

Effects of Superplasticizer and Viscosity-Modifying Agent on Fresh Concrete Performance of SCC at Varied Ambient Temperatures

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Abstract. Varying ambient temperatures in plants or on construction sites during casting of SCC can cause serious problems affecting the fresh concrete performances, such as rheological properties and setting time, with consequences for the hardened properties in the structure. By sensible choices of the components, the robustness of SCC mixtures against temperature variations can be improved. However, this aspect has not been the focus of intensive research yet. In this study the effects of varied ambient temperatures on the early performance of differently composed SCC mixtures are investigated, with emphasis on changes in rheology, early deformations, heat evolution and setting. Focus is placed on the study of the influence of the polycarboxylate ether molecule type as well as different viscosity-modifying agents on the temperature robustness. Effects on the relevance for practical concrete applications are evaluated, which will provide a reliable framework of possible actions on the appropriate use of admixtures for SCC.

Introduction

It is often stated that self-compacting concrete (SCC) can only function well, when the mixture composition is perfectly adjusted and the ambient conditions are within narrow limits. Thus, SCC is typically limited to precast applications, although the technology offers many opportunities for the construction site as well. The flow properties of SCC are controlled by the composition of paste and aggregates as well as their respective ratio in the concrete. Regarding the rheology of the paste matrix, the adsorption of superplasticizer molecules on the surfaces of clinker phases and early hydrate phases plays an important role [1, 2]. In case of SCC, polycarboxylate ether superplasticizers (PCE) are mostly used. Positively charged clinker and reaction phases, like C₃A and ettringite, interact with the negatively charged backbones of the PCE molecules [3]. In this process, superplasticizer

molecules compete with the sulphate ions and interact with the calcium ions in the pore solution [4, 5]. The processes are time dependent, since newly built reaction phases, e.g. ettringite, provide additional adsorption surfaces. The higher the anionic backbone charge density, the quicker the molecules adsorb on surfaces. The lower the charge density, the slower but the more polymers can adsorb. In case of high dosages, some molecules will not adsorb directly but time dependent [3, 6]. Typically highly charged PCEs are used for quick performance over a short period of time, whereas lowly charged PCEs are used if flow retention is required. Sensible choice of PCE at particular ambient conditions can optimize the flow performance or the robustness against varying total water contents resulting from either poor production control or varying moisture contents of the components. An optimized PCE for particular conditions, however, does not inevitably have to be the best choice at differing ambient conditions. At varied temperatures, the hydration can be accelerated or slowed down, which affects the interaction between PCE, cement and hydrates significantly.

In the case of ready-mix concrete, surrounding conditions may change unexpectedly, and it is not possible to have an individual optimum superplasticizer modification for all expectable situations. Robustness is often only linked to the performance stability against variations in quality and quantity of the concrete's constituents such as water, cement, admixtures, aggregates, or human and technological shortcomings during casting [7-11]. The stability against ambient climatic conditions at otherwise identical specifications is only rarely observed. The interaction between PCE and mineral components is highly affected by the ambient temperature. Hence, the relevant question for casting on site is not only, which PCE can optimize the performance, but also which SCC mixture parameters can buffer negative effects caused by temperature dependent varying binder-PCE-interactions. In this, the impact of additions and viscosity-modifying agents (VMA) has to be considered. Additions may also provide positive surface charges, causing interactions with PCE. VMA has strong impact on the rheology of cementitious materials, overlapping or interfering with the effects of PCE [12]. In order to better understand temperature effects, systematic investigations were performed at varied temperatures with a powder type SCC and a VMA stabilized SCC. Focus was put on rheological concrete properties as well as on setting, heat evolution and autogenous deformations.

Experimental Setup and Investigations

Two characteristic concrete mixture compositions were generated, which are demonstrated in Table I:

- The powder type mixture (POW) used in the investigations is a modification of an SCC, originally developed without any VMA according to the approach of Okamura [13]. In order to better point out effects of VMA, in the modified concrete (POW) the limestone filler content of the original

Okamura type was reduced by 50 kg/m^3 . The missing filler was compensated by VMA. By this modification, yielding a water-powder ratio of 0.31 and a total powder content of still 560 kg/m^3 , the basic characteristics of a powder type SCC remain largely untouched, while the role of VMA for the functioning of the SCC is increased.

The mixture called COM is a combined approach between powder and admixture stabilization. The powder content is higher than in ordinary concrete but significantly smaller than in the POW mixture. Due to the missing powder, high contents of VMA are required to achieve segregation stability and self-compacting flow properties.

These basic mixture compositions were then adjusted by combination of three types of PCE and two types of VMA, in such a way that a slump flow diameter between 650 and 700 mm was obtained 30 minutes after mixing. This specification was made in order to provide sufficient workability retention with regard to the casting on the construction site, where temperature changes are most likely to occur. The PCEs in use are commercial products with comparable side chain and backbone length, differing characteristically in their graft chain density, which determines the backbone's ionic strength and thus the adsorption velocity. For a better display of the results, this paper focuses only on the PCEs with highest and lowest charge density (PCE1 and PCE2), since SCC with the medium charge density polymer always performed within the range of these. Viscosity-modifying agent VMA1 was based on modified potato starch, whereas VMA2 was based on Diutan Gum. When introduced into water only, both VMAs increase plastic viscosity but only VMA2 generates a significant yield stress. When added to water-solid suspensions, both VMAs significantly increase plastic viscosity and yield stress [12, 14]. Thus, particle immobilization (VMA1) and fluid-phase stabilization (VMA2) can be distinguished. Table II provides an overview of the characteristics and dosages of admixtures to achieve the defined flow performance.

Rheological concrete investigations were performed by using a CONTEC Rheometer-4SCC. The rheometer is an impeller based transportable system, which measures the electric current at varied rotational speed [9]. When applying a Bingham curve on the results, qualitative information about yield stress (G-Yield) and viscosity (H-Viscosity) of flowable concrete can be obtained. Changes of the rheological properties can be displayed qualitatively, but the results cannot be converted to fundamental rheological units as possible with a co-axial cylinder rheometer. The rheological test protocol is given in Table III. The first step includes 5 seconds of pre-shearing in order to assure measuring at steady state. In order to avoid deviations due to the change of the rotational speed, only the last 4 seconds of each step were used for the calculation of the Bingham curve. The rheometric investigations were conducted in a large climate chamber at 5, 20 and 30°C . 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

Table IV. Mixing protocol for concrete investigations.

Step	Duration [s]	Action
1	60	Dry mixing
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

The early age properties were determined by measuring setting, autogenous deformations as well as heat evolution of the mixtures at 5, 20 and 30°C. Since the particular effects of VMA on the early properties go beyond the scope of this paper, the presented results focus on the influence of PCE. For these demonstrated tests, binder paste was used. Since the sand used in the basic concrete mix design (Table I) did neither provide high contents of fines nor large surfaces compared to the powders, consideration of the powder fraction from sand and water absorption of sand and aggregates would only modify the paste composition to small extent. Hence, the pastes for these tests were generated from cement, limestone filler, water and superplasticizers to the same volumetric ratio as in the concrete mixture given in Tables I and II.

Since the particular adjustment of admixtures was conducted on SCC, the thus generated pastes, if sand and aggregates were added, can be considered to function properly at 20°C. The aim of the demonstrated research was to learn more about the influence of the PCE molecule type on the paste components and to illuminate effects taking place on paste level. Therefore the pastes were not furthermore changed characteristically or optimized. Particularly the PCE-powder ratio should remain untouched in order to point out effects of the PCE modification and to avoid that observed effects are rather resulting from differing PCE solid contents. Furthermore, the water-powder ratios were not changed to better distinguish characteristics of powder type and combination type binders. However, without the stabilizing effect of the sand and aggregates, the COM pastes tended to segregation, which had to be avoided since this would critically affects the measurement of the deformations and the setting. In order to safely avoid segregation of the COM specimens at all observed temperatures, the VMA contents were increased by factor 2 compared to the concrete mixes. By this, the general characteristics of the pastes, such as the ratio of powder to water and solid PCE, respectively, remained untouched. Since the VMA content was kept constant for all paste tests, this allowed observing the effect of different PCE types. It has to be stated that the effects observed with these pastes do not have to be representative for the respective concretes, since numerous influencing factors

have been excluded. To which extent the demonstrated results provide validity on full concrete scale will be subject of future research.

For the investigations of the setting, an automatic Vicat device was used. Measurements took place under water at particular temperature. Early deformations were measured with a shrinkage cone, where the mortar is given into a cone tapered downwards. On the flat top surface, a laser reflector is placed, measuring continuously the change in height. The top angle of 60° allows for similar deformations in height and width. Only the cone walls can be tempered, therefore the investigations were conducted in a climate chamber at particular temperature. In order to avoid exchange with the surrounding air, the cones were fully covered by foil. Since the minutes between mixing and first measurement remain undefined, a quantitative determination of the deformations is not possible. The method, however, provides information on rate of deformation. It cannot distinguish between deformations caused by settlement or shrinkage. When a sensible starting time for the observations can be defined (e.g. after final set) the deformations can be quantified. The heat flow investigations were performed in an isothermal heat flow calorimeter type TAM Air. The cells were calibrated to the particular investigation climate. The above described tests were conducted in parallel from one single mixture in order to avoid effects resulting from different test conditions. A repeatable mix regime that has proven to homogenize the powder well was applied constantly. Each test was conducted at least twice for each mixture and admixture adjustment.

Results and Discussion

Yield stress was influenced much more by the surrounding conditions and the admixture adjustment than viscosity. Therefore, the demonstrated results focus on G-yield, which can be linked to the slump flow behaviour of the mixes. Figure 1 shows the evolution of the G-Yield of the POW mixtures with time depending on temperature, PCE and VMA. At 5°C neither PCE type nor VMA type affect the performance and the performance retention of the POW mixes. At higher temperatures PCE1 retains the yield stress constantly, whereas PCE2 causes a time dependent increase of the yield stress. The latter effect is boosted by higher temperature. Due to the performance loss at 30°C no further measurement could be conducted later than 30 minutes, when PCE2 was used. Generally the influence of VMA is negligible. Only at 20°C in combination with PCE2, VMA1 provides better yield stress retention than VMA2. Figure 2 shows the respective results for the COM mixtures. Due to the higher content of VMA, their performance depends on both PCE and VMA type. At 5°C concrete with PCE2 provides a significantly lower yield stress than with PCE1. This effect occurs in comparable magnitude for both VMA types. In addition, concrete with VMA1 provides significantly lower yield stress than with VMA2. Both stabilizing agents provide characteristic retention behaviour, which is independent of the PCE type. VMA1 causes constant

stiffening, whereas VMA2 causes an initial stiffening effect which reduces again with increasing time. Effects of VMA and PCE superpose so that the only mixture that can be considered self-compacting is the mixture with PCE2 and VMA1.

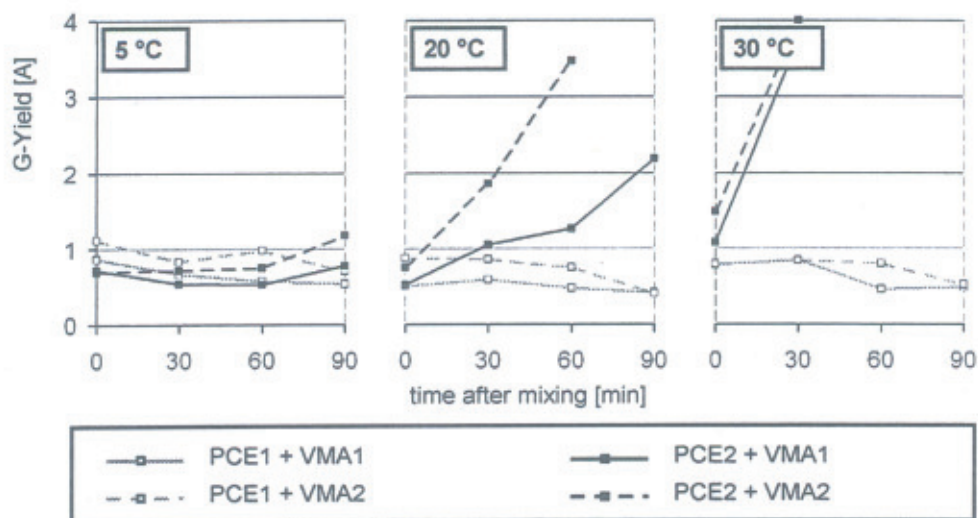


Figure 1. POW mixtures at varied temperatures, PCEs and VMAs.

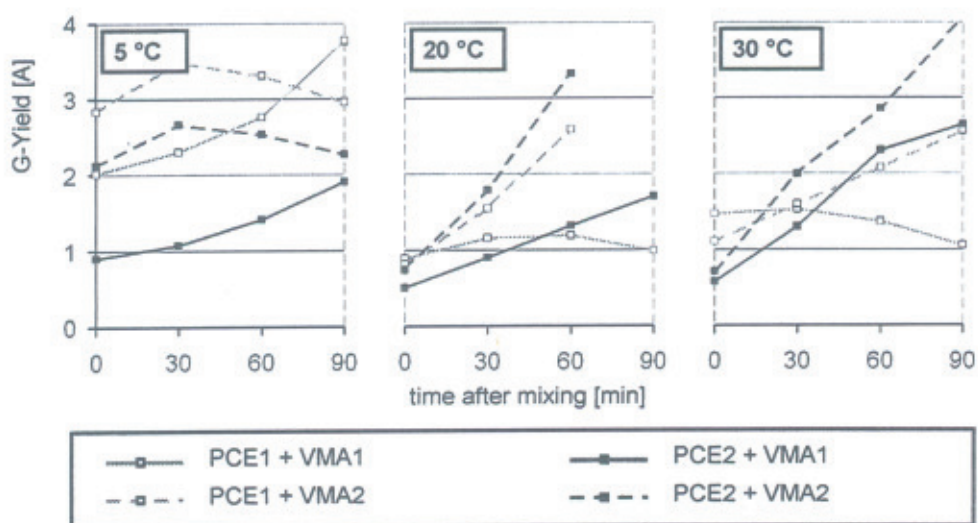


Figure 2. COM mixtures at varied temperatures, PCEs and VMAs.

At 20°C the influence of the VMA on yield stress is much stronger than the effect of the PCE. Independent of the PCE type, both mixes with VMA1 retain the performance better than those with VMA2. At 30°C, effects of both, VMA and PCE, can be noticed. Initially PCE2 provides much lower yield stress than PCE1 but then the yield stress increases quickly. PCE1 generally provides better yield

stress retention. Mixtures with VMA1 provide lower yield stress. The only mixture that performs well over the whole time includes PCE1 and VMA1.

The results presented in Figures 1 and 2 can be explained by PCE adsorption that depends on hydration progress and backbone charge density as well as on the stabilizing mechanism caused by the mix design and the VMA. Since the flow behaviour of the POW mixture is strongly dependent on particle distribution and optimized water content, the influence of low temperatures on the yield stress is small. The hydration is slowed down and thus the adsorption of polymers on hydration phases is low. Therefore the influence of the PCE type is negligible. At higher temperatures, the hydration takes place much quicker, causing stronger effect of the PCE type. The highly charged polymers of PCE2 are quickly consumed so that any further hydration causes stiffening, whereas the lower charged PCE1 still provides polymers for adsorption in the solution. Hence, PCE1 generally provides better robustness against temperature effects. The influence of the VMA is generally low on the POW mixtures, since it is only added in small amount. The flow performance of the COM mixtures depends rather on the VMA than on the optimum adjustment of particles and water demand. Since the COM mixtures provide water in overabundance, the temperature effect on the performance of VMA2, which rather stabilizes the fluid phase, is much stronger than on VMA1, which immobilizes the particles. At low temperatures, precipitation of aluminates and solubility of sulphates is slowed down as well as their reaction. Therefore, less adsorption sites are available for the PCE molecules than at higher temperature, when ettringite can be shaped quickly. Hence the PCE with high backbone charge density performs significantly better than the one with low charge density. Since the performance loss related to the initial performance of both PCEs is comparable, it can be assumed that even after a long period of time no distinct adsorption of PCE1 takes place. This can be explained by anions from the pore solution occupying the adsorption spaces for the polymers. Effects of VMA superpose the PCE performance, and VMA2 causes a distinct performance loss. Hence, only the combination of PCE2 and VMA1 performs stable at low temperature. At 20 and 30°C the hydration proceeds faster and the PCEs' dependency on the hydration process gains prominence. This causes low initial yield stress combined with poor performance retention for SCC with highly charged PCE. With increasing temperature, the hydration is accelerated causing increasingly poorer performance retention at the use of PCE2. Since the flowability of these mixtures is supplementary determined by the high available volume of water, however, the significance is much smaller than it is for the POW mixtures.

In summary, the POW mixtures provide stable performance at a wide temperature range, when a low charge density polymer is used, whereas a highly charged polymer might cause poor performance retention at high temperatures. COM mixtures require a highly charged polymer at cold temperatures to provide workability at all, while at higher temperature the influence of the PCE is less significant. Hence, POW mixtures are very robust at low temperatures and prone to

failure at high temperature against effects of the PCE type. Vice versa, COM mixtures are sensitive against PCE effects at low temperatures and more robust at high temperatures. However, since the used PCE also determines the overall amount of adsorbable polymers in the bulk system, and the adsorbed surfaces influence the hydration progress, the effect of the PCE continues still after casting, since it can have a strong influence on the setting behaviour.

Figure 3 demonstrates the influence of the PCE on the setting behaviour for the COM mixtures at 5 and at 30°C. In order to provide comparable flow properties of the concrete, the low charge backbone PCE has to be added in significantly higher solid content (see Table II). Therefore, compared to PCE2, the setting is significantly retarded, since at full consumption of PCE more molecules occupy the surfaces of hydration products, thus slowing down the setting. This observation fits in with the results of the heat flow calorimetry. Retarding effects that were caused by the choice of PCE and the respective amount of solid molecules could qualitatively be observed at the heat flow curves as well. In order to underline this, the first derivative of the heat flow was calculated, which can be entitled as the heat flow rate (Figure 4). For all temperatures the maximum heat flow rate peak occurs at the time of the final set, which underlines the strong correlation between heat evolution and setting. This is valid for all observed temperatures.

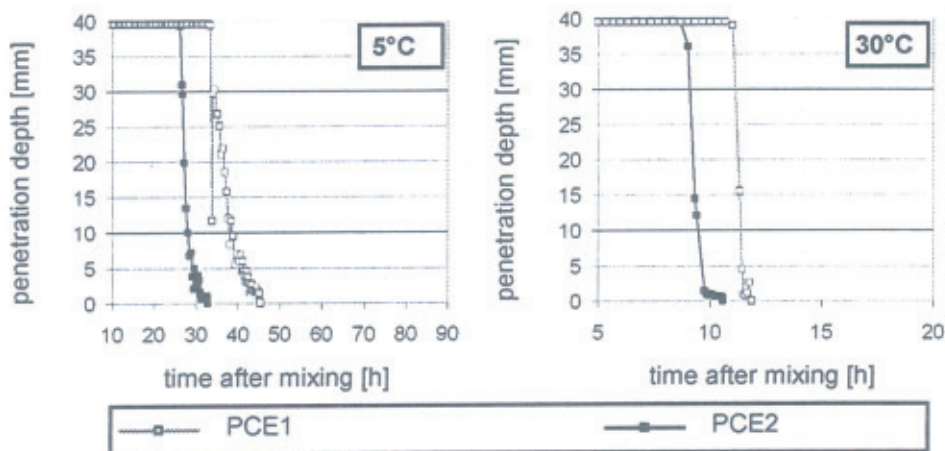


Figure 3. Needle penetration depth at 5 and 30°C of COM paste.

The time dependency of the autogenous deformations, the deformation rate, which when approaching zero indicates the transition towards a slow deformation process, was strongly related to temperatures. At 5°C the approximation towards zero occurred for the demonstrated examples of the COM pastes around 44 hours at 5°C and around 21 hours at 30°C, independent of PCE type or solid content. If deformation progresses are independent of the PCE solid content but the final set is strongly depending on the PCE solid content, this suggests taking a closer look at those deformations after the final set. Deformations occurring earlier take place still in plastic state, which makes the occurrence of lasting cracks unlikely. After

the final set, deformations take place in elastic state while the strength is still low, making the mortar prone to cracks in particular at this time.

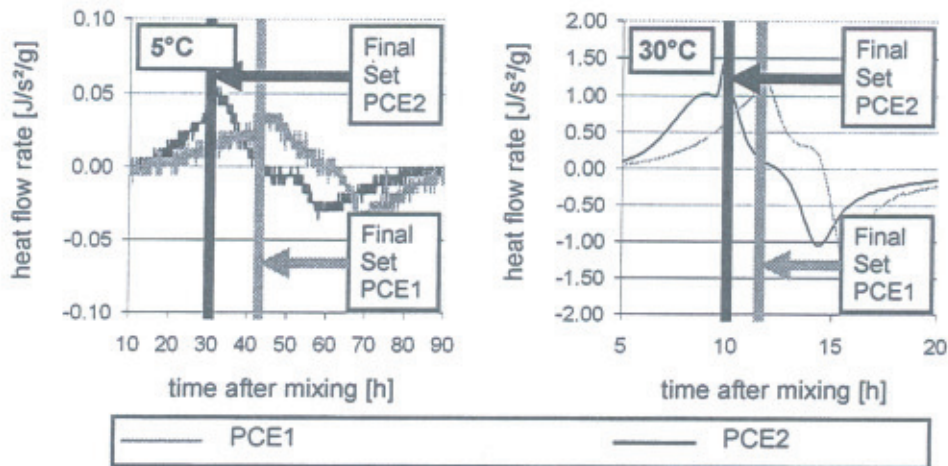


Figure 4. Heat flow rate depending on PCE type compared to time of final set.

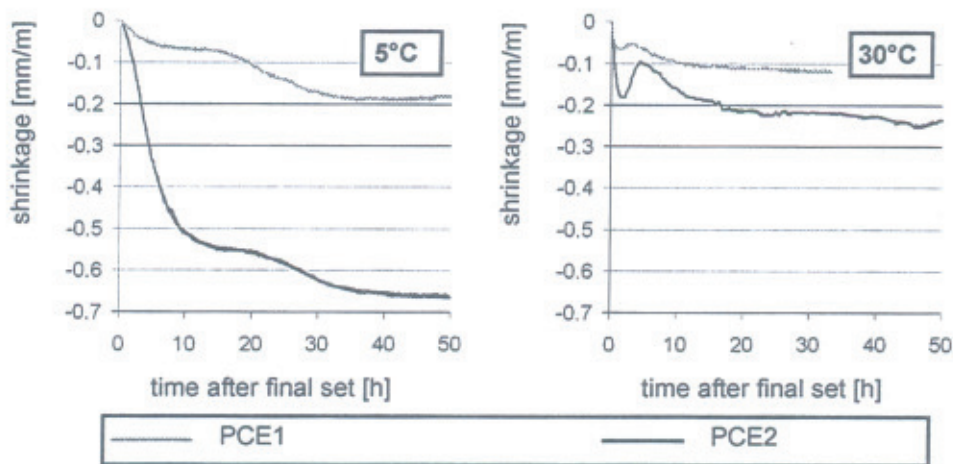


Figure 5. Deformations after final set depending on PCE type.

Figure 5 shows the deformations of the mortars with PCE1 and PCE2 that only occur after the final set at low and high temperatures. Since at all temperatures the shrinkage rate approaches zero with PCE1 and PCE2 approximately at the same time, but PCE2 always sets much earlier than PCE1, the highly charged PCE2 produces larger deformations than the lowly charged PCE1 at this stage. The higher amount of polymers that is required to provide the demanded concrete flow performance with PCE1 reduces the susceptibility to early cracks due to set retardation. Furthermore, the shrinkage deformations after the final set are generally higher at 5°C than at 30°C. This effect can be attributed to a slower development of stiffness at low temperatures, causing low resistance against deformations over a longer period of time. Temperature effects on deformations

after setting are more prominent with PCE2. The deformations at 5°C are roughly two times as high with PCE1 and roughly three times as high with PCE2 as at 30°C. The earlier setting due to the lower amount of polymers occurs most significantly at low temperatures (Figure 3). The long period of time between the setting of PCE1 and PCE2 at 5°C causes that the influence of temperature on deformations after setting is significantly higher on pastes when the highly charged PCE is used.

Summary and Outlook

Rheological investigations as well as investigations of early properties of two types of SCC at varied temperatures and at varied admixture compositions have shown that although the performance of all modifications was comparable at 20°C, significant performance differences occur at varied temperatures.

- Since temperature effects on the performance of SCC are mainly initiated by the temperature dependent hydration velocity, robustness improvement can be achieved by sensible choice of a fitting PCE polymer.
- At low temperatures, the powder type SCC is less affected by the choice of PCE, whereas at high temperatures PCE with high ionic strength of the backbone can cause rapid stiffening.
- The VMA type SCC requires a highly charged PCE at low temperatures, whereas at high temperatures the effect of PCE is less prominent.
- Besides temperature effects that can be related to PCE, temperature effects on the VMA have to be considered for the VMA type SCC. In the demonstrated research, starch ether was less prone to temperature effects than Diutan Gum.
- Since the charge density of the polymers' backbone also determines the amount of solids that have to be added to achieve certain flowability, the required PCE for a defined flow performance strongly affects the early concrete properties.
- Higher PCE solid contents slow down the setting and the heat flow. While it is likely that at 20 and 30°C these effects are not of practical importance, at low temperatures, the delay can be crucial.
- Since early deformations in the observed pastes are rather temperature and mixture dependent but, unlike the setting, less affected by the polymer type, retarded setting helps minimizing the risk of early cracks.

The research has shown that a reasonable mixture composition as well as the admixture setup can improve the robustness against effects of the ambient temperature on performance and performance retention. Furthermore, influences on the early properties caused by the superplasticizer type have been shown. These results, however, were demonstrated on the basis of binder pastes, which do not have to be representative for the respective concrete mixes, particularly at low temperatures, which in combination with the high PCE contents caused severe set

retardation. In order to show the relevance for the concrete scale, they have to be validated by concrete tests in future investigations.

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