Casting process improvement by optimization of mixture composition and high range water reducing agent modification

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ABSTRACT:

Since its invention in the early 1990's, self-consolidating concrete has never become well established in the ready-mix sectors worldwide. The reason for this can be mainly found in the fact that the sophisticated compositions are sensitive against changing environments. This lack of robustness can be attributed to the interaction between cement hydration reaction and high range water reducing agent (HRWRA). Understanding the relevant mechanisms that control the initial flow performance as well as the flow retention helps optimizing SCC mixtures that perform either steadily in one specific environment or that perform largely similarly at steadily changing environments.

This paper depicts how HRWRAs interact with clinker and hydration phases and discusses the important role of the charge density of a polycarboxylic HRWRA in the way the rheology is affected. Based on rheometric results and observations of the Vicat setting times, it is shown that increasing charge densities of the HRWRA and decreasing water to powder ratios (w/p) reduce the flow retention and have lesser retarding effect on the setting. Based on the discussion, optimization procedures for the mixture composition and the HRWRA modification are suggested to achieve optimized performance for varying environmental situations or highest robustness for specific conditions.

Keywords: Polycarboxylate, cement hydration, adsorption, mixture composition, environmental conditions

INTRODUCTION

The flow properties of SCC are determined by a range of factors. The type, quantity and composition of the aggregate, the water/solid particle ratio of the binding agent paste plus the interactions between the binding agent components and polymer admixtures are to be found amongst these. Due to their strong effect on the reduction of the yield stress, usually, HRWRAs based on polycarboxylate ethers (PCE) are incorporated into SCC mixture compositions. The PCE molecules are composed of a negatively charged polycarboxylate backbone and a number of ethylene oxide grafts. Due to the anionic backbone, the polymers are adsorbed on positively charged surfaces. The latter are mostly created on aluminate and ferrous clinker phases as well as on monosulfate and ettringite hydration phases [1, 2]. The actual dispersing effect, however, is caused by steric repulsion of the particles through the side chains and backbone depending on the adsorption figure [3].

The addition of HRWRAs mainly has an effect on the yield stress of a cementitious system. Yield stress changes can be detected mainly by changes of the slump flow behavior. The lower the yield stress, the wider the slump flow diameter. The quantity of adsorbed molecules correlates linearly with the resulting slump flow [4, 5]. This correlation holds true independent of the polymer geometry [6]. HRWRA molecules, which cannot be adsorbed, are inefficient for the dispersion. PCE competes for adsorption sites with anions in the pore solution. Particularly, sulfate ions from the set retarder and alkali sulfates from the clinker also strive to adsorb on positively charged surface exposed areas [7, 8].

However, both the solubility of the ions as well as the adsorption and desorption processes are dependent on time and boundary conditions such as the environmental temperature or the mixing intensity. The reaction products generated during initial and early hydration yield new surfaces for the adsorption of HRWRAs. Ettringite, in particular, exhibits a high positive zeta potential, thus offering large adsorption sites with time [2]. The time effect of the ettringite formation on the adsorption of PCE is illustrated schematically in Fig. 1. The higher the polymer's anionic charge density may be, the more efficiently it can be adsorbed; the lower it is, the greater the delay in adsorption; yet, the more polymers can be adsorbed. If – as in the case of SCC – very high dosages of HRWRA are required, significant quantities of PCE do not adsorb immediately, since there are not enough adsorption sites available. Adsorption takes place over the longer period of hydration time as soon as new, additional adsorption sites have grown with significant effect on the time dependent flow properties.

The charge density, thus, is the determining parameter for a PCE in terms of its efficiency to reduce the yield stress at a certain point in time. Higher charged PCE molecules are adsorbed more efficiently and less easily desorbed again. However, also the time dependent performance of the dispersing effect of PCEs is determined by the charge density. At an early stage, highly charged PCEs can be adsorbed in large quantities, whilst low charge density PCEs are partially repulsed or desorbed by the anions found in the solution. The non-adsorbed PCEs remain in the pore solution and thus cannot contribute to dispersion. However, a constant growth in the specific surface of cement particles occurs during the induction period [9]. Even during the dormant period steady hydration takes place, though at relatively slow velocity. In the course of time, morphological changes take place on the particle surfaces, overgrowing adsorbed PCEs thus making them lose their effectiveness. Therefore highly charged PCEs lose their effectiveness rapidly despite their strong effect on the early yield stress reduction. Low charge density PCEs are initially adsorbed at lower rate. However, the non-adsorbed polymers can be adsorbed onto the newly created hydration products over a delayed period of time, and thereby contribute to a long retention of the plasticizing effect.

Consequently, highly charged PCEs are well suited for the field of precast components, which demand for a rapid dispersion effect, and where any retention of the flowability after finishing the casting process is, in fact, rather undesirable. PCEs with a lower charge density are suited to uses in the ready-mix concrete sector. These are typically not quite as effective in plasticizing as highly charged polymers, but can nonetheless retain the consistency over the required period of time.

If a particular flow property is stipulated at a defined point in time, a high charge density PCE will be able to attain this with lower solid particle contents than a low charge density PCE. In a simplified way, one can imagine that a certain total charge quantity has to be adsorbed in order to generate charge equilibrium at a defined point in time. With a higher charge density, as a consequence, fewer polymers are required to attain this equilibrium. Due to effects over time, competitive adsorption, and also the effect of adsorbed PCEs on the growth of hydrates, this simplification does not fully render the complex situation but it helps to qualitatively illustrate the influence of the PCE charge density on the required amount of polymers to achieve a stipulated yield stress reduction.

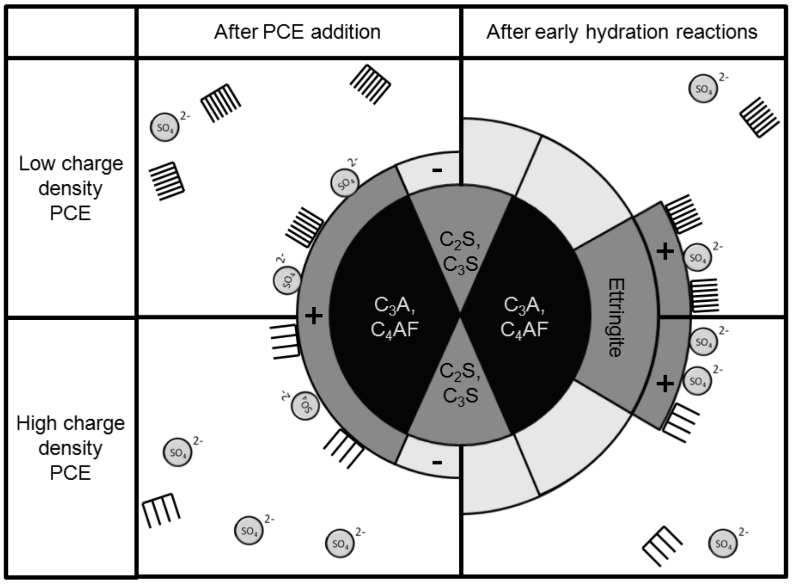

Figure 1 — Influence of charge density and hydration on the adsorption of PCE.

The flow properties of SCC are not only dependent on the charge density of the HRWRA. Today, a wide range of different types of SCC has established. They distinguish significantly in their total volume of paste components. Depending upon the mixture composition approach, also the water to powder ratio (w/p) typically varies significantly. SCCs rich of powder typically operate at a low w/p to avoid segregation. They can be characterized by low yield stress and high viscosity. SCCs designed with lower powder contents typically require higher w/p values in order to increase the total paste volume. Most often, they need to be amended by supplementary stabilizing agents and can be characterized by a relatively higher yield stress and at the same time relatively lower plastic viscosity.

The w/p, however, can supplementary have a strong influence on the rheology of SCC as well as on the retention of the workability. In order to establish a robust casting process fitting in with the particular specifications of a construction site, it is of utmost importance to be aware of the parameters that control the rheology of SCC in the course of time. Based on experiments with two characteristically differing SCC types with varied PCE charge densities as well as on their respective paste compositions, the interacting effects determined by the w/p and the PCE modifications shall be illustrated and explained, and conclusions with practical relevance shall be drawn.

EXPERIMENTIAL WORK

Two characteristic SCC types were generated, one of which is rich of powder and can be classified as powder type SCC (POW). The other concrete has significantly lower w/p and can be classified as stabilizing agent type SCC (STA) according to the Japanese regulations [10]. The pastes were generated from an ordinary Portland cement (OPC) and limestone filler. The utilized sand was washed sand so that its contribution to the powder fraction was negligible. Quartzitic washed aggregate was used with a maximum grains size of 16 mm (0.63 in).

The mixture compositions of the concretes as well as the observed paste calculated from the mixture composition of the stabilizing agent type can be found in Table 1. These concrete types were adjusted by means of differently charged PCE HRWRAs, which all consist of identical backbones. The different charge densities were achieved by varying the grafting degree as well as the number of polyethylene units in the grafts. All PCEs are commercial products and no specific information can be provided. Their charge density can thus be described only qualitatively. Their properties are given in Table 2. The PCEs were added in the specific amounts that generated slump flow values between 650 mm (24.6 in) and 700 mm (27.6 in) 30 minutes after mixing. These dosages are given in Table 3.

The rheological properties were determined using a Rheometer-4SCC for concrete measurements. By measuring the torque at varied rotational speeds, under assumption of Bingham behavior, the equipment allows to calculate a flow curve, which provides qualitative information about yield stress (G-Yield) and plastic viscosity (H-Viscosity). The measurement profile can be taken from Table 4. Only the measurements of the last four seconds of each speed step were utilized to calculate the Bingham curve.

Table 1 ─ Mixture composition of SCCs and paste of STA.

Constituent	Unit weight	POW		STA	
		SCC	Paste	SCC	Paste
	kg/m³ (lb/ft³)	kg/m³ (lb/ft³)	kg/m³ (lb/ft³)	kg/m³ (lb/ft³)	kg/m³ (lb/ft³)
Cement	3125 (195.1)	310 (19.4)	804 (50.2)	350 (21.8)	987 (61.7)
Limestone filler	2735 (170.7)	250 (15.6)	649 (40.5)	130 (8.1)	367 (22.9)
Water	1000 (62.4)	175 (10.9)	454 (28.3)	175 (10.9)	494 (30.8)
Sand 0-4 mm	2650 (165.4)	808 (50.4)	-	848 (52.9)	-
Aggregate 4-16 mm	2600 (162.3)	791 (49.4)	-	831 (51.9)	-

Table 2 ─ Characteristics of the varied PCE.

	PCE-LC	PCE-MC	PCE-HC
Charge density	low	medium	High
Graft chain length	medium + low	medium + low	medium
Grafting degree	high	medium	low
Solid content	30%	23%	20%

Table 3 ─ HRWRA adjustment to achieve slump flow values of SCC between 650 mm and 700 mm after 30 minutes.

	PCE-LC	PCE-MC	PCE-HC
POW	0.62% bwoc	0.55% bwoc	0.38% bwoc
STA	0.68% bwoc	0.61% bwoc	0.44% bwoc

Table 4 ─ Setup for rheometric concrete investigations.

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

Table 5 ─ Variations of the dosages and types of HRWRA in paste tests.

		PCE-LC	PCE-MC	PCE-HC
Identical solid content	COM	0.42% bwoc	0.42% bwoc	0.42% bwoc
Similar yield stress	COM	0.66% bwoc	0.61% bwoc	0.42% bwoc
	POW	-	-	0.36% bwoc

In order to further observe the influence of the PCE charge density beyond the workability period, investigations on the paste of the STA mixture were conducted in an automatic Vicat device (Toni Technik). The mixture composition can be found in Table 1. In order to distinguish between the influence of the charge density of a PCE and the respective amount of PCE, two observation series were set up at varied PCE dosages. In a first series, the effective polymer contents were kept identical regardless of the effect on the flow properties. In the second series, the PCE was added in the same amount as required to achieve slum flow values in concrete between 650 mm (24.6 in) and 700 mm (27.6 in) 30 minutes after mixing. In order to observe the influence of the mixture composition, the investigation was also conducted with the high charge density PCE for the COM and the POW paste in the respective amount that was required to fulfill the specified slump flow diameter in concrete. The admixture dosages used in these tests can be taken from Table 5. The dosages slightly vary from those in Table 2, the reason for which is based in the use of a differently operating viscosity modifying agent in the paste tests than used for the concrete tests. However, the deviations in the PCE dosage between paste and concrete tests are negligibly small.

RESULTS AND DISCUSSION

Rheological properties

Analyzing the required amounts of PCE to achieve the specified flow properties gives a first indicator about the different performances of the varied PCEs (Figure 2). For both mixture composition types, the addition amounts decrease with increasing charge density. This confirms the initially mentioned effect of the charge density on the amount of required PCE polymers. However, it can also be found that for both mix design types the required amount of the low and medium charge PCEs are in the same order of magnitude, while a significantly lower amount of the high charge density polymer was required, indicating that it is likely that the low and medium charge density PCEs may behave similarly, while a distinctive performance difference can be expected with the high charge density PCE.
The results of the rheological measurements over a period of 90 minutes of time are shown in Figures 3 and 4. It has to be noted that the absolute G-Yield and H-Viscosity values between POW and COM shall not be compared between the mixture composition types, since the method does not allow a reliable distinction between characteristically differing mixture compositions. However, for one and the same mixture composition, observed variations are significant, as long as they can be allocated to the effect of the HRWRA.

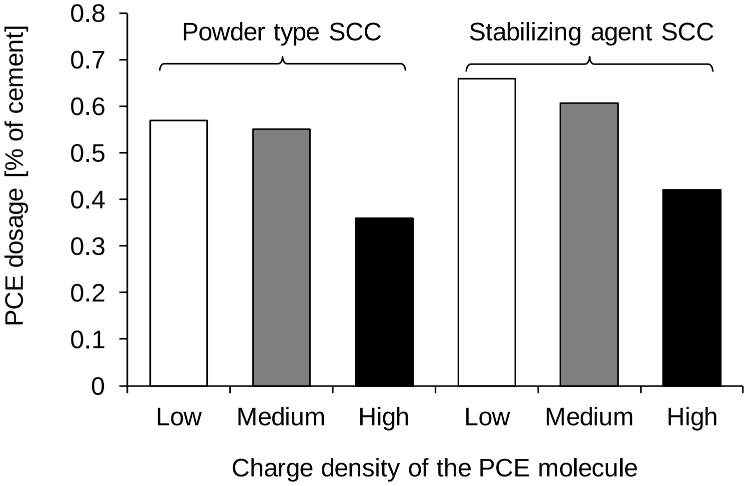

Figure 2 — Required PCE dosages to achieve slump flow diameters between 650 mm and 700 mm.

Yield stress is typically affected by particle interactions, while viscosity is often mainly affected by changes of phase volumes. The use of differently charged PCEs therefore can be expected to mainly affect the G-Yield rather than the H-Viscosity. This is confirmed by the Figures 3 and 4. Apart from an initial effect of each PCE on the H-Viscosity in general, an ongoing increasing H-Viscosity can be observed regardless of the SCC type or the charge density of the PCE (Figure 3). However, the rate of increase is very similar for all PCE types. At the same time, distinct time-dependent effect can be observed for both SCC types regarding the G-Yield (Figure 4).

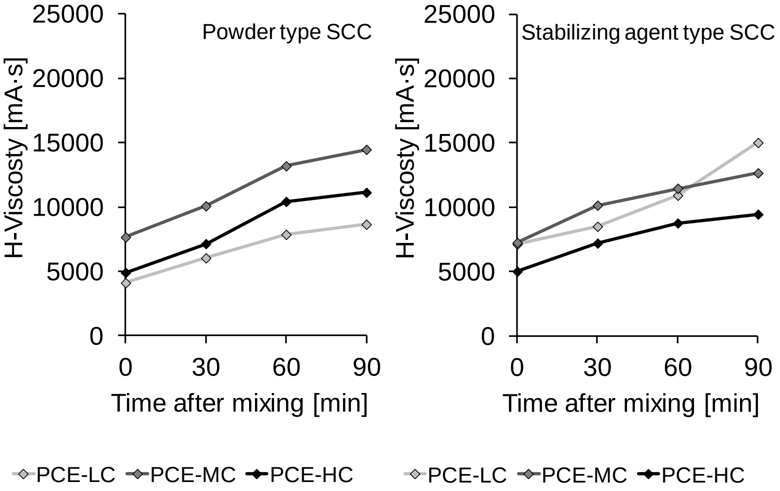

Figure 3 — G-Yield values of the POW and STA mixture over a time of 90 minutes.

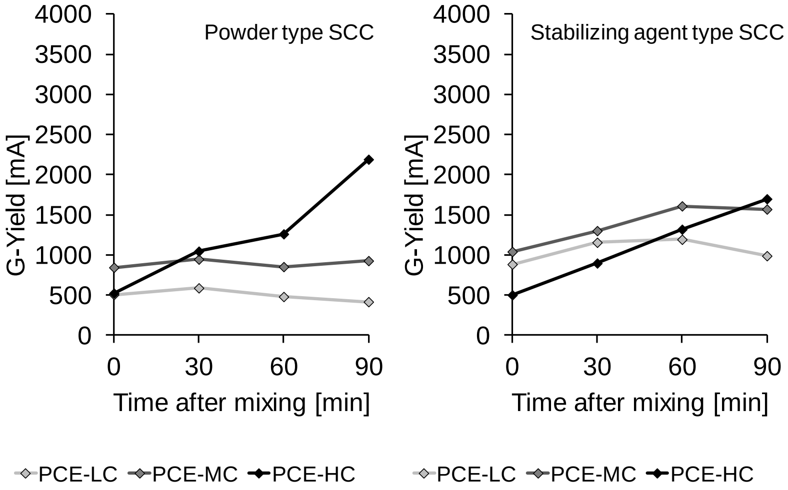

Figure 4 — G-Yield values of the POW and STA mixture over a time of 90 minutes.

The time resolved performance of the low and medium charge density PCEs are very similar for both mixture compositions, while the SCCs incorporating the high charge density PCE show a more rapid increase of the G-Yield values. This confirms the introduced effect of the charge density on the time dependent flow performance of SCC. The mechanism is illustrated in Figure 5. The higher charge density polymers are adsorbed rapidly onto the surfaces of aluminate and ferrous phases as well as on very early hydration products, mainly ettringite and monosulfate. However, due to the hydration these early adsorbed PCEs become ineffective by morphological changes of the surfaces. The lower charged PCEs first maintain ineffectively in the solution and thus are capable to develop their dispersing effect over a longer period of time.

Besides the effect of the differently charged PCEs there is a clear difference in the quality of the more rapid stiffening of the mixtures incorporating high charge density PCE. The powder type mixture shows significantly more rapid increase of the G-Yield. In order to understand this effect, the w/p has to be taken into account. The mode of operation of powder type SCCs is based on a dense packing of particles and narrow distances that need to be filled by the fluent phase. Stabilizing agent types have significantly larger distances between the particles and a higher volume needs to be filled up with fluid. As soon as there is no more sufficient free PCE available to effectively disperse the particles, the effect of the available water volume becomes dominant. Due to the low w/p of powder type SCCs, particles become less and less mobile among each other with ongoing hydration. The same effect occurs significantly less pronounced for stabilizing agent SCCs due to the significantly larger water volume in the entire system. This effect is illustrated in Figure 6.

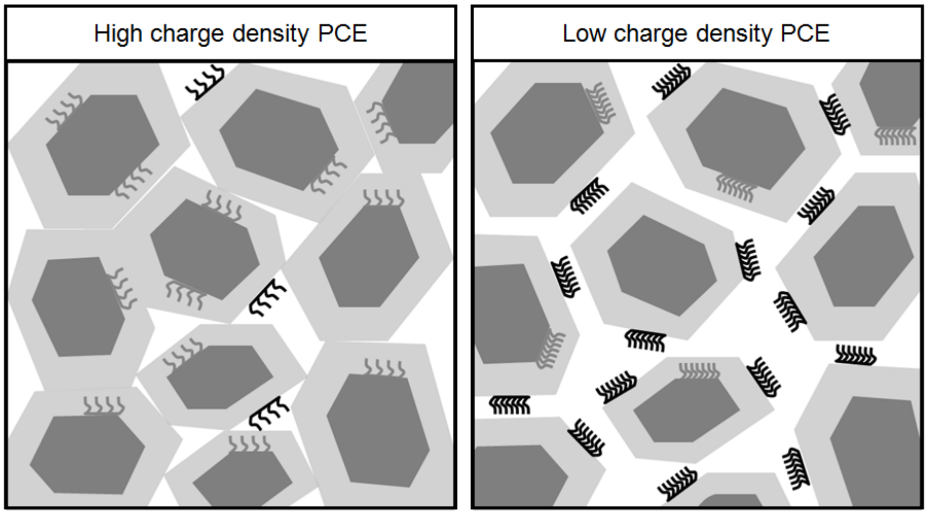

Figure 5 — Effect of the charge density of PCE on the time dependent dispersion of paste.

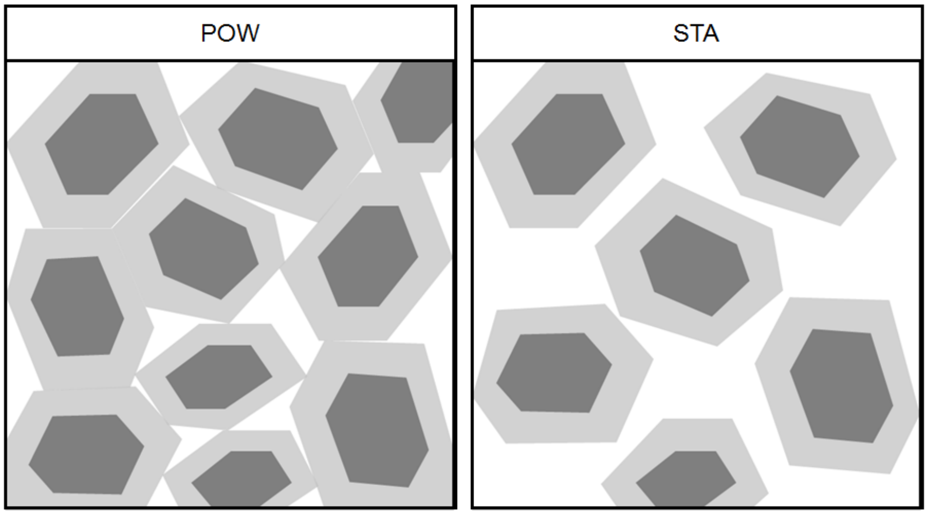

Figure 6 — Effect of w/p on the time dependent dispersion of paste.

For the same reason, it is assumable that the retention of the low yield stress for the POW mixtures in case of low and medium charge PCE is better than in the STA mixtures. The ongoing dispersing effect of the time delayed adsorbing polymers may cause micro-segregation in the pastes of the STA concrete due to the high water volume. This effect also causes that stabilizing agent types perform poorly at very low temperatures, when the adsorption of PCEs is hindered due to the slow velocity of the hydration reaction [11].

Setting and early hydration

Today, there is no clarification, why PCEs slow down the hydration. The modes of operation discussed in literature are hindrance of alite dissolution, possible calcium ion complexation, prevented C-S-H precipitation, and changed growth or nucleation of hydrates.[12-15]. It is well known that increasing PCE dosages intensify hydration process retardation.[16-18]. However, there is little awareness of the great effect that the charge density of a PCE on the extent of delay in the further course of hydration has. The results of the set experiments are shown in Figure 7. If the three differently charged PCEs are added in identical effective agent contents (0.42% bwoc), it can be observed that the different PCEs affect the setting in different ways. The lowest charge density PCE sets most early but the highest charge density PCE shows similar behavior with only a small time shift in both initial and final setting. The medium charge density PCE, however, causes a stronger set retardation. The lack of a systematic influence of the charge density of the set retardation clearly indicates that the charge density solely might not be a reasonable parameter to be linked to the mechanisms that control the set retardation.

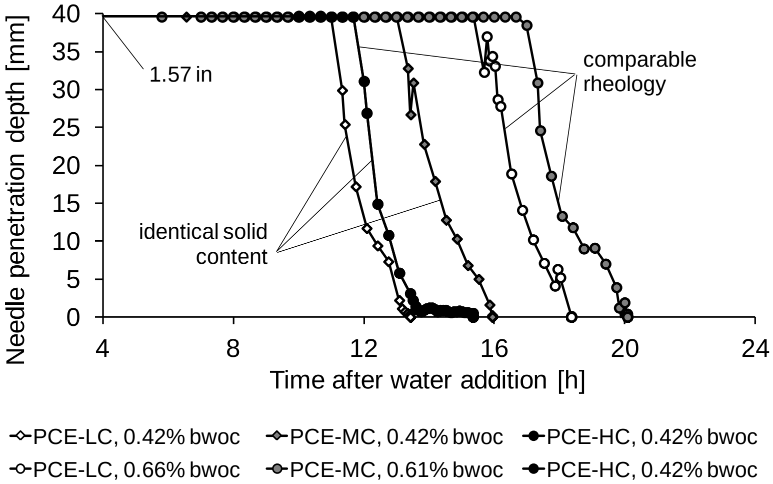

Figure 7 — Effect of charge density and dosage of PCE on the setting of SCC paste.

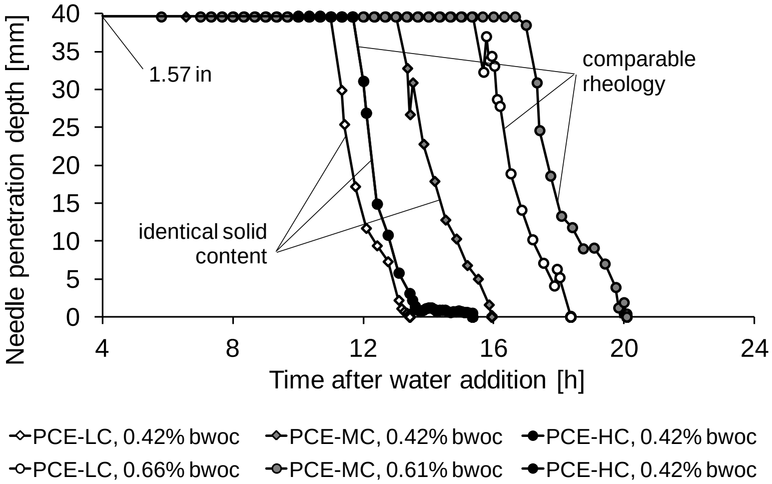

Figure 8 — Effect of the mixture composition on the setting of SCC paste.

However, any effect of the polymer setup is negligible in contrast to the dominant influence of the amount of polymers required for the specified flow properties. If, as shown in Figure 7, the differently charged PCEs are added in the effective amounts that are required to adjust similar slump flow values, all of a sudden, the influence of the charge density can be identified. The high charge density PCE causes significantly earlier setting, while the low and medium charge density polymers cause a shift of the setting times between three and four hours. The time effects thus are dominated by effects caused purely by the amount of PCE in the system. Since the high charge density PCE can be adsorbed more efficiently, significantly lower amounts are required to achieve the specified slump flow value. The low and medium charge density polymers provide similar properties and are required in similar amounts thus having similar effects on the set retardation.

For production of SCC, PCEs are usually added with focus on the rheological properties. Therefore, despite the fact that obviously the effect of the PCE geometry on the setting might be complex, the charge density is the most influencing parameter caused by the fact that obviously any polymer's effect is outweighed by the influence of the amount of PCE polymers. In this context, higher charge density PCEs show less retarding effect on the hydration than lower charge density PCEs.

The setting behavior is furthermore influenced by the mixture composition. Figure 8 shows the setting of the pastes in case of a POW and STA type SCC with high charge density. While the high powder paste POW sets around 9 h, the STA paste sets around 13 h. One influence on the earlier setting of the POW mixture is the lower PCE dosage required to adjust similar flow properties, however, the PCE dosages are in a similar order of magnitude with 0.36% bwoc and 0.42% bwoc. It is therefore unlikely that the lower PCE dosage in the POW mixture can be solely responsible for the distinct effect on the setting. The filler used in the investigations is limestone filler. Limestone filler is known to accelerate setting due to providing crystallization seeds in the finest components. Furthermore, PCE can be adsorbed on limestone filler as well, thus withdrawing part of the PCE from the interaction with the cement hydration. Finally, the STA concrete can be assumed to be retarded due the higher w/p ratio, which causes that, despite the lower water to cement ratio of STA, a higher water volume can interact with the cement particles.

Conclusions for practical applications

For the practitioner on the construction site it is important to consider aspects like haul time and casting time, which may vary from construction site to construction site and demand individual workability adjustments. The longest retardation of the workability and the setting can be achieved by using a high w/p mixture with low charge density PCE; the shortest workability time and the earliest setting can be achieved by using a high powder content mixture with a high charge density PCE. Changing any of these parameters, either charge density of the PCE or w/p of the mixture may affect the workability and set retardation following the rule: the higher the charge density of the PCE or the lower the w/p, the shorter the slump flow retention and the earlier the setting. The observations from Figure 4 indicate that particularly at low w/p, the influence of the charge density of the PCE may have a strong effect on the slump flow retention, while the high powder content can be assumed to contribute positively to earlier setting. Figure 8 indicates that in the present results, the mixture composition again has a strong influence on the set retardation, with powder rich mixes showing significantly earlier setting, while at the same time, the mixture composition influence on the retardation, as shown in Figure 4 is not comparably strong. These observations are illustrated in a simplified way in Figure 9. Since in the investigations ordinary Portland cement and limestone filler, which is considered to be largely inert, were used, the demonstrated effects can be assumed to have qualitative validity for a wide range of SCC mixture compositions. However, further effects may overlap.

CONCLUSIONS

Investigations on two types of SCC with different w/p ratios and their respective pastes were conducted. In the tests, the influence of differently charged PCE HRWRAs was observed on the time dependent rheology and the setting.

- The charge density of the PCE strongly affected the retention of the flow properties. While both SCC types showed enduring performance with the low and the medium charged PCE, the yield stress increased rapidly with high charge density PCE.
- PCE effects on the time dependent flow properties were qualitatively similar regardless of the mixture composition type.
- More rapid stiffening could be observed for the powder type SCC. This effect was explained by the denser particle packing in the fluid phase, which fosters immobilization of particles due to hydration based morphological changes.
- In general effects that cause performance retention caused set retardation as well. Increasing water to powder ratios as well as decreasing charge densities of the PCE caused more extended setting times.
- The effect of the charge density of the PCE on the setting is limited to its effect on the yield stress reduction efficiency. In this context, lower charge PCEs need to be added relatively in higher amounts. These higher amounts finally cause the set retardation.
- The powder type SCC showed significantly earlier setting. The reason for this may be found in the lower w/p ratio, the lower PCE demand, as well as the utilization of limestone filler, which is known to accelerate the setting.

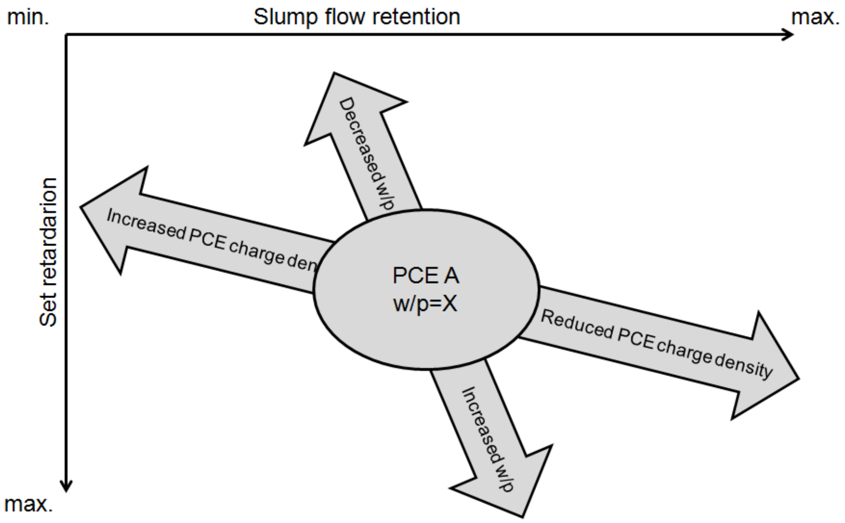

Figure 9 — Influence of the PCE and the w/p on flow retention and set retardation.

The above observation can help optimizing the casting process of SCC according to individual specifications. For short haul and casting times and a rapid construction site progress a powder rich SCC with a high charge density can be considered as the best choice. If the casting process demands for enduring flowability retention and slow de-molding can be accepted, a high w/p mixture with low charge density should be preferred. The charge density and the mixture composition both can help finding the optimum adjustment for particular construction site conditions.

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