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Influence of Environmental Temperatures on the Performance of Polymeric Stabilising Agent in Fresh Cementitious Materials

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Abstract. Stabilising admixtures are commonly used additives in repair mortars and grouts. Beyond this, such type of admixture is increasingly used in concrete and other cementitious materials. In particular when fresh mortar or concrete properties have to be adjusted reliably, stabilising agents can be beneficially used to improve workability and robustness of the mixture. The mode of operation of these admixtures varies, rather affecting either the liquid phase or the solid particles in the dispersion, both causing strong interactions with the mortar or concrete system, and significant changes in their rheological behaviour. Furthermore, these are strongly affected by the environmental temperature during the casting process. In the paper the effect of temperature on the performance of stabilising agents in cementitious systems is presented and how performance changes affect fresh and hardening mortar or concrete properties. Particular attention is placed on interactions between stabilising agents and superplasticizers. Results are discussed with special focus on self-compacting concrete.

Introduction

During the last 15 to 20 years the variety of approaches to the mixture composition of self-compacting concrete (SCC) has changed world wide. The ancestor SCC, the so called powder type SCC, has often been replaced in favour of less powder rich concrete, which gains stability by addition of admixtures often called viscosity modifying agents (VMA) or viscosity enhancing agents (VEA). Since these admixtures do not affect solely viscosity but may also have strong impact on yield stress, in this paper they are referred to as stabilising agents.

According to [1] for mortar and concrete applications, commonly polysaccharides are in use. The variety of these products is huge. Some different types and their effects on fresh and hardened properties are described in [1-5]. Their mode of operation can be distinguished between adsorption, association and intertwining [1]. However, more than the mode of operation, for the user the effect in the whole cementitious system is of importance. Typically stabilising agents affect the rheological behaviour of mortar or cement providing stability against segregation or higher robustness against production parameters. Stabilisation can either be increased by affecting rather the fluent phase directly [4] or the particles in the fluent phase [5], both affecting yield stress and viscosity of mortar or concrete.

Rheological modifications are typically generated on purpose. However, it is also reported of earlier or later setting and retarded strength development [1, 3, 6-8]. These effects are not comprehensively understood today. It is said that retarded setting may be caused by adsorption of stabilising agents on cement particles, modifying the precipitation of minerals [1]. Also the dependency on the individual composition of stabilisers is reported. According to [9] the calcium binding capacity, causing complexation, and a possible chelation due to alkaline instability, which is also reported by [6], may play a certain role in the retardation. Results with cellulose ethers, however, only showed negligible calcium binding capacity and high stability against high alkaline media. It is also reported that there is a dependency on the clinker composition. [10] found out that the retardation is the stronger, the lower the C_3A content of the cement is. A typically decelerated retardation of Portlandite and CSH was linked to the stabilisation of ettringite and gypsum caused by the admixtures. However, they found out that depending on the composition of the polymer acceleration and retardation can be observed, Variations in the setting behaviour were also reported in combination with superplasticizer [1, 7, 11].

The effect of stabilising agent on rheological properties of mortar and concrete is extensive, depending on the type and modification of stabilising agent. In the evaluation of rheological effects it has been shown that consideration of the whole mortar or concrete system is important since effects occurring distinctively in paste can be overcompensated by supplementary effects resulting from the whole compound [8]. With regard to the practical application, it is therefore important to observe the rheological effects of admixtures in the mortar or concrete system. The effect on the setting behaviour is comparably large and only fairly understood to date. The available knowledge today is based on investigation at constant climate. The presented paper focuses on the effect of varied temperatures on two types of stabilising agents in presence of differently modified superplasticizers. The influence on the rheological behaviour is demonstrated using the example of an SCC with low powder content. The setting behaviour is observed on cement pastes with and without superplasticizer.

Experimental Investigations and Specifications

Materials Setup. For the tests, two differently working stabilising agents were selected. Stabiliser 1 (St1) is based on potato starch ether, Stabiliser 2 (St2) is a microbial polysaccharide. The main characteristic difference between them is the effect on yield stress and viscosity. Fig. 1 demonstrates this under assumption of Bingham behaviour for both stabilising agents mixed on the one hand with water only and on the other hand with water-cement dispersion. It has to be noted that Bingham behaviour is a simplification since factually both stabilisers cause shear thinning behaviour at low shear rates. Nevertheless this simplification gives a good overview about the behaviour of each stabilising agent. At an admixture amount that causes comparable viscosity when added to water only, St1 does not generate a yield stress, whereas St2 does. When particles are dispersed in the same solutions, both stabilising agents generate a distinct yield stress. Compared to St1, St2 affects yield stress stronger than viscosity.

Furthermore two types of polycarboxylate ether superplasticizer (PCE) with varying charge density of the backbone were chosen for the investigations. The backbone charge determines the adsorption velocity of superplasticizers on clinker phases and early hydration products and thus influences the time dependent rheological performance as well as the setting. Table 1 provides a detailed overview of the used admixtures.

Table 1 : Used admixtures

Admixture type	Code	Characteristics and effect
Stabilising agent	St1	Modified starch, mainly immobilising particles
	St2	Biopolymer, mainly affecting rheology of the fluid phase
Superplasticizer	PCE1	Low backbone charge density, slower adsorption
	PCE2	High backbone charge density, quicker adsorption

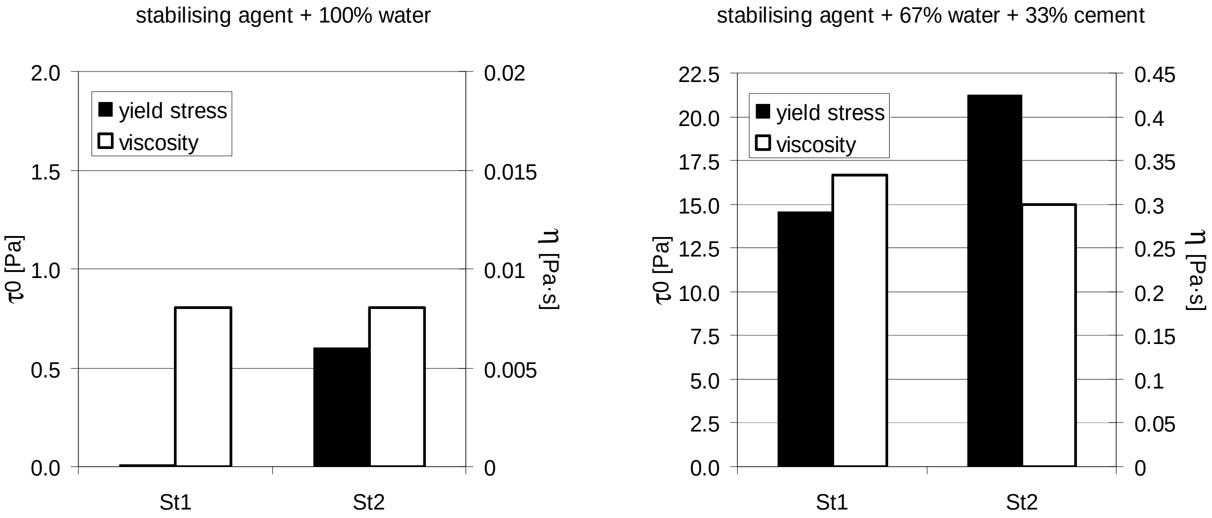

Figure 1: Influence of St1 and St2 on rheology of water and water-cement suspensions

Table 2 : Basic SCC mixture composition

Component	Portland Cement*	Limestone filler	Water	Sand 0-4 mm	Aggregate 4-16 mm
Proportion [kg/m³]	350	130	175	848	831
* CEM I 42.5, total alkali content: 0.89 wt.-%, Clinker comp. (Bogue) [wt.-%]: C_3S=56; C_2S=20; C_3A=8; C_4AF=7					

Table 3 : Admixture modifications

Modification	Stabilising agent	PCE type	Characteristics
Mod 1	St1	PCE1	Starch ether + low charge density
Mod 2	St2	PCE1	Biopolymer + low charge density
Mod 3	St1	PCE2	Starch ether + high charge density
Mod 4	St2	PCE2	Biopolymer + high charge density

Table 4 : Mean values of concrete temperatures at different temperatures and time steps.

Environmental temperature	Directly after mixing	30 minutes after mixing	90 minutes after mixing
5 °C	10.2 °C	9.3 °C	8.3 °C
20 °C	23.9 °C	22.4 °C	22.1 °C
30°C	32.8 °C	30.0 °C	29.2 °C

Rheology. For the investigations of the rheological performance, focus was placed on self-compacting concrete. A basic mix design, shown in Table 2, was modified by appliance of different admixture compositions generated from the two types of stabilising agents and PCEs. The modifications were adjusted in such way that each SCC provides a slump flow diameter higher than 650 mm at 20 °C 30 minutes after mixing. No adjustment of the admixtures took place at varying temperatures. The particular modifications are shown in Table 3.

The investigation were conducted in a climate chamber providing sufficient space for a 50 l mixer as well as the raw materials, personnel and equipment for several fresh concrete tests, which were conducted in parallel to the presented research. Investigations were performed at 5, 20 and 30 °C environmental temperature, directly, 30, 60, and 90 minutes after mixing.

Before the tests were performed, all mixture components were stored for at least 24 hours in each particular climate. Water was exactly adjusted to each temperature. It has to be noted that due to mixing, the fresh concrete temperature was not identical to the environmental temperature, and that it was changing within time.

Table 4 gives a survey of the mean values of the fresh concrete temperatures at each particular surrounding temperature. The standard deviations of the measurements were smaller than 0.3 °C. The table shows that the environmental temperature does not truly render the fresh concrete temperature and that time dependent adjustment takes place. However, each fresh concrete temperature range is characteristic at each environmental temperature and can be clearly distinguished. Hence in the presentation of the figures the environmental temperature is utilised instead of the fresh concrete temperature.

Fresh concrete analyses were conducted by help of a mobile concrete rheometer of the type ConTec Rheometer-4SCC. By measuring the torque in mA at varied rotational speeds and appliance of a Bingham approach, this equipment allows drawing qualitative conclusions on yield stress and viscosity of the mixes. It does not provide real physical measurands, and the results in this paper, which can only provide qualitative information on the properties, are thus referred to as G-yield and H-viscosity, respectively.

Setting. The influence of type and amount of stabilising admixtures was observed in dependence of the environmental temperature. Pastes from cement and water were investigated, modified with and without superplasticizer (PCE1). The mixes without superplasticizer were adjusted to w/c=0,55 those with PCE to w/c=0,40. The dosages of St1 were added in amounts that fit into the range provided by the data sheet of the producer. Since according to the data sheet of the producer St2 has to be added in much lower contents than St1, only the two lower contents accord to the producer's data sheet. The two higher dosages were added to see how both admixtures behave at comparable polymer contents. The dosages are related to the water content of the mixes.

The tests were conducted by help of a programmable automatic Vicat device allowing temperature control of the surrounding water storage and continuous logging of the penetration depth. This enables to observe the full penetration curve between initial and final set. Since the times between initial and final set were comparable for all mixes at each particular temperature, the time at which a needle penetration depth of 20 mm was reached was chosen to represent a median between initial and final setting times.

Results and Discussion

Rheology. Fig. 2 shows the time dependent rheological performance of SCC at 5 °C. Each stabilising agent affects the rheological performance of the SCC characteristically. St1 keeps yield stress much lower than St2. However, with St1 the initial yield stress increases steadily with time, whereas with St2 yield stress increases at 30 minutes but reduces hereon to the initial value again. These effects are independent of the PCE type. Generally PCE1 causes higher yield stresses and higher viscosities than PCE2 but no interaction between the stabilising agent and PCE takes place affecting the yield stress. However, St2 increases viscosity disproportionately higher in combination with PCE1. Whereas with focus on yield stress, the SCC with PCE2 and St1 provided good self-compacting properties, the other mixtures can not be considered as self-compacting without limitation.

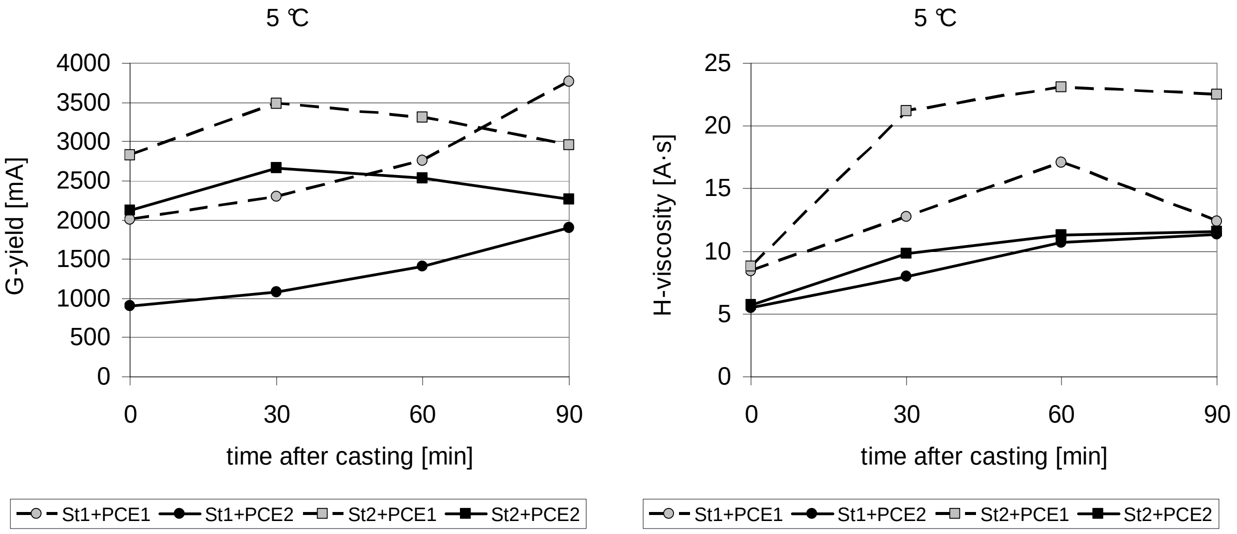

Fig. 2: Rheological performance of SCC with different stabilising agents and PCE types at 5 °C

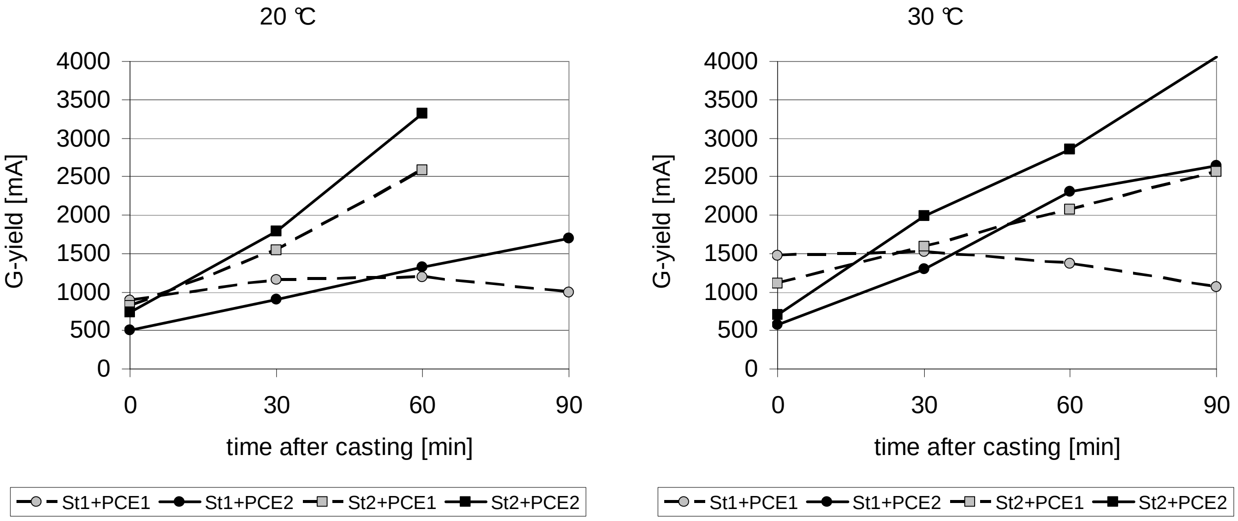

Fig. 3: Qualitative changes of yield stress due to stabilising agent and PCE at 20 and 30 °C

At 20 and 30 °C, no significant effect on viscosity changes, neither of PCE nor of stabilising agent type, can be observed. This differs with regard to yield stress. Figure 3 shows the time dependent yield stress development of SCC with different admixtures at both temperatures. At 20 °C the influence of the stabilising agent predominates over the effect of PCE. The quickly adsorbing PCE causes lower initial yield stress than the slower adsorbing PCE but poorer retention with time. This effect is independent of the stabiliser type. Both SCCs with St2 showed much quicker increase of the yield stress independent of the PCE in use. Later than 60 minutes these mixes were no longer measurable since they became too stiff and could no longer be considered as self-compacting. The retention of the yield stress is much better with St1. In combination with the low charge density PCE, a uniform performance can be retained for the whole observation period of 90 minutes.

At 30 °C the effect of the superplasticizer gains importance again. Without regard to the engaged stabilising agent, PCE2 causes significantly lower initial yield stress that increases rapidly, whereas PCE1 shows higher initial yield stress, which is only slightly increasing. Nevertheless it can be observed that independent of the PCE type St1 retains the initial yield stress better than St2. The latter effect can be observed for all temperatures in the tests. Practically without corresponding adjustment St1 causes higher robustness against temperature variations. This observation could be underlined by separate slump flow and V-funnel tests. Nevertheless at 30 °C, caused by low yield stress and viscosity, an initial segregation tendency could be observed in case of the use of St1, which was not observable with St2 [12]. Furthermore the stability against segregation could not be retained over longer period of time, which may cause problems at low temperatures, when setting is significantly retarded.

Setting. The influence of the stabilising agent type on the setting at varied temperature ranges is relatively small for the tested specimens compared to the influence of superplasticizer. In the mixes without superplasticizer only negligible delayed setting can be observed for both stabilisers and for all observed temperatures. This slight retardation can be observed without systematical correlation to the added amount, which means that such effect is caused solely by the presence of stabilising agent but not influenced by the amount. Considering the short setting times of these mixes, in particular at 20 and 30°C, such a retardation does not play a crucial role in building practice.

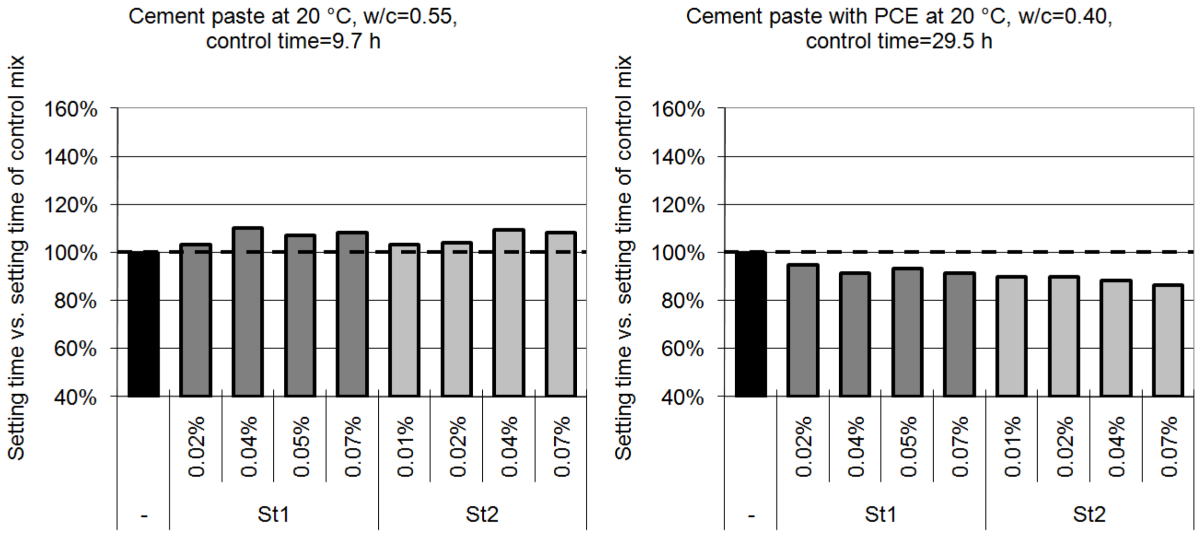

Fig. 4: Influence of the presence of superplasticizer on the setting at 20 °C

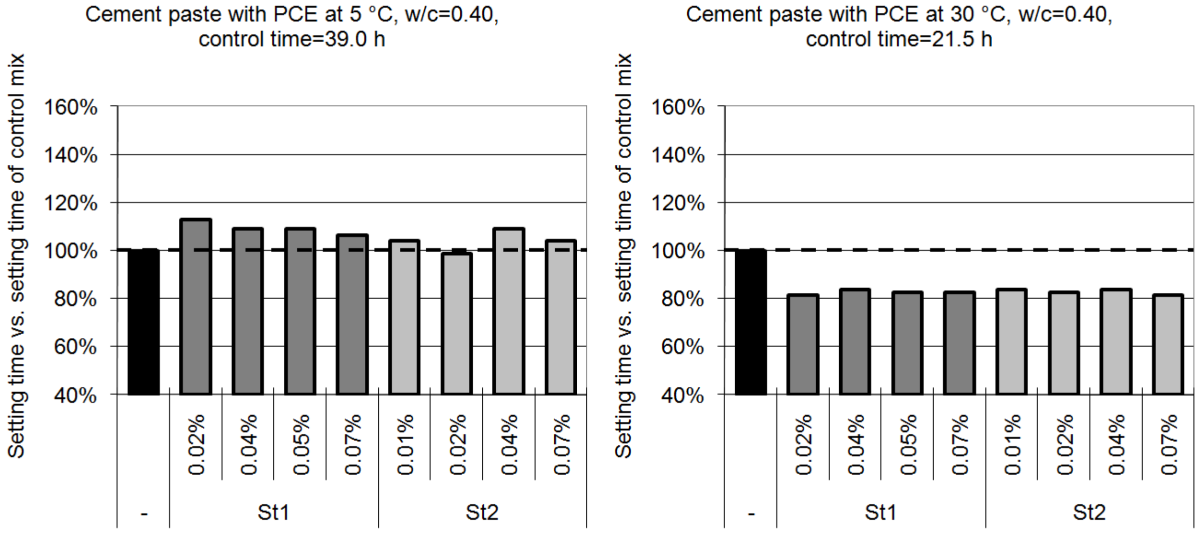

Fig. 5: Influence of PCE on the setting at 5 and 30 °C

When superplasticizer is added supplementary to stabilising agent, the behaviour changes. Fig. 4 shows a comparison between mixes with and without superplasticizer at 20 °C. The figures demonstrate mixes with different amounts of stabilising agent in comparison to a control mix without stabiliser, which is defined as 100% value. In presence of superplasticizer (Fig. 5), both stabilising agents cause retarded setting at 5 ° and accelerated setting at 20 and at 30 °C. The latter effect was stronger at 30 °C. Increasing amounts of stabilising agent do not intensify these effects.

It is reported that retardation of the setting is depending on the adsorption of stabilising agent molecules on cement particles. The behaviour of the investigated stabilising agents without superplasticizer matches to these observations. The strong temperature dependency in case of mixes with both, stabilising agent and PCE, suggest that an additional effect takes place, which only affects the PCE performance in the pore solution, overcompensating the retarding effect of the stabilising agents' adsorption. Focusing on the dormant period, it is thinkable that despite of the retarded hydration of aluminates due to adsorption of stabilising agent, the stabilising agent induced increased viscosity of the pore solution or locking effects reduce the mobility of PCE molecules in favour of a quicker adsorption of sulphate ions on C_3A hydrated phases. This would otherwise be disturbed by competitively adsorbing PCE molecules. Since the hydration of C_3A is significantly slower at very low temperatures such as 5 °C, this effect retreats into the background and the adsorptive effect of the stabilising agent predominates, causing retarded setting at very low temperatures. This, however, can only be considered as rough hypothesis, which cannot be quantified by means of the conducted investigations.

Conclusions

In the presented paper the influence of varied environmental temperatures on the effect of two types of stabilising agent in combination with superplasticizer on rheology and setting is demonstrated. With regard to the influence of temperature on the performance of SCC the following items can be stated:

- At 5 °C the influence of both, superplasticizer and stabilising agent, is strong. A quickly adsorbing PCE generally provides lower yield stress and viscosity than a slowly adsorbing PCE. The performance differences induced by PCE are retained throughout the whole observation time. The stabiliser based on modified potato starch generally generates lower yield stress than the microbial polysaccharide. The influence of each stabiliser on yield stress is not affected by the PCE modification. In combination with PCE1, unlike with PCE2, St1 keeps viscosity lower than St2.
- At 20 and 30 °C the viscosity of the SCC is not markedly affected by the modification of stabilising agent.
- At 20°C the influence of the stabilising agent on yield stress overbalances the effects of the different PCE modifications. Generally St1 retains yield stress significantly lower than St2.
- At 30°C the effect of superplasticizer predominates over the effect of stabilizing agent. After significantly lower values in the very beginning, the yield stress with PCE2 increases quickly, whereas the initial yield stress with PCE1 is higher but increases only slightly within the observation time. Generally St1 causes lower yield stresses than St2.
- Concerning the setting, both stabilisers slightly retard without superplasticizers. The retardation is a general effect caused by the presence of stabiliser and not by the amount.
- In presence of superplasticizer both stabilising agents cause retarded setting at 5 °C and accelerated setting at 20 and 30 °C. The accelerating effect is stronger with higher temperature.

Considering that the influence of stabilising agent on setting is generally only fairly understood and results are not always consistent, the presented results on setting raise several questions that cannot be answered without further research. A rough idea to the accelerated setting in presence of PCE by reduced mobility of the PCE in the pore solution is suggested. In this context the influence of the molecules structure of the PCE could gain importance and should be observed in future investigations.

The only admixture combination that provided self-compacting performance at least for 60 minutes throughout the whole temperature range between 5 and 30 °C was the combination of the quickly adsorbing PCE with the modified potato starch stabiliser. Nevertheless the microbial polysaccharide seemed to avoid segregation more reliably. Robustness against such huge temperature variations is not a typical requirement of SCC. Considering that admixture amounts typically can be modified with respect to particular climatic conditions, the presented investigations and results provide useful information for the use of admixture combinations and possible modifications in case the environmental temperature varies.

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