Influences of superplasticizer modification and mixture composition on the performance of self-compacting concrete at varied ambient temperatures

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ABSTRACT

The fresh behaviour of self-compacting concrete (SCC) at varying temperatures differs from that of normal vibrated concrete. This is because the rheology of SCC depends not only on degree of cement hydration, but also on the adsorption of superplasticizers – mostly polycarboxylate based polymers (PCE) -, which is affected by the time and hydration progress. Due to the variety of PCEs and mixture compositions for SCC a prediction of the rheology at varying temperatures is complicated. The charge densities of PCEs as well as the water to solid ratio in the paste are identified to be the main decisive parameters for robust fresh concrete properties.

Rheometric concrete investigations with different SCC mixture compositions and varied anionic charge densities of the PCE were conducted. SCC which is rich in powder components showed robust performance at low temperatures while SCC with low powder content was favourable at high temperatures. High charge density PCE pointed out to be very robust at low temperatures but at high temperatures it significantly reduced the flow retention. Low charge density PCE could not generate self-compacting properties at low temperatures but retained the flow performance over sufficiently long time. Based on considerations about particle interactions and adsorption mechanisms of PCEs, the relevant processes are explained and options for the development of robust mixture compositions for individual temperature ranges are itemised.

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1. Introduction

In addition to cost, one major obstacle to the extensive usage of self-consolidating concrete (SCC) within the ready-mix industry is the high complexity of its constituents working together. The high complexity and the sometime unpredictable performance upon changes of ambient or processing parameters can make SCC less robust than vibrated concrete. For successful applications of SCC at the construction site, it should be robust with respect to variations in processing parameters and the environmental boundary conditions.

Robustness is typically understood as stability against variations in quality and quantity of the constituents or as the capability to absorb human or process-technological uncertainties [1–5]. Most influences can be overcome by a good quality control system, improved logistics and process technologies. These can be directly controlled by the staff. However, the environmental conditions during the whole concreting process can only be predicted by

weather forecast, but moderate to rapid temperature changes at the construction site can cause trouble during SCC casting. The robustness of ready-mix concrete with respect to such environmental temperatures can thus be considered as a major key to improving the acceptance of SCC technology for ready-mix applications.

1.1. Importance of consideration of the ambient temperature

As reported by Brameshuber and Übachs [6] already slight changes of the temperature might already cause serious problems for the workability or the durability of SCC. From that point of view temperature dependent performance changes are generally critical for pre-cast and ready-mix or construction site concreting. However, the range of temperatures that are likely to occur during casting is much wider in the field of the ready-mix concrete.

The annual temperature differences are of importance in case of casting the same concrete mixture composition at different periods of the year. However, temperatures can also strongly vary throughout a single day, which is even more critically for concreting. For example, the "Digitaler Umweltatlas Berlin, 2001" [7] provides

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data from July 8, 1991 where daily temperatures measured at a height of 2 m varied within 24 h depending upon the location between 10.2 and 17.5 °C. Khayat et al. report about SCC that was cast in Montreal during at a day when ambient temperatures varied between 10 °C in the night and 30 °C during the day [8].

The annual as well as the daily temperature changes are a serious threat to SCC, since the handling of performance loss is much more delicate than it is for normal concrete. While for vibrated concrete stiff consistencies can be partly compensated by higher or longer vibration, vibrating SCC can cause segregation which would likely deteriorate the structure even more than inadequate filling.

In order to safely cast SCC on the construction site the specific effects of the environmental temperature on the flow properties of SCC need to be taken into account, and mixture compositions need to be developed that are robust against varying temperatures.

1.2. Influence of temperature on the workability of normal concrete

Upon addition of water to a cementitious system metal ions, calcium ions (Ca^{2+}), sulphate ions (SO_4^{2-}) hydroxide ions (OH^-), and smaller amounts of aluminates and silicate are interacting in the solution [9–13]. Within short time a gel like layer, which is rich of alumina and silica, forms around the surfaces of the cement grain and within approximately 10 min ettringite forms stubby rods on the surfaces of the grain and in the solution. The latter are generated from sulphate and calcium aluminate reaction. Depending upon the sulphate and aluminate contents, alumina, ferric oxide mono-sulphate phase (AFt), ferric oxide tri-sulphate phase (AFm) or gypsum can occur. The most significant AFt and AFm phases at this point in time are ettringite and monosulphate, respectively. After this initial reaction, a dormant period occurs for several hours at which no significant amounts of new reaction products are building. Despite the use of the word dormant period reactions yielding morphological changes on the surfaces take place. According to Locher [10] ettringite undergoes re-crystallisation during the dormant period although no new reaction products are built or chemical reactions take place. This is brought in context with loss of workability. According to Yamada et al. [14] the specific surface of cement paste increases steadily throughout the first 120 min after water addition. The latter changes take place quicker at high temperature and slower at low temperature. Hence, temperature acts as accelerator or retarder of reactions, typically generating a quick loss of workability at high temperature and extended workability time at lower temperatures.

1.3. Influence of temperature on the workability of SCC

The formerly mentioned effects of temperature on the workability basically taking place in the binder paste are generally valid for SCC and normal concrete likewise. The major difference between SCC and normal concrete is the high amount of superplasticizer (SP) that is required for SCC to provide a sufficiently low yield stress for self-compacting properties. For SCC typically SPs with polycarboxylic backbone (PCE) are typically used. SPs adsorb on the surfaces of cement and mineral particles [15–20]. As all common types of SPs provide a negatively charged backbone as adsorbing unit they are typically attracted by positively charged surfaces or upon flow by areas providing a positively charged zeta potential (ζ). According to Yoshioka et al. [21] adsorption of SPs predominantly takes place on the surfaces of C_3A and C_4AF initially [21] as well as on monosulphate and ettringite, of which ettringite provides the highest ζ [22]. If in case of SCC high amounts of SP are added to the mixture significant amounts of PCE do not adsorb immediately but with time shift upon formation of ettringite. This means that ettringite, which reduces the workability of a cementitious system without SP, virtually provides flowability in a system incorporating high amounts of SP.

Finally two opposing effects act in parallel in SCC, which are determined by the temperature. While increasing temperature

Fig. 1. Difference between normal concrete and SCC at exposure to varying temperatures.

negatively affects the workability by accelerating the hydration, the accelerated growth of ettringite quickly provides large adsorption sites for SPs, which again positively affects the flowability. Decreasing temperatures positively affect the workability retention but as a result of slow hydration might not generate sufficient adsorption sites for SPs so that they remain ineffectively in the solution.

Hence, as presented in Fig. 1 the temperature dependent behaviour of concrete without or with only small amounts of SP is always determined by the way, temperature affects the hydration. For concrete containing high amounts of SP varying concrete temperatures affect the hydration velocity and the adsorption of SP, while both effects oppose each other.

1.4. Research objectives

As shown in Fig. 1, the flow performance of SCC can be linked to the adsorption behaviour of PCE. Today's PCEs are very versatile and occur in a wide variety of molecular architectures with influence on the charge density of the polymer. The latter property affects the adsorption tendency over the course of time with strong effects on the rheology and the slump retention. This important influence of the molecular architecture of PCEs is very often neglected in research but is responsible for many observed effects induced by temperature influences. Furthermore, SCC occurs in numerous variations and the respective water to powder compositions may vary strongly. This study aims at better understanding the role of the SCC mixture composition and PCE specification for the temperature depending behaviour.

To point out the importance of mixture composition and of the PCE specification, literature on the flow properties of SCC at different temperatures is surveyed and discussed. The experimental work is presented thereafter.

2. Experiences with SCC at varying temperatures

2.1. Practical experiences with SCC at varied temperatures

There are only few reports available that provide data from real site applications about the concrete performances in the context of the casting temperature.

Khayat et al. [8,23] investigated SCC used for the repair of retaining wall elements in Montreal cast with two types of SP based on polynaphtalene sulphonate (PNS) and PCE. The concrete with PNS was cast at ambient temperature of 14 °C. The respective slump flow diameters reduced from 640 to 540 mm within 60 min of casting. The concrete with PCE was cast at ambient temperature of 6 °C and the slump flow diameters increased within the first hour from 600 mm to 660 mm. This emphasises the difficulty to predict the response of SCC at varying temperatures as well as the importance to consider the superplasticizers as critical factor for the performance.

Heunisch et al. examined SCC castings for inner shells of tunnels [24]. The mixtures incorporated PCE superplasticizers. The concrete temperatures were kept between 8 °C and 25 °C. Concrete temperatures, average slump flow diameters, and V-funnel efflux times were recorded on the mixing plant as well as on the construction site. Fig. 2 shows slump flow values and V-funnel efflux times vs. concrete temperatures based on the recorded data in the report. It can be clearly seen that as a result of the transportation the range of measurable temperatures is much wider than the range of the mixing plant. Both data sets show a strong and quite linear correlation between concrete temperature and slump flow diameter such way that increasing concrete temperatures coincide with smaller slump flow diameters. Regarding the V-funnel efflux
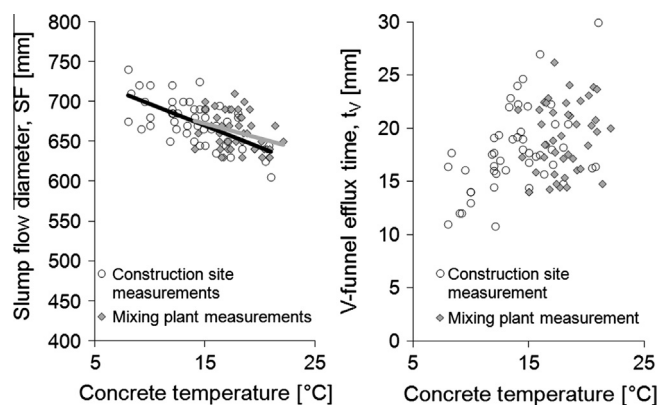
Fig. 2. Influence of concrete temperature on slump flow diameters and V-funnel efflux times after data by Heunisch et al. [24].

times the scatter is much larger, which might be a result of greater measurement inaccuracies of the methods. However, a trend towards longer efflux times with increasing temperatures is identifiable.

2.2. Research experiences on paste and mortar level

Temperature effects on the fresh concrete properties were studied by several researchers with a variety of results. Most of the research was done on paste or mortar.

Based on research of cement pastes blended with and without silica fume (SF), a water to cementitious materials ration (w/cm) of 0.35, and SP based on PNS Jolicoeur et al. investigated the effects of temperature and PNS addition on the rheological properties on the retention of slump area and viscosity as well as on the adsorption of polymers [17]. Temperatures were varied between 0 and 40 °C. Regardless of the PNS amount the influence of the temperature on the initial mini slump area at a particular PNS dosage was low in case of the cement without silica fume. In case of cement with silica fume increasing temperatures in the range between 10 and 40 °C correlated with reduced areas. Investigations of the fluidity ($1/\eta$) showed that rising temperatures caused a high increase of the initial fluidity in case of cement without silica fume. The inverse could be observed for cement with silica fume even though the slope was much smaller. The authors concluded that in case of PNS added in excess to a saturation dosage the time dependent rheology is related to the PNS concentration in the solution. However, paste fluidity is affected by temperature in a sometimes non-linear and unpredictable fashion which means other effects might enhance or oppose effects of adsorbed SP.

Yamada investigated the influence of temperatures of 5, 20, and 30 °C on ordinary Portland cement (OPC) pastes with w/c 0.3 and 1.0% PCE by mass of cement compared to non-superplasticized paste with w/c 0.5 [14]. Without PCE the flow area decreased at all temperatures between 0 and 120 min. With PCE at 5 and 20 °C within the same time span an increase of the flow area could be observed while the flow areas remained stable. The authors showed that increasing amounts of PCE adsorb with time. The initial adsorption as well as the increase was the smallest at 5 °C while 20 and 30 °C behave similarly. By varying the sulphate ion concentration in the solution, they showed that PCE adsorption is strongly depending on the sulphate ions content in the pore solution. Based on these results, the authors developed a model based on the factors BET surface change and the sulphate ion concentration. At low temperatures the high initial sulphate ion content outweighs the relatively small change of the surface yielding

increasing flowability with time. At high temperatures the effect of the rapidly increasing surface area prevails, causing a time dependent loss of flowability.

Roncero et al. observed the influence of temperatures between 5 °C and 45 °C on the flow properties of ordinary cement paste with w/c 0.33 and two different SPs based on PNS and a copolymer of oxyethylene–oxypropylene [25]. Rheological properties were determined by using a Marsh cone (ASTM C 939-87). It was shown that increasing SP addition reduced the efflux times until a saturation point at which the efflux times increased again. Increasing temperatures reduced the flow times. At initial saturation level the retention of the flow time was investigated additionally and did not increase strongly for both SPs below 25 °C and increased more pronounced for higher temperatures. The authors concluded that the adsorption of SP polymers is basically depending on the particles' surface area and that upon saturation no further flowability can be provided. As a result at low temperatures, where poor flow properties could be observed, the addition of supplementary SP could not improve the flowability.

Brameshuber and Übachs investigated the influence of different PCE modifications on mortars from OPC with w/c 0.55 at 5, 10, 15, 20, and 30 °C [6]. The observed six different polymers varied in backbone length and side chain length. After adjustment to comparable slump flow values at 20 °C the mixes were investigated in a rotational rheometer at different temperatures at constant shear rate for 90 min. The initial shear resistance at low temperatures was higher than at higher temperatures with time delayed liquefaction. Furthermore the polymer modifications showed a wide range of temperature dependent effects, which could not systematically be linked to the polymer structure. In another publication the authors also discussed data from ramp tests, which provide qualitative data about the development of yield stress and plastic viscosity [26]. Here at 20 °C and 30 °C a Bingham approach could well describe the rheological properties. At 10 °C the mortar showed shear thickening behaviour. The authors attributed the observed effects to possible influences of the graft chain lengths the polymers.

Strong effects of the mixture temperature on the rheological properties and their retention are also reported by Svavarsson and Wallevik [27] based on well cement slurries with w/c 0.8 for slurries without SP and w/c 0.66 for slurries with SP at 20, 40, and 60 °C. Increasing temperatures came along with higher initial yield stress and more rapid increase of the yield stress with time. A trend towards higher viscosity with increasing temperature could also be observed. The authors state that workability is depending on two parameters, which are time and temperature.

This was endorsed by Petit et al. [28–32] based on rheometric analyses of micromortars with a maximum grain size of 315 μm, w/c 0.53 and w/c 0.42, and SP based on PNS and PCE. The authors showed that yield stress increased with time in a linear way when PNS was used. Initial yield stress and time dependent behaviour were qualitatively comparable for all temperatures. The authors concluded that temperature basically acts as a catalyst to accelerate or slow down hydration, determining the time depending flow performance. The behaviour with PCE was different. Above a specific threshold temperature yield stresses increased rather linearly with time. Below that temperature an initial retention or even reduction of yield stress could be observed until approximately 30% of the dormant period had passed, after which yield stress increased again. Various mixture compositions were investigated showing individual and widely differing threshold temperatures between 15 and 33 °C. The authors concluded that the threshold temperature that yields workability retention is mixture specific.

Based on OPC pastes with w/c 0.33 Fernandez-Altable and Casanova [33] observed the influence of SP content, admixture addition time, and temperature on the rheological properties directly after mixing. The study showed that a delayed addition of PCE reduced the apparent viscosity and the yield stress. The performance difference between early and delayed addition was prominent at low PCE additions and diminishing with increasing additions. The effect was related to fewer intercalates into early forming mineral layers.

Nehdi and Al Martini developed a prediction model for oscillatory yield stress depending upon temperature, mixing time, and SP type [34]. PCE, melamine sulphonate superplasticizer, and PNS were varied. The w/c was 0.38. OPC was used for the experimental part. Within the observed temperature range between 22 and 45 °C and the observed combinations of particular superplasticizers and the particular cement the predicted results fitted in with the measured values with reasonable accuracy when individual models for each SP were chosen. The rheological measurements pointed out that increasing temperatures produced higher yield stresses at particular SP content. The temperature influence was strongest with ML, followed by PNS and it was lowest for PCE.

Schmidt et al. [35–37] compared paste and mortar calculated from an SCC mixture composition containing OPC, limestone filler (LSF), and fly ash (FA). The influence of temperature and supplementary admixtures to PCE such as shrinkage reducing agent (SRA) and viscosity modifying agent (VMA) on the flow properties was observed. Fig. 3 shows that VMA significantly reduced the Haegermann flow spread diameter d_{SF}, while supplementary SRA improved the flow properties again. SRA showed particularly positive effects on the flow properties at high temperatures. These effects were significantly less prominent in case of mortar tests. With mortar the admixture compounds showed no significant influence at low temperatures. At 20 °C and at 30 °C each supplementary admixture component contributed to a reduction of the slump flow diameter with higher impact at 30 °C. In paste systems effects of the admixtures were strong while influences of the temperature were small. In mortar systems increasing temperatures caused significant loss of performance. The authors concluded that although admixtures can strongly affect the flow performance of pastes this does not inevitably need to have significance for concrete or mortar. Reason for this might be that effects on paste rheology are overcompensated by the rheology of the aggregate granules. It is therefore most important to evaluate observations made on paste level against its relevance for the concrete level.

2.3. Research experiences with concrete level

Höveling and Lohaus compared J-ring spread values of two SCCs with high powder contents and a flowable concrete with lower powder content and different w/c [38]. The SCC with highest
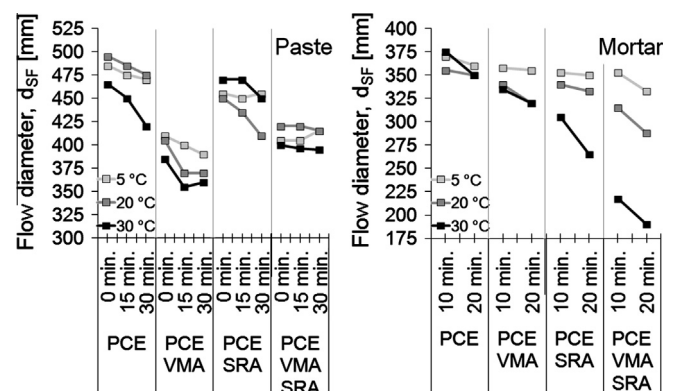

Fig. 3. Slump flow values of paste and mortar generated from this paste depending upon time and admixture setup based on the data after Schmidt et al. [37].

powder content lost flow performance during the first 60 min but remained flowable at 20 °C. At 30 °C the SCC was no longer workable after 60 min. The SCC with slightly lower powder content showed similar behaviour but less workability loss at 30 °C. At 5 °C for both high powder content SCCs the initial diameters were significantly smaller than at higher temperatures. However, with time the values approximated the values measured at 20 °C. In general, lower temperatures correlated with increasing t_{500} times. This observation correlates to the paste observation of Fernandez-Altable and Casanova [33].

Assaad and Khayat studied the effect of the casting rate and the concrete temperature on the formwork pressure for SCC [39] with mixes with w/c 0.4. The SCCs were observed at 10, 20, and 30 °C. The PCE content was identical for 10 °C and 20 °C and slightly higher for 30 °C. Temperature effects on the slump flow values were negligible. However, the time dependent evolution of the lateral pressure indicated that increasing temperatures accelerated the decline of the initial formwork pressure and also led to earlier times at which the lateral pressure drops significantly.

Golaszewski and Cygan compared paste and cement generated from two different paste compositions containing LSF at 5 °C, 20 °C, and 30 °C [40]. One paste was composed with w/cm 0.3 the other with 0.4. Regardless of the w/cm both pastes exhibited the lowest flow spread values at 20 °C. The paste with higher w/cm generated comparable higher spread values, whereas the spread diameter of the paste with lower w/cm at low temperatures was in the same range higher as it was noticed in the other mixture, but at 30 °C the increase was most prominent. A systematic effect of the temperature on paste could not be observed. In another step the paste was filled up with aggregates up to 16 mm. The volumetric ratio of paste to aggregate was varied between 1.15 and 1.85 and slump flow values were measured 20 and 60 min after water addition. Due to the ratio variation, the powder contents varied between 476 kg/m^3 and 720 kg/m^3. At all temperatures and for both paste compositions increasing volumes of aggregates caused wider slump flow diameters. Increasing temperatures reduces the slump flow as well as the time dependent performance retention. The concretes showed identical effects as the pastes at low temperatures. However, high temperatures caused stiffening of the concretes for all modifications. The authors concluded that temperature increase has negative effects on the workability of SCC and that the consideration of solely paste might lead to inaccurate conclusions.

Schmidt and Kühne presented V-funnel efflux times for three different SCC modifications with w/cm 0.35 containing different FA contents replacing cement [37,41]. At 5 °C and 30 °C for all mixtures higher efflux times than at 20 °C were measured. However, while at 30 °C the longer efflux duration could be linked to high viscosity at 5 °C the longer efflux time was a result of segregation of aggregates which blocked the funnel nozzle. The segregation tendency at low temperature coincided with reduced slump flow diameters and a rapid loss of workability with time.

Results of different SCCs were presented in another study of the same authors. These are shown in Fig. 4 [42]. The presented mixtures exhibited w/cm 0.36 and varied only in type and amount of VMA. Initially and over the course of time a strong loss of performance could be observed at 5 °C. However, at 30 °C both mixtures show significantly wider slump flow diameters than at 20 °C and approximated with time towards similar slump flow values. The increase of the slump flow correlated with a noticeable but uncritical segregation brim during the initial slump flow test. At cold temperatures within 15 min a retarded liquefaction took place.

Weisheit et al. investigated the effect of temperature on the rheological properties by observing slump flow values and V-funnel times. These were compared to results from a rotational concrete rheometer [43]. The SCC contained only cement as powder
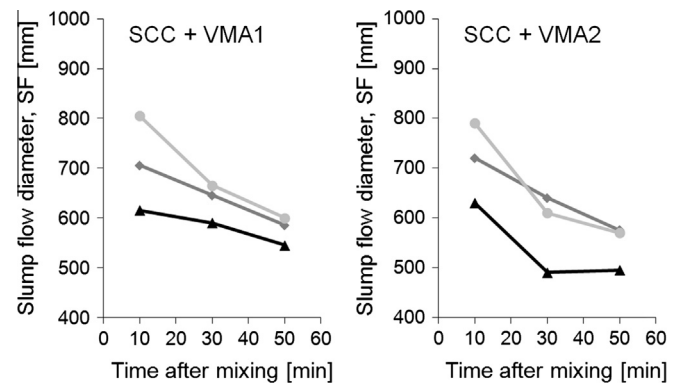

Fig. 4. Slump flow test results at varied temperature for mixes composed with different VMA types and contents.

component and w/c 0.45. The cement used for the investigations was blast furnace cement (CEM III). Increasing temperatures caused wider slump flow diameters and reduced the yield stress. Comparing V-funnel times to the qualitative results for the viscosity indicated that viscosities were lowest at 20 °C. In a second step the authors adjusted identical slump flow at all temperatures by adding or reducing PCE. They found that highest contents of PCE were required at cold temperatures and lowest at high temperatures. With these performance adjusted mixtures rheological tests were repeated, showing a significant gain in flow properties within the first 30 min at cold temperature and a marked loss at high temperatures.

Al Martini and Nehdi compared the influences of temperatures between 22 °C and 45 °C on the rheological properties of OPC paste and concrete both with w/cm 0.38 [44]. Measurements were made 20, 50, 80, and 110 min after water addition, during which the paste and cement was continuously mixed. The PCE saturation dosage at which further addition of PCE does not further reduce the yield stress was more or less identical for cement paste at all temperatures. Below this dosage the yield stress increased quickly with time. This occurred more pronounced at 35 °C and 45 °C than at 22 °C. For concrete the saturation dosage increased with increasing temperature. The authors concluded that PCE should be added at the saturation dosage at high temperatures, in order to make sure that time and accelerated hydration do not negatively affect the rheological properties.

Ghafoori and Diawara observed the influence of temperature on the performance of the same SCC mixture composition modified by three different PCE and VMA contents [45]. Based on the observations a flow chart was developed, explaining temperature effects based on the adsorption of superplasticizers per specific surface area. This chart is similar to the explanation model of Yamada et al. [14] amended by influences of the water content and the respective contribution of the aggregates.

2.4. Discussion of research experiences

Most of the studies discussed before observe the rheological properties only at a single step in time. This is not sufficient to describe the temperature dependent effects. This is also fortified by Göller et al. [20], who confirm that the retention ratio is the main parameter affected by superplasticizer type, w/c, and ambient temperature. The initial flow might differ strongly from the time dependent performance.

All authors are in agreement about the temperature affecting the adsorption of SPs on particles. According to most authors, the latter is influenced by the initial and the time dependent specific surface of the paste, which differs depending upon the particular

mixture temperature from slow increase at low temperatures toward quick increase at high temperature.

However, neither the specific surface of the paste or its growth nor the adsorption of PCE is fully adequate to describe the behaviour of PCE sufficiently.

SPs do not only adsorb on cement particles. Several authors report about possible intercalation of PCE into AFm phases yielding so called organo-mineral phases (OMP) [18,46,47]. Intercalated PCE can no longer contribute to flowability. In order to cope with this conflict, Flatt and Houst [18] suggest to better chose the word consumption of PCE instead of adsorption. This consumption of PCE is not automatically linked to improved flowability, as the steric dispersion is only provided by those polymers being adsorbed at the outer particle areas.

As presented by Plank and Hirsch [22] after initial adsorption on C_3A and C_4AF, PCE molecules mainly adsorb on surfaces of AFm and AFt, as they provide positively charged zeta potentials (ζ), AFt providing the highest ζ. The adsorption on C–S–H, which can also take place upon high Ca^{2+} ion concentrations in the solution is negligible, as the amount of adsorbable polymers compared to the high specific surface area of C–S–H is small. Hence, a high surface area by itself does not automatically promote the adsorption of PCE. However, it is certainly evident that surface growth is to a large part caused by the ongoing hydration of ettringite or its re-crystallisation with time during the so called dormant period at which C–S–H hydration is reduced to a rate close to zero. It is now depending upon the amount of PCE in the system whether AFm and AFt growth contributes to or adversely affects the flowability. At high concentrations of PCE it is likely that hydration causes stiffening when insufficient PCE is available, due to morphological changes of the particle surfaces and hydrates filling up the gaps between particles upon hydration in the solution, which according to Winnefeld et al. is fostered by PCE addition [48]. At excess PCE time delayed adsorption of PCE causes improved flowability.

As neither the adsorbed part of the consumed PCE can be precisely determined nor can the influence of the surface growth on the rheological properties be easily predicted, the adsorption of PCE per surface area cannot precisely predict the influence of the temperature on the flow properties of SCC. However, qualitatively the results should correlate well with real observations. Intercalations can be assumed not to play a major role for temperature related influences. They occur less prominently with PCE than with other SPs due to lower charge densities and longer graft chains. If specific performance properties are adjusted their negative effect can be ignored as long as the mixing regime remains identically. Finding a general rule in which way temperature affects intercalations, is difficult to discuss, as this might be much more dependent on the individual cement chemistry, particularly the C_3A content and surface, and the set retarder's solubility. Increasing temperatures might either foster growth of ettringite due to quicker precipitation of sulphate ions, which would yield a lower amount of intercalates. It could also foster the hydration of monosulphate, thus creating more intercalates, as the reactivity of the aluminates is improved. Also the surface growth definitively affects the workability. It is likely that the C–S–H hydration generally affects the workability negatively. Also ettringite and monosulphate show negative effects on the flowability, depending upon the amount of PCE they only undergo a certain early period at which they can show indefinite behaviour.

Due to the specific role of the ettringite growth it is thus problematic to observe only a single step in time to evaluate temperature effects. E.g. as in Fig. 4, the flow performance changes significantly with time. A single step in time can thus only be an arbitrary choice, which is not sufficient to explain phenomena. This is particularly a problem when rheological properties are investigated immediately after mixing. The flow properties directly after

mixing can be strongly affected by thixotropy and time shifted influences of the steady high shear force in the mixer, which affects the formation of AFm, AFt, and secondary gypsum.

E.g. Schmidt et al. report about reasonably good flow properties at cold temperatures, when the concrete was tested directly after mixing, while the flowability rapidly went down within the next minutes [37,41]. Furthermore, effects of mixing time can be assumed to play a significantly higher role for the measurements immediately after mixing. As seen in Fig. 5, during the first 20 min the influence of the mixer type plays an important role for the performance of SCC. From these results, SCC with high powder content seems to be more flowable after mixing at high intensity shearing in an intensive mixer compared to a compulsory mixer. Considering later steps in time the performance approximated for both mixer types.

Hence, a comprehensive observation of temperature effects can only be conducted when time aspects are considered adequately. The latter are diffused by the hydration of mainly ettringite and with minor importance monosulphate. Considering the important role of AFm and AFt most aforementioned studies neglected that PCE superplasticizers are markedly more versatile in their configurable appearance than elder generations of SPs. Backbone and graft chemistry as well as their lengths can be modified largely independent from each other. A good overview about different solution structures of PCE molecules is given by Plank et. al. [19]. Only in the studies by Brameshuber and Übachs attention was paid to the influence of the molecular structure [6]. However, their observations did not lead to a simple regularity and the authors could only conclude that the graft chain length might have a certain not tangible influence on the temperature dependent behaviour of SCC.

The role of the polymeric structure is clarified in an important study published by Schober and Flatt on the rheological properties of SCC with validity for paste and concrete [16,49]. This study was supplemented by a case study published by Schober and Mäder [50]. The first result of practical importance is that there is a largely linear correlation between slump flow diameter and amount of adsorbed polymers. The second important result is that upon adsorption the flow performance is no more significantly influenced directly by the molecular structure. The adsorption is mainly determined by the anionic charge of the polymer and the charge density of the backbone. The latter is confirmed by a study of Plank and Hirsch [22]. In this context the graft chain length indirectly affects the flow properties as the grafting degree determines the charge density of the backbone, and thus the adsorption properties.

Also the time dependent adsorption of PCE is depending on the charge density. As presented by Yamada and Hanehara [51] and by Plank et al. [19] SPs adsorb in competition with sulphate ions.
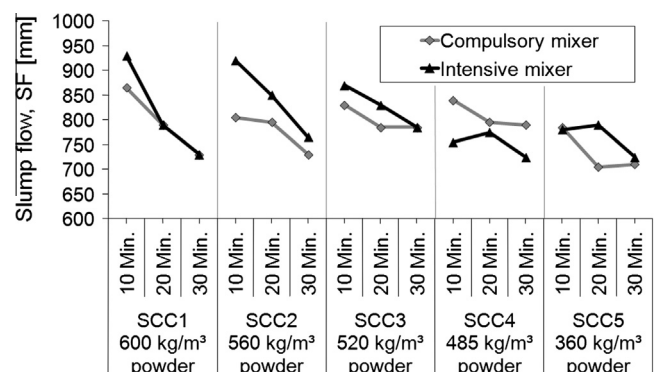

Fig. 5. Slump flow performance of different mixture compositions depending on the mixer type.

Although the adsorption of PCE is partly determined by entropic effects [52,53], the adsorption is to a large part driven by electrostatic attraction between the backbone and the opposite charge of the adsorption site. High charge densities of the backbone favour the adsorption of PCE, while PCE with low charge density of the backbone might be pushed back by sulphate ions to remain firstly ineffective in the solution. However, the significantly higher amount of low charge density polymers remaining in solution can be adsorbed over the course of time upon hydration of ettringite.

The influence of the delayed adsorption of PCE is illustrated in Fig. 6 considering the aforementioned mechanisms. This process clarifies the role of the charge density of the PCE. High charge density causes early and favoured adsorption of PCE with quicker consumption by ongoing hydration. Low charge density causes delayed adsorption but retarded consumption. As the temperature accelerates or slows down the hydration and thus the occurrence of new adsorption sites it is becoming evident that the charge density of the polymer can be identified as the driving influencing factor for the performance of SCC at varying temperature.

Another aspect determining the flow properties is the mixture composition of the SCC itself. In general SCC with high powder content and low w/cm has a low yield stress and a high viscosity while viscosity modifying agent type SCC typically has a higher yield stress but low viscosity. Powder-rich SCC and powder-poor SCC distinguish significantly in how strongly PCE affects rheology. The flow properties of powder type SCC are resulting from an optimised particle packing while the water has mainly a lubricating role. For this type of concrete the effectiveness of a dispersing agent is of highest importance. In viscosity modifying agent type SCCs particles are typically less densely packed. The higher viscous fluid phase contributes much more to the flow properties. As the contribution of PCE to rheological properties might vary depending upon the mixture composition type it is likely that the before mentioned influence of the PCE charge density also varies depending on the mixture composition type. This would also explain controversial observations that were made in concrete tests [37,38,40,41,43].

Schmidt and Kühne [42] and Weisheit et al. [43] report about poor flow performance at low temperature and wider flow values with increasing temperature, while Golaszewski and Cygan [40] report about contrary behaviour. The latter behaviour was also reported by Ghafoori and Diawara [45]. However, as the tests took place immediately after mixing these might be of limited significance. Taking a closer look at the mixtures employed by Golaszewski and Cygan all mixtures that can be compared to an identical mixture at different temperatures contain powder contents higher than 535 kg/m^3, most of which contain powder contents between 600 and 700 kg/m^3. The mixture compositions from Schmidt and Kühne and Weisheit et al. contain powder contents between

420 kg/m^3 and 480 kg/m^3. The first results can thus be attributed to SCC, which rather represents a powder type, while the latter rather represent viscosity modifying agent types. The results give a hint that in considering temperature dependent effects on SCC the mixture composition type can have a decisive role in which way PCE affects the rheology. The results of Lohaus and Höveling [38] support this observation. Both investigated mixtures with high and medium powder content exhibited smaller flow diameters at cold temperatures. However, in case of high powder content the difference to 20 °C was small while with low powder content it was pronounced. Another aspect, which also recommends to closer observe mixture composition influences, is the fact that SCCs with high powder contents typically contains high amounts of fillers that contribute to accelerated hydration by acting as hydration seeds. At last, it has to be considered that depending on the ζ of fines in the individual pore solution PCE does not only adsorb on cement but also on fillers [54]. It is hence likely that strong differences between powder type SCC and viscosity modifying agent type SCC should be observed at varying temperatures, at least in case the filler contributes to dispersion.

The influence of the charge density was not yet subject to intensive research in general and no publication is known to the author that distinguishes between different charge densities in the context with temperature dependent workability. The present study was conducted to illustrate effects resulting from differently modified PCEs paying special attention to the mixture composition type.

3. Experimental investigations

3.1. Matter of investigations

In order to gain new information on how the PCE charge density and the mixture composition affect the rheology at varying temperature, two concrete mixtures were developed, one of which represents a typical powder type SCC (POW). The other concrete represents a combination type SCC with low powder content (COM). Both mixtures were made from the same raw material components. These mixtures were modified with different PCEs. These characteristically differ in their anionic charges. The rheology was observed at 5 °C, 20 °C, and 30 °C.

3.2. Powder properties

The cement used for the tests was an OPC (CEM I 42.5 R) according to EN 196. The bulk density of the material was determined by He-pycnometry as 3123 kg/m^3. The Blaine value was determined according to EN 196-6:1990 as 4110 cm^2/g. The water demand to
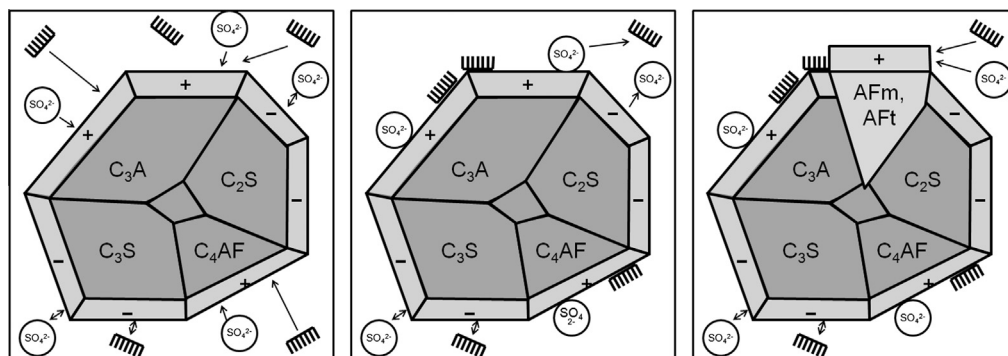

Fig. 6. Competitive adsorption of PCE and sulphate ions.

meet the standard stiffness was determined according to EN 196-3:1995. A summary of the materials properties is given in Table 2.

The chemical composition of the cement was determined according to EN 196-2:2005 and the resulting clinker composition calculation according to the modified Bogue calculation after Taylor [55] is given in Table 1.

The bulk density of the limestone filler was 1735 kg/m³ (He-pycnometry), the Blaine value was 5130 cm²/g (EN 196-6:1990). The chemical composition of the LSF was measured by X-ray fluorescence method (μ-XRF) as given in Table 3. The particle size distributions of the cement and the LSF measured by laser granulometry are given in Fig. 7.

3.3. Sand and gravel

Washed and fractioned sands and aggregates were used. As a result the powder contents of the sand and aggregates are negligible. At delivery the sands and aggregates were fully dried and stored at room climate afterwards. Hence, no significant amount of water was absorbed on the aggregates. The grading curves of the single fractions are given in Fig. 8. The sand and gravel densities measured according to EN 1097-6 were determined as 2600 kg/m³.

3.4. Superplasticizers

The PCEs used for the investigations are commercially available products. All polymers contain identical polycarboxylic backbones

Table 1
Clinker phase composition of the CEM I based on the modified Bogue calculation according to Taylor [55].

Clinker phase	Modified Bogue calculation [55] (%)
C_3S	61.8
C_2S	20.5
C_3A	6.2
C_4AF	7.7
Sum:	96.1

Table 2
Physical properties of the CEM I 42.5 used for the tests according to the producer.

Property	Unit	Value
Fineness (Blaine)	cm²/g	4110
Density	kg/m³	3123
Water demand	%	28.5
Compressive strength, 1 day	MPa	23
Compressive strength, 2 days	MPa	37
Compressive strength, 7 days	MPa	50
Compressive strength, 28 days	MPa	61

Table 3
Oxide composition of the total limestone filler from XRF measurement.

Oxide	Percentage (%)
Na_2O	3.27
MgO	0.61
Al_2O_3	0.46
SiO_2	1.47
P_2O_5	2.19
SO_3	0.34
K_2O	0.54
CaO	90.68
TiO_2	0.05
Fe_2O_3	0.4
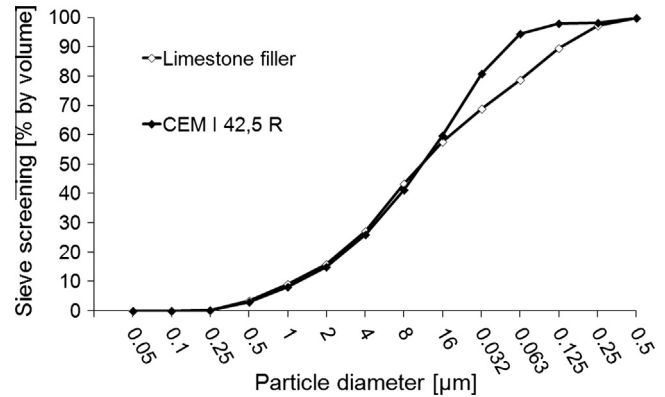
Fig. 7. PSD of CEM I 42.5 R and limestone filler used for the investigations.
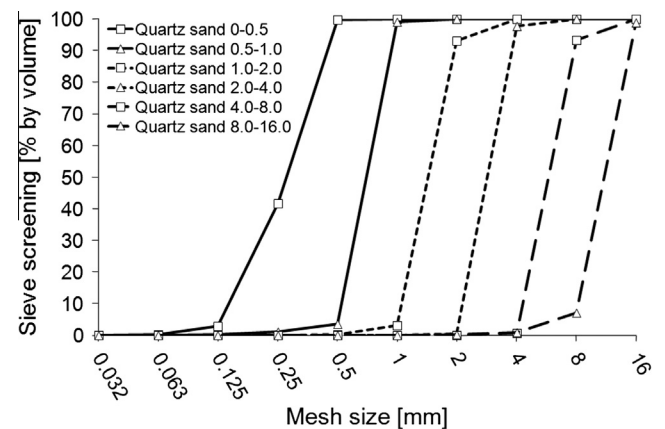
Fig. 8. Grading curves of the sand and aggregate fractions.

in chemistry and length. The graft chains consist of polyethylene oxide, which vary for each polymer in length. Blends of different graft chain lengths are possible, which have minor influence on the polymers' charge densities. The major effect determining the charge density of the employed PCEs, however, is the grafting degree, which is high for the low charge density polymer and low for the high charge density polymer. The medium charge polymer has a grafting degree in between. Details about the PCEs are given in Table 4.

3.5. Viscosity modifying admixture

A VMA based on modified potato starch was used for the mixtures. Their dosages can be found in Table 6.

3.6. Concrete compositions

Each concrete was adjusted by PCE addition to have a slump flow value between 650 and 700 mm at 20 °C and 30 min after mixing. No specification was made regarding the V-funnel time, since the focus of the research is the PCE performance and PCE mainly affects yield stress.

Regardless whether the mixture composition was POW or COM the grading of the aggregates was kept identical. Due to the lower total powder content of the COM mixture the integral grading curve varies from the curve of the POW composition (Fig. 9). Table 5 shows the mixture composition of the POW and the COM mixtures. Table 6 shows the PCE dosages required to achieve the specified flow properties 30 min after mixing.

Table 4
Specifications of the polycarboxylic superplasticizers.

	Low charge PCE	Medium charge PCE	High charge PCE
Abbreviation	LC	MC	HC
Backbone	Polycarboxylate ether (PCE), identical for all modifications		
Graft chains	Polyethylene oxide (PEO)		
Recommended dosage	0.2–3.0% bwoc		
Density at 20 °C	1.07 ± 0.02 g/cm^2	1.05 ± 0.02 g/cm^2	1.05 ± 0.02 g/cm^2
Solid content (%)	30	23	20
pH at 20 °C	6.5 ± 1.0	6.5 ± 1.0	6.5 ± 1.5
Max. chloride content	0.10% by weight		
Max. alkali content	1.5 M.-% (Na$_2$O-eq.)	1.2 M.-% (Na$_2$O-eq.)	1.3 M.-% (Na$_2$O-eq.)
Graft chain length	Medium + low	Medium + low	Medium
Grafting degree	High	Medium	Low
Backbone charge density	Low	Medium	High
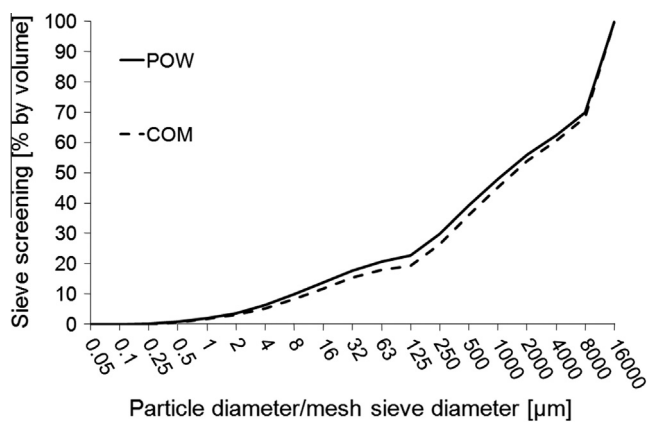
Fig. 9. Integral grading curves of the COM and POW mixtures.

3.7. Test specifications

The rheometric investigations were conducted in a large climate chamber at 5, 20, and 30 °C and at a constant relative humidity of 50% RH for all temperatures. The mixer as well as the rheometric equipment was placed in the chamber and all tests were conducted directly in the chamber at the particular climate conditions.

In advance it was ensured that the raw materials including water were adjusted to the particular test climate. 30 l of concrete were mixed for the tests in a compulsory mixer. The mixing regime can be found in Table 7.

The stirrer speed was adjusted to 70 rounds per minute. Rheometric investigations were made 0, 30, 60, and 90 min after the mixing with a CONTEC Rheometer-4SCC. By interpreting the electric current measured by the device at varied rotational speeds qualitative results about yield stress and viscosity can be obtained expressed as relative values G-yield in mA and H-Viscosity in mA s,

Table 5
Final mixture composition of the mineral components.

	Density (kg/m^3)	POW[a]		COM[b]	
		Weight per m^3 (kg/m^3)	Volume per m^3 (l/m^3)	Weight per m^3 (kg/m^3)	Volume per m^3 (l/m^3)
CEM I 42.5 R	3125	310	99	350	112
Limestone filler	2735	250	91	130	47
Water	1000	175	175	175	175
Air	–		20		20
Sand (0.1–0.5 mm)	2600	320	123	336	129
Sand (0.5–1.0 mm)	2600	184	71	193	74
Sand (1.0–2.0 mm)	2600	184	71	193	74
Sand (2.0–4.0 mm)	2600	120	46	126	48
Aggregate (4.0–8.0 mm)	2600	120	46	126	48
Aggregate (8.0–16.0 mm)	2600	671	258	705	271
Fresh concrete density		2334		2334	

[a] POW: Powder type mixture based on high powder content low w/p and.
[b] COM: Combination type mixture based on moderately high powder content relatively higher w/p and stabilising agent.

Table 6
Final mixture composition of the admixtures to achieve a slump flow value between 650 and 700 mm at 20 °C and 30 min after mixing.

Superplasticizer	Ionic backbone strength	POW			COM		
		PCE % bwoc	PCE solids % bwoc	VMA % bwoc	PCE % bwoc	PCE solids % bwoc	VMA % bwoc
PCE LC	Low	2.05	0.62	0.018	2.25	0.68	0.120
PCE MC	Medium	2.40	0.55	0.018	2.64	0.61	0.120
PCE HC	High	1.90	0.38	0.018	2.20	0.44	0.120

Table 7
Mixing regime throughout the conducted tests.

Step	Duration (s)	Action
1	60	Dry mixing of all powder components
2	60	Addition of 2/3 of total water
3	30	Wet mixing + addition of VMA
4	60	Addition of remaining water mixed with PCE
5	30	Scraping walls of mixing pan
6	120	Mixing
7	120	Resting phase
8	120	Mixing

respectively. Due to the undefined shear field in the rheometer and the non-Newtonian behaviour of the concretes, a sound conversion over a wide range of consistencies into fundamental units in Pa and Pa s is not possible. However, due to the qualitative affinity of the relative values and the fundamental values, changes in G-yield and H-viscosity likewise represent changes into the same direction for yield stress and plastic viscosity. The measurement regime is given in Table 8. The first step includes 5 s of pre-shearing of the SCC before the actual measurement starts in order to avoid effects of the starting torque to assure measuring at steady state. In order to avoid unreasonably high deviations due to the change of the rotational speed, only the last 4 s of each step were used for the further interpretation based on the assumption that the concrete behaves like a Bingham fluid.

Prior to testing the rheological properties at 30 min the concrete was fed back to the mixer and stirred intensively. By this the transportation to the job-site in a truck mixer should be simulated. For later testing times the concrete was only gently stirred in the rhe-

Table 8
Rheological test regime for the rheometric temperature investigations.

Step	1	2	3	4	5	6	7	8	9
Speed (s^{-1})	0.45	0.40	0.35	0.30	0.25	0.20	0.15	0.10	0.05
Duration (s)	10	5	5	5	5	5	5	5	5

ometer with a brick trowel in order to avoid effects of possibly separated aggregates.

Furthermore, concrete cubes ($15 \times 15 \times 15$ mm^3 according to EN 12390-1:2001) were cast directly after the measurement that took place after 30 min. The cubes were covered with foil and remained in the climatic chamber until the end of the test. After 90 min they were stored in the concrete laboratory at 20 °C until de-moulding after 24 h. After de-moulding they were stored under water at 20 °C according to EN 12390-2:2001 until testing.

It has to be noted that due to mixing the fresh concrete temperatures were not identical to the adjusted ambient temperatures and the temperatures were changing with time. The fresh concrete temperatures were not measured regularly but randomly for at least four different mixture modifications per temperature at 0, 30, and 90 min after mixing. The average values and the standard deviations for each time and temperature are presented in Table 9.

4. Results

4.1. Results of the powder type SCC

A strong influence of the PCE modification on the yield stress can be observed for the powder type mixes shown in Fig. 10. At 5 °C the initial yield stress is maintained throughout the whole observation time with all PCEs. Only minor variations of yield stresses can be observed between the PCEs directly after mixing. The meaningfulness of these very early results, however, should not be over-interpreted, since directly after mixing thixotropy effects and lack of adsorption equilibrium of the PCEs might diffuse the results. Considering the total observation period of 90 min no significant influence of the PCE modification can be observed.

This differs for the medium charged PCE. In general the yield stresses are higher than with PCE LC. At 5 °C and 20 °C the yield stress retention is very good. The initial flow performance can be maintained throughout the observed 90 min. At 30 °C, however, an increase of the yield stress from 1000 mA to approx. 1500 mA can be observed. This is maintained until 90 min.

Table 9
Average concrete temperatures at different times compared to the ambient temperatures.

Ambient temperature (°C)	Directly after mixing		30 min after mixing		90 min after mixing	
	Mean value (°C)	Standard deviation	Mean value (°C)	Standard deviation	Mean value (°C)	Standard deviation
5	10.2	0.67	9.3	0.36	8.3	0.22
20	23.9	0.26	22.4	0.16	22.1	0.27
30	32.8	0.26	30.0	0.29	29.2	0.35

Fig. 10. G-Yield vs. time of POW mixes for PCE LC, PCE MC, and PCE HC.

The most pronounced effects of the different temperatures can be observed for the high charged PCE. While at 5 °C the initial performance can be held throughout the whole observation time, at 20 °C the yield stress increases in a linear way from 500 mA initially to 2000 mA. This indicates that the concrete is difficult to handle at 90 min. The mixture with the high charge density shows a G-yield of approx. 1000 mA initially but rapidly stiffens, so that the G-yields is already higher than 3500 mA after 30 min. It is not self-compacting any more at this point in time. Any later measurement failed since the consistency was too stiff for a measurement with the Rheometer-4SCC.

Fig. 11 shows the respective H-Viscosities. The viscosity data is less precise to interpret quantitatively. Therefore, differences in H-viscosity values at identical time steps will not be interpreted. However within one series changes in the value with time can be identified. For the POW mixtures no effect of the PCE on the viscosity can be observed depending upon the PCE modifications. All mixtures show initial H-viscosities in the range of approximately 5000 mA s and 7500 mA s. H-viscosities increase steadily with decreasing gradient until values are reached between approximately 9000 mA s and 15000 mA s.

4.2. Results of the combination type SCC

Also for the combination type concretes a significant effect of the PCE modification on the temperature dependent behaviour of the SCC can be identified. The results for G-yield for the different PCE modifications are shown in Fig. 12. SCC with PCE LC shows relatively steady values at 20 °C. Initially as well as after 90 min the G-yield is approximately 1000 mA. The values in between are

slightly higher. At 30 °C the initial value is 1500 mA and decreases with time until 1000 mA after 90 min. At 5 °C the initial G-yield value is approximately 2000 mA, increases steadily with time and reaches a value above 3500 mA after 90 min. At this temperature the workability was poor at all observed times and a thin layer of segregated paste could be observed in the concrete.

When the medium charged PCE is used, an increase of the G-yield with time can be observed at all temperatures. At 20 °C and 30 °C the performance is quite similar. The initial values are approximately 1000 mA. They increase steadily with decreasing slope. The values after 90 min are 1500 mA at 20 °C and 2000 mA at 30 °C. At 5 °C the initial yield stress with PCE MC is 1500 mA, thus higher than at 20 °C and 30 °C. It is retained over the first 30 min and then increases rapidly.

With PCE HC similar behaviour can be observed at 5 °C and 20 °C. At 20 °C the initial G-yield is 500 mA and increases in quite linear manner to a value of approximately 1700 mA after 90 min. At 5 °C the initial yield value is around 1000 mA and increases steadily with time until a value of about 2000 mA is reached. At 30 °C the initial G-yield is 500 mA, which is similar to the initial value at 20 °C, but it increases more rapidly over the course of time, so that after 60 min the G-yield values already lies approximately at 2300 mA. At 90 min the G-yield is approximately 2600 mA.

For the H-viscosity results (Fig. 13) it can be observed that the influence of the PCE modification is negligible. Only at 5 °C and for SCC with low charge density PCE a performance significantly differing from the other modifications can be observed. The decrease of the curve from 60 to 90 min, however, is most likely caused by the high stiffness of the concrete that caused incomplete shear and thus faulty rheometric measurement results at 90 min.
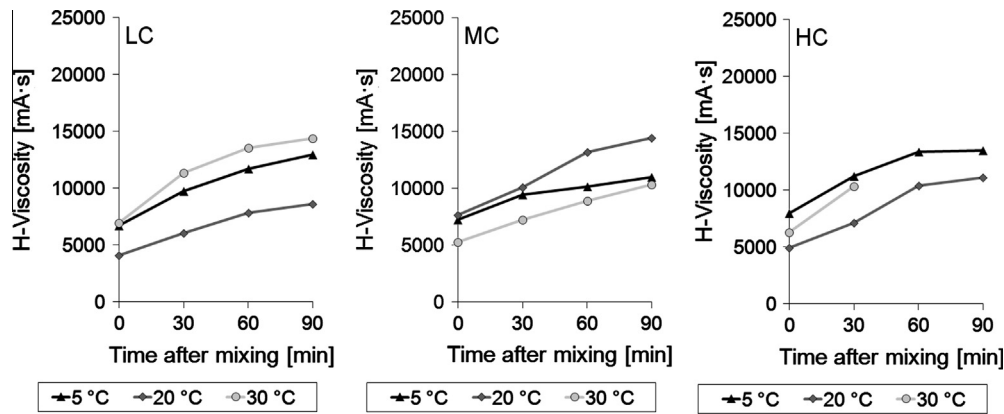

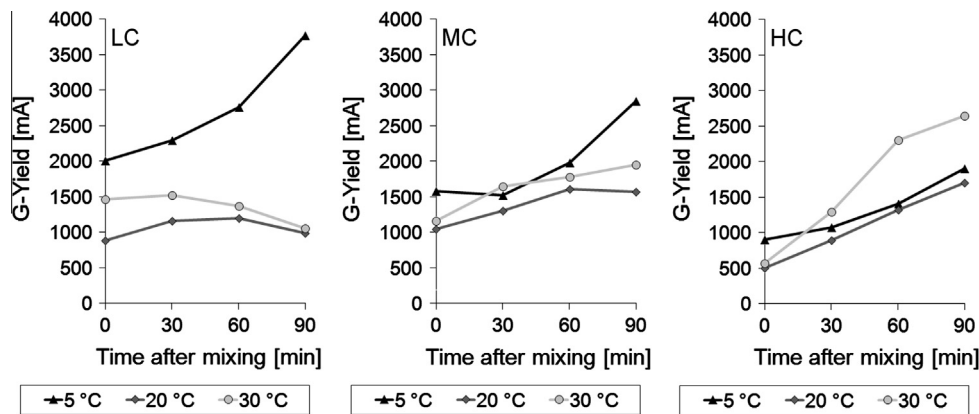Fig. 11. H-Viscosity vs. time of POW mixes for PCE LC, PCE MC, PCE HC.

Fig. 12. G-Yield vs. time of COM mixes for low, medium, and high charge density PCE.
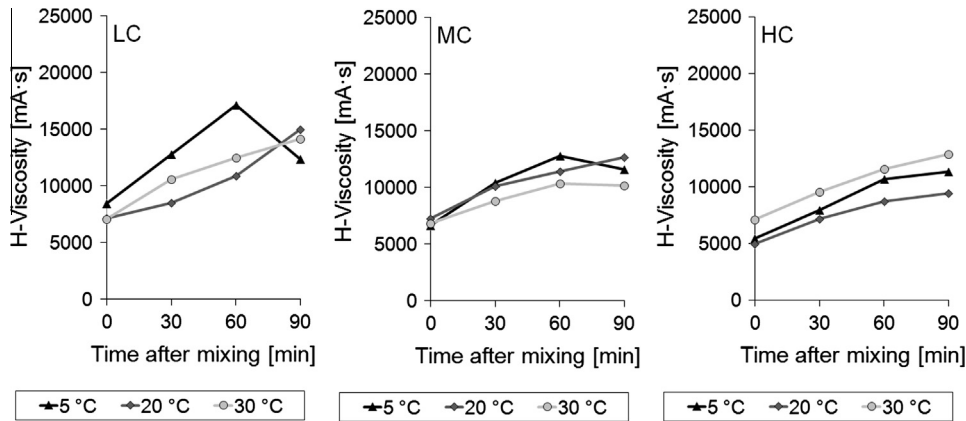
Fig. 13. H-Viscosity vs. time of COM mixes for low, medium, and high charge density PCE.

However, also when the 90 min value is omitted the viscosity of SCC with PCE LC increases more rapidly than with the other PCEs. This is another result of the segregation that could be observed. The segregated aggregates accumulate on the lower part of the bucket yielding high yield stresses and higher viscosities.

All H-viscosity values increase with time. Apart from the above mentioned strongly segregating mixture with PCE LC at 5 °C, at all temperatures the difference between the initial value and the value after 90 min is approximately 5000 mA·s. The curves' time dependent characteristics are similar at all temperatures. However, it can also be observed that in general the viscosities reduce with increasing charge densities.

5. Discussion of the results

The results confirm the initial hypothesis that temperature related effects on SCC should only be made in a distinguished way and that special attention has to be paid on the PCE modification and the mixture composition. The observed results simultaneously verify and falsify previous research results focusing on concrete, e.g. by Weisheit et al. [43], Golaszewski and Cygan [40], or Nehdi and Al Martini [34]. This means many research results so far show validity for the specific mixture setup observed, in particular for one specific PCE and one specific mixture composition. These results, however, do not inevitably have to have evidence for mixture compositions and PCE modifications that differ significantly.

Numerous effects induced by either the mixture composition, the temperature, or the PCE modification, can be observed. The POW mixture shows quite similar time dependent yield stresses at 5 °C and 20 °C but significant effects of the PCE at 30 °C. The COM mixture shows quite similar time dependent yield stresses at 20 °C and 30 °C, but significant effects at 5 °C.

For POW mixtures the influence of the PCE modification on yield stress is negligible while a certain effect of the polymers can be observed for the COM mixture. This effect is induced by the different stabilising mechanisms of the different mixture compositions. POW mixtures have a higher particle packing density and are stabilised by the low water to powder ratio. Water is only added in a volume that is required to provide flowability. The particle distances upon flow are limited so that the influence of the PCE is small.

The influence of PCE on viscosity is generally small since their adsorption mainly affects the yield stress. Nevertheless, certain effects can be observed for the COM mixtures. These have a higher water to powder ratio. Thus, the stability of the system depends not only on STAs but also on the dispersion and repulsion of the

PCEs. The better adsorption ability caused by higher charge densities causes better particle repulsion. This gives better mobility among the particles.

A basic dependency between the flow properties and the charge density can be observed. Although for many environmental conditions no clear effects of the charge density can be observed, due to similar performances with all charge densities, this is getting clear at the particular cases when clear differences can be observed between the low charge polymer and the high charge polymer. In this case, the medium charged polymer behaves always in between these performances. E.g., as shown in Fig. 15 for the COM mix at
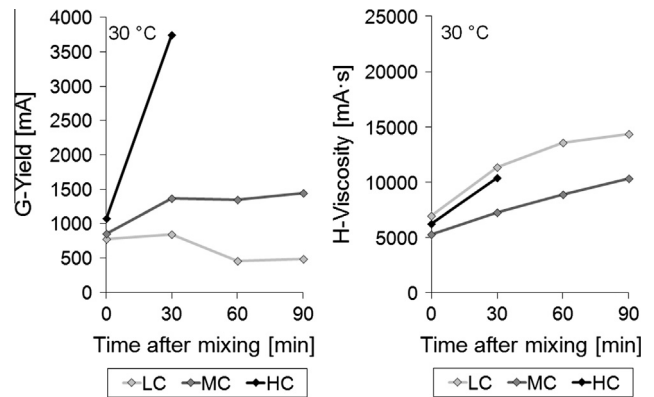

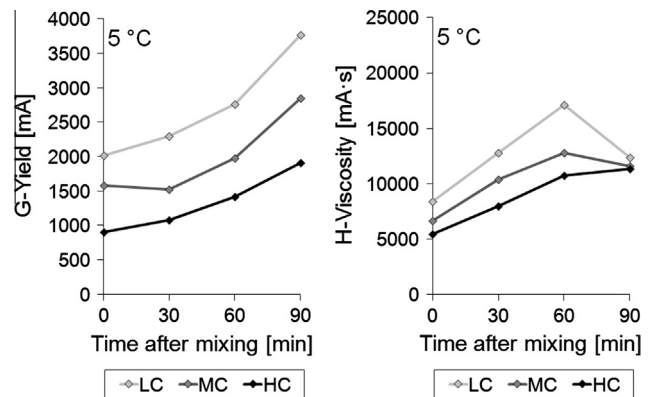**Fig. 14.** G-Yield and H-viscosity of POW SCCs at 30 °C.

Fig. 15. G-Yield and H-viscosity of COM SCCs at 5 °C.

Table 10
Summary of SCC performances at varied temperatures.

Mixture type	Temperature (°C)	Charge density of the PCE			Specific observations
		Low	Medium	High	
POW	5	Good flowability	Good flowability	Good flowability	
		Good retention	Good retention	Good retention	
	20	Good flowability	Good flowability	Good flowability	
		Good retention	Good retention	Medium retention	
	30	Good flowability	Good flowability	Only initial flowability	Mixture sensitive to PCE charge density
		Good retention	Medium retention	Minimal retention	
COM	5	No flowability at all	Good flowability	Good flowability	Mixture sensitive to PCE charge density
		Medium retention	Medium to poor retention	Medium retention	
	20	Good flowability	Good flowability	Good flowability	
		Good retention	Medium retention	Medium retention	
	30	Good flowability	Good flowability	Good flowability	
		Good retention	Medium retention	Medium to poor retention	

5 °C, PCE HC generates low yield stress and PCE LC high yield stress and the curve of PCE MC runs between these curves. The curve characteristics are very similar. In Fig. 14, for the POW mixture at 30 °C, it can be seen that the yield stress retention is good for PCE LC, very poor for PCE HC, and in between for PCE MC.

There is no specific influence that can be considered as critical for the performance in general. The majority of all modifications generated good or medium flow performance and the retention was acceptable. Table 10 provides an overview of all setups with regard to flowability in general and the retention of the G-yield.

Two specific combinations of admixture setup and temperature ranges distinguish clearly from all other mixtures. These are concerning the powder type mixture at 30 °C and the combination type mixture at 5 °C. At these temperatures a clear influence of the PCE modification can be observed. Apart from these specific cases, all other mixtures show good or medium flow and performance retention properties. In general, it seems that apart from the mentioned special cases, the POW mixtures show better retention of the performance.

At 30 °C the powder type with the high charge PCE shows poor retention of the flow properties. The yield stress values for this particular combination of mixture composition and temperature is shown in Fig. 14. While the flow performance with the low charge density PCE is very good throughout the whole time the retention of the yield stress reduces with increasing temperatures. At 30 °C the stiffening takes place so rapidly that already at 30 min the consistency is too stiff to provide flowability.

At 5 °C the low charge density polymer shows no flowability at all in case the low charge density polymer is used. The G-yield values and the respective H-viscosities are shown in Fig. 15. The only PCE that generates good flow properties and long performance retention is the high charge density polymer. The medium charged polymer can generate good initial flow but the performance reduces with time. The low charge density polymer cannot generate good flow properties at all.

As described, the reduced flow properties do not only negatively affect the workability properties but they have tangible effect on the mechanical strength of the resulting hardened concretes. The mixtures, with significantly poorer workability properties were compacted less than the other mixes. This finally affects the mechanical properties. The 28d-strength values of the POW mixes were significantly lower at 30 °C in case the high charge PCE was used (Fig. 16). The same is valid in similar magnitude for the COM mixture at low temperature in case the low charge density polymer is used (Fig. 17). The medium charge density polymer at cold temperatures also shows poorer strength properties, confirming that at cold temperatures a very high charge density is required for the PCE to generally yield flowability when the SCC exhibits a high water to solid ratio.
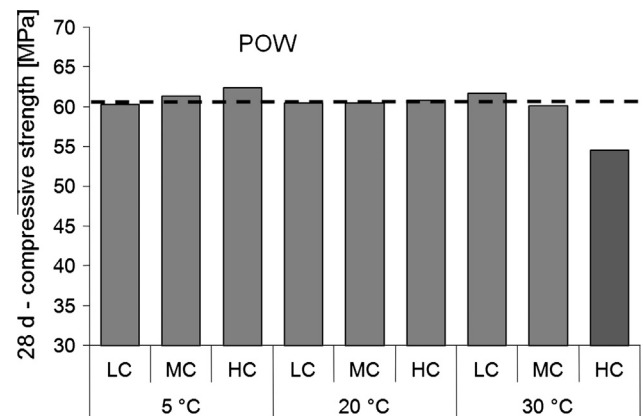

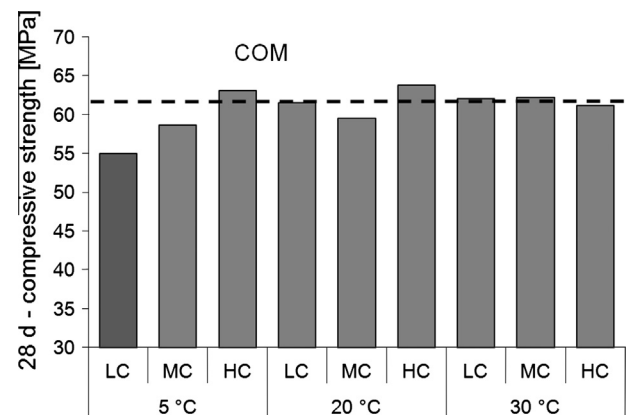**Fig. 16.** Compressive strength results for the observed POW SCCs.

Fig. 17. Compressive strength results for the observed COM SCCs.

6. Explanation of the observed effects based on the charge density of the PCE and the water to solid ratio

6.1. Differentiation between the mixture composition types

In order to understand why powder type and combination type SCC have different temperatures at which they are sensitive to the PCE modifications and why admixtures with specific charge densities cannot provide sufficient flow properties, it is important to take a closer look at the characteristics of each mix.

The characteristic difference between the mixture compositions observed in these tests is the water to powder ratio. The POW mixture has the higher powder content. As a result the particles

are arranged densely in the fluid and have limited mobility among each other. The COM mixture has a lower powder content while the water volume is identical to the POW mixture. As a result particles have larger distances and better mobility among each other as illustrated in Fig. 18.

6.2. Systems with low water/solid-ratio at high temperature

In systems with low water to solid ratio the mobility of the particles is limited. Upon addition of PCE the charge density determines the adsorption behaviour. While no critical effect of the PCE charge density can be observed at lower temperatures a distinct influence occurs at high temperature.

As shown in Fig. 19 PCE with low charge density adsorbs only partly while a distinct part of the polymers remains in solution. They are yet pushed aside by ions with higher anionic charges, most prominently SO_4^{2-} [19,51]. Furthermore, low charge density polymers typically contain a higher number of graft chains, thus a more complicated geometry, which supplementary fosters the slow early adsorption capacity. These polymers do not have any effect on the flowability at this time. The high temperature accelerates the hydration, which quickly causes the formation of C–S–H, AFm, and AFt that increase the specific surface area of the particles. The crystals growth and crystal modifications change the morphology of the particles which annihilates the effect of the already adsorbed polymers and furthermore reduces the mobility of the particles. The large number of PCEs that did not find adsorption sites and remained ineffectively initially can now adsorb with time on the newly formed crystals, mainly ettringite and monosulfate, thus maintaining the repulsion of particles. This leads to a sufficiently lasting retention of the flow properties.

In contrast a highly charged polymer will adsorb rapidly at higher rate as shown in Fig. 20. A smaller part of the polymers will remain ineffectively in the solution. This causes high flowability di-

rectly upon addition and can even generate strong segregation initially. The quickly adsorbed PCEs are quickly consumed and overgrown due to rapid hydration fostered by the high temperature. Morphological changes of the surfaces quickly reduce the mobility of the particles. The PCEs that did not yet adsorb cannot maintain the repulsion of particles and thus a low yield stress cannot be maintained.

Finally, the major driving force for the performance loss at high temperature is the dense particle packing combined with the rapid hydration. The only possibility in this case to provide good flow properties is choosing low charge PCE.

6.3. Systems with high water/solid ratio at low temperature

In systems with high water to solid ratio the mechanism is different. Differing from the powder-rich systems that exhibit a sensitive performance at high temperatures the problems occur at low temperatures. Here again the adsorption of PCE determines the flow properties but the driving force for poor flowability is induced by segregation.

A low charge density polymer adsorbs only partly (see Fig. 21) while a significant part of the polymers remains ineffectively in the pore solution. At low temperatures the hydration is slowed down. This means C–S–H, AFm, and AFt only grow slowly. As a result only few new adsorption sites for the not yet adsorbed PCEs can be generated so that the large number of unadsorbed polymers does also not find adsorption sites with time. The steric repulsion of the particles is not sufficient to stabilise them in the fluid. Upon flow particles cannot be kept in distance and block each other, which reduces the mobility, thus causing poor flow properties. This can be seen in the high yield stress results.

The described problem of poor flowability due to lack of repulsion capacity can be overcome by the use of a high charge density PCE. As illustrated in Fig. 22 high charge density PCE will be quickly
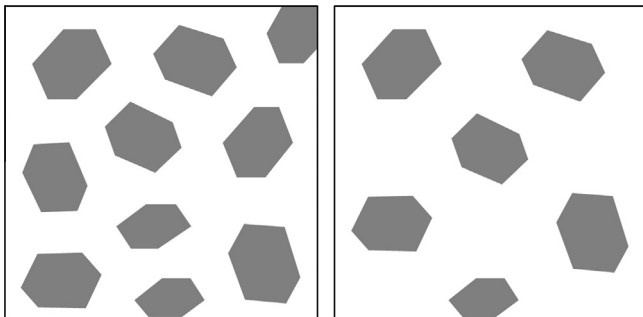

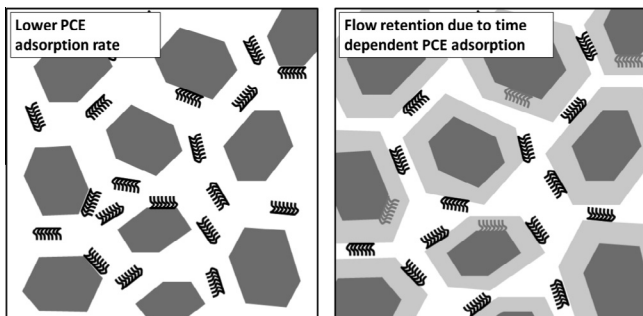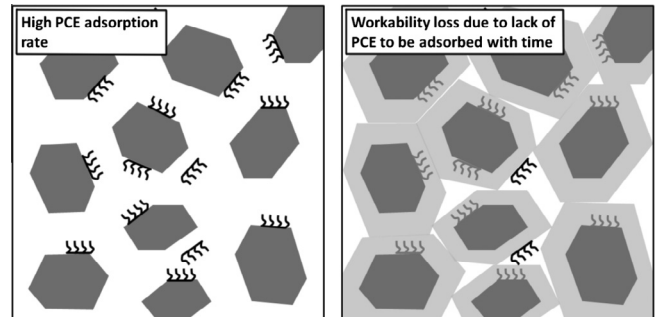**Fig. 18.** Qualitative arrangement of particles in the POW mixture (left) and the COM mixture (right).

Fig. 20. Poor flow performance retention caused by high initial adsorption of high charge PCE and rapid hydration progress in powder-rich systems at high temperature.
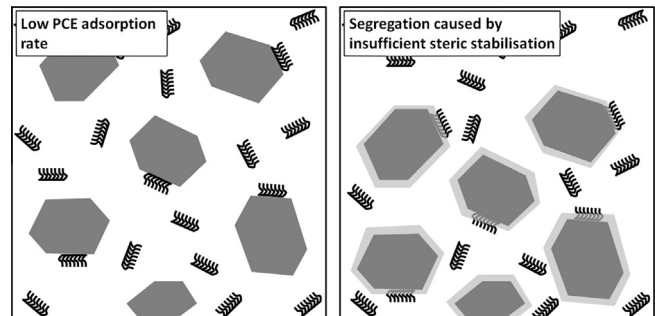

Fig. 19. Good flow performance retention due to time shifted adsorption of low charge PCE in a powder-rich system at high temperature.

Fig. 21. Poor flow performance of water-rich systems at low temperatures caused by low initial and time-shifted adsorption of low charge PCE.
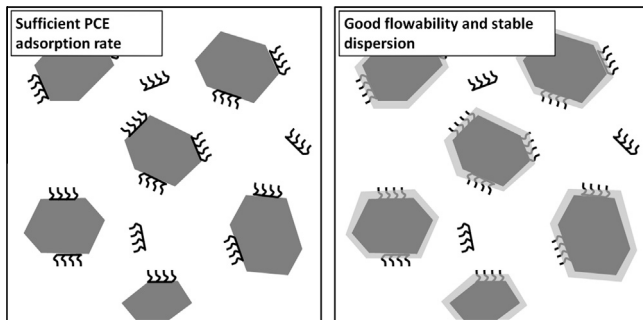
Fig. 22. Good flow performance of water-rich systems at low temperatures caused by high initial adsorption of high charge PCE.

adsorbed on the particles and the few early formed hydration phases. Due to the stronger adsorption tendency, it is depending to a lesser degree on the formation of new adsorption sites by the hydration process and can thus provide good flow properties.

7. Conclusions

The results presented herein confirm that the fresh properties of normal concrete, for varying temperatures, differ from those of self-compacting concrete. A simple transfer of knowledge of normal concrete to self-compacting concrete is not possible. One major difference between normal concrete and self-compacting concrete is the extensive use of SP in the latter. Differing from normal concrete, SP is an essential component for the functioning of SCC. The admixture performance, however, is strongly affected by the environmental temperature, since the temperature related hydration rate affects the rate of the adsorption as well as the amount of adsorbable polymers. Hence, a simple description of the temperature induced fresh behaviour of SCC is not possible. Temperatures affect mixture compositions with high water to powder ratios differently than mixture compositions with low water to powder ratios. Depending upon the mixture composition the charge density of a PCE has a different effect.

The results of the rheometric investigations at varied admixture adjustments at different temperatures show that the charge densities of PCE as well as the mixture compositions need to be taken into account for a robust temperature performance of SCC. The following observations were made:

- In order to assess temperature influences and qualitatively predict the flow properties of SCC it is important to distinguish between mixture compositions with low and high water to powder ratio.
- At low temperature a powder rich mixture showed good performance and to be not significantly affected by the PCE's charge density. However, at high temperature the powder-rich concrete is prone to quickly lose flow properties.
- The situation is exactly inverted for mixtures containing low powder contents. They perform significantly more robust and are less affected by the PCE modification than powder rich mixtures at high temperatures. In return, they are prone to failure at low temperature.
- Regardless of the water to powder ratio low charge density polymers appear to be the best choice at high temperature since they are consumed slower than high charge polymers.
- In return high charge density polymers adsorb quickly, even when the formation of new adsorption sites takes place slowly. Hence, regardless of the mixture composition type, highly charged PCEs can be considered as the best choice for low temperatures.

- For each critical combination of temperature and mixture composition, however, the SP's charge density affects the functionality of the SCC.
- For the similar PCEs considered herein, PCEs with a charge density that lies between two charge densities will also perform in between the thresholds given by the higher and lower charge density PCEs in terms of flow and flow retention.
- A powder rich concrete fails at high temperature, when a high charge density polymer is used. It functions properly when a low charge polymer is used. The reason is the time shifted adsorption of the low charge polymer, which yields good flow properties, even when the particles specific surfaces increase rapidly.
- A mixture with low powder content fails at low temperatures when a low charge polymer is used. It works properly when a high charge polymer is used. The reason is that low temperatures cause a slow hydration process, so that insufficient new adsorption sites appear for the low charge PCEs to be adsorbed. High charge PCE can be adsorbed directly and does not need supplementary sites to be generated over the course of time to provide flowability.

For the applier of SCC this gives two ways of improving the robustness, depending on the individual boundary conditions. Often producers do not vary their SPs but they are open to cast various concrete mixtures. Other producers may provide several SP modifications that can be varied according to the required specifications. Then again it has to be distinguished whether an optimised performance is required at a particular temperature or whether a high robustness is required for a wide range of temperatures.

In case the SP may be varied for high temperatures it can be advised to use a low charge PCE in order to provide sufficiently long lasting flowability. For low temperatures a high charge density PCE is the best choice in order to ensure that PCE molecules adsorb quickly on particles.

In case the PCE is a fixed parameter the best choice of concrete at high temperatures is a concrete mixture composition with high water to powder ratio. In this case the influence of the PCE modification, which is most likely unknown to the user, is minimised. At low temperatures a powder-rich mixture composition should be chosen so that the SCC is not depending on a quick adsorption of PCE. This yields independence of the charge density of the PCE.

The medium charged PCE showed to operate in between the performances that were generated by the higher and the lower charged PCE, respectively. Hence, for general temperature robustness a medium performance PCE can be considered as the best choice.

A high level of knowledge is required in order to assure good performance of SCC at varying temperatures. In particular understanding the effect of the charge density of a PCE seems to be the key to develop high robustness and optimised performance of SCC with regard to the casting on the construction site.

References

[1] bibm, CEMBUREAU, EFCA, EFNARC, and ERMCO. The European guidelines for self-compacting concrete – specification, production and use. <http://www.efnarc.org>.
[2] Terpstra J. Stabilizing self-levelling concrete with polysaccharide additive. In: SCC'2005-China: 1st international symposium on design, performance and use of self-consolidating, Concrete; 2005. p. 207–213.
[3] Wallevik OH, Kubens S, Mueller F. Influence of cement-admixture interaction on the stability of production properties of SCC. In: 5th international RILEM symposium on self-compacting concrete, Ghent, Belgium; 2007. p. 211–16.
[4] Nunes S, Figueiras H, Milheiro Oliveira P, Coutinho JS, Figueiras J. A methodology to assess robustness of SCC mixtures". Cem Concr Res 2006;36:2115–22.

[5] Hamada D, Hamai T, Shimoda M, Shonaka M, Takahashi H. Development of new superplasticizer providing ultimate workability. In: 8th CANMET/ACI international conference on superplasticizers and other chemical admixtures in concrete, Sorrento, Italy; 2006. p. 31–50.

[6] Brameshuber W, Uebachs S. The influence of the temperature on the rheological properties of self-compacting concrete. In: 3rd International RILEM symposium on self-compacting concrete, Reykjavik, Iceland; 2003. p. 174–83.

[7] SenStadtUm, Digitaler Umweltatlas Berlin. Senatsverwaltung für Stadtentwicklung und Umweltschutz Berlin; 2001. p. <http://www.stadtentwicklung.berlin.de/umwelt/umweltatlas/da404_01.htm#Abb2>.

[8] Khayat KH, Petrov N, Morin R, Thibeault M, Bissonnette B. Comportement du béton autoplaçant fibré dans la réfection du passage inférieur du Viaduc Jarry-Querbes à Montréal. In: 8e Journées Scientifiques du (RF)²B, Montreal; 2007. p. 32–47.

[9] Scrivener K. The microstructure of concrete. Mater Sci Concr 1989:127–61.

[10] Locher FW, Richartz W, Sprung S. Erstarren von Zement. Teil I: Reaktion und Gefuegeentwicklung. Zement-Kalk-Gips Int 1976:435–42.

[11] Chen W. Hydration of slag cement – theory, modeling and application. Enschede: University of Twente; 2006.

[12] Taylor HFW. Hydration of portland cement. In: Telford T, editor. Cement chemistry. Thomas Telford Publishing; 1997. p. 187–224.

[13] Gartner EM, Sabio S, Perez J-P, Equilibria in the system calcium hydroxide-calcium sulphate-alkali sulphate-water at 5–30 °C, and their relevance to portland cement hydration in the presence of superplasticizers. In: 11th International Congress on the Chemistry of Cement, Durban, South Africa; 2003. p. 635–44.

[14] Yamada B, Yanagisawa T, Hanehara S. Influence of temperature on the dispersibility of polycarboxylate type superplasticizer for highly fluid concrete. In: 1st international RILEM symposium on self-compacting concrete, Stockholm, Sweden; 1999. p. 437–48.

[15] Houst YF, Flatt RJ, Bowen P, Hofmann H. Influence of superplasticizer adsorption on the rheology of cement paste. In: International symposium on: the role of admixtures in high performance concrete, Monterrey, Mexico; 1999. p. 387–02.

[16] Schober I, Flatt RJ. Optimizing polycaboxylate polymers", in 8th canmet/aci international conference on superplasticizers and other chemical Admixtures in Concrete, Sorrento, Italy; 2006. p. 169–84.

[17] Jolicoeur C, Sharmann J, Otis N, Lebel A, Simard MA, Pagè M. The influence of temperature on the rheological properties of superplasticized cement pastes. In: 5th CANMET/ACI international conference on superplasticizers and other chemical admixtures in concrete, Rome, Italy; 1997. p. 379–91.

[18] Flatt RJ, Houst YF. A simplified view on chemical effects perturbing the action of superplasticizers. Cem Concr Res 2001;31:1169–76.

[19] Plank J, Bassioni G, Dai Z, Keller H, Sachsenhauser B, Zouaoui N. Neues zur Wechselwirkung zwischen Zementen und Polycarboxylat-Fließmitteln. In: 16th International conference on building materials – ibausil, Weimar, Germany; 2006. p. 579–98.

[20] Göller F, Dikty S, Hamada D. The relationship between retention stability and chemical structure of PCE. In: Ninth ACI international conference on superplasticizers and other chemical admixtures in concrete, Seville, Spain; 2009. p. 249–60.

[21] Yoshioka K, Tazawa E-I, Kawai K, Enohata T. Adsorption characteristics of superplasticizers on cement component minerals. Cem Concr Res 2002;32:1507–13.

[22] Plank J, Hirsch C. Impact of zeta potential of early cement hydration phases on superplasticizer adsorption. Cem Concr Res 2007;37:537–42.

[23] Khayat KH, Petrov N, Morin AJR, Thibault M. Performance of SCC used in the repair of retaining wall elements. SCC; 2005. p. 1003–1013.

[24] Heunisch M, Hoepfner M, Pierson M, Dehn F, Orgass M. Selbstverdichtender Beton (SVB) im Straßentunnelbau. Bergisch Gladbach 2008(8).

[25] Roncero J, Gettu R, Vazquez E, Torrents JM. Effect of superplasicizer content and temperature on the fluidity and setting on cement pastes. In: International symposium on: the role of admixtures in high performance concrete, Monterrey, Mexico; 1999. p. 343–56.

[26] Brameshuber W, Uebachs S, Spoerel F. Selbstverdichtender Beton – Temperatureinflüsse und Schalungsdruck bei Frischbeton, Verformungseigenschaften bei Festbeton. In: Forschungskolloquium des Deutschen Beton- und Bautechnikvereins, Darmstadt; 2004. p. 214–19.

[27] Svavarsson HG, Wallevik OH. Geothermal well cementing: the effect of temperature and time on workability loss vol. 12. Reykjavik, Iceland; 2004.

[28] Petit J-Y, Khayat KH, Wirquin E. Coupled effect of time and temperature on variations of yield value of highly flowable mortar. Cem Concr Res 2006;36:832–41.

[29] Petit J-Y, Wirquin E, Duthoit B. Influence of temperature on yield value of highly flowable micromortars made with sulfonate-based superplasticizers. Cem Concr Res 2005;35:256–66.

[30] Petit J-Y, Wirquin E, Vanhove Y, Khayat K. Yield stress and viscosity equations for mortars and self-consolidating concrete. Cem Concr Res 2007;37:655–70.

[31] Petit JY. Effet de la temperature, des superplastifiants et des ajouts sur les variations rheologiques des micromortiers et betons auto-compactants. In: Faculté de génie, Département génie civil, Université de Sherbrooke and Faculté des sciences appliquées, Filière génie civil, Université d'Artois. vol. PhD Sherbrooke, Canada: Université de Sherbrooke and Université d'Artois; 2005.

[32] Petit J-Y, Wirquin E, Khayat KH. Effect of temperature on the rheology of flowable mortars. Cem Concr Compos 2010;32:43–53.

[33] Fernandez-Altable V, Casanova I. Influence of mixing sequence and superplasticiser dosage on the rheological response of cement pastes at different temperatures. Cem Concr Res 2006;36:1222–30.

[34] Nehdi M, Al Martini S. Estimating time and temperature dependent yield stress of cement paste using oscillatory rheology and genetic algorithms. Cem Concr Res 2009;39:1007–16.

[35] Schmidt W, Kuehne H-C, Meng B. Performance and interactions of admixtures for SCC exposed to different climatic conditions. In: Concrete under Severe Conditions: Environment & Loading, Tours, France; 2007. p. 979–86.

[36] Kuehne H-C, Schmidt W, Meng B. The influence of temperature on self-compacting concrete in presence of superplasticizer and additional admixtures. In: 5th International RILEM symposium on self-compacting concrete, Ghent, Belgium; 2007. p. 405–10.

[37] Schmidt W, Kühne HC. Einfluss der Verarbeitungstemperatur auf die Eigenschaften von SVB bei Verwendung von Fließmittel und weiteren Zusatzmitteln. Betonwerk + Fertigteil-Technik 2007:40–9.

[38] Lohaus L, Hoeveling H. Robustimprovement für selbstverdichtenden beton (SVB). In: 15th International Conferenz on Building Materials - ibausil, Weimar, Germany; 2003. p. 177-87.

[39] Assaad J, Khayat K. Effect of casting rate and concrete temperature on formwork pressure of self-consolidating concrete. Mater Struct 2006;39:333–41.

[40] Golaszewski J, Cygan G. Einfluss der Temperatur auf die Verarbeitbarkeit selbstverdichtender Betonmischungen. BWI – Betonwerk International 2009:40–6.

[41] Kühne HC, Schmidt W. Der Siebtrennversuch nach prEN 12350-11. Beton 2007;57:448–54.

[42] Schmidt W, Kühne HC. Wechselwirkungen zwischen Zusatzmitteln und mineralischen Komponenten in selbstverdichtendem Beton beim Betonieren in unterschiedlichen Temperaturen. Betonwerk Int: BWI 2009;2:32–8.

[43] Weisheit S, Waldmann D, Greger M. Influence of environmental conditions on the rheological properties of SCC. In: 6th international RILEM symposium on self-compacting concrete and 4th North American conference on the design and use of SCC; 2010. p. 453–60.

[44] Al-Martini S, Nehdi M. Rheology of superplasticized cement paste and concrete subjected to high temperature and prolonged mixing time. In: 6th International RILEM symposium on self-compacting concrete and 4th North American conference on the design and use of SCC, Montreal, Canada; 2010. p. 461–69.

[45] Ghafoori N, Diawara H. Influence of temperature on fresh performance of self-consolidating concrete. Construct Build Mater 2010;24:946–55.

[46] Keller H, Plank J. Zusammenhang zwischen Intercalation und Wirkung von Polycarboxylat-Fließmittel bei früher und später Zugabe. In: Jahrestagung der Fachgruppe Bauchemie, Siegen; 2007. p. 69–77.

[47] Plank J, Dai Z, Zouaoui N, Vlad D. Intercalation of polycarboxylate superplasticizers into C3A hydrate phases. In: 8th CANMET/ACI international conference on superplasticizers and other chemical admixtures in concrete, Sorrento, Italy; 2006. p. 201–14.

[48] Winnefeld F, Zingg A, Holzer L, Pakusch J, Becker S. Ettringite-superplasticizer interaction and its impact on the ettringite distribution in cement suspensions. In: Ninth ACI international conference on superplasticizers and other chemical admixtures and tenth aci international conference on recent advances in concrete technology and sustainability issues, Seville, Spain; 2009. p. 420.1–420-17.

[49] Schober I, Flatt RJ. Optimierung von polycarboxylat-ether polymeren. In: 16th international conference on building materials – ibausil, Weimar, Germany; 2006. p. 93–100.

[50] Schober I, Mäder U. Selecting the optimum HRWR for SCC. In: 2nd North American conference on the design and use of Self-Consolidating Concrete (SCC) and 4th international RILEM symposium on self-compacting concrete, Chicago; 2005. p. 39–45.

[51] Yamada K, Hanehara S. Working mechanism of polycaryboxylate superplasticizer considering the chemical structure and cement characteristics. In: 11th international congress on the chemistry of cement, Durban, South Africa; 2003. p. 538–49.

[52] Plank J, Sachsenhauser B, de Reese J. Experimental determination of the thermodynamic parameters affecting the adsorption behaviour and dispersion effectiveness of PCE superplasticizers. Cem Concr Res 2010;40:699–709.

[53] Plank J, Sachsenhauser B. Experimental determination of the thermodynamic parameters affecting the adsorption behavior and dispersion effectiveness of PCE-superplasticizers. In: Ninth ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete - Supplementary Pappers, Seville, Spain; 2009. p. 87–103.

[54] Rickert J, Herrmann J. Zemente mit mehreren Hauptbestandteilen – Wechselwirkungen mit PCE-Fließmitteln. In: vdz Fachtagung "Betontechnik" Düsseldorf: vdz; 2011.

[55] Taylor HFW. Modification of the Bogue calculation. Adv Cem Res 1989;2:73–7.