

Correlation between setting, heat evolution, and deformations of cementitious binder systems depending on type and amount of superplasticizer

¹Schmidt W^{1*}

¹BAM Federal Institute for Materials Research and Testing, Berlin, Germany

²Brouwers HJH

²Eindhoven Technical University, Eindhoven, Netherlands

¹Kuehne H-C and ¹Meng B

Abstract

Today polycarboxylate ether based superplasticizer (PCE) is commonly used in concrete technology when high flow properties and water reduction are specified. The ionic strength of the polymers' backbones determines the adsorption behaviour of polymers on clinker and early hydration products. The amount of required polymers for specified flow properties and the performance over the time of casting is thus determined by the molecular structure of the superplasticizer. The time depending consumption of polycarboxylate ether polymers strongly affects the reaction of aluminates and sulphate ions as well as the hydration process in general. Hence, the choice of polymers for particular flow properties greatly affects the very early properties of cementitious materials such as setting, heat evolution and autogenous deformations.

In order to better understand how PCEs influence the early properties, mixes from cement, limestone filler, viscosity modifying agent and water were varied with a high and a low charge density superplasticizer in differing amounts. Results are presented from measurements with an automatic Vicat device, an isothermal heat flow calorimeter, and shrinkage cones. Tests were conducted at 5, 20, and 30 °C.

It is shown that in presence of PCE the final set correlates well with the inflexion point of the heat flow curve, which emphasises the interrelation between C-S-H formation and setting. No such clear correlation can be found for the initial set, which is attributed to the fact that the initial set is rather a rheological than a structural phenomenon, so that other effects overlap with C-S-H formation. The results demonstrate that for a given polymer concentration low charge density polymers yield earlier setting than high charge polymers. However, this influence is overridden by the influence of the total amount of polymers in a cementitious system. Since PCE is typically added according to rheological specifications, and low charge PCE typically requires higher amounts of polymers than high charge PCE for comparable flow performance, low charge PCE retards setting more than high charge PCE.

The paper furthermore points out that there is no significant influence of the polymer type or amount on the early deformations. Since type and amount strongly affect the hydration, it is demonstrated that early setting causes higher strain after the final set. It is hence concluded that higher PCE solid contents reduce the risk of early cracks that occur at time of setting, when a solid structure has already been formed but without resistance against cracks yet.

Originality

The paper focuses on early hydration processes and the way they are affected by chemical admixtures. In terms of hydration history, the focus is placed on the period between fresh concrete and hardened concrete. The paper thus mainly contributes to the main topics of the 13th ICCI "Properties of fresh and hardened concrete", considering the effects of chemical admixtures on rheology, hydration, setting and deformations. However, since the effects cannot be extracted from micro-structural developments, the paper also contains numerous links to the main topic "Hydration and microstructure".

Chief contributions

To date most research that observes cement superplasticizer interactions focuses on rheological properties. Only few published papers deal with the properties after casting until final set. Typically general differences of mixtures with polycarboxylate ether superplasticizers are investigated versus mixtures without. Aspects of particular molecule types and respective ionic backbone charge densities are less focused in research. The results of this paper help improving mixtures with regard to early hydration effects and sensitivity against early crack formation.

Keywords: Polycarboxylate superplasticizer, setting, heat evolution, autogenous deformation

¹ Corresponding author: Email wolfram.schmidt@bam.de Tel +49 30 8104 3210, Fax +49 30 8104 1717

Introduction

The adsorption of superplasticizers based on polycarboxylate ether (PCE), which are commonly used today, has strong influence on the flow properties of cementitious systems, particularly on its yield stress. The driving force for the reduction of the yield stress is the amount of adsorbed superplasticizer molecules (Schober and Flatt, 2006, Schmidt *et al.*, 2010). The adsorption process again, is influenced by the molecular architecture, which determines the anionic charge density of the polymers (Plank and Hirsch, 2007, Plank and Sachsenhauser, 2006). Since PCEs compete with the sulphate ions in the pore solution for adsorption, the charge density determines whether preferentially sulphate ions or PCE molecules adsorb. Typically a high charge density polymer is used in order to provide maximum flowability very early, when flow retention is not required, while a low charge density may not provide maximum flowability at early stage, but it can retain the flow performance over a long period of time (Schmidt *et al.*, 2009a, Schmidt *et al.*, 2010).

However, the charge density of a polymer also affects the number of polymers required to achieve a specified flow property. Thus, an identically charged adsorption site attracts a higher number of lowly charged than highly charged polymers. For a given flow value of a cementitious system, typically a higher amount of polymers is required, when a low charge density PCE is used (Note that this is valid for the solid content since the water-to-solid ratios of bulk superplasticizers differ).

The influence of PCE on the early hydration is not limited to the period in which the workability properties are of importance. It is known that an increasing amount of PCE prolongs the dormant period and retards setting (Wadsö, 2005, Schmidt, 2008, Zingg *et al.*, 2009). Locher *et al.* (1980) concluded that the setting is basically driven by the recrystallisation of ettringite with elongated crystals bridging the gap between particles, thus initiating setting still during the dormant period. Today the setting is rather attributed to the formation of C-S-H (Taylor, 1997), although the bridging effect of ettringite, described in Locher *et al.* maintains relevance, since it affects the workability and its retention, particularly, when superplasticizers are present (Schmidt *et al.*, 2009b, Schmidt *et al.*, 2010). Furthermore, intercalation of superplasticizers into C₃A reaction products consumes polymer molecules (Plank *et al.*, 2006) so that they can no longer interact with the ongoing hydration process that causes setting effects.

To date, it is controversially discussed, which mechanisms lead to the dormant period and the onset of the C₃S hydration. Bullard and Flatt (2010) investigated two leading theories, which emerged to well describe the phenomena. One theory describes that a metastable phase forms a passivation layer, which suppresses further growth of C-S-H. The other theory explains that reaction sites are deactivated by the adsorption of protons. Both models are in line with published research results, however furnish different prediction results with and without portlandite (Ca(OH)₂). However, other theories exist, as well.

The reason for the prolonged dormant period due to superplasticizer addition is also controversially discussed. Different effects can be found in the literature: hindrance of C₃S dissolution, possible calcium ion complexation, prevented C-S-H precipitation, and changed growth of hydrates (Lothenbach *et al.*, 2007, Pourchet *et al.*, 2007, Zingg, 2008). Recent research by Sowoidnich and Rößler (2009) has shown that hindered dissolution of C₃S is unlikely and that the hydration retardation in presence of superplasticizers is rather an effect of constrained growth of C-S-H nuclei due to unadsorbed PCE.

However, not only the amount but also the type of PCE affects the early hydration. The setting behaviour can be changed markedly by the PCE type (Zingg *et al.*, 2009, Schmidt *et al.*, 2009a). In Schmidt *et al.* (2009a), it was shown that with identical amounts, cement mixes with low charge density PCE exhibit earlier initial and final setting times than mixes with high charge density PCE.

When PCE amount and type determine the early hydration and the related properties, such as setting at otherwise identical conditions, the question emerges also, in which way the early deformations are affected by different PCE types. This paper shall highlight effects resulting from the polymer structure of the PCE on early hydration and on the autogenous deformations of cementitious pastes.

Methods

Investigations were conducted with pastes from cement and limestone filler and a water-to-powder ratio of 0.365 (Table 1). The components' ratios were calculated from a self-compacting concrete's mixture composition. Viscosity modifying agent (VMA) based on microbial polysaccharides, was used to avoid segregation during the setting and deformation tests. Two commercial PCE superplasticizers from the same product group were used in the tests. These are comparable in their graft length but characteristically differing in the grafting degree, and thus the anionic charge density. The low charge density polymer is abbreviated PCE LC, the high charge density polymer PCE HC. Their added amounts were adjusted to a slump flow value of the respective concrete between 650 and 700 mm after 30 minutes, which yields an addition of 0.62% solids for PCE LC and of 0.38% solids for PCE HC (Table 1, columns 1 and 3). Since the superplasticizer addition was adjusted to a flow performance after 30 minutes, when a significant interaction of aluminates and sulphates had already taken place, it can very roughly be assumed that 0.62% of PCE LC and 0.38% of PCE HC occupy comparable charges on clinker and hydrates.

Not only the charges but also the total amount of solids may have an influence on the system. Therefore another modified mix was generated with PCE LC such that the amount of solids was identical with the amount of solids of PCE HC, regardless of the resulting flow properties. This mixture, designated PCE LC-0.38%, can be found in the second column of Table 1.

The mixes were investigated in an automatic Vicat device according to EN 196-3:2005 (Toni Technik), an isothermal heat flow calorimeter (TAM Air) and two parallel shrinkage cones (Schleibinger), of which the surface was sealed to prevent drying of the paste. The latter device measures the height loss of a specimen with a laser reflector. Due to the 30° angle of the apex of the cone, which is turned downwards, radius and height deform to the same rate, when isotropic shrinkage is assumed. The Vicat specimens were stored under water throughout the whole test in water tempered to the testing temperature. The calorimeter was calibrated to each particular climate, which made it necessary to store the whole device in a climate chamber for the measurements at 5 °C, in order to avoid condensation. The shrinkage cones were stored in a climate room adjusted to each particular climate for all investigations. All components were adjusted to the testing temperature before mixing. The mixing, however, was conducted at 20 °C. Each test was repeated twice out of the same batch.

Table 1: Mixture composition and admixture variations

Mixture composition of the binder			
	PCE LC-0.62%	PCE LC-0.38%	PCE HC-0.38%
Cement [kg/m ³]		1044	
Limestone filler [kg/m ³]		389	
Water [kg/m ³]		523	
Admixture adjustment			
	PCE LC-0.62%	PCE LC-0.38%	PCE HC-0.38%
PCE bulk [% by weight of cem.]	2.25	1.38	1.90
PCE solids [% by weight of cem.]	0.62	0.38	0.38
VMA [% by weight of water]	0.04	0.04	0.04

Results and Discussion

Initial and final set according to Vicat occur significantly earlier, when the high charge PCE is used (Figure 1). This effect however, is basically caused by the lower polymer content that is required to achieve the specified rheological properties. When the low charge PCE is used at the same solid content as the high charge PCE, initial set takes place earlier at all temperatures than in the case the high charge PCE is used. This observation is in line with the observations presented in (Zingg *et al.*,

2009), where the setting is defined as the onset of the increasing heat flow curve. This point is much closer to the initial than the final set. Observing the final set (Figure 1) shows a different picture. Independent of its molecular structure, PCE LC-0.38% and PCE HC-0.38% have comparable final set times at all observed temperatures, whereas the times significantly diverge with PCE LC-0.62%. Hence, the final set seems to be much more affected by the total amount of polymers than by their molecular structure. This may fit in with the observations presented by Sowoidnich and Rößler (2009), that show that the retardation of the C_3S hydration is not caused by blocked hydration due to adsorption but rather by modified crystal growth due to the presence of not adsorbed, excess PCE.

The Vicat results are confirmed by heat flow calorimetry (Figure 2). For a better overview, in these figures, vertical lines of the same grey level as the heat flow curves represent the respective final Vicat setting times. The retardation of pastes with PCE LC-0.62% is significant. At identical solid contents the heat flow curves behave similar, independent of the PCE type. The earlier increase of the heat flow curves with PCE LC-0.38% compared to those with PCE HC-0,38% is in line with the earlier respective initial set from the Vicat test. At identical solid content, the low charge density polymers cause slightly earlier setting than those with the high charge density. This confirms the results shown in Zingg *et al.* (2009) and Schmidt *et al.* (2009a). The effect occurs more pronounced at 30 °C. However, the influence of the charge density is significantly lower than the influence of the solid content. Considering that PCE is typically added in order to achieve required flow properties, it can be stated that in practical applications, high charge density PCE will retard setting less, due to the fact that less solids are required to achieve the flow specifications.

The different characteristics of the sulphate depletion peaks suggest that temperature, and PCE type and amount, strongly affect the early interaction between aluminates and sulphates, and that intercalations of PCE into C_3A hydrates might play a certain role. However, a discussion of the sulphate depletion peak would go beyond the scope of this paper.

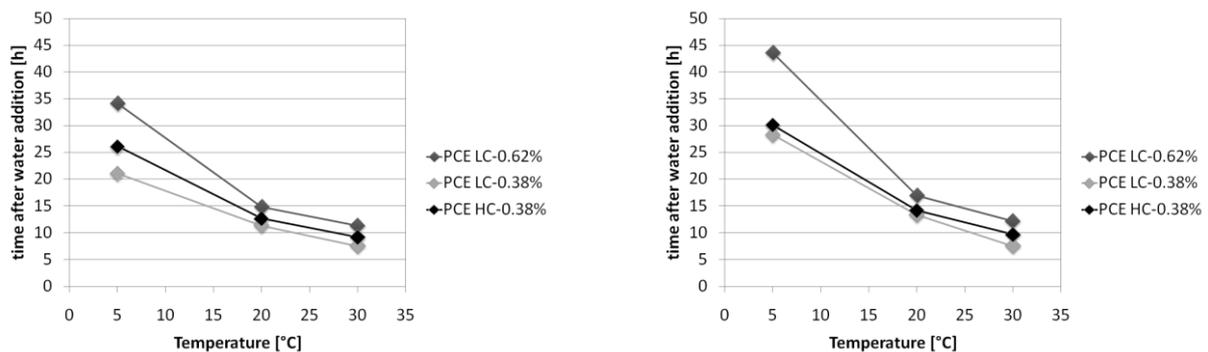


Figure 1: Initial (left) and final (right) set according to the Vicat needle penetration test

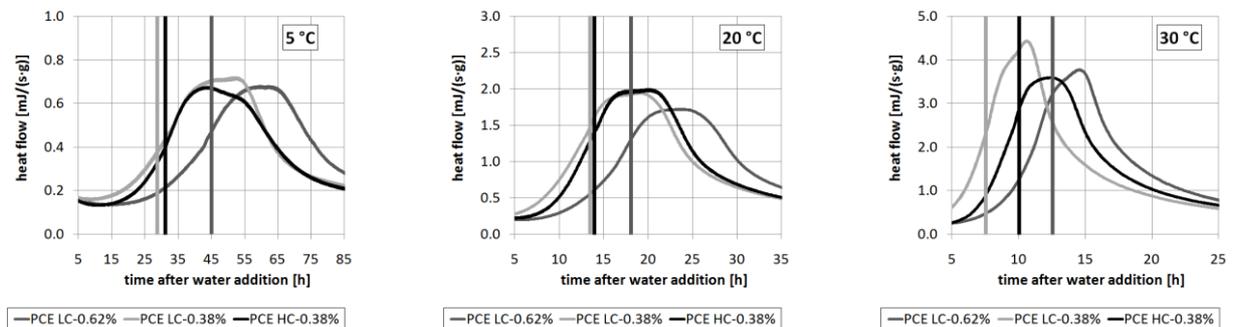


Figure 2: Heat flow curves at varied temperature, and PCE type and content compared to the final set

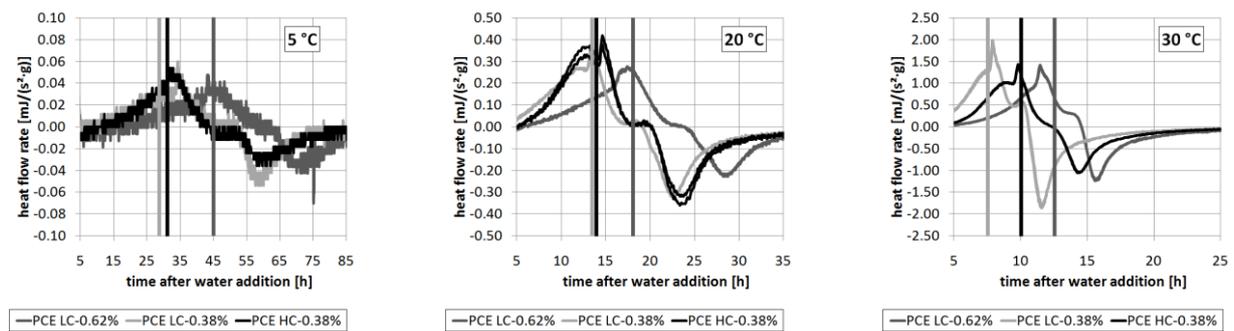


Figure 3: Heat flow rate curves with varied PCE amounts and modifications at different temperatures

The time of final setting varies between the first third and the second third of the period marked by the onset and the maximum heat flow. In order to better analyse the exact time of the final set, the first derivative of the heat flow curve was calculated. From a physical point of view its unit J/s^2 may appear meaningless. However, as it is the second derivative of the energy with respect to time, it can be interpreted as a kind of energy acceleration curve. Regardless of the physical meaning, such a curve helps to identify distinctive points of the heat flow curve more clearly. The curves, which are described here as heat flow rate, are demonstrated in Figure 3. The final set according to Vicat takes place very close to the maximum of the heat flow rate curve, which is the inflexion point of the heat flow. This is also valid, when the final set deflects distinctively from the half distance between onset and maximum of the heat flow curve. This relation but without PCE was already described by Taylor (1997). No prominent ettringite reactions take place during this period, which emphasises the strong interrelation between the formation of C-S-H and the final set. The occurrence of the final set very close to the inflexion point of the heat flow shows that the decelerated hydration due to increasing densification of the microstructure, which reduces the mobility of reaction partners, takes place in parallel to the formation of a solid macrostructure.

Unlike the final set, a relation between initial set according to Vicat and heat flow cannot be observed. Whereas the final set is a prominent step during early hydration representing the transition from a plastic to a solid state, the initial set according to Vicat is rather a rheological phenomenon. For example, it would be easily possible to generate a highly viscous yield stress fluid that hinders the needle to drop to the bottom without any formation of a solid structure. For all samples, the initial set takes place at a time, when the heat flow curve already increases significantly, yielding the conclusion that also the initial set is indeed driven by C-S-H formation, as also described by Ylmén *et al.* (2009). However, there is not an identically clear correlation between heat flow and Vicat results regarding the initial set as it is for the final set. It is thus also likely that other effects, affecting the rheology, like the re-crystallisation of ettringite (Locher *et al.*, 1980), may overlap with the C-S-H formation.

In parallel to the observations of hydration and setting, the early deformations were studied. The test setup cannot distinguish the sources of these deformations, which are basically caused by settlement, and chemical and autogenous shrinkage. These are typically driven by the water-to-powder ratio, the particle size distribution, and the presence of surface active agents. The mixes used in this study have identical water-to-powder ratios and particle size distributions, and all mixes contain superplasticizers. As a result, the rates of deformation after water addition at particular temperature do not strongly differ, independent of the amount of PCE or its molecular architecture. In contrast to this, as shown before, these parameters strongly affect the time of the final set. Hence, the question arises, of which magnitude deformations occur after the final set has taken place. These deformations are most critical, since concrete is already in a solid state but the strength is still low. This makes the system prone to cracks caused by restrained deformations.

Figure 4 displays those deformations at three temperatures occurring after the final set according to Vicat. At 20 °C deformations after the final set are generally low for all three mixes. PCE LC-0.38%

exhibits higher deformations than PCE LC-0.62% at 5 °C and PCE HC-0.38% yields the largest deformations. At 30 °C again the PCE LC-0.62% has the lowest strain, PCE HC-0.38% exhibits higher and PCE LC-0.38% highest deformations. At all temperatures PCE LC-0.62% shows very low deformations, whereas the other modifications show significantly higher strains at 5 and 30 °C. The earlier setting of those mixes with lower content of polymers cause that a larger part of the deformations takes place when the pastes are already in a solid state. For the paste with higher polymer content the opposite is true: The majority of deformation take place in a still plastic state of the material. A higher solid content of PCE polymers, thus, reduces the risk of early cracks due to retarded setting. Hence, it can be concluded that, if the workability specifications are fixed, a low charge density polymer is beneficial, as a higher PCE solid content is required.

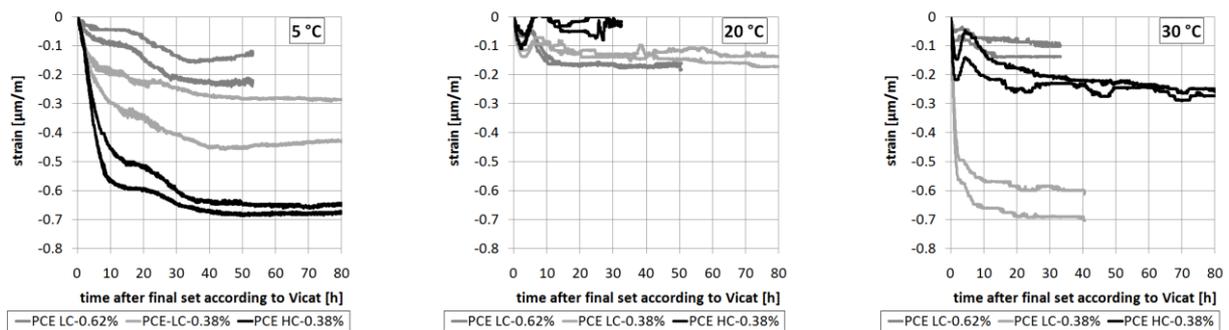


Figure 4: Strain occurring after the final set according to Vicat

Conclusions

Investigations of setting, heat evolution and early deformations have been conducted at identical paste mixtures, modified with a high charge density PCE at 0.38% solid content and a low charge density PCE at 0.38% and 0.62% solid content.

The observation of the setting times according to Vicat show that the final set is influenced by the type as well as by the amount of PCE. However, as the influence of the polymer type at identical solid content of polymers is rather small, the influence of the total amount of PCE more than clearly outweighs this influence. PCEs are typically added to mixes in order to achieve specified flow properties, i.e. a given flow rate. It can thus be concluded that, in spite of the positive effect of their molecular structure, low charge density PCEs yield higher retardation of the setting than high charge PCE, since the latter typically demands less solids for identical flow properties.

The influences of the PCE type on the setting is confirmed by the heat flow curves. A good correlation between the final set and the inflexion point of the heat flow curve can be demonstrated. This emphasises that the final set is predominantly driven by the formation of C-S-H.

The initial set shows less systematic interrelations with the heat evolution. As differing from other methods, the initial set according to Vicat is more related to rheological phenomena than to effects of a solid structural build-up. Other reactions (like crystalline transformation of ettringite) may superpose with effects of C-S-H formation. This distorts the interpretation of the initial set when the Vicat method is used. The effect of the polymer modification and particular the required amount of solid PCE for specified flow performances is significant. However, at identical mixture compositions, there is no such significant influence of the PCE modification or amount on early deformations. As a result, higher contents of PCE solids reduce the risk of early cracks, since the formation of a solid structure is delayed and a bulk of quickly occurring large deformations takes place still in plastic state of the paste. The research was conducted with cement-limestone filler pastes, including VMA, calculated from real application self-compacting concrete compositions, which means, the PCE content was high. Hence, it

cannot be excluded that at lower PCE contents other conclusions can be drawn. Furthermore, the influence of the limestone filler and the VMA addition was not explicitly discussed. However, the results are in line with those of other researchers (with and without PCE). The demonstrated results may thus contribute to a field of research, which to date is still highly controversially discussed.

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