

Interaction of Polycarboxylate-based Superplasticizers and Cements: Influence of Polymer Structure and C₃A-content of Cement

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Abstract

Superplasticizers are commonly used in modern cementitious building materials like self-compacting concrete. However, there are still many unsolved problems concerning cement/superplasticizer compatibility like poor flow behaviour, early slump loss or strong retardation.

The objective of this study is to link the molecular structure of polycarboxylate-ether type superplasticizers with their performance in cementitious systems in order to develop new enhanced products.

Different experimental superplasticizers have been synthesized and applied in cement pastes. The examined cements differed mainly in their C₃A-content. Various methods have been used to characterize the cement-superplasticizer interactions, like rheological measurements, conduction calorimetry, and determination of the adsorption isotherm by TOC analysis, as well as XRD and TGA measurements.

As result of this study, characteristic correlations between molecular structure of the superplasticizer and C₃A-content of the cement with respect to adsorption behaviour, rheology and retardation could be determined.

1 Introduction

Superplasticizers are commonly used in concrete technology to improve the rheological properties of cement pastes, mortars and concretes. On one hand, they enable the production of concretes with special workability properties like self-compacting concrete. On the other hand, superplasticizers allow concrete mix designs with very low water/cement ratios. Thus, high performance concretes with very high strength and durability can be achieved. The new generation superplasticizers with enhanced properties are comb-shaped polycarboxylate-based polymers. They are adsorbed on the cement particles and act as dispersants by electrostatic and mainly steric repulsion effects as demonstrated by Uchikawa et al. [1].

The workability properties of cement pastes, mortars and concretes with the addition of superplasticizers are depending on various parameters. On one hand, the type, the chemical composition and the molecular structure of the admixture [2-5] influence the rheological properties (e. g. yield stress, viscosity, concrete slump). On the other hand, the chemical composition of the cements (especially C₃A-content and the availability of soluble sulphates during workability time), their specific surface, the presence of mineral additions or of other types of admixtures as well as the

hydrate phases formed during early hydration affect the behaviour of superplasticizers in cementitious systems [6-13].

Despite the increasing number of ongoing research projects, there are still many unsolved problems when using superplasticizers in cementitious systems. Effects like poor flow behaviour, early slump loss, strong retardation or flash set may be the result of an incompatibility between the binder and the superplasticizer.

The objective of this study is to link the molecular structure of polycarboxylate-ether type superplasticizers with their performance in cementitious systems. To address the influence of cement chemistry on the performance of the entire system, three cements with different C_3A -contents were used in the experiments.

2 Materials

Different experimental superplasticizers of polycarboxylate ether (PCE) type (copolymers of methylpolyethyleneglycole-methacrylate and methacrylic acid) were synthesized with varying length and density of the polyether chains. Fig. 1 shows the chemical structure of the superplasticizers used in this study. During the polymerization step the molar concentrations of all monomers were kept constant to ensure the same reaction kinetics in all examples. Due to the molecular weight difference of the macromonomers used here, this led to different final solids contents, which was compensated in all experiments. Therefore, all dosages given in this paper are referring to the dry matter of the admixture.

Molecular weight of the polymers was determined by size exclusion chromatography. Table 1 shows the characteristics of the polymers. It is important to note that the charge density of the polymer increases with decreasing side chain density and with decreasing side chain length, leading to an increasing amount of free carboxylic groups. The superplasticizers were applied as sodium salts. Before they were used in the experiments, a de-foaming agent and a fungicide were added to all polymers.

Three ordinary Portland cements CEM I 42.5 N according to European Standard EN 197-1, see table 2, were used in this study. They exhibit a varying C_3A -content of 1% (L-OPC), 8% (M-OPC) and 10% (H-OPC) according to Bogue calculations as well as different ratios Al_2O_3/SO_3 (1.9, 1.7 and 2.1, respectively). Tricalciumsilicate (Alite) was purchased commercially.

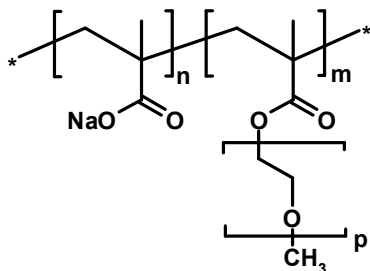


Fig. 1: Chemical structure of the experimental superplasticizers (copolymers of methylpolyethyleneglycole-methacrylate and methacrylic acid, sodium salts)

$m:n = 1:2, 1:4, 1:6; p = 23, 102$

Table 1: Properties of the applied PCE-superplasticizers

polymer	length of side chain ρ	density of side chains m:n	M_n ¹ g/mol	M_w ² g/mol	PDI ³ M_w/M_n -	solid content mass.-%
PCE 23-1:2	23	1:2	8700	25600	2.9	25.5
PCE 23-1:3	23	1:4	7900	20200	2.6	17.4
PCE 23-1:4	23	1:6	7600	18900	2.5	13.8
PCE 102-1:2	102	1:2	16800	78000	4.7	46.3
PCE 102-1:3	102	1:4	15100	71000	4.6	28.4
PCE 102-1:4	102	1:6	14600	67000	4.6	21.0

¹ M_n = number-average molecular weight

² M_w = mass-average molecular weight

³ PDI = M_w/M_n = polydispersity index

Table 2: Characteristics of the cements CEM I 42.5 N used in this study

	CaO	MgO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Na ₂ O	K ₂ O	SO ₃	CO ₂	L.O.I.	free lime	sp. surf.
	wt.-%	wt.-%	wt.-%	wt.-%	wt.-%	wt.-%	wt.-%	wt.-%	wt.-%	wt.-%	wt.-%	cm ² /g
L-OPC	61.2	1.8	18.7	4.3	6.2	0.13	1.0	2.3	2.56	2.75	0.47	3560
M-OPC	63.4	1.8	20.0	4.8	2.5	0.10	0.94	2.8	1.85	2.29	0.76	3150
H-OPC	61.8	2.1	19.2	5.4	2.8	0.33	0.95	2.6	2.79	3.35	1.14	3090

3 Methods

For the rheological experiments a Paar Physica MCR 300 rheometer was used. A cylindrical measuring geometry according to ISO 3219 with a cup and a rotating bob was applied (measuring gap 1.13 mm, ratio outer/inner radius 1.08, serrated surface with a depth of 100 μm) to measure the flow curves. To blend the cement with water and superplasticizer, a Braun kitchen blender (Multiquick 5550 M CA) was used. 300 grams of cement were taken for each measurement. The water/cement ratio (w/c) was kept at 0.35. The mixing procedure was set at 30 seconds of mixing at stage 6, a 30 second pause then 30 seconds of mixing at stage 6 again. Afterwards the cement paste was transferred into the rheometer cup with a spoon. The measuring system was then lowered into the cup, and the cup was covered with a solvent trap to keep humidity high during the experiment. The temperature of the paste was controlled by a water bath and kept constant at 20°C. The measurement started 5, 30 and 60 minutes after water or the admixture containing solution was added to the cement. First, one minute of pre-shearing at a shear rate of 100 s^{-1} was performed. After that, a flow curve with shear rates between 100 and 0.1 s^{-1} was recorded. Apparent yield stress and plastic viscosity were calculated according to the Bingham model.

The remaining paste from each experiment was used to determine the adsorption of the polymer after 5, 30 and 60 min on the cement particles by

the solution depletion method. The alkaline pore solution was removed through a 0.45 μm Nylon filter by pressure filtration and stabilized by adding 9 ml of 0.1 mol/l hydrochloric acid to 1 ml of pore solution. The total organic contents (TOC) of these solutions were measured using a Shimadzu TOC-Analyzer 5000A. The percentage of polymer adsorbed on the cement was calculated from the TOC contents using a reference measurement of the aqueous polymer solution. The TOC content of the plain cement pastes (e. g. due to the presence of grinding aids) was taken into account.

A conduction calorimeter (Thermometric TAM Air) was used to determine the rate of hydration heat liberation at 20°C during the first 72 hours. 6.00 grams of cement were weighed into a flask and 2.10 ml of water or the admixture containing aqueous solution (w/c = 0.35) were added. The mixing was done by a small stirrer for two minutes. The flask was then capped and placed into the calorimeter. From the calorimetric curve the onset of the acceleration period was determined as described in [5].

For some pastes, the time depending hydration behaviour over time was studied by X-ray diffraction (XRD) and thermogravimetric analysis (TGA). 30 g of cement and 10.5 ml of water or the admixture containing aqueous solution (w/c = 0.35) were placed in a plastic container and mixed by hand with a spatula for two minutes. The hydration was stopped by submersion of the pastes in acetone, filtering, washing the residue with acetone and drying at 40 °C for three days. Afterwards the samples were ground to < 0.063 mm. TGA (Mettler-Toledo TGA/SDTA 851) was carried out in N₂ on about 10 mg of sample at 20 °C/min up to 980 °C. XRD patterns were measured with a Panalytical X'pert Pro powder diffractometer in a 2 θ -range of 5-80°.

4 Results and discussion

4.1 Paste rheology

The apparent yield stresses after 5 min hydration time are displayed in the left column of fig. 2. The results after 30 and 60 min are not reported here, as they are not much differing from the data after 5 min. It was found that yield stresses of all pastes increase only slightly with time.

With increasing side chain density of the superplasticizers the needed dosages to reduce apparent yield stress of the pastes to values below \approx 5 Pa increase. Concerning the polymers with side chain densities of 1:2, the yield stress does not reach such a low value but remains - depending on the cement type - on a plateau between 10-20 Pa (PCE 23-1:2) or does not show any reduction (PCE 102-1:2) at all.

The length of the side chains has only a minor influence on the rheology of the examined cement-PCE-combinations. Yamada et al. [2] used superplasticizers with a related structure. The authors found in their system that longer side chains gave lower yield stresses and lower plastic viscosities. In a previous study [5] an improvement of rheology with increasing side chain length was found only for PCEs with quite short side chains. Only

the results obtained in this study for the polymers with side chain densities of 1:2 indicate that longer side chains lead to lower yield stresses. However, this can be regarded probably as an effect of poor polymer adsorption due to low charge densities of the PCEs with side chain densities of 1:2.

The plain cement pastes show yield stresses of about 30 Pa (L-OPC, M-OPC) and 55 Pa (H-OPC), respectively. The paste of cement with the highest C_3A -content (H-OPC) shows the highest yield stress, as this system is expected to produce the highest amount of ettringite during very early hydration. The production of ettringite consumes a reasonable amount of the mixing water, thus reducing the amount of free pore solution and increasing the solid content of the paste.

Compared with the other two cements, higher yield stresses occur in pastes made from the high- C_3A -cement for a certain polymer dosage especially when only low dosages of PCE are applied. The dosage of PCE needed to lower the apparent yield stress of the pastes to values below ≈ 5 Pa is higher for H-OPC compared to the other cements.

4.2 Superplasticizer adsorption

The adsorption isotherms determined after 5 min hydration are shown in fig. 2 (right column). The amount of polymer adsorbed does not change significantly between 5 min and 30 or 60 min, respectively, which agrees well with other studies on similar systems by Winnefeld et al. [5] and Lothenbach et al. [14]. Thus it can be concluded that the adsorption of the polymers used in this study is a very rapid process and that there is not much further adsorption occurring after the initial adsorption. A previous study [5] revealed that the superplasticizer adsorption is strongly dependent on the molecular weight of the polymer. It was found by size exclusion chromatography that PCE fractions with a higher molecular weight adsorb preferably on the cementitious phases.

The different behaviour of the polymers concerning rheology is related to their adsorption properties. Strictly speaking “adsorption” is not the correct term, as a part of the consumed polymer is according to Flatt and Houst [9] coprecipitated with early cement hydration products (e. g. monosulphate) and thus not effective for dispersion. This is especially the case when there is an insufficient sulphate supply during early hydration. From the cements used in this study the high C_3A -cement (H-OPC) is the most likely to act in this way.

The saturation point in the adsorption isotherms is generally reached for polymer dosages between 0.2 and 0.3 wt.-%, with the exception of polymer PCE 102-1:2 that hardly does not adsorb at all.

In general, PCEs with shorter side chains and lower side chain density adsorb to a larger extent on the cement particles. This could be expected when the charge density of the polymers is taken into account, which increases with decreasing side chain length and with decreasing side chain

density as determined experimentally by Plank et al. [4] for PCEs with the same architecture.

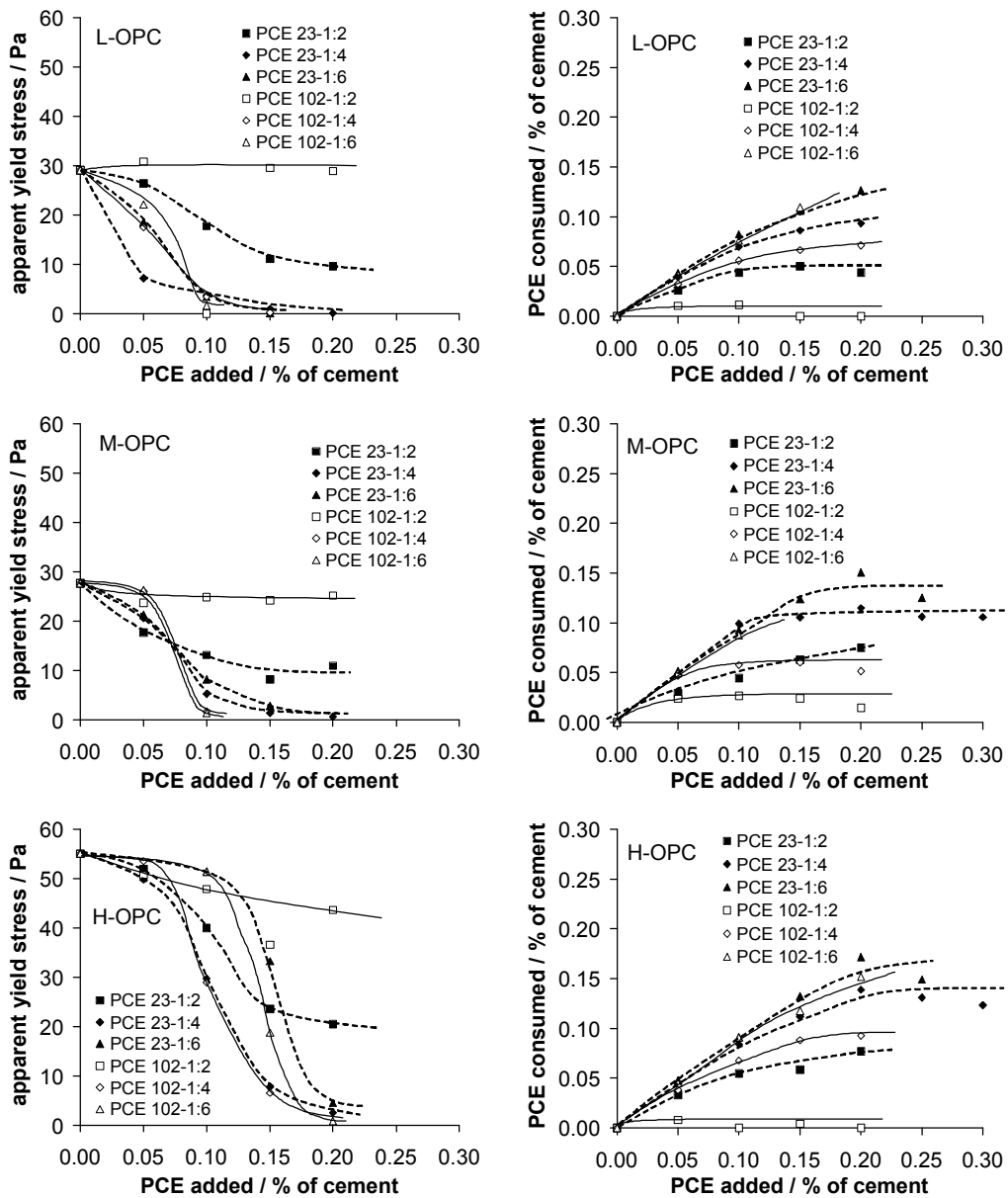


Fig. 2: PCE-type and dosage on yield stress (left column) and superplasticizer adsorption (right column) of the cement pastes at a sample age of 5 min; from the top to the bottom: L-OPC, M-OPC, H-OPC

With increasing aluminate content of the cement the amount of polymer adsorbed is increasing. This agrees well with findings of Yoshioka et al. [11], who examined the adsorption behaviour of superplasticizers on pure clinker phases. Their study revealed that superplasticizers adsorb pref-

erably on C_3A and C_4AF and their hydration products and to a much lesser extent on the calcium silicate phases.

4.3 Influence of superplasticizer on cement hydration

Besides the workability improvement, the influence of superplasticizers on cement hydration is of special importance in concrete technology. Fig. 3 gives the influence of PCE side chain length and side chain density on the hydration heat flow during the first 72 hours of hydration of L-OPC pastes with 0.3% of superplasticizer added.

The plain cement paste without any addition of PCE shows a dormant period associated with a relatively low heat flow until about two hours of hydration. This is followed by an increase in heat evolution over several hours towards a maximum after about 13 hours, mainly due to alite hydrating to calcium silicate hydrates. The sulphated depletion peak (usually occurring some hours after the main hydration peak) is almost not visible for this cement due to its low C_3A -content.

In general, all examined superplasticizers retard the hydration of the cement compared to the plain paste. Furthermore, the main hydration peak seems to be broader in the superplasticizer containing samples compared to the plain paste. In the case of additions of 0.3% polymer, the dormant period is prolonged between 2 hours (PCE 102-1:2) and 17 hours (PCE 23-1:6).

Despite the fact that the PCE superplasticizers adsorb preferably on the aluminate phase and its hydration products, they retard mainly the alite hydration. This is displayed by the TGA data shown in fig. 4. In the paste without addition of PCE, the formation of portlandite starts at a hydration time of 4 hours. In the system with PCE portlandite begins to occur after 18 hours. However, after 28 days no significant difference in the amount and kind of hydration products formed can be observed. XRD measurements on the same samples (data not shown in this paper) confirmed these results. In a different study by Lothenbach et al. [14] we found that PCE superplasticizers retard the dissolution of alite strongly, thus delaying the formation of portlandite and C-S-H. However no retardation of the dissolution of the aluminate phase or of the precipitation of ettringite is observed.

A decreasing side chain length of the grafted polymers leads to an increase of the retarding effect. Similar results are reported by Yamada et al. [2], who found an increase of the final setting of cement pastes containing polycarboxylate-based PCEs with decreasing side chain length. Kirby and Lewis [3] determined an increasing retardation of the onset of the acceleratory period with decreasing side chain length.

A lower side chain density causes an increasing retardation of cement hydration as well. The effects of PCE side chain length and side chain density can be explained by the adsorption behaviour of the polymers that is related to their charge density. An increasing adsorption of the polymers on the cementitious phases leads to a stronger retardation of cement hy-

dration. A further explanation for the only slight retarding effect of PCEs with long side chains is that in the PCE with long side chains most of the mass of the polymer is concentrated in the non-adsorbing backbone. Thus, the coverage of the surface of the cement with a PCE with long side chains is much less compared to a PCE with short side chains, assuming that the total amount of polymer adsorbed is the same in both cases.

The amount of PCE present in the cement pastes influences the onset of the acceleration period as well, depending on the chemical composition of the cement (fig. 5). Increasing additions of superplasticizers lead to a stronger retardation of cement hydration. The influence of PCE dosage on retardation is more pronounced for polymers with shorter side chains and with lower side chain densities. The polymer with the long side chains and the highest side chain density (PCE 102-1:2) shows almost no retardation even at an addition of 0.3 wt.-% of polymer. In contrary, the polymer with short side chains and the lowest side chain density (PCE 23-1:6) causes the most pronounced dependence of retardation on PCE dosage and effects cement hydration kinetics stronger than all other PCEs investigated in this study.

The effect of PCEs on hydration kinetics gets more pronounced with decreasing C_3A -content of the cement (fig. 5). As mentioned above, the PCEs affect mainly alite hydration, but adsorb preferably on the aluminate phases. This apparent discrepancy can be explained by the effect that in low C_3A -cements less polymers are adsorbed on aluminate phases and thus more polymers are available to interact with tricalcium silicate and its hydrates. To confirm the interaction between PCEs and C_3S , the hydration heat flow during the first 7 days of hydration of pure C_3S -pastes with 0.2% of superplasticizer added was examined (fig. 6). The results reveal that the structure/effect relations of PCEs discussed above are valid for pure C_3S as well. The dormant period is even more prolonged than for the low- C_3A - cement, indicating the strong interaction between PCEs and the hydration kinetics of C_3S .

Mollah et al. [8] proposed three different mechanisms for the retarding effects of superplasticizers on cement hydration: (i) adsorbed superplasticizer molecules hinder the diffusion of water and calcium ions at the cement-solution interface, however adsorption on C_3S is much less pronounced in comparison to C_3A [11], (ii) calcium ions form complexes with the polymer molecules which prevent nucleation and precipitation of calcium containing hydrate assemblages, but there is not much evidence of calcium ions forming strong complexes with PCEs [14], and (iii) the dispersive action of superplasticizers changes growth kinetics and morphology of hydrate phases. Another possible mechanism of retardation is that the PCEs change the morphology and the density of the hydrate layer covering the clinker grains during early hydration, as shown in [16,17] by the investigation of the hydration of pure clinker phases by transmission X-ray microscopy without and with the presence of PCE-based superplasticizers.

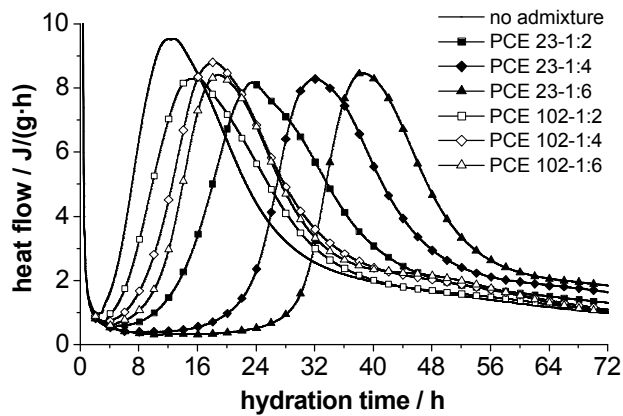


Fig. 3:
Conduction calorimetry
of L-OPC-pastes with
0.3% additions of PCE

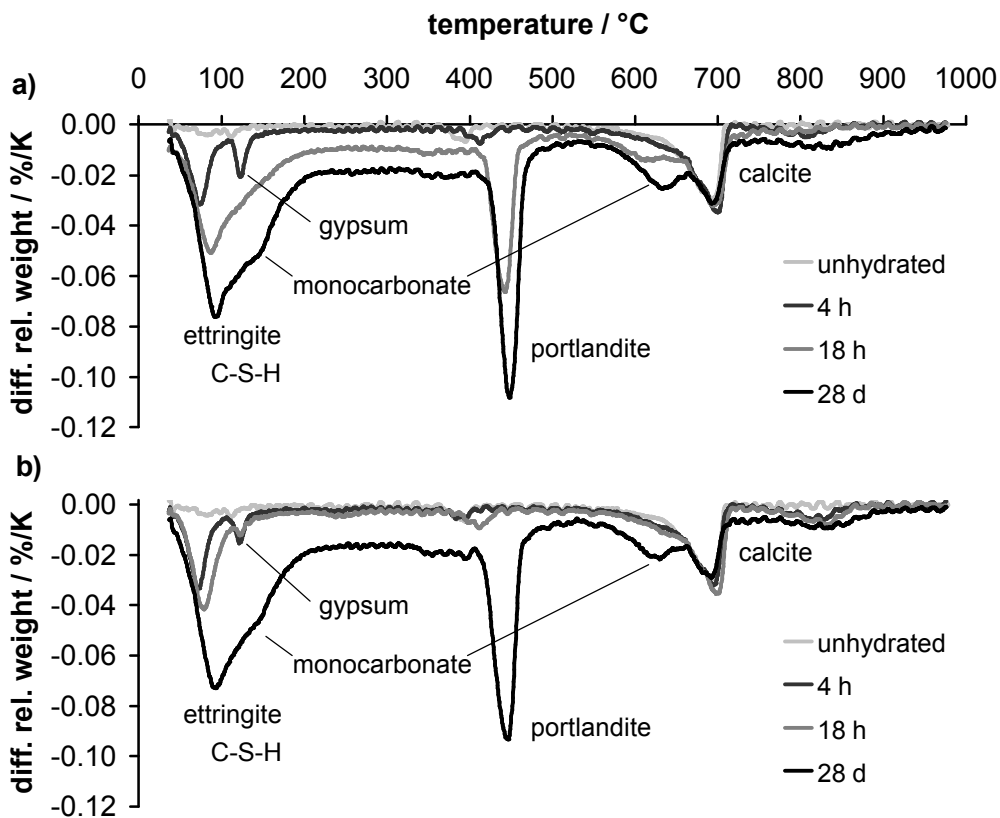


Fig. 4: Differential thermogravimetric analysis of medium C_3A - OPC pastes (M-OPC) at w/c 0.35
a) without addition of superplasticizer and
b) with addition of 0.2% PCE 23-1:6

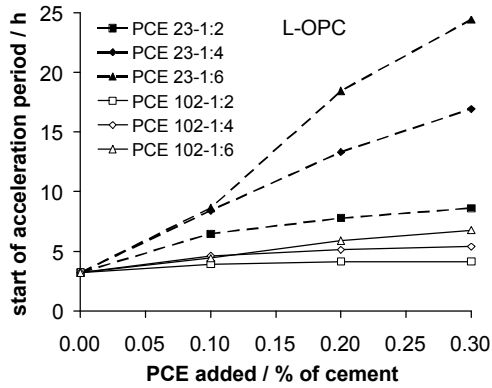


Fig. 5: Influence of PCE-type and dosage on the start of the acceleration period

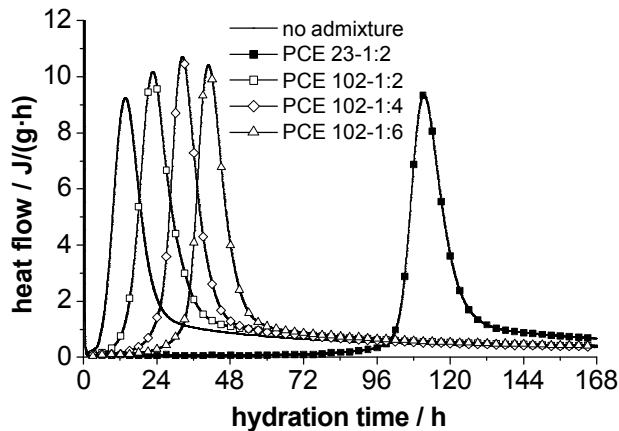
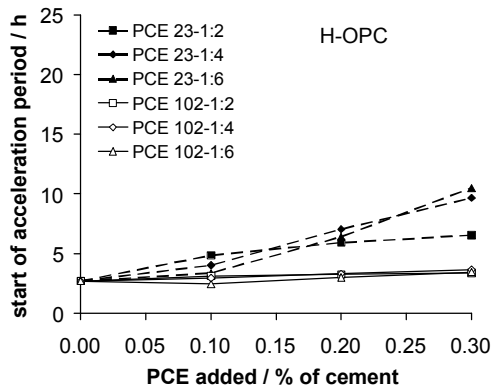
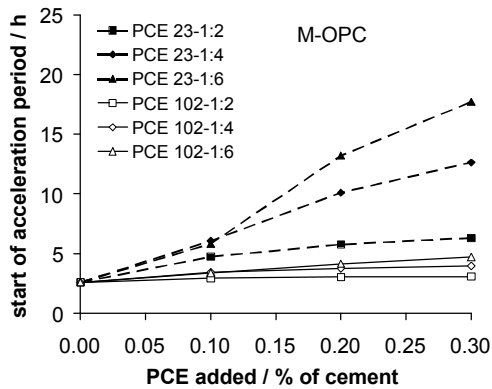


Fig. 6: Conduction calorimetry of C_3S -pastes with 0.2% additions of PCE; water/ C_3S = 0.35; pastes with PCE 23-1:4 and PCE 23-1:6 are retarded more than 168 hours

5 Conclusions

The interactions of superplasticizers based on polycarboxylate ethers (PCE) with different Portland cements have been examined with various methods like rheology, pore solution analysis and conduction calorimetry. The results reveal that the adsorption of the polymers on the cement clinker phases and their hydration products plays a key role concerning rheology and early cement hydration. It can be controlled by changing side chain density, side chain length or the molecular weight of the polymer.

It was found that a decreasing density of the PCE side chains enhances cement paste workability. The length of the side chains has only a minor influence. All superplasticizers retard the hydration of the Portland cements used in this study. The dormant period is prolonged with decreasing length and with decreasing density of the side chains. The adsorption measurements revealed that polymers with higher charge density adsorb to a larger extent. The charge density of the PCEs increases with decreasing side chain length and with decreasing side chain density. The amount of adsorbed polymer can be directly linked to the retardation effect.

With increasing C_3A -content of the cement the amount of polymer adsorbed is increasing. However, a cement with a higher C_3A -content needs higher additions of superplasticizer to the paste, mortar or concrete compared to cement with a lower C_3A -content to achieve the same workability. The reason for that might be the incorporation of a reasonable amount of PCE in early cement hydration products (e. g. monosulphate) especially when using a high- C_3A cement with an insufficient sulphate supply during early hydration. The effect of PCEs on hydration kinetics gets more pronounced with decreasing C_3A -content of the cement. The PCEs affect mainly the alite hydration, but adsorb preferably on the aluminate phases. Thus, in low C_3A -cements more polymers are available to interact with tricalcium silicate and its hydrates.

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References

- [1] H. Uchikawa, S. Hanehara, D. Sawaki, The role of steric repulsive force in the dispersion of cement particles in fresh paste prepared with organic admixture, *Cem Concr Res* 27 (1) 1997 37-50
- [2] K. Yamada, T. Takahashi, S. Hanehara, M. Matsuhisa, Effects of the chemical structure on the properties of polycarboxylate-type superplasticizer, *Cem Concr Res* 30 (2) 2000 197-207
- [3] G.H. Kirby, J.A. Lewis, Comb polymer architecture effects on the rheological property evolution of concentrated cement suspension, *J Am Cer Soc* 87 (9) 2004 1643-1652
- [4] J. Plank, R. Schwerd, D. Vlad, A. Brandl, P. Chatziagorastou, Kolloidchemische Aspekte zur Verflüssigung von Zementleimen mit Polycarboxylaten, in: *Proceedings 6. GDCh-Tagung BAUCHEMIE*. Erlangen, Germany, 7-8 October 2004: GDCh Monographie Vol. 31. pp. 58-69
- [5] F. Winnefeld, S. Becker, J. Pakusch, T. Götz: Polymer structure / concrete property relations of HRWRA, in: *Proceedings 8th CANMET/ACI International Conference on Recent Advances in Concrete Technology*, Montréal, Canada, May 31 - June 3, 2006, Suppl. Vol., pp. 159-177

- [6] C. Jolicoer, M.-A. Simard, Chemical admixture-cement interactions: phenomenology and physico-chemical concepts, *Cem Concr Comp* 20 (2-3) 1998 87-101
- [7] S. Hanehara, K. Yamada, Interaction between cement and chemical admixture from the point of cement hydration, absorption behaviour of admixture, and paste rheology, *Cem Concr Res* 29 (8) 1999 1159-1165
- [8] M.Y.A. Mollah, W.J. Adams, R. Schennach, D.L. Cocks, A review of cement - superplasticizer interactions and their models, *Adv Cem Res* 12 (4) 2000 153-161
- [9] R.J. Flatt, Y. Houst: A simplified view on chemical effects perturbing the action of superplasticizers, *Cem Concr Res* 31 (8) 2001 1169-1176
- [10] K. Yamada, S. Ogawa, S. Hanehara, Controlling the adsorption and dispersing forces of polycarboxylate-type superplasticizer by sulphate ion concentration in aqueous phase, *Cem Concr Res* 31 (3) 2001 375-383.
- [11] K. Yoshioka, E. Tazawa, K. Kawai, T. Enohata, Adsorption characteristics of superplasticizers on cement component minerals, *Cem Concr Res* 32 (10) 2001 1507-1513
- [12] W. Prince, M. Espagne, P.-C. Aïtcin, Ettringite formation: A crucial step in cement superplasticizer compatibility, *Cem Concr Res* 33 (5) 635-641
- [13] F. Puertas, H. Santos, M. Palacios, S. Martínez-Ramírez, Polycarboxylate superplasticiser admixtures: effect on hydration, microstructure and rheological behaviour in cement pastes, *Adv Cem Res* 17 (2) 2005 77-89
- [14] B. Lothenbach, F. Winnefeld, R. Figi, Thermodynamic modelling of the influence of superplasticizers on the hydration of Portland cement, in: *Proceedings of the 12th International Congress on the Chemistry of Cement*, Montréal, Canada, July 8 and 13, 2007, in press
- [15] A. Zingg, F. Winnefeld, P. Gasser, A. Kaech, J. Pakusch, S. Becker, L. Holzer, Cryo-microscopy for fresh cement pastes: First results and comparison with conventional SEM and ESEM techniques, in: *Proceedings 8th Canmet/ACI International Conference on Superplasticizers and other Admixtures in Concrete*, Sorrento, Italy, October 29 - November 1, 2006, in press.
- [16] R. Trettin, K.G. Böttger, J. Thieme, C. Schmidt, F. Winnefeld, J. Rieger, S. Becker: Röntgenmikroskopie: eine effektive Methode zur in-situ Untersuchung der frühen Hydratation von Tricalciumsilicat, in: *Proceedings 6. GDCh-Tagung BAUCHEMIE*, Erlangen, Germany, October 7-8, 2004, GDCh Monographie Vol. 31, pp. 135-139.
- [17] M. Geyer, R. Trettin, K.G. Böttger, J. Thieme, S. Becker, Sorption von definierten Polycarboxylaten an synthetischen Hydratphasen, in: *Proceedings 6. GDCh-Tagung BAUCHEMIE*, Erlangen, Germany, October 7-8, 2004, GDCh Monographie Vol. 31, pp. 206-209.