhéologiques de liants minéraux pour la construction civile comme le béton ou le mortier. Puisque les super plastifiants sont devenus une technologie à la mode, de nos jours la consistance du béton est de plus en plus ajustée afin de présenter des caractéristiques de fluidité. Celles-ci s'accompagnent souvent d'un risque de ségrégation qui peut être évitée de manière effective en additionnant des agents stabilisant en plus des super plastifiants.

© Appl. Rheol. 23 (2013) 52903 DOI: 10.3933/ApplRheol-23-52903

Les agents stabilisant sont typiquement basés sur des polysaccharides tels que la cellulose, la gomme de sphingan, ou l'amidon. L'amidon se distingue clairement des autres polysaccharides par son effet sur la rhéologie qui est principalement du à une forte influence de l'amylopectine sur la dispersion et la stabilisation des particules. Sur la base d'études rhéologiques de suspensions calcaires et de ciment possédant différents ratios volumétriques d'eau et de solide, le mode d'opération de l'amidon de pomme de terre modifié est expliqué et comparé à celui de la gomme de sphingan. On montre que l'effet stabilisant de l'amidon sur une dispersion de grosses particules dépend principalement du ratio eau/solide et qu'au-delà d'un certain seuil de volume de particule, l'amidon affecte principalement la contrainte seuil dynamique des dispersions, tandis que la viscosité plastique reste moins affectée. L'effet de la gomme de sphingam dépend moins du volume en particules et présente un plus grand effet sur la viscosité plastique que sur la contrainte seuil. Dans les systèmes incorporant des super plastifiants, les influences des deux agents stabilisants ont peu d'impact sur la contrainte seuil, tandis que les deux agents maintiennent leurs effets sur la viscosité plastique.

Key words: cement, limestone, rheology, stabilising agent, coarsely dispersed systems, diutan gum, starch ether

1 INTRODUCTION

1.1 IMPORTANCE OF POLYSACCHARIDES IN CONCRETE TECHNOLOGY

Superplasticizers can be considered as the key to most significant innovations in cement and concrete technology during the last decades since they allow optimising the rheology without changing the water content, which is relevant for the strength and durability of concrete. Innovations such as Self-Compacting Concrete (SCC), Ultra-High Performance Concrete, or Reactive Powder Concrete were only achievable due to the intensive use of superplasticizers (SPs). Today, for high performance applications, polycarboxylate ethers (PCE) are typically used but often they need to be supplemented with stabilising admixtures (STA) in order to avoid uncontrolled segregation. A major problem of flowable concrete is segregation, fostered by the wide range of diameters of mortar and concrete constituents ranging in size from nm to cm. In order to avoid dynamic segregation upon flow, flowable concrete types typically contain higher contents of fines than normal concrete. However, this cannot effectively avoid segregation at rest, which is particular a problem induced by the retarding effect of superplasticizers. Furthermore the material costs as well as the shrinkage tendency are increased. Therefore, concepts with lower powder contents, incorporating PCE superplasticizers and supplementary rheology modifying admixtures are becoming more and more popular and important.

According to a milestone paper by Khayat [1] for mortar and concrete applications, commonly polysaccharides are in use as polymeric STAs. The variety of these products is huge. Often cellulose, gums from plants or microbes as well as starches are used as basic components. Typically, the mode of operation of STAs in mortar systems is explained by their capability to be adsorbed on water. Increasing molecular weights yield higher water retention properties [2, 3]. The cementitious pore solution at fresh state exhibits pH-values higher than 13. It is therefore typically assumed that most polysaccharides may be incompatible with the hydration of cement due to degrading in the high alkaline surrounding of the cement paste or loss of effectiveness due to shrinkage in presence of metal ions [2, 4, 5]. Izumi [4] investigated a number of polysaccharides and showed that from one specific polysaccharide, the majority of STAs exhibit decreasing viscous behavior in solution with increasing ion concentration. Pourchez found adverse results with regards to the stability of different cellulose derivatives, which showed high stability in alkaline surrounding [6]. In general, the threat of a high ionic solution is well known to the producers of commercial STAs, so that the available products on the market can be considered as sufficiently stable

1.2 STARCH ETHER AND SPHINGAN GUM STABILISING AGENTS

Starch is a polysaccharide, which typically consists of two types of macromolecules composed of differently linked glucose monomers. Though,

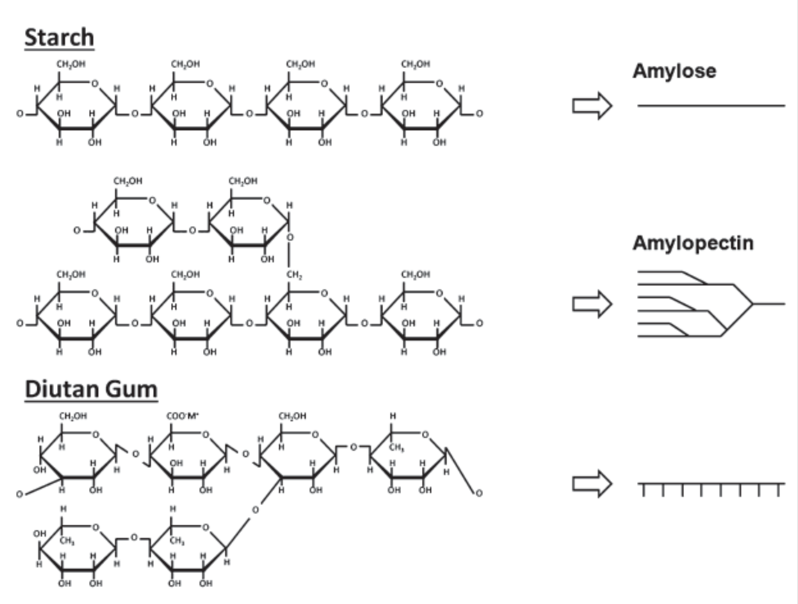


Figure 1:
Chemical and macromolecular structures of starch and diutan gum.

chemically identical to cellulose, the starch strands as well as the macromolecular structure differ in a pronounced way. The glucose units of cellulose are arranged in alternating order, while they are arranged identically for starch. Furthermore, cellulose strands are mostly linear, while starch consists of two types of macromolecules, amylose and amylopectin. Amylose is a largely linear polymer with regularly repeated hydroxide bonds as shown in Figure 1. For the more complex macromolecule amylopectin, the majority of bonds are constituted by hydroxide bonds as well. However, hydroxymethyl bonds are reported every 12 to 17 glucose units [7] or every 15–30 glucose units [8]. As a result, a tree like structure as shown in Figure 1 forms in solution. Amylose molecules occur 200 to 1000 times more often than amylopectin but amylopectin has an approximately 1000 times higher degree of polymerisation than amylose, thus the radius of gyration of amylopectin is about 10 times higher than that of amylose (see Table 1). For typical starches (apart from waxy maize starch, which has 100% amylopectin), about 80 % by weight are constituted by amylopectin. For construction materials starches have to be made cold-water soluble. Furthermore, for application in the high pH-environments of cementitious systems, starches need to be stabilised by ether or ester bond in the hydroxyl groups. Typical modifications are conducted by ethylene oxide, propylene oxide, or sodium mono chloracetate reactions. Such stabilisation is typically made for the reason to reduce the tendency for retrogradation and to minimise intermolecular interactions [9].

Diutan gum is a microbial polysaccharide. The backbone consists of the repeated configuration of rhamnose, glucose, glucoronic acid, glucose units [10]. A carboxylate group attached to the glucuronate gives anionic charges to the backbone of diutan gum [5]. The side chains of diutan gum, which consist of two linked rhamnose units, are attached to each second glucose unit [5, 10]. These are considered to sterically shield the carboxylic acids, thus avoiding cross-linking by calcium ions. The structure of the polymer is given in Figure 1 in comparison to starch. Diutan belongs to the group of sphingans, which all exhibit the same backbone structure. However, only welan and diutan are considered to be compatible with the cement hydration since they are stable in high pH systems. They distinguish in their main chain length and side chain geometry [5, 11]. Since only few reports about diutan gum in cementitious systems are available, the review part discusses experiences with welan gum as well. Due to their structural similarity experiences with welan can be qualitatively assigned to diutan as well.

Based on the data provided by Swinkels [12], the molecular weight of starch is in the range of 2 to 2.5 million g/mol mainly caused by the amylopectin molecules with a degree of polymerisation of 2,000,000. The average molecular weight of commercial diutan lies between 2.88 and 5.18 million Da [5, 10]. Starch ethers and diutan gum distinguish significantly in their appearance (Figure 1). Diutan gum has a linear main chain with regular side chains. Starch consists of the two aforementioned differently sized macromolecules. Diutan incorporates anionic charges, while typical starches for cementitious systems can be considered as non-ionic (but there are also carboxymethyl-starches on the market). As a result of these differences, it can be assumed that the modes of operation of the STAs differ greatly.

Khayat attributed effects of sphingans to the binding of water, which in return increases the viscosity of the cementitious system [1]. Despite the chemical similarity between starch and cellulose, in cementitious systems, the performance of cellulose compares much more to

Table 1:
Typical technical specifications of starch and diutan gum based on [5, 8-12, 32].

	Potato starch		**Diutan gum**
	Amylose	**Amylopectin**	
Content	~ 20%/wt	~ 80%/wt	-
Molecular mass [u]	50000 - 500000	10000000 - 100000000	2900000 - 5200000
Radius of gyration [nm]	~30	50 - 500	N/A

the performance of sphingans. As will be discussed later, this is likely to be linked to the linear structure of the cellulose as well as to the fact that often cellulose derivatives used in construction materials are amended by carboxylic groups. For sphingan and cellulose, Khayat distinguished between three modes of operation, which occur in coarsely dispersed cementitious systems depending upon the concentration [13]:

- Adsorption: Polymers adhere to and immobilise water.
- Association: Molecules form a network, causing gellation, which blocks the water motion.
- Intertwining: At low shear rates, polymer chains intertwine and entangle. This effect is basically limited to high addition amounts.

Sonebi observed marked shear thinning behavior in mixes incorporating SP and sphingan gums [14, 15]. This effect was more pronounced with diutan gum than with welan gum, which was attributed to the higher molecular mass. The study shows that diutan gum significantly increases the apparent viscosity particularly at low shear rates. It is assumed that the long chains of diutan entangle and intertwine at low shear forces. At higher shear rates, the polymers direct into the flow direction, which lowers the apparent viscosity again. Rajayogan [16] and Terpstra [17] published studies that show the suitability of starch ether as a STA for cementitious materials. According to Simonides and Terpstra [18], the stabilising mechanism of starch ethers differs greatly from diutan gum. As shown in Figure 2, the mode of operation is basically attributed to the effect of the amylopectin, which spreads out in solution into its tree-like structure, thus keeping particles in distance, to avoid segregation. The effect therefore mainly affects the yield stress at rest and does not show strong influence on the plastic viscosity. Based on this, it is assumable, that differing from cellulose or diutan gum, the molecular weight of starch may play a minor role for the stabilising effect and that the ratio between amylose and amylopectin may be of significantly higher importance.

The former observations, however, clearly contradict to observations of Rajayogan et al., who observed a large increase of the plastic viscosity due to starch [16]. A major difference between the mixtures that were observed in these studies were the amounts of starch in the mixture compositions, the water to powder ratios as well as the binder to aggregate ratios. Simonides and Terpstra were using self-compacting concrete (SCC) with a powder content of 400 kg/m^3 and a water to powder ratio of 0.47. The starch dosage was 0.06 % of the powder. Rajayogan et al. were using much higher powder contents between 550 and 650 kg/m^3 with water to powder ratios ranging between 0.34 and 0.40. The starch dosages ranged between 0.11 % and 0.23 % of the powder. Hence, the systems observed by Rajayogan et al. had significantly higher particle packing and higher starch contents. It can be assumed that the effect demonstrated in Figure 2 is the major effect of stabilisation in relatively fluent systems as observed by Simonides and Terpstra. At higher powder densities and lower water volumes and higher starch contents, the space filling effect of starch might be outweighed by intertwining and association of polymers. It is, however, questionable, if stabilising agents are required at all in high powder systems.

In a former comparison between water-STA systems and water-cement-STA systems under the assumption of Bingham behavior, it was shown by Schmidt et al. that diutan generated a significant yield stress in water, while starch only showed relatively negligible effects. Upon addition of particles, however, the starch strongly increased the yield stress [19]. It can therefore be concluded that both admixtures work on different modes of operations. Diutan gum mainly affects both, viscosity and yield stress through binding high amounts of water. The thus increased apparent viscosity of the fluent phase finally affects the rheology of the overall system. In contrast to that, starch mainly affects the yield stress in presence of particles and much lesser the viscosity. It does not bind high amounts of water but can affect the rheology upon addition of particles significantly. Hence, starch and diutan in mortar like systems can be distinguished between (a) stabilising of particles (starch) and (b) stabilising of the fluent phase (diutan gum).

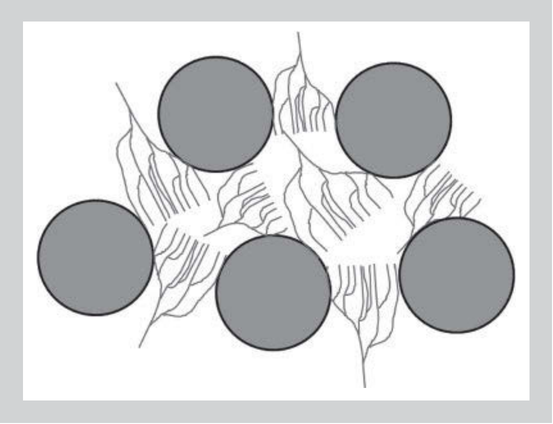


Figure 2: Stabilising mechanism of starch ether and effect on yield stress after Simonides and Terpstra [18].

1.3 POLYSACCHARIDES IN PRESENCE OF PCE

Modern flowable concrete and mortar types contain high amounts of SPs, typically PCE. PCEs are comb polymers consisting of a polycarboxylic backbone and polyethylene oxide graft chains. Their dispersing mechanism is based on their adsorption on positively charged surfaces and a steric hindrance of the particles upon adsorption. 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. Furthermore, they adsorb preferably on newly formed hydration phases upon addition of water such as ettringite and monosulfate, which occur by reaction of water, gypsum and calcium aluminate phases. Their effect on yield stress is very pronounced, while they only show little influence on the plastic viscosity.

Some polysaccharides such as cellulose, welan and diutan gum are known to provide anionic charges, which makes them adsorb on particles [1, 5, 20, 21]. It is reported that the adsorption of present SPs avoids the adsorption of diutan gum [5], however, there are also results that suggest that adsorption still takes place to certain amount in presence of superplasticizers [14]. The anionic charges generally suggest that interactions between the polymers can take place or that adsorption occurs competitively between both types of polymers. Khayat showed that small changes of naphthalene based SP dosages had large effects on the apparent viscosity in welan stabilised systems [1]. With increasing content of Welan gum, the robustness against variations in the SP dosage could be significantly increased. In return, higher amounts of SP were required to achieve similar reduction of the apparent viscosity. Yammamuro et al. investigated the interactions of SPs with adsorptive and non adsorptive STAs [3]. The non adsorptive STA did not at all affect the adsorption of SPs, while increasing amounts of adsorptive STA reduced the adsorption of SPs significantly. The authors concluded that competitive adsorption takes place between SPs and adsorptive STAs. Results by Phyfferoen et al. shown that indeed diutan gum STA shows a tendency to adsorb on cement particles. This effect, however, shall be eliminated in presence of SPs [5, 22]. Interactions are assumed to be hindered by steric shielding of the anionic charge by the double rhamnose side chain. Also starch is reported to be found adsorbed on cementitious particles, however, to significantly lesser extent. By adding PCE, the adsorption could be avoided [23], and a strong influence of starch on the yield stress in presence of PCE could be observed. As a possible explanation for this effect, the authors suggest depletion forces due to unadsorbed polymers.

Table 2: Technical specifications according to the producer data sheets of the PCE and the STAs used for the investigations.

Name	Commercial name	Description	Form	Bulk density	pH
PCE	Glenium Sky 591	Polycarboxylic backbone with polyethylene grafts	30% solids in water	1.07 ± 0.02 g/cm^2	6.5 ± 1
ST1	Foxcrete S 100-F	Starch ether	Powder	400 kg/m^3	11 - 12 (100 g/l H_2O)
ST2	Kelkocrete DG-F	Diutan gum	Powder	n/a	n/a

PCEs and STAs distinguish strongly from each other. PCEs may have molecular weights between 10,000 and 200,000 g/mol and typically gyratory radii between 5 and 150 nm [24 – 28], while for different polysaccharide STAs for application in cementitious systems molecular weights between 300,000 and 5,000,000 g/mol and gyratory radii between several tenth and 500 nm are reported [4, 5, 12, 20]. Due to the enormous variety of products of SPs and STAs, it is difficult to detect generally valid laws regarding possible interactions between these polymers. However, a good understanding is important, since an increasing trend to use both types of admixtures in parallel can be observed on the side of the concrete engineers as well as of blenders of admixtures for the market.

1.4 MOTIVATION OF THE INVESTIGATIONS

The use of polysaccharides can effectively avoid segregation and increase the robustness against unavoidable scatter in the constituents' qualities. The performance of polysaccharides in mortar can depend upon the water to solid ratio. Furthermore, interactions between superplasticizers and STAs are possible and understanding the combined effects becomes increasingly important for the concrete industry. However, interactions between STAs and PCEs have not been matter of intensive research yet. Based on rheometric experiments, the characteristic differences between non-adsorptive and adsorptive stabilising agents based on starch and diutan gum shall be discussed without and in presence of superplasticizers and in systems with varied water to solid ratios.

2 MATERIALS AND METHODS

2.1 ADMIXTURES

The STAs that were used are commercially available polysaccharides. The STA abbreviated ST1 is a starch derivative and has been subject of research in the field of SCC in the past years [17, 18, 29]. ST2 is a diutan gum and has also been subject of research in the field of cement and concrete technology [5, 14, 15, 30]. Commercial pure polycarboxylate ether with a solid content of 30 % was used as superplasticizer. Technical specifications of the admixtures are given Table 2.

2.2 MATERIALS AND MIXES

Investigations were conducted on water-limestone systems and water-cement systems with different water to solid ratios. The powders' particle size distributions and oxide compositions can be found in Figure 3 and Table 3, respectively. Figure 3 also shows results of slump flow tests of the used cement and limestone when supplemented by water at their respective water demand according to the Puntke method [31] at increasing PCE solid additions. The flow induction of LSF happens at significantly lower dosage and the maximum spread flow diameter occurs at lower dosage and is wider than with cement, which indicates that significantly higher amounts of PCE can be adsorbed on cement and that the dispersing forces of PCE are lower in cementitious systems than in LSF-systems. Nevertheless, the basic mechanism of dispersion can be observed for both powders, so that depending on the observation type, limestone filler systems can possibly replace cementitious systems without the negative effect of the rapid change of rheology due to the ongoing cement hydration.

The STAs were observed in water only, and in water to powder systems at medium and high powder content. For all investigations, STA was first dissolved in water. Due to the different water demands of LSF and cement, their volumes were varied between 0, 33.3 % and 50.0 %, and 0, 25.0 % and 40.0 %, respectively. Furthermore the combined influence of PCE and STA was studied for each powder at the highest observed powder concentration. In these investigations, the PCE solid contents were varied for LSF between 0.06 % and 0.30 %, which approximately are the dosages required to induce flow and to achieve maximum spread flow according to Figure 3 (right). For cement, the same dosages were chosen and supplemented by a dosage of 1.20 %. Here the first dosage represents a very low PCE dosage, and the latter dosages represent the onset and the maximum. In the LSF investigations, the STA content was fixed at 0.5 % of the water. However, due to the significantly higher efficiency of ST2, for the cement tests more diverse dosages were chosen. ST1 was varied between 0.5 % and 5 %, ST2 was varied between 0.05 % and 0.5 %, each percentage related to the water content. In flowable cementitious systems 0.5 % for ST1 and 0.05 % for ST2 represent typical dosages for use as stabilising agent, while significantly higher dosages would only be used for special applications. The mixture proportioning for the LSF tests and the cement tests is given in Table 4 and Table 5, respectively.

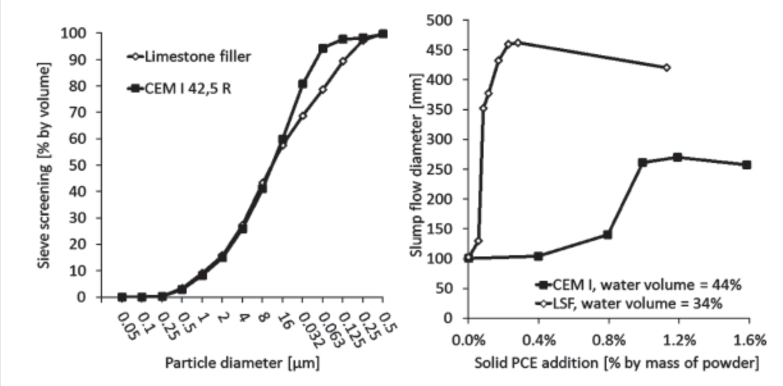


Figure 3: Grading of the CEM I and limestone filler used for the investigations and slump flow diameters of cement and limestone filler of pastes with Punkte-water demand [31] at varying PCE additions.

Table 3: Oxide compositions of the used cement and limestone filler (¹based on wet chemistry according to DIN EN 196-2, ²determined with XRF).

Oxides	Cement (CEM I 42.5 R)¹	Limestone filler²
CaO	62.80%	90.68%
SiO_2	20.56%	1.47%
$Al2O_3$	4.36%	0.46%
Fe_2O_3	2.27%	0.40%
MgO	2.14%	0.61%
Mn_2O_3	0.03%	-
Na_2O	0.28%	3.27%
K_2O	0.95%	0.54%
Ti_2O	0.20%	0.05%
P_2O_5	-	2.19%
SO_3	3.45%	0.34%

Table 4: Conducted tests with STAs and LSF at varied powder contents (ST1: 0.5 % by weight of water, ST2: 0.05 % by weight of water).*

Water [vol %] + ST*	100	66.7	50.0	50.0	50.0
LSF [vol %]	-	33.3	50.0	50.0	50.0
PCE solids [% bwo LSF]	-	-	-	0.06	0.30

Table 5: Conducted tests with STAs and cement at varied powder contents (ST1: 0.5 % by weight of water, ST1: 5.0 % by weight of water, ST2: 0.05 % by weight of water, ST2: 0.5 % by weight of water).*

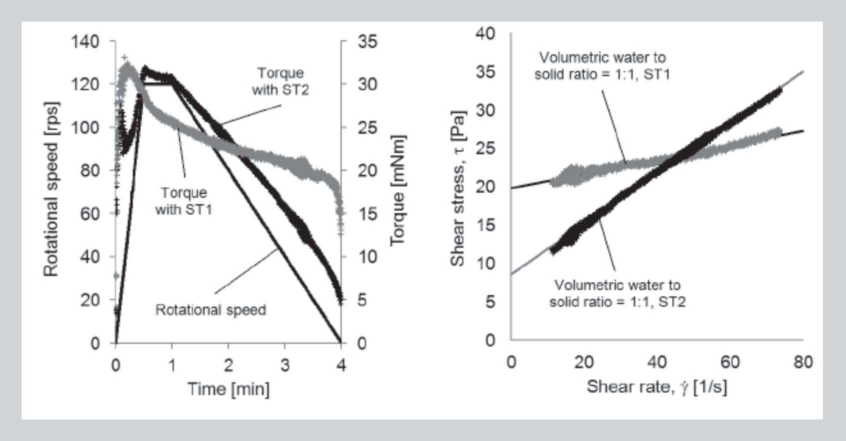
Water [vol %] + ST*	100	66.7	50.0	50.0	50.00	50.00
Limestone filler [vol %]	-	25.0	40.0	40.0	40.0	40.0
PCE solids [% bwo cement]	-	-	-	0.06	0.30	1.20

Figure 4 (above):
Wide gap basket cell, as used for the rheometric investigations (sketch by Schleibinger).

2.3 RHEOMETRIC EQUIPMENT AND MEASUREMENTS

A Couette type viscosimeter was used with a double gap cell as shown in Figure 4. A network structured grid as shear body induces a flow that is largely based on the cohesion between the fluid layer on the wall and the fluid. This minimises wall slip effects, which typically limit the use of standard geometries for coarsely dispersed systems, and allows measurements up to a maximum grain size of 1–2 mm. A ramp profile was established as shown in Figure 5 and the values at decreasing shear rates were used to calculate yield stress τ_o and plastic viscosity η_{pl} based on the assumption that the fluids largely show Bingham behavior. A Bingham interpretation is assumed to not truly render the performance of STAs, particularly at low shear rates and in the water-STA systems only. However, the strength of the Bingham model is the clear differentiation of the yield stresses, and the effect on yield stress is assumed to be one of the major distinction item between ST1 and ST2. Furthermore, the Bingham approach is the most commonly used model in cement and concrete technology and the observed systems showed Bingham behavior over a wide range of shear rates.

Figure 5:
Measurement for the observation of the influence of solid particles with sample measurement results (left) and sample flow curves and Bingham approximations (right).



Since shear forces strongly affect the cement hydration and the adsorption of polymers, for cementitious systems it is of utmost importance to keep the measurement time as short as possible. The applied profile is considered to be a reasonable compromise between precision and compactness. Due to the initial formation of ettringite and monosulfate, the performance of PCE in cementitious systems can change rapidly during the first 3–5 minutes. In order to make sure that the cementitious systems were stable the measurements were conducted not earlier than 10° minutes after water addition.

3 RESULTS AND DISCUSSION

Figure 6 shows yield stresses and plastic viscosities for ST1 and ST2 for different water to solid ratios compared to identical water-limestone suspensions without stabilising admixture. It can be clearly observed that ST1 does not strongly affect τ_o compared to a mixture without STA, when added to water only and to a mixture with only 33.3 % solids. At the same time, with ST2 in water only a clear yield stress can be observed, which increases only slightly at low solid content. For mixtures with high solid content, ST1 increases τ_o strongly, while the effect of higher powder contents is only small for ST2. Despite the strong effect of ST1 on τ_o upon addition of high solid contents, η_{pl} is only slightly affected. A pronounced increase of η_{pl} can be observed at high solid contents with ST2, although at the same time the increase of τ_o is small.

Regarding the yield stress, at 0 % solids, the starch system does not distinguish from the control system with water, and starch only increases η_{pl} slightly. At 50 % of solids, τ_o increases prominently, while the increase of η_{pl} is relatively low. This clearly indicates that for ST1 a threshold for the solid particle amount exists, which triggers the rapid increase of τ_o, which cannot solely be explained by the higher particle volume, since then η_{pl} would exhibit at least a similarly strong increase. This is clearly not the case in Figure 6. Since the polymer concentration in water is main-

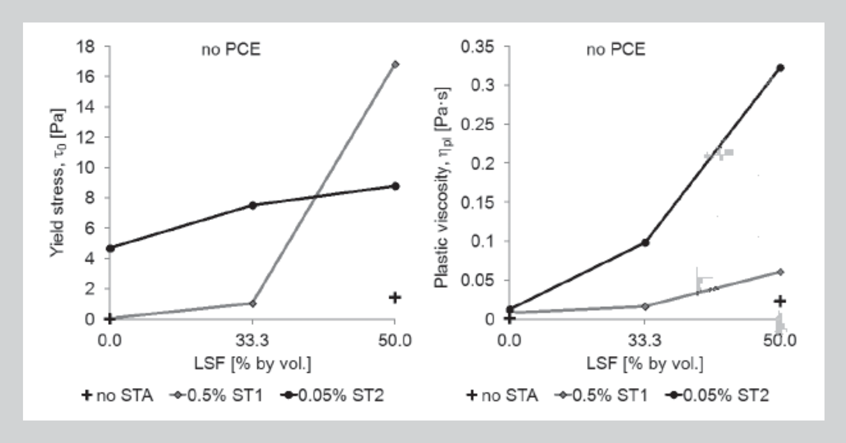


Figure 6 (above):
The influence of the solid content of LSF on yield stress and plastic viscosity when mixed without stabilising agent, with ST1 and with ST2.

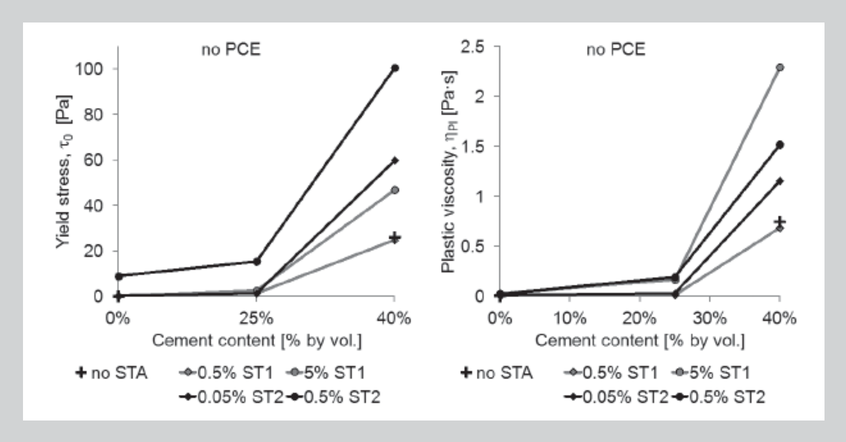
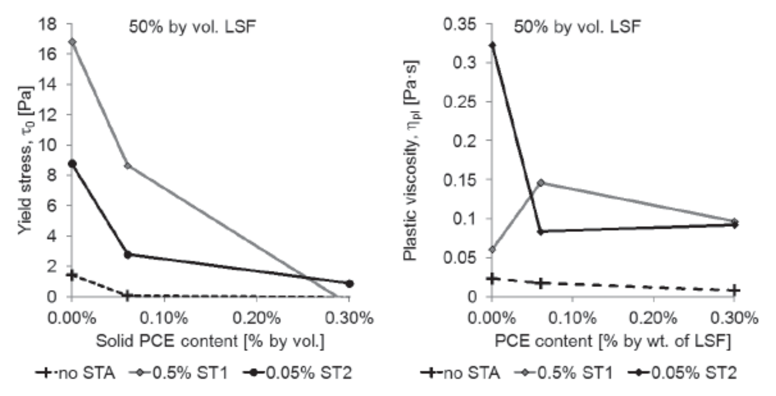


Figure 7:
The influence of the solid content of cement on yield stress and plastic viscosity when mixed without stabilising agent and different amounts of ST1 and ST2.

tained for all tests, intertwining of polymers does not seem to be the driving force for the significant yield stress increase. Without doubt the effect of depletion forces as described in [23] induced by non-adsorbed starch molecules cannot be neglected in the discussion. However, due to the large molecule size of the amylopectin, depletion forces may be mainly induced by the a multiple smaller amylose. Another mechanism that can explain the observed effect would be rather a particle-amylopectin-particle lattice effect, which is activated by the closer particle distance of LSF, when added above a threshold dosage. The cause is similar to that of depletion, large particles cannot access a zone in between two particles, however, the forces are lesser induced by osmotic pressure but rather by the pure size of the molecule. This means, the huge amylopectin structures act like springs – or rather like deformable particles – between the finest particles, as shown in Figure 2. In this context it may be negligible whether the amylopectin can be found adsorbed or non-adsorbed on particles. Adsorption of starch on cement is reported in literature [23]. As starch can be attracted on surfaces with positive zeta potentials [33], it is assumable that it can be adsorbed on limestone fillers as well. The adsorption of small molecules such as amylopectin would add a steric repulsive component, which contradicts to the observation, though such effect cannot be excluded. In case amylopectin adsorbs, this would add a bridging component to the mechanism. However, considering the tree-like structure of amylopectin as well as its enormous size in the order of magnitude of finest particles, the number of adsorbed branches would be small compared to the non-adsorbed branches, which would make bridges relatively flexible. Furthermore, similar behavior was observed by the authors for a high number of differently modified starches regardless of the presence of different charges, which also indicates that the effect of starch on rheology is not predominantly induced by adsorption mechanisms.

Due to the flexibility, upon shear, the interparticular mobility remains good so that low viscosity can be maintained despite high yield stresses. Nevertheless, the rapid increase of τ_o at high solid content also indicates that starch polymers might entangle at dense particle packing. The latter would explain why Rajayogan et al. [16] found – differing from the results presented here – high viscosity induced by starch at low w/p (volumetric water to powder ratio). The diutan gum based ST2 strongly immobilises water and forms a network. Thus, it strongly stiffens the fluid even at no or low solid contents. At higher particle dosages, the network maintains stable so that additional solids do not significantly increase the yield stress. Nevertheless, the strong increase of viscosity at high solid contents points out that also entanglement of the polymers or between polymers and particles takes place, which reduces the mobility of particles.

In the cementitious systems (Figure 7), ST1 shows similar behavior as in the limestone system. At low cement volume, no significant effect on τ_o can be observed. For the low dosage of ST1, τ_o is even lower than in the reference system without STA. Also η_{pl} is slightly lower than in a system without STA, however, at a 5 % dosage of ST1 η_{pl} is strongly increased due to higher particle volumes. It can be assumed that at such a high dosage entanglement of the starch molecules acts against the motion of particles. While in absence of PCE the effect of ST1 is similar in LSF and cement systems, the behavior of ST2 with different solid types needs further discussion. The influence of the particle solid content on η_{pl} is similar to the LSF system. In case of 0 and 25 % cement, ST2 also shows similar behavior in terms of τ_o as in the LSF system at 0.5 % ST2. At lower



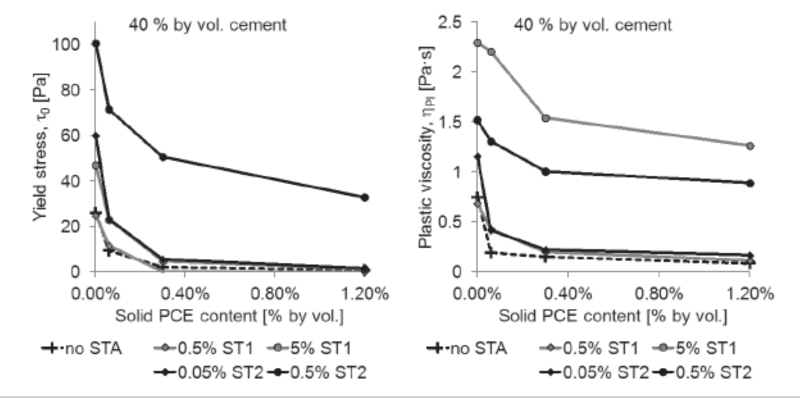


Figure 8 (above): The influence of the PCE content on yield stress and plastic viscosity of LSF-water systems in presence of ST1 and ST2, and without stabilising agent.

Figure 9: The influence of the PCE content on yield stress and plastic viscosity of cement-water systems in presence of different amounts of ST1 and ST2, and without stabilising agent.

dosage of ST2, no significant effect on τ_o can be observed. However, at both dosages at 50 % particle content, τ_o is increased significantly towards values above the yield stress induced by ST1. This is a clear distinction between the LSF system and the cement system. The reason for this might be explained by the stronger attraction forces of the cement (and monosulfate and ettringite in particular) causing more adsorbed ST2 polymers and stronger bonds, which bridge the particles. It can thus be concluded that the stabilising mechanism of ST1 may be more complex than that of ST2, since the enormous size and the special tree-like structure of the amylopectin supplement the stabilising mechanism by an additional particle-polymer interaction, which is triggered by a threshold particle density. ST2 mainly interacts with the fluent phase of a dispersed system, however, with major effect on η_{pl} at increasing solid concentrations. In cementitious systems at higher solid concentration, the anionic character of the polymer may cause a strong tendency to adsorb and increase τ_o by bridging.

In presence of PCE the behavior of both STAs differs (Figure 8 and Figure 9). Already small amounts of PCE significantly reduce τ_o of the pastes regardless of the STA type. Already at the low dosage of 0.06 % of PCE in LSF and cement systems, the yield stresses are approximately bisected. It is noteworthy that differing from the LSF system, in the cementitious system 0.5 % of ST1 exhibits the same yield stresses as cementitious systems without any STA. With further addition of PCE the yield stress values approximate the values of systems without PCE. Above a PCE dosage of 0.3 % in the cementitious system, only the system with 5 % ST2 can maintain a significantly higher yield stress than the water system without STA. In the LSF system, the addition of PCE causes an increase of η_{pl} at 0.06 % PCE, while a significant drop of η_{pl} can be observed for ST2. The latter effect may be induced by the competitive adsorption of PCEs. Further addition of PCE does not significantly modify η_{pl} values for both STAs in LSF.

In comparison to the LSF systems, the addition of PCE causes a significant drop of η_{pl} of the starch systems. It is assumable that in the LSF system only little or no adsorption of ST1 takes place, while in the cementitious system more ST1 can be found adsorbed without PCE. Therefore, effects of competitive adsorption occur more pronounced in the cement system. For the systems with ST2 the influence of the PCE is similar in the LSF and cement system with the difference that in the cement system the slope for the loss of η_{pl} is smaller at low dosages than in the LSF system, which underlines the observation that cement gives a stronger tendency for the ST2 to adsorb. For all mixes with STA η_{pl} remains higher than in the reference system without water. At the same time with the exception of ST2 at 0.5 % dosage at high PCE dosages the effect of the STAs on τ_o is small. Different dosages of ST1 only show little effect on τ_o, while the increase of η_{pl} at higher dosages is very pronounced. Higher dosages of ST2 affect both τ_o and η_{pl} towards significantly higher values. At dosages of 0.5 % for ST1 and 0.05 % for ST2, which can be considered as typical values for the stabilisation of cementitious systems, the behavior of both STAs in presence of PCE is very similar. However, differing behavior could be observed for systems without PCE.

Without doubt the rheometric investigations can only indicate effects, and due to the systems' complexity, it may be impossible, to clearly separately observe single parameters that control the effect of stabilising agents. The latter is particularly valid for the starch stabilising agents due to the extremely differing characteristics of amylose and amylopectin. Based on the present results the following main mechanisms are suggested to account for the observed rheological effects. For ST1 it is concluded that the amylopectin is the main driving parameter for the stabilisation (although supplementary mechanisms may overlap). The stabilising mechanism is considered to be similar to a filler effect with the difference that the filling medium amylopectin remains deformable under shear forces (Figure 10). This mechanism needs a sufficient volume of particles in order to become active. The PCE causes better dispersion of the solids, thus reducing τ_o significantly. Since the amylopectin molecules remain in the solution, they continue hindering motion between particles, which causes that η_{pl} is largely unaffected for LSF and lesser than the yield stress for cement by PCE (Figure 10).

It can be assumed that the major effect of ST2 on yield stress is caused predominantly by water immobilisation, which is the reason, why ST2 increases τ_o and η_{pl} significantly without presence or at low solid particle volumes. At higher particle volume, a rapid increase of τ_o can be observed for cementitious systems, which is assumed to be caused by bridging effects caused by adsorption (Figure 11). Upon addition of SP, indeed, as suggested by Phyfferoen [5], the adsorption of ST2 seems to be reduced. Therefore, the stabilising mechanism in presence of PCE is very similar to that of ST1 (Figure 11).

4 SUMMARY

Investigations were conducted to demonstrate the difference in the stabilising mechanism of STAs based on potato starch (ST1) and diutan gum (ST2) on coarsely dispersed systems. It was shown that it is very important to distinguish between flowable systems with and without adsorptive superplasticizers. While diutan gum effectively stabilised water at low solid particle systems, starch required a certain threshold particle volume in the fluid to significantly affect the yield stress. At high solid content starch effectively increased the yield stress. The same effect could be observed for diutan gum in presence of cement but much lesser in presence of LSF. The addition of PCE significantly reduced the yield stress and the plastic viscosity regardless of the STA. Beyond dosages of 0.06 and 0.3 % for LSF and cement, respectively, an increase of the PCE dosage did not cause any further reduction of yield stress and plastic viscosity.

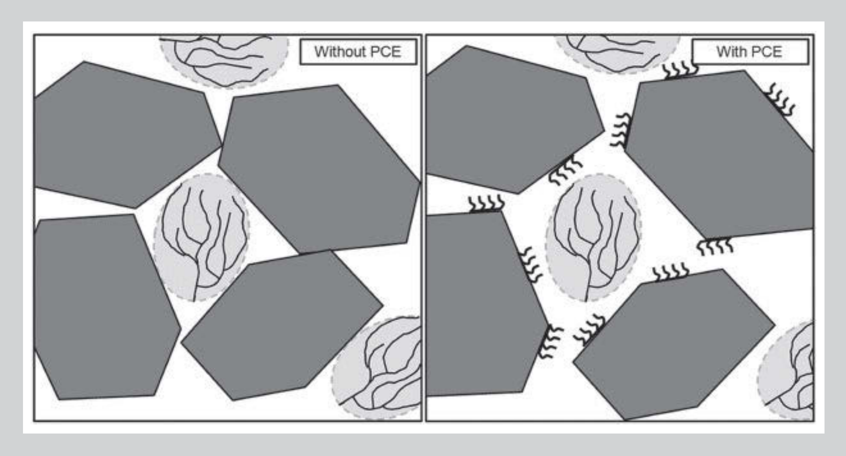


Figure 10 (above): Suggested stabilising mechanism of amylopectin without and with PCE.

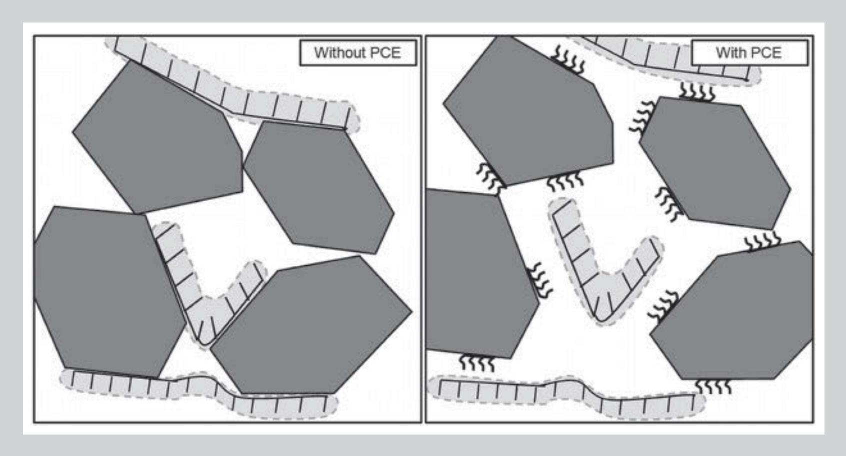


Figure 11: Suggested stabilising mechanism of diutan gum without and with PCE.

In limestone fillers systems ST1 and ST2 were shown to only partly render the behavior in cementitious systems. At low powder volumes and without presence of PCE, limestone filler systems showed qualitatively similar behavior. However at higher powder content and in presence of ST2 the cementitious systems exhibited significantly higher yield stresses, which is most likely caused by stronger bridging effects. In presence of PCE similar observation could be made for the effect of the PCE dosage on performance of ST1 and ST2 for the yield stress. For the plastic viscosity, however, qualitative differences were observed for ST1. The performance differences of the two stabilising agents appeared more pronounced in absence of PCE. In presence of PCE, at dosages of 0.5 and 0.05 % for ST1 and ST2, respectively, both STAs showed similar behavior. At higher dosages of starch the effect on yield stress was small, while a significant increase of the plastic viscosity could be observed. For high dosages of diutan gum yield stress and plastic viscosity could be significantly increased.

The results underline that in coarsely dispersed systems particle interactions significantly contribute to the stabilising mechanism of starch, while diutan functions by immobilising the fluent phase between the particles and by bridging. Upon addition of high amounts of PCE, however, the effects induced by both STAs are similar. Compared to diutan gum, starch is more complex for the use in cementitious systems, since its performance depends on factors such as the particle size distribution and the water to solid ratio. However, since its influence seems to be more independent of the adsorption of particles, it might less interfere with PCE adsorption.

The obtained results are based on the assumption that a Bingham approach can sufficiently describe the stabilising agents' rheological properties. However, particularly at low shear rates, is can be assumed that the observed stabilising agents show clear non-linear behavior. Furthermore, it was observed that particularly the stabilising effect of starch can be reduced over the course of time (e.g. when, due to cold temperatures, the stability is not supported by hydration). Therefore, for future research, it is important to put focus on the behavior particularly at low shear forces.

ACKNOWLEDGEMENTS

The authors would like to thank the reviewers for their thorough and constructive input, including suggestions for supplementary observations, which surely increased the value of this study.

REFERENCES

[1] Khayat KH: Viscosity-enhancing admixtures for cement-based materials – An overview, Cement Concrete Composites 2 (1998) 171–188.

[2] Pourchez J, Peschard A, Grosseau P, Guyonnet R, Guilhot B, Vallee F: HPMC and HEMC influence on cement hydration, Cement Concrete Res. 2 (2006) 288–294.

[3] Yammamuro H, Izumi T, Mizunuma T: Study of non-adsorptive viscosity agents applied to self-compacting concrete, 5th CANMET/ACI International Conference on Superplasticizers and other chemical Admixtures in Concrete (1997) 427–444.

[4] Izumi T, Dikty S, Yamamuro H: Properties of New Polysaccharide as a Thickener for Concrete, 8th CANMET/ACI International Conference on Superplasticizers and other chemical Admixtures in Concrete (2006) 105–116.

[5] Phyfferoen, A, Monty, H, Skaggs B, Sakata N, Yanai S, Yoshizaki M: Evaluation of the biopolymer, Diutan gum, for use in self-compacting concrete, First North American Conference on the Design and Use of Self-Consolidating Concrete (2002) 141–146.

[6] Pourchez J, Govin A, Grosseau P, Guyonnet R, Guilhot B, Ruot B: Alkaline stability of cellulose ethers and impact of their degradation products on cement hydration, Cement Concrete Res. 36 (2006) 1252–1256.

[7] Bechthold A, Seibel, J: Stärke (RD-19-03654) (2012) www.roempp.com.

[8] Lander V: Amylopektin (RD-16-03559) (2012) http://www.roempp.com.

[9] BeMiller JN, Huber KC: Starch – Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag (2000).

[10] Coleman R, Patel Y, Harding N: Identification and organization of genes for diutan polysaccharide synthesis from Sphingomonas sp. ATCC 53159, Journal of Industrial Microbiology & Biotechnology, 4 (2008) 263–274.

[11] Sonebi M, McKendry D: Effect of Mix Proportions on Rheological and Hardened Properties of Composite Cement Pastes, Open Construction Build. Technol. J. 2 (2008) 15–23.

[12] Swinkels JJM: Composition and Properties of Commercial Native Starches, Starch – Stärke 37 (1985) 1–5.

[13] Khayat KH, Ghezal A: Effect of viscosity-modifying admixture-superplasticizer combination on flow properties of scc equivalent motar, 3rd International RILEM Symposium on Self-Compacting Concrete (2003) 369–385.

[14] Sonebi M: Rheological properties of grouts with viscosity modifying agents as diutan gum and welan gum incorporating pulverised fly ash, Cement Concrete Res. 9 (2006) 1609–1618.

[15] Sonebi M: Rheological characterization of cement-based materials pastes containing Diutan Gum and limestone powder, 12th International Congress on the Chemistry of Cement (2007).

[16] Rajayogan V, Santhanam M, Sarma BS: Evaluation of hydroxy propyl starch as a viscosity-modifying agent for self compacting concrete, 3rd International RILEM Symposium on Self-Compacting Concrete (2003) 386–394.

[17] Terpstra J: Stabilizing self-levelling concrete with polysaccharide additive, SCC'2005-China: 1st International Symposium on Design, Performance and Use of Self-Consolidating Concrete (2005) 207–213.

[18] Simonides H, Terpstra J: Use of innovative starch ethers for paving blocks and other concrete products, Concrete Plant + Precast Technology 9 (2007) 38–45.

[19] Schmidt W, Brouwers HJH, Kühne, H-C, Meng B: Influence of Environmental Temperatures on the Performance of Polymeric Stabilising Agent in Fresh Cementitious Materials, Key Engineering Materials 466 (2011) 97–104.

[20] Brumaud C, Baumann R Schmitz M, Roussel N: Influence Of High Molar Mass Polymers On The Rheological Behavior Of Fresh Cement Pastes, ICCC 13th International Congress on the Chemistry of Cement (2011).

[21] Fugmann B, Lützen A: Cellulose (RD-03-00833) (2012) http://www.roempp.com.

[22] Phyfferoen A, Skaggs CB: Optimizing the use of welan gum in cementitious and gypsum-based systems, ConChem – International Exhibition & Conference (1997) 193 – 202.

[23] Palascios M, Flatt R, Puertas F, Sanchez-Herencia A: Compatibility between Polycarboxylate and Viscosity-Modifying Admixtures in Cement Pastes, 10th International Conference on Superplasticizers and Other Admixtures in Concrete (2012) 29 – 40.

[24] Zingg A, Winnefeld F, Holzer L, Pakusch J, Becker S, Figi R, Gauckler L: Interaction of polycarboxylate-based superplasticizers with cements containing different C3A amounts, Cement Concrete Comp. 3 (2009) 153 – 162.

[25] Plank J, Bassioni G, Dai Z, Keller H, Sachsenhauser B, Zouaoui N: Neues zur Wechselwirkung zwischen Zementen und Polycarboxylat-Fließmitteln, 16th International Conference on Building Materials – ibausil (2006) 579 – 598.

[26] Plank J, Hirsch C: Impact of zeta potential of early cement hydration phases on superplasticizer adsorption, Cement Concrete Res. 4 (2007) 537 – 542.

[27] Giraudeau C, D'Espinose De Lacaillerie J-B, Souguir Z, Nonat A, Flatt RJ: Surface and Intercalation Chemistry of Polycarboxylate Copolymers in Cementitious Systems, J. Am. Ceramic Soc. 11 (2009) 2471 – 2488.

[28] Winter CAJ: Untersuchungen zur Verträglichkeit von Polycarboxylaten mit den Hydratationsverzögerern Citrat und Tartrat und zur Wirkung der Caseinfraktionen α-, β- und κ- Casein im ternären Bindemittelsystem Portlandzement-Tonerdeschmelzzement-Synthetischer Anhydrit, TU-München, München (2007).

[29] Terpstra J: Stabilizing low-viscous self-compacting concrete, 2nd North American Conference on the Design and Use of Self-Consolidating Concrete (SCC) and 4th International RILEM Symposium on Self-Compacting Concrete (2005) 47 – 53.

[30] Zhang J, Weissinger EA, Peethamparan S, Scherer GW: Early hydration and setting of oil well cement, Cement Concrete Res. 7 (2010) 1023 – 1033.

[31] Puntke W: Wasseranspruch von feinen Kornhaufwerken, Beton 5 (2002) 242 – 248.

[32] Burchard W:Polysaccharides – Structural diversity and functional versatility, Marcel Dekker (2005).

[33] Izaguirre A, Lanas J, Álvarez JI: Behaviour of a starch as a viscosity modifier for aerial lime-based mortars, Carbohydrate Polymers 80 (2010) 222 – 228.