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Alexandre Govin, W. Schmidt, Marie-Claude Bartholin, Phillipe Grosseau. Effect of guar gum derivatives combined with superplasticizers on properties of portland cement-pastes. 2nd International Conference on Bio-Based Building Materials and 1st International Conference on ECOlogical valorisation of GRAnular and FIBrous materials (ICBBM ECOGRAFI 2017), Institut Pascal - ; Université Blaise Pascal ; Polytech Clermont-Ferrand, Jun 2017, Clermont-Ferrand, France. pp.55-61. hal-01548245

HAL Id: hal-01548245

<https://hal.science/hal-01548245v1>

Submitted on 27 Jun 2017

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EFFECT OF GUAR GUM DERIVATIVES COMBINED WITH SUPERPLASTICIZERS ON PROPERTIES OF PORTLAND CEMENT-PASTES

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Abstract

Chemical admixtures allow to the create a variety of fresh and hardened state properties in cementitious materials. In the case of self-compacting concrete, plasticizers or superplasticizers are introduced with the aim to decrease the yield stress and the viscosity of the materials. However, in order to prevent segregation and bleeding, and to improve the water retention of cement-based system, stabilizing agents or viscosity agents are often introduced in addition. Among these admixtures, polysaccharides are most commonly used.

The aim of this study is to provide an understanding of competitive or synergetic effects induced by the combination of hydroxypropyl guar stabilizing agents (HPG) and superplasticizers on cement pastes. Two polycarboxylate superplasticizers (PCE) exhibiting different charge densities and one HPG were studied. It was found that the combination of HPG with PCE superplasticizer strongly affects the rheological behavior of cement pastes. Despite the presence of HPG, the viscosity of the pastes strongly decreased with increasing dosage of PCE until it became close to the viscosity of a cement paste with PCE only. However, the use of HPG in combination with PCE allows maintaining a significant yield stress in the cement paste compared to PCE alone. The increase in the charge density of the PCE seemed to amplify the drop of the viscosity and to reduce the gain on the yield stress induced by HPG.

The results also highlight a delay in the setting-time of the cement paste by adding HPG and PCE. The delay induced by HPG is significantly lower than that generated by PCEs. However, the combination of the both kind of admixtures leads to a slightly shorter setting-time compared to the PCE alone.

Keywords:

Admixtures, Rheology, Hydration, Polysaccharides, Guar derivatives, Superplasticizers

1 INTRODUCTION

In order to obtain specific properties, from the fresh state to the hardened material, the formulations of cementitious materials become more and more complex by combining several kinds of admixtures. Since many years, cementitious materials with high flowability have been developed for the economic and technical advantages they bring. Dispersing admixtures such as superplasticizers are commonly used in the formulation of ready mixed concrete, High or Ultra-High-Performance Cementitious Materials (HPCM, UHPCM), or Self-Compacting Concrete (SCC). These admixtures can dramatically reduce the amount of mixing water while maintaining workability or increasing workability without loss of performance [Hanehara 1999, Yamada 2000, Burgos-Montes 2012]. Commonly, polycarboxylate ethers (PCE) are used as superplasticizers to disperse cement particles in concrete and mortar [Ramachandran 1995]. Due to the

anionic charges in the backbone chain, the PCE can adsorb on surfaces of cement and hydration phases. After adsorption, steric repulsion of the particles through the side chains and the main chain leads to the dispersing effect [Yamada 2000, Plank 2007]. However, the use of highly flowable mixtures may lead to segregation or excessive bleeding and eventually durability issues. In order to enhance the sedimentation resistance yet maintaining high fluidity, viscosity-enhancing admixtures (VEA) or stabilizing agent (STA) are frequently introduced within the formulations [Rols 1999, K. H. Khayat 1997, Lachemi 2004, Sonebi 2006]. Among these admixtures, natural polysaccharides or their derivatives (such as sphingane gum, starch derivatives, cellulose ethers or guar gum derivatives) are used. The incorporation of STAs is useful to ensure sagging resistance for thick application on vertical support, and to allow sufficient fluidity for normal pumpability by supplying shear thinning rheological behavior [Paiva 2006]. Indeed,

these admixtures provide, generally, high yield stress and apparent viscosity at low shear rate but low resistance to flow at high shear rate [Khayat 1998]. However, their mode of action is not fully understood, and results are sometimes contradictory, since they are affected by multiple parameters such as solid volume fraction, polymer content, pore solution chemistry and particle surface parameters.

The consideration of environmental concerns, the reduction of greenhouse gas emissions and energy consumption lead the cement industry to develop more and more complex formulations. Consequently, a greater control of the formulation and a better understanding of the effects of all admixtures in a formulation are necessary. Indeed, an understanding of the mechanism of action of the admixtures is a way to improve the selection of admixtures in relationship with the practical applications. However, most of the academic studies focused on the effect of individual admixture, despite competitive adsorption which can occur inhibiting the intended effect [Plank 2008] or positive interaction which can promote the efficiency of the polymers [Recalde Lummer 2012, Bessaies-Bey 2016].

The objective of this paper is to improve the understanding of synergetic or competitive effect between hydroxypropyl guar and polycarboxylate-based superplasticizers.

2 MATERIALS AND METHODS

2.1 Mineral products

The investigations were carried on water-cement system. The cement used for this study was an ordinary Portland cement, referenced as CEM I 42.5 R (CEMEX) according to the European standard EN 197-1. The chemical composition was determined X-ray fluorescence spectroscopy and the resulting clinker composition according to the modified Bogue calculation according to Taylor [Taylor 1989] is given in Tab. 1.

Tab. 1: Oxide composition (% weight) of the investigated cement determined by XRF and clinker phase composition according to the modified Bogue calculation.

Chemical composition (% wt)				Phase composition (% wt)	
Oxides	XRF	Oxides	XRF	Phases	XRD (Rietveld)
CaO	62,80	Na ₂ O	0,28	C ₃ S	61,8
SiO ₂	20,56	K ₂ O	0,95	C ₂ S	20,5
Al ₂ O ₃	4,36	TiO ₂	0,2	C ₃ A	6,2
Fe ₂ O ₃	2,27	SO ₃	3,45	C ₄ AF	7,7
MgO	2,14	LOI	2,40		

2.2 Organic admixtures

Guar gum is a high molecular weight, hydrophilic, non-ionic natural polysaccharide extracted from the endospermic seed of *Cyamopsis tetragonolobus*. Guar

gum consists in a D-mannopyranose backbone with random branchpoints of galactose. Hydroxypropyl guar (HPGs) are obtained from the original guar gum via an irreversible nucleophilic substitution, using propylene oxide in the presence of an alkaline catalyst (Fig. 1). Thanks to its branched-chain structure and the lot of hydroxyl groups, guar gum exhibits a high chemical reactivity and is soluble in cold water. Moreover, guar gum is extracted by simple thermo-mechanical process, leading to a low impact on the environment of the HPGs manufacturing.

The chemical modification of the original guar gum requires normal reaction conditions of temperature and pressure, does not generate large quantity of by-products, and requires minimal purification procedure [Biasotti 2014].

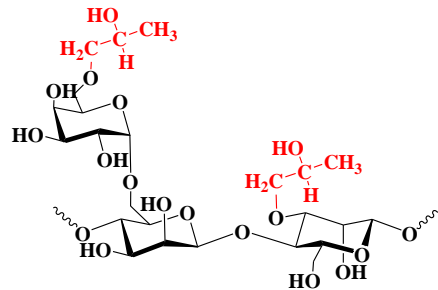


Fig. 1: Molecular structure of HydroxyPropyl Guar.

In this paper, one HPG, provided by Lamberti S.p.A., was studied. The molecular weight is of around $2 \cdot 10^6 \text{ g} \cdot \text{mol}^{-1}$ and the molar substitution ratio (MS) is low [Pointot 2013]. This HPG was chosen because of its good adsorption on the cement particles [Govin 2016].

Two polycarboxylate-based superplasticizers (PCE) were tested (Glenium Master Sky 591 called PCE_{LC} and Glenium Master Sky 595 called PCE_{HC}). Since these two polymers are commercial products, no details of the chemical composition were given by the manufacturer (BASF). A qualitative description is given in Tab. 2.

Tab. 2: Qualitative description of the PCEs used.

	PCE _{LC}	PCE _{HC}
Backbone	Polycarboxylate ether (PCE)	
Side chains	Polyethylene oxide (PEO)	
Side chain length	Medium + low	Medium
Grafting degree	High	Low
Backbone charge density	Low	High
Solid content (%)	30	20

These superplasticizers were chosen because of their difference in the charge density, since it is one of the major influencing parameters for the performance of superplasticizers [Plank 2008]. For the following, LC and HC mean low charge and high charge density, respectively.

2.3 Preparation of fresh pastes

The investigations were carried on cement pastes. The water-to-cement ratio (W/C) was kept constant and fixed at 0.4. Deionized water was used for all the experiments. The hydroxypropyl guar was dry-blended with the cement, hand-premixed during one minute, before adding liquid. When superplasticizers were used, they were added into the dry mix with the water. The amount of water contained into the PCE solution was deduced from the mixing water in order to keep constant the liquid-to-solid ratio. The mixing was made in mixer, in accordance to EN 196-1. All the dosages in admixture were expressed in percent by weight of cement (% bwoc). The studied dosages were 0.1, 0.2 and 0.3% bwoc and 0.1% bwoc for PCEs and HPG, respectively.

All tests were carried out at a controlled temperature since rheological behavior of the cement paste and setting-time are temperature-dependent. A control test was also performed with cement without admixture.

2.4 Rheological behavior

The rheological measurements were performed with a Rheometer Viskomat NT (Schleibinger Geräte), in a room thermostated at 20 °C. The rheological properties of fresh pastes were investigated with a double gap cell and a basket probe composed of a structured grid (Vogel cell) (Fig. 2(a)). The gap thickness was about 6 mm.

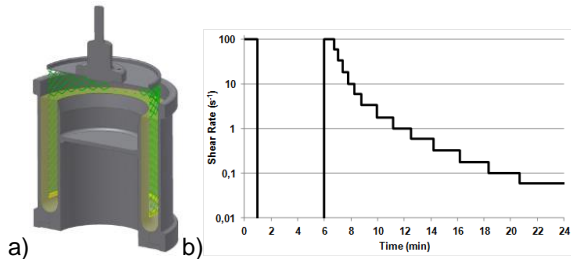


Fig 2: Double gap cell and the basket probe (a) and experimental protocol (b) used for the rheological measurements.

The paste was introduced into the measurement system at the end of the mixing cycle and was then held at rest. At 9 min the experiment was started. The mortar was first pre-sheared for 1 min at 100 s⁻¹ in order to re-homogenize the sample and to eliminate its shear history because of potential thixotropic character of cementitious materials [Phan 2006, Roussel 2012]. After a period of rest of 5 min, the rheological measurements were started. The imposed shear rate was 14 decreasing steps from 100 s⁻¹ to 0.06 s⁻¹ (Fig. 2(b)). The measuring time was adjusted for each shear rate, in order to obtain a steady state.

The shear stress (τ) was expressed as a function of the shear rate ($\dot{\gamma}$) and the Herschel-Bulkley model was applied to fit the experimental data and used to describe cement rheological behavior [Herschel 1926]:

$$\tau = \tau_0 + K\dot{\gamma}^n \quad (1)$$

where τ_0 corresponds to the yield stress, K the consistency coefficient and n the fluidity index which

characterizes shear-thinning or shear thickening behavior of the paste. In addition, the residual viscosity, as defined by [Hot 2014], was determined.

$$residual\ viscosity_{(\dot{\gamma})} = \mu_{app} - \frac{\tau_0}{\dot{\gamma}} \quad (2)$$

Where μ_{app} is the apparent viscosity ($=\tau/\dot{\gamma}$), τ_0 is the yield stress.

The residual viscosity does not take into account the contribution of the energy needed to overcome the attractive interaction colloidal forces and to destroy the inter-particle network, characterized by the yield stress [Hot 2014].

2.5 Adsorption measurements

The adsorption isotherms were determined using the depletion method. The non-adsorbed polymer remaining within the pore solution was quantified. The pore solution was extracted from the cement pastes by means of centrifugation, 15 min after contact between water and cement. The first step consisted in the centrifugation of around 150 g of cement paste at 5000 rpm for 5 min. The supernatant was, afterward, centrifuged again at 14500 rpm for 10 min. It is worth noting that the amount of missing polymer into the pore solution was called "adsorbed" for the rest of the paper, despite that a small part of polymer could be intercalated into hydrates due to early chemical interactions [Flatt 2001]. Moreover, adsorption does not mean that the polymer becomes active in dispersing due to possible multilayer adsorption.

TOC measurements:

The supernatant was diluted with hydrochloric acid solution at 0.1 mol.L⁻¹. The TOC was determined by combustion at 850 °C with a Vario-TOC Cube (Elementar). The device was calibrated thanks to reference solutions of HPG and PCE.

SEC measurements:

Since the TOC measurements do not allow to quantify the amount of each polymer, an original method was developed. The size exclusion chromatography analysis (SEC) was used to separate the two polymers (superplasticizer and polysaccharide) and to quantify the amount of PCE into the pore solution. After calibrating of the both analysis methods, the subtraction of the SEC results to TOC results gives the amount of polysaccharide into the pore solution.

SEC analyses were carried out on a Waters apparatus equipped with a pump Waters 916. The eluent was a 0.5 mol.L⁻¹ NaCl solution, on-line degassed. The flow rate was set to 0.5 mL.min⁻¹. A column Shodex OHPak SB-806M-HQ was used and kept at 50°C in an oven. Detection was achieved thanks to a refractometer-type detector Waters 2410.

2.6 Determination of the setting-time

The setting-time (Vicat) was carried out using ToniSET Expert (Toni Technik). The diameter and the weight of the needle were 0,5 mm and 300 g, respectively. The samples were stored at 20°C into water during all the experiment.

3 RESULTS AND DISCUSSION

3.1 Adsorption measurements

It was first checked that the SEC method provides the same adsorption isotherms than TOC analysis (Fig. 3). The results show a good correlation between the both methods, validating the use of SEC to quantify the amount of PCE remaining into the pore solution.

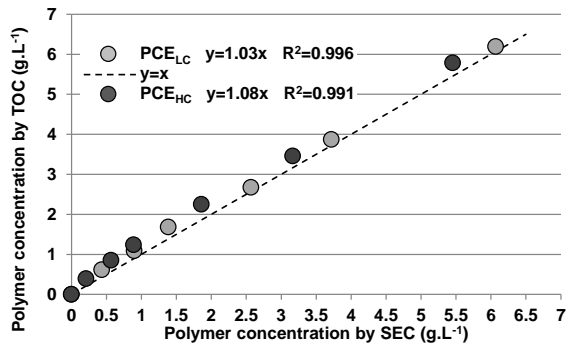


Fig. 3: Comparison of SEC and TOC methods for the quantification of PCE adsorption.

The adsorption isotherms obtained by SEC analysis for the both PCEs (high charge and low charge) are shown on Fig. 4. The adsorption measurements of PCEs are represented by Langmuir model (solid line). The results show that the adsorption of PCE_{HC} is higher than that of PCE_{LC}, which is coherent with the charge density of the two PCEs [Plank 2008, Dalas 2015] and the size of the molecules (result not shown here).

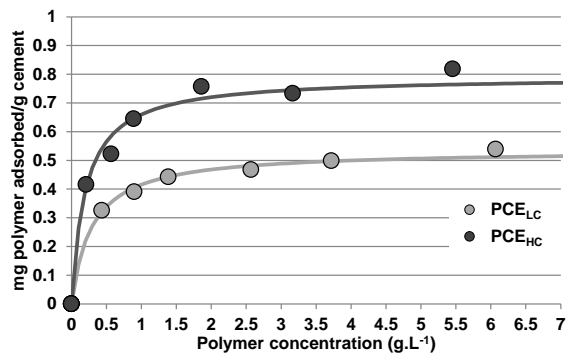


Fig. 4: Adsorption isotherm of PCE_{LC} and PCE_{HC} alone.

The amounts of PCEs adsorbed in presence of a constant amount of HPG (0.1% bwoc) are shown on Fig. 5 and Fig. 6. The adsorption isotherms of PCEs and HPG (0.1% bwoc) alone are also represented for comparison. HPG exhibits an adsorption of 0.74 mg/g, whereas the adsorption of PCE reaches 0.55 mg/g and 0.82 mg/g for PCE_{LC} and PCE_{HC}, respectively. However, due to the great difference in molecular weight between HPG and PCEs (between 5 and 10 times), more molecules of PCE than HPG are adsorbed. The results highlight that both admixtures are able to adsorb even when they are added together in the cement pastes. The combination of the PCE, exhibiting the lowest charge density (PCE_{LC}), with HPG leads to a modification of the adsorption of the

two polymers (Fig. 5). Indeed, for the both admixtures, their amounts adsorbed are lower when the two polymers are introduced together in the mix than when they are introduced separately. By increasing the dosage of PCE_{LC} from 0.1% to 0.3% bwoc, the adsorption is reduced of 7% to 5% and 13% to 20% for PCE_{LC} and HPG, respectively.

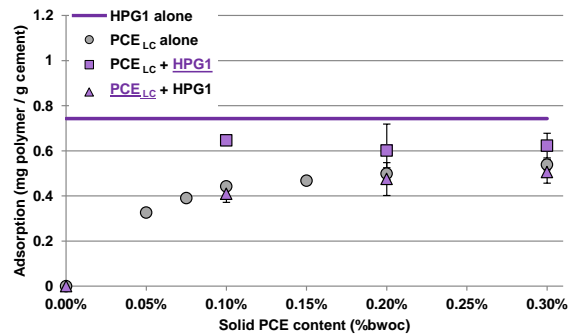


Fig. 5: Adsorption isotherm of HPG alone, PCE_{LC} alone, HPG and PCE_{LC} when they are combined.

When the charge density of PCE increases (PCE_{HC}), the adsorption of the PCE seems to be unmodified by the presence of the HPG (Fig. 6). It appears obviously that the adsorption of the HPG is strongly reduced by the presence of the PCE_{HC}. The drop of adsorption ranges from 37% to 56% when the dosage of PCE increases from 0.1% to 0.3% bwoc. These values correspond approximately to three times those obtained with the low charge density PCE.

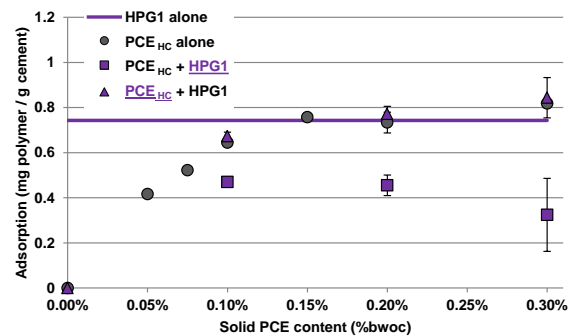


Fig. 6: Adsorption isotherm of HPG alone, PCE_{HC} alone, HPG and PCE_{HC} when they are combined.

All the measurements were realized with a high dosage in PCE (>0.1% bwoc) leading to a high surface coverage of the cement particles. This surface coverage becomes more and more close to the surface saturation when the dosage in PCE increases (Fig. 4). In these conditions, competitive adsorption between organic admixtures should occur [Bessaies-Bey 2016]. The results show clearly that the affinity of the polymer with the cement particles is a key factor in the competitive adsorption. The polymer with the highest affinity adsorbs first, leaving the remaining surface available for the second admixture. In the case of increasing dosage in PCE_{HC}, the available surface for the polysaccharide decreases, leading to a decreasing adsorption of HPG. When the charge density of the PCE is lower, the gap of affinity between

the PCE and the polysaccharide is reduced, and competitive adsorption occurs.

3.2 Impact of admixtures on the rheological properties of fresh pastes

Fig. 7 and Fig. 8 show the evolution of the relative yield stress, extracted from Herschel-Bulkley model, and the relative residual viscosity for all the studied pastes (without and with admixture). The relative value (yield stress or residual viscosity) corresponds to the ratio of the value obtained for the admixed pastes to the value determined for the non-admixed cement paste. The use of increasing dosage in PCEs leads to continuous decrease in the yield stress and residual viscosity. The charge density of PCE impacts the evolution of the yield stress and the residual viscosity. Indeed, pastes admixed with PCE_{HC} exhibit a lower yield stress and a lower residual viscosity than pastes admixed with PCE_{LC}. This result is in agreement with the higher adsorption of PCE_{HC} which improves the steric repulsions and limits the contacts between cement particles. In our case, cement pastes admixed with 0.1% and 0.2% of PCE_{HC} give similar rheological behaviors than cement pastes admixed with 0.2% and 0.3% of PCE_{LC}, respectively. Consequently when the charge density of PCE decreases, higher dosage in PCE is required to obtain the same rheological behavior, and thus same slump flow [Schmidt 2015].

The results show also that the presence of 0.1% of HPG leads to an increase in both yield stress and residual viscosity. It was shown that HPG is able to bridge two cement particles which conducts to an increase of the yield stress [Govin 2016]. Moreover, the viscosity of the pore solution is increased by the HPG coils remaining into the pore solution.

When the PCEs are combined with HPG, a general decrease in the yield stress and the residual viscosity is observed with increasing dosage in PCE. However, the yield stress is always higher than with PCE alone. Moreover, the impact of the dosage in PCE depends on the charge density of the PCE. For PCE_{HC}, a continuous decrease in the yield stress is observed, whereas a plateau followed by a decrease is noticed for PCE_{LC}. These tendencies are consistent with the adsorption results. The great reduction in HPG adsorption induced by PCE_{HC}, leads to the progressive replacement of the bridging by the steric repulsions, and consequently, to the drop of the yield stress. In the case of the lowest dosage in PCE_{LC}, we showed that the reduction in adsorption of HPG and PCE was low. The reduction in HPG adsorption could be sufficiently low to maintain enough bridging and thus a similar yield stress than with HPG alone. At higher dosage in PCE_{LC}, the steric repulsion induced by the superplasticizer adsorbed could be responsible to the decrease in the yield stress.

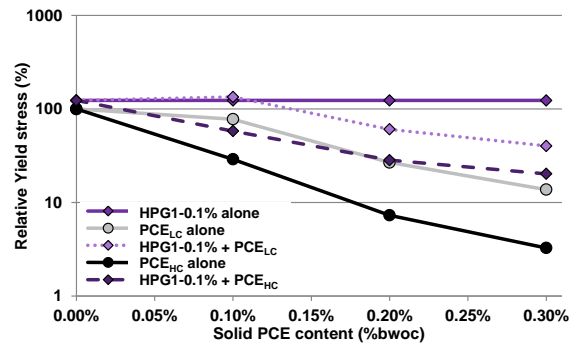


Fig. 7: Yield stress as a function of solid content of PCEs.

The combination of HPG with PCE_{LC} induces a low modification of the residual viscosity compared to the use of PCE_{LC} alone. However, the viscosity of this pore solution is quite similar than that obtained with HPG alone (results not shown here). This result indicates that the modifications of the colloidal and electrostatic forces induced by the PCE are greater than the modification of the hydrodynamic forces induced by the polysaccharide. For highly charged PCE, the increase in the pore solution viscosity induced by the reduction in HPG adsorption can justify the greater residual viscosity observed when the pastes are admixed with the combination of PCE and HPG compared to the PCE alone.

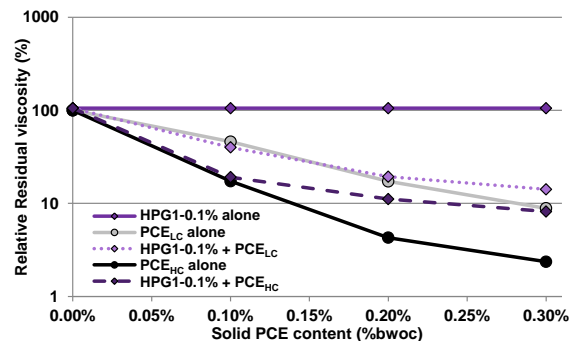


Fig. 8: Residual viscosity as a function of solid content of PCEs.

3.3 Impact of admixtures on the setting-time of fresh pastes

Fig. 9 shows the impact on the initial setting-time for increasing dosages in PCEs, with or without HPG. Due to the strong impact on the setting-time of the dosage in PCE, each value has been normalized in reference to the corresponding setting-time obtained with the corresponding PCE and corresponding dosage, without HPG (100%). In these conditions, a value lower than 100% indicates an acceleration of the setting-time in comparison to the same formulation without HPG. When the cement paste is admixed with the HPG alone, a delay (≈ 12 min) in the setting-time is observed. However, it is worth noting that this delay is strongly lower than that induced by PCE alone (> 3 h for the lowest delay).

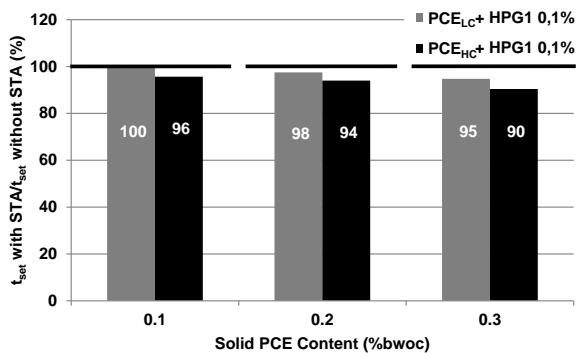


Fig. 9: Effect of HPG combined with increasing dosage in PCEs on the initial setting-time. (— Reference corresponds to the setting-time obtained with the corresponding PCE and corresponding dosage, without HPG)

The results show that the combination of PCE with 0.1% of HPG leads to a lower retardation than pure PCE. This indicates that an interaction between both admixtures could have occurred, leading to a reduction of the delay in the setting-time. The same tendency was also observed with the use of other polysaccharides such as starch and diutan gum [Schmidt 2016]. According to the authors, the mobility of the PCE in the pore solution could be reduced by the presence of the polysaccharide in the pore solution to the benefit of more sulfate ion adsorption. Thus more ettringite could precipitate. This assumption was strengthened by Stroh et al. [Stroh 2016]. The higher amount of aluminate hydrate phases precipitated could lead, at later stage, to a higher adsorption of PCE. Hence, after a few hours of hydration a lower amount of PCE is thus available in the solution to modify the C-S-H reaction.

This proposed mechanism is not in contradiction to the lower observed PCE adsorption in the presence of HPG at early stages (e.g. in Fig. 5) since the lower adsorption after 15 minutes positively triggers the hydration reaction that causes higher adsorption at later stages. Furthermore, the adsorption measurements highlight that, depending on the introduced dosage and the nature of the PCE, the remaining amount in PCE, into the pore solution, ranges between 35 to 85%, indicating that after adsorption, a significant amount of PCE is still available to interact with cement hydration at later stage. Dalas et al. also showed that some PCEs can only slightly slow down the ettringite precipitation, but, PCEs strongly increase the specific surface area of ettringite [Dalas 2015]. This implies that the potential adsorption of PCE could be strongly increased at later stage on aluminate hydrates. However, to conclude on the real mechanism, further experiments are necessary.

4 SUMMARY

This paper deals with the effect of the combination of PCEs and HPG on the adsorption, rheological behavior and setting-time of cement pastes. The results show that the combination of HPG with PCE

superplasticizer strongly modifies the rheological behavior of cement pastes. Despite the presence of HPG, the relative viscosity of the pastes decreased with increasing dosage in PCE. However, it allows maintaining a significant yield stress in the cement paste compared to PCE alone. The increase in the charge density of the PCE seemed to amplify the drop of the viscosity and to reduce the gain on the yield stress induced by HPG.

The results also highlight that the combination of the both kind of admixtures lead to a slightly shorter setting-time compared to the PCE alone.

5 ACKNOWLEDGMENTS

The authors would like to acknowledge Lamberti S.p.A. and BASF for the admixtures they provided.

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