The ettringite – superplasticizer interaction and its impact on the ettringite distribution in cement suspensions

By

F. Winnefeld, A. Zingg, L. Holzer, J. Pakusch, S. Becker

Synopsis: In terms of workability of cement based materials, ettringite formation is of major importance. Thus, the interaction between polycarboxylate-ether based superplasticizers (PCE) and various pure cement clinker and hydrate phases is investigated by means of rheological, adsorption and zeta potential measurements. Microstructural analysis of fresh pastes is carried out using cryo-microscopic methods.

The rheological results reveal that the ettringite phase is dominating the workability properties of cement suspensions as the PCE shows high affinity to adsorb onto ettringite surfaces.

The dispersive effect of PCE in cement suspensions is mainly governed by electrostatic and/or steric repulsive forces evoked by the PCE molecules. This effect can be observed by cryo-microscopy on high-pressure frozen cement suspensions. Without PCE, ettringite tends to agglomerate with the tricalciumsilicate rich clinker particles due to their opposite zeta potential. Therefore, the ettringite is inhomogeneously distributed in the OPC suspension. This distribution pattern changes completely in the presence of PCE, where the ettringite crystals now are mainly present in the interstitial pore space.

These results underline that the ettringite phase and its dispersion in the fresh cement paste is acting as the major key mineral concerning workability issues for cement applications.

Keywords: adsorption isotherms, cryo-microscopy, cryo-SEM, cryo-FIB, ettringite, microstructure, polycarboxylate-ether, rheology, superplasticizer, zeta potential
Frank Winnefeld is a senior researcher at the Concrete/Construction Chemistry Laboratory at the Swiss Laboratory of Material Testing and Research (Empa), Dübendorf, Switzerland. His research has been focused on the chemistry, hydration, and rheology of cementitious systems.

Anatol Zingg did his PhD at ETH Zurich (Dept. of Material Sciences) and Empa. His PhD project on cement-superplasticizer interactions was focussed on new methods in the field of cryo-SEM and on high-pressure freezing and financed by BASF SE, Ludwigshafen, Germany. Now at Holcim Group Support Ltd., Holderbank, Switzerland, he is in charge of product innovations in the field of cement – admixture interactions.

Lorenz Holzer is a senior researcher, formerly at Empa’s Concrete/Construction Chemistry Laboratory, now at Empa’s High Performance Ceramics Laboratory. His research has been focused on 3D-microscopy, image analysis, pore structures and particles size distributions.

Joachim Pakusch is head of global R&D "Polymers for Construction" at BASF SE in Ludwigshafen/Germany.

Stefan Becker was responsible for the global product development of HRWRA within BASF’s Business Unit Functional Polymers. As a senior manager in BASF Future Business GmbH he is in charge of business development for medical device materials now.

INTRODUCTION

The use of superplasticizers improves the workability of mortar and concrete systems for demanding industrial applications. The addition of superplasticizers is aiming at two objectives: first, superplasticizers enable to control the flow properties, which are of major importance for the design of e.g. self-compacting concretes, and second, superplasticizers allow the reduction of the water to cement ratio without losing the workability in order to reach high concrete strength and durability.

Although the influence of PCE on cementitious systems has been extensively investigated (1-12), many questions remain unsolved concerning the influence of superplasticizers on the early microstructural development, the nucleation and growth of hydrate phases, the dissolution of clinker phases, the admixture adsorption behaviour and the interparticle forces. Due to the complexity of this multi-mineral system, the influence of superplasticizers has been increasingly investigated on simplified systems (pure clinker and hydrate phases) (13-17) and model suspensions (18,19). Those studies deliver important information about e.g. influence of superplasticizers on nucleation and growth of hydrate phases, adsorption of superplasticizer on specific phases and influence of superplasticizers on electrostatic and/or steric repulsive forces. However, the possibility of simplification is limited if one wants to obtain relevant results, because of the complex chemical processes involved in cement suspensions.

In terms of rheology, the interparticle forces play a decisive role (2,19-21). Those forces govern the behaviour of two approaching particles whether the particles attract or repel each other. A key role plays the zeta potential which gives the electrostatic potential at the surface, where the particle is separated from the surrounding solvent. Particles with opposite or low zeta potentials attract each other and tend to form agglomerates. Depending on their architecture and dosage, superplasticizers can have a strong influence on the workability properties of fresh cement pastes. Adsorbed molecules on the particle surface modify the zeta potential, strengthening the electrostatic potential or evoking steric repulsion. Both effects hinder the particles to agglomerate and thus, result in lower viscosities.

Long range particulate structures of dispersed and agglomerated systems are closely associated with interparticle forces between the different mineral particles (22-24). Most of the microstructural investigations of cement suspensions at early hydration times have been carried out on filter residues or in-situ experiments in an ESEM (25,26), wet cell (e.g. Quantomix WETSEM cell) (27) or on plunge frozen samples (28). However, none of the methods used enables the investigation of original particulate structures in cement suspensions. Recently, the advantage of high-pressure freezing of fresh cement pastes combined with the use of advanced cryo-microscopy has been described in several studies (29-31). On one hand, cryo-preparation allows preserving the original particle arrangement of long
range structures and on the other hand, cryo-SEM enables to gain high resolution images of very fine structures and cryo-FIB (Focused Ion Beam) nanotomography enables even the quantification of particle size distributions.

In this study, a laboratory made fine cement and its interaction with different PCEs is characterized concerning the workability of the suspensions by PCE adsorption analysis, rheology and zeta potential measurements. Calorimetric data provides information about the delay of the main hydration period induced by the presence of PCE, whereas the hydration products are investigated by thermogravimetric and X-ray diffraction analyses. Suspensions of pure phases (ettringite, C₃S, C-S-H) are examined by means of rheology, PCE adsorption isotherms and zeta potential. The study of specific defined phases aims to improve the understandings about the influence of PCE on the microstructural evolution of cement suspensions during the early hydration and its link to macroscopic data like rheology or setting behaviour. Cryo-microscopic data from high-pressure frozen cement suspensions are presented in order to illustrate the link between the findings of interparticle behaviour of C₃S, C-S-H and ettringite phase with specific microstructural phenomena.

This paper sums up the findings from several previous studies (9,12,17,29-32).

**MATERIALS**

**Portland cement**

In order to obtain representative microstructural analyses of cement suspensions with cryo-FIB, it is important to decrease the particle size of cement. Therefore, a fine cement was produced by grinding a normal Portland cement CEM I 42.5 N with a laboratory rotating disc mill (Siebtechnik GmbH, Germany) to a medium diameter d₅₀ of 9 µm (d₁₀=0.6 µm and d₉₀=37.6 µm). To avoid undersulfatisation, gypsum was added to a total SO₃ wt.-% of 3.9. The chemical analysis of the laboratory cement is given in table 1. The fine cement exhibits a specific density of 3.07 g/cm³ and a specific surface area (Blaine method according to EN 196-6) of 5640 cm²/g.

**Pure phases**

C₃S was purchased commercially. Ettringite and C-S-H were synthesized. Prior to the synthesis analytical grade Ca(OH)₂ (Fluka) was burned at 1000°C for 12 hours to CaO and then ground below < 63 µm.

Ettringite was obtained by precipitation from solutions containing stoichiometric contents of CaO and Al₂(SO₄)₃·16H₂O (Fluka) in excess of deionized water. After 14 days, the precipitate was filtered, dried at 37°C and afterwards ground below 45 microns. XRD and TGA analysis confirmed the product to be ettringite.

C-S-H with a molar ratio Ca/Si = 1.3 was obtained by precipitation from solutions containing stoichiometric contents of CaO and SiO₂ (Aerosil 200, Degussa) in excess of deionized water. After 21 days, the precipitate was filtered and dried at 40°C. Afterwards the C-S-H was ground below 45 microns. XRD and TGA analysis proofed the precipitated material to be C-S-H.

**Superplasticizers**

For this study, three comb-shaped polycaboxylate-type superplasticizers (PCE) were synthesized. Methylpoly-ethyleneglycole copolymers (side chains) were grafted on a methacrylic acid copolymer (backbone). The polymer architecture is varied by using different side chain densities and lengths. The chemical structure is shown in fig. 1. All dosages given in this paper refer to the solid content.
EXPERIMENTAL

Rheology

The cement suspensions were prepared by blending the fine cement with water (water/cement 0.35) with and without added superplasticizer by hand for two minutes. The pure phases were mixed with synthetic pore solution (K: 444 mmol/l, Na: 40 mmol/l, Ca: 10 mmol/l, OH: 104 mmol/l, SO\(_4\)\(^2-\): 200 mmol/l) with and without superplasticizer. For the various materials, different water/solid ratios had to be applied in order to obtain a workable paste (ettringite = 1.3, C\(_3\)S = 0.4, C-S-H = 0.95).

For the rheology experiments, a Paar Physica MCR 300 rheometer was used. For the fine cement pastes a cylindrical geometry was applied. The rotating bob was serrated with 0.1 mm deep vertical lines. The gap between the rotating bob and the cylindrical beaker was 1.13 mm with a ratio between outer and inner cylinder radius of 1.08. For the pastes made from the pure phases, a plate-plate geometry was used. The rotating plate exhibited a rough surface (100 µm). The gap between the plates was 1 mm. The temperature was controlled by a water bath and kept at 20°C. A solvent trap protected the sample from water evaporation. The measurements were taken 10 minutes after blending, performing 1 minute pre-shearing at a shear rate of 100 s\(^{-1}\). Afterwards, a flow curve with shear rates between 100 and 0.1 s\(^{-1}\) was recorded. Apparent yield stress and plastic viscosity were calculated using the Bingham model.

Admixture adsorption isotherms

To determine the PCE adsorption isotherms, the same sample preparation procedure as for the rheology samples was used. 10 minutes after mixing, the liquid phase was removed through a 0.45 µm Nylon filter by air pressure filtration and was stabilized by adding 9 ml of 0.01 mol/l HCl. The total organic content (TOC) of the samples was determined by a Sievers 5310 C apparatus (pure phases) or a Shimadzu TOC-Analyzer 5000A (fine cement). The consumed amount of PCE was calculated from reference measurements of aqueous polymer solutions.

Zeta potential

The investigations were carried out using the ZetaProbe (Colloidal Dynamics Inc.), which works on the basis of the electroacoustic method. Prior the sample measurements, pH-meter (4.01, 7.01 and 10.01) and flow-through measurement cell (KSiW-standard, provided by Colloidal Dynamics Inc.) were calibrated. The titration unit was washed prior to the use with the titrant to insure its purity. All samples were stirred and pumped constantly in order to prevent segregation.

For the investigation of the impact of PCE on the zeta potential of the fine cement paste (water/cement ratio 0.5), concentration series with constant titration increments of diluted PCE solutions were measured. Note, that this experimental setup measures the impact of delayed PCE addition, whereas in the other techniques the PCE was added into the mixing water. In a preliminary test series, the fine cement paste used for this study was found to yield a stable zeta potential after 15 minutes of hydration.

For the pure phases, PCE titration experiments were carried out on suspensions with solid volume fractions around 2% and with synthetic pore solution as solvent. The PCE concentrations ranged from 0.01 to 0.20 wt.-% with titration increments of 0.01 wt.-%.

The zeta potential is highly sensitive to the chemical composition of the solution such as ionic species, pH and conductivity. Solutions with high ionic concentrations evoke strong background signals which can not be neglected. Consequently, background measurements were carried out for the different solutions. Subsequent to each experiment, the zeta potentials were recalculated with the corresponding background files.

Conduction calorimetry

The heat evolution during early hydration of the fine cement was measured using an isothermal heat flow calorimeter (Thermometric TAM Air) at a constant temperature of 20°C. All samples consisted of 6 g of cement and 2.1 g of
deionised water (water/cement ratio of 0.35) and were mixed outside the calorimeter for 2 minutes with a small stirrer. The PCE was added to the mixing water prior the addition to the cement. The flask with the cement suspension was then capped and placed into the calorimeter. The heat flow was recorded for 48 hours.

Hydration studies by thermal analysis and X-ray diffraction

The hydration kinetics of the fine cement with and without addition of PCE was examined by thermal analysis and X-ray diffraction analysis. The samples with water/cement ratio of 0.35 were mixed like in the rheology experiments and stored in sealed containers at 20°C. The hydration was stopped after several hydration times between 6 and 24 hours, respectively, by submerging the cement suspension in acetone. The stopped samples were dried at 40°C for three days and then ground to < 63 µm.

Thermogravimetric analysis (Mettler-Toledo TGA/SDTA 851) was carried out under nitrogen atmosphere at heat rates of 20°C/minute up to 980°C. The weight fractions of ettringite (~80°C) and portlandite (~440°C) were estimated from the weight losses at the characteristic temperatures. X-ray diffraction analyses (XRD) were performed using a Panalytical X’Pert Pro powder diffractometer equipped with an X’Celerator detector in a 2θ-range of 5-80°.

Cryo-microscopy

All suspensions of the fine cement exhibited a water/cement ratio of 0.5 and were mixed by hand for 2 minutes. PCE solution was premixed with the water prior to the addition of the cement. During hydration, the samples were kept stored in 100% relative humidity conditions in order to avoid drying. All hydration times (5 minutes to 2.5 hours) were within the dormant period. The cement suspensions were filled into small brass specimen carriers for subsequent cryo-fixation.

The hydration of the cement suspensions was stopped by high-pressure freezing with a HPF 010 (Bal-Tec Inc.). In contrast to other cryo-methods such as e. g. plunge freezing, the freezing under 2 kbar pressure (33,34) allows to preserve the original long range particle structures, which is important for investigations on the spatial distribution of clinker and hydrate particles in the suspension. The complete sample preparation procedure is described in (29-31).

For the investigations by cryo-SEM (scanning electron microscope) the high-pressure frozen samples were fractured and coated in a BAF 060 (Bal-Tec Inc.) and then transferred into a HR-FEG Leo 1530 Gemini (Carl Zeiss SMT AG). For the investigations on cryo-FIB cross-sections, the high-pressure frozen samples were fractured and transferred to the chamber of a Strata FEI dual-beam FIB (contains separate ion and electron beam).

RESULTS

Macroscopic properties of fine cement suspensions and impact of PCE molecular architecture

Fig. 2 shows the influence of the different PCE superplasticizers on apparent yield stress and plastic viscosity of the fine cement pastes. PCE 102-2 (low charge density) does hardly affect apparent yield stress and plastic viscosity, whereas PCE 23-6 and PCE 102-6 (both PCEs exhibit higher charge densities) show a good and similar ability to lower yield stress and viscosity of the cement pastes. The slight increase of the viscosity in the case of PCE 102-6 at a dosage of 0.1 weight-% of cement is probably due to different influence on the initial hydration compared to PCE 23-6.

The poor performance of PCE 102-2 can be explained by its adsorption behaviour (fig. 3). It does hardly adsorb and thus has no strong influence on apparent yield stress and plastic viscosity. In contrary, the PCE 23-6 and PCE 102-6 have not reached the saturation point at an admixture dosage of 0.4 weight-%. The poor adsorption of PCE 102-2 is due to its low charge density compared to the other superplasticizers, and that the accessibility of the carboxyl-groups for a PCE with high side chain density is hindered.
The zeta potential (fig. 3) of the plain cement paste is around -4 mV. The titration of the cement paste with the higher charged PCE 23-6 and PCE 102-6 leads to a zeta potential shift towards zero charge. Saturation concentrations are reached at about 0.2 wt.-% referred to cement. This shift of zeta potential towards zero is in agreement with (35), where very long side chained PCE’s are proved to change the negative even into positive zeta potentials. In contrast, PCE 102-2 with lower charge density reaches saturation only above about 0.5 wt.-% referred to cement. However, according to the adsorption data, the molecules do hardly adsorb and thus, the adsorption data are in contrast to the zeta potential data. Two mechanisms could explain the data: i) weak adsorption of the molecules (such as London forces, ion (particle surface) – dipole (PCE) bonds) on cement and hydrate particles, measurable with the ZetaProbe, but too weak to resist filtration-methods and ii) strong influence of the PCE on the structural properties of the pore water (viscosity, surface tension, cluster structure).

The fluidizing effect of PCE may be associated with undesired retardation of the hydration and associated delayed setting times. In fig. 4 the heat evolutions of the plain fine cement paste and the pastes containing 0.4 weight-% of PCE 23-6, PCE 102-2 and PCE 102-6 respectively are shown. The presence of PCE delays the onset of the acceleration period between 2 hours (PCE 102-2) and 4 hours (PCE 23-6). Decreasing side chain density (PCE 102-6 < PCE 102-2) and shorter side chains (PCE 23-6 < PCE 102-6) prolong the setting times, whereas the latter effect is more pronounced. The presence of highly charged PCE (23-6 and 102-6) does not only shift the main hydration peak of the fine cement pastes, but also changes the peak shape. The peaks are the sum of simultaneous ongoing hydration processes of different clinker phases and thus, interpretations of peak shape and its changes in presence of PCE are difficult. Generally it is assumed, that PCE molecules preferably adsorb on C\textsubscript{3}A, C\textsubscript{4}AF and their hydration products. However, they mainly retard C\textsubscript{3}S hydration (9,36,37), thus delaying the formation of C-S-H and portlandite.

These findings are supported by TGA (figs. 5, 6) and XRD (results not shown). The formation of portlandite has already started in the plain cement suspension after 6 hours, whereas in the cement suspension containing PCE, no (PCE 23-6) or only little (PCE 102-6, PCE 102-2) portlandite is formed at this time. In spite of delayed portlandite formation, the hydrate phase assemblages of cement suspensions containing PCE do not significantly differ from the plain cement suspension in their amounts of portlandite at a sample age of 24 hours, except for the cement suspension with PCE 23-6, which shows the strongest retardation effect among the PCEs applied.

In contrast, no delay of ettringite formation nor significant differences in the amount of ettringite precipitated are observed when the plain cement paste is compared with those containing PCE.

The results obtained from the laboratory made fine cement are in good agreement with previous investigations using the same or similar polymers in suspensions of various commercial normal Portland cements (8,9,12). Thus, it has been proven that the laboratory made fine cement behaves comparable to industrial products, which is of relevance concerning the cryo-experiments described below.

Interaction of pure phases with superplasticizer

The plastic viscosities of C-S-H (solution/C\textsubscript{3}S wt.-ratio = 0.95) and ettringite (solution/ettringite wt.-ratio = 1.3) suspensions are shown in fig. 7. Data obtained from C\textsubscript{3}S (solution/C\textsubscript{3}S wt.-ratio = 0.4) is given in (17). For all three phases, the addition of PCE 102-2 with high side chain density and length shows only low impacts on the plastic viscosity, whereas PCE 23-6 and PCE 102-6 very efficiently fluidize the suspensions. At higher PCE concentrations of these PCEs (0.3 weight-% referred to solid), the viscosities of the ettringite suspensions are below 0.1 Pa\textperiodcentered s. This is not the case for the C-S-H phase, where at higher PCE concentrations (0.3 weight-% referred to solid) the viscosity remains at 0.5 Pa\textperiodcentered s. However, the viscosities of the different solids in suspension are not directly comparable to each other because of the different experimental set-ups (i. e. different water/solid ratio).

Adsorption isotherms of PCE on C-S-H and ettringite are shown in fig. 9. It can be observed, that the PCE 102-2 with high side chain density and length does hardly adsorb on any of the phases (fig. 6, top right). The higher charged PCE 23-6 and PCE 102-6 show comparable adsorption isotherms. Thus, the PCE molecules with similar side chain to backbone ratio but different side chain length do not exhibit significantly different adsorption behaviour. However, there is a significant difference of PCE adsorption ability between the silicate and the aluminate phases. The ettringite phase shows high adsorption ability for PCE 23-6 or PCE 102-6 molecules, the saturation
point has not been reached at a PCE addition of 0.4 weight-% referred to the solid. In contrary, C-S-H shows saturation concentration at 0.1 wt.-%. C<sub>3</sub>S shows a similar behaviour like C-S-H (17).

In synthetic pore solution, the zeta potential of ettringite (fig. 8) is about -12 mV. However, in 0.1 M KOH, it is found that the zeta potential of ettringite is slightly positive (17). Thus, it can be concluded that the presence of SO<sub>4</sub><sup>2-</sup> ions (originating from the synthetic pore solution) leads to a charge inversion of the ettringite phase. The zeta potential shifts towards -4 to -2 mV with increasing PCE concentration. The influence of PCE molecules on the zeta potential of ettringite shows only minor dependency of the PCE architecture – all PCE types reached their saturation concentrations around 1 wt.-% PCE referred to the solid material. This is in contrast to the adsorption data, where PCE 102-2 does hardly adsorb. The plain C-S-H suspension exhibits a slightly positive zeta potential of 2 mV in synthetic pore solution. The zeta potential of C-S-H in synthetic pore solution is not significantly influenced by the addition of PCEs. With increasing PCE concentration, the zeta potential of the suspension remains constant and positive.

A comparison of the data from the pure phases with those obtained from the fine cement reveal that the zeta potential and the rheology of bulk cement suspensions are dominated by ettringite.

**Cryo-microscopy of cement suspensions**

Cryo-FIB enables the investigation of well-defined cross-sections, because the exposed microstructure is not biased by selective fracturing along zones of weaknesses. Hence, cryo-FIB delivers a more representative microstructural insight compared to high resolution cryo-SEM or ESEM investigations. Cryo-FIB cross sections can be a basis for estimations of volume fractions from different grain-populations. In fig. 10 spatial distribution of large unhydrated clinker particles and small hydration phases are demonstrated for two different samples: a non-dispersed (without PCE) and a well dispersed (with PCE 23-6) cement paste.

In the non-dispersed cement paste (hydrated for 24 minutes), two populations of particles can be distinguished (fig. 10 left), based on size, shape and grey-scale: the population with larger particles (size of 2-5 microns) consists of mostly bright-grey, polygonal shaped grains. These are interpreted as mostly unhydrated clinker grains. The population with the smaller particles (<500 nm) appears in a slightly darker grey level and can be interpreted as early hydration products. The small particles are not dispersed in the interstitial space (as in fig. 10 right), but they are attached to the surface of the unhydrated clinker particles. The density of attached particles varies. Locally they can form very dense layers, where single particles can hardly be distinguished. In other places they form very loose formations, where individual prismatic particles can be identified. The larger clinker particles either show clean boundaries or a dark, irregularly shaped rim, whereas the large clinker particles are randomly distributed and the small particles at (sub-) µm-range are flocculated. Thus, agglomerates consisting of the smaller particles form bridges between the neighbouring clinker particles. The size of the agglomerates is typically between 1-3 microns.

In well dispersed cement pastes (fig. 10 right, hydrated for 6 min) the interstitial pore space between the larger clinker particles contains well dispersed crystals that are typically smaller than 500 nm. Those small crystals are very numerous and almost evenly sized. In contrast to the non-dispersed system (compare fig. 10 left), the clinker particles in the dispersed system show clean boundaries, almost without any hydration rims. Only few small particles are attached to the boundaries of the larger particles. Since the small particles do not form agglomerates, the flocculation of the larger particles has not yet started. The small particles in the interstitial pore space correspond to the fraction of submicron particles. The small particles in the interstitial pore space are interpreted as fresh precipitates that have formed within the first 6 minutes.

Based on high resolution cryo-SEM, important morphological details can be observed which are relevant for the interpretation of the smaller particle population that was previously described as hydration products based on cryo-FIB cross-sections (see fig. 10). This additional information is illustrated for the dispersed and the undispersed system, hydrated for 6 minutes and 24 min, respectively, in fig. 11.

Besides the large, fractured clinker particle and the vitrified pore solution of the system with PCE (fig. 11 left), two different types of hydration products can be distinguished as displayed in the close-up image of these hydrates (fig
The euhedral crystals are hexagonal and short-prismatic and typically have a length of 100 to 500 nm. The thickness of these crystals is variable. Based on their morphology, these crystals can be identified as ettringite. The second population of hydration products consists of finer and fibrous minerals (possibly C-S-H), which are agglomerated and partially intergrown with ettringite crystals. At higher magnification (fig. 11 top right) it can be observed, that the smaller, fibrous crystals are covering an assemblage with numerous larger ettringite crystals. The small fibrous crystals have a thickness of 20-40 nm and they are randomly oriented and distributed on the surface of the larger ettringite. In the case of the PCE containing samples, the surface of the clinker grain appears mostly free of hydration products, whereas when no PCE is added, the clinker surface is covered by ettringite and C-S-H (fig. 11 bottom right). This observation agrees very well with the findings from the cryo-FIB experiments (fig. 10).

**DISCUSSION**

The polycarboxylate-ether (PCE) adsorption and rheology measurements combined with heat evolution analysis of cement suspensions demonstrate that PCE architectures like PCE 102-6 with low side chain densities (enhanced workability) combined with long side chains (less undesired retardation effects) are favoured for applications where an enhanced superplasticizer especially for a precast concrete application is needed. Low side chain density is correlated with high anionic charges which lead to strong adsorption of the molecules on clinker surfaces. The polyethylene-oxide side chains evoke steric forces and prevent the formation of agglomerates.

The presence of adsorptive PCE greatly affects the rheological properties of cement suspensions. Rheological properties such as e.g. viscosity and yield stress are closely associated with the particulate structures of cement suspensions. Investigations on this relationship urges for non-destructive sample preparation. In this study the high-pressure freezing technique is successfully modified from life sciences. This freezing technique enables the preservation of long range microstructures by vitrification of the aqueous phase. Additionally, the FIB nanotomography (focused ion beam) method is modified for cryo experiments on high-pressure frozen cement suspensions. Cryo-FIB investigations illustrate the differences of a non-dispersed cement suspension and a well dispersed cement suspension containing PCE. Without PCE, agglomerates (1-3 µm) consisting of small particles are formed immediately after initial hydration, and the interstitial pore space (frozen aqueous phase) remains free of submicron particles. In presence of PCE, ettringite is well dispersed in the interstitial pore space.

However, cryo-FIB is not sensitive enough to resolve very fine structures below 100 nm. Therefore, high resolution cryo-SEM is applied. It enables to investigate these individual crystals, particle surfaces, morphologies of hydration layers and small agglomerates on a qualitative level. It is found that the small agglomerates mainly consist of ettringite with intergrown C-S-H needles. In addition, the colloidal phase in the interstitial pore space may play an important role concerning nucleation of hydrates. After two hours of hydration, numerous nuclei are embedded in a complex mixture of C-S-H gel and PCE network structure which pervades the interstitial pore space. Those nuclei and other embedded particles are immobilized by the C-S-H gel and PCE network structure.

The interfaces between clinker particles and hydrate phases are of major importance concerning the dispersion mechanisms during early hydration. High resolution cryo-SEM reveals that C-S-H needles may act as glue between ettringite crystals and lead to the formation of small agglomerates. The zeta potentials of the silicate phases (tricalciumsilicate, calcium silicate hydrate) are slightly positive, whereas the zeta potential of the aluminate phase (ettringite) is negative. These opposite potentials lead to attraction between C₃S and ettringite, C-S-H and ettringite particles which could be confirmed by cryo-microscopic analysis. It is observed that the ettringite crystals tend to cover the clinker surfaces. In presence of PCE, the zeta potential of ettringite is reduced whereas the zeta potentials of C₃S and C-S-H remain constant. However, the experiments on single phase suspensions do not show only PCE adsorption but also decreased viscosities for all three phases. Thus it is hypothesized that the anionic PCE molecules adsorb at the positive charged shear plane and/or Stern layer of C₃S and C-S-H particles and consequently, can not be detected by zeta potential measurements. In contrast, the zeta potential of ettringite is influenced by the PCE adsorption on the positive charged ettringite surface. Independently on the type of PCE adsorption, the steric forces induced by the polyethylene-oxide side chains of the PCEs hinder the particles to agglomerate. Consequently, dis-
persed ettringite is floating as individual crystals in the interstitial pore solution as demonstrated by cryo-FIB experiments.

CONCLUSION

The comparison of the zeta potentials of ettringite and plain cement suspensions reveals that ettringite is the dominating mineral phase with respect to that property. In cement suspensions without PCE, ettringite is coating the clinker particles and thus, strongly influences surface properties of the larger clinker particles. In presence of PCE, the ettringite is mainly present in the aqueous phase between the clinker particles. It represents to control a large part of the surface area which again dominates the zeta potential and thus the rheology of the cement suspension.

These results underline that the ettringite phase and its dispersion in the fresh cement paste is acting as the major key mineral concerning workability issues for Portland cement applications.

REFERENCES


Table 1 — Chemical composition of the laboratory made fine cement

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<th>CaO wt.-%</th>
<th>MgO wt.-%</th>
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Table 2 — Characterization of the polycarboxylate ether superplasticizers

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<th>Mₘ₂</th>
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<td>78000</td>
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<td>46.3</td>
<td>4.2x10⁻⁴</td>
</tr>
<tr>
<td>PCE 102-6</td>
<td>102</td>
<td>6:1</td>
<td>14600</td>
<td>67000</td>
<td>4.6</td>
<td>21.0</td>
<td>1.1x10⁻³</td>
</tr>
</tbody>
</table>

¹ Mₙ = number-average molecular weight  
² Mₘ = mass-average molecular weight  
³ PDI = Mₙ/Mₘ = polydispersity index  
⁴ calculated values, corresponds also to minimum mmol/l Na which is added to the solid-solvent system by titration, direct addition

Figure 1 — Chemical structure of the superplasticizers used; back bone unit (n) to side chain unit (m) 2:1, 6:1 and number of PEO units (p) in the side chains of 23 and 102.
Figure 2 — Apparent yield stress (left) and plastic viscosity (right) of dispersed fine cement suspensions as function of PCE concentration.

Figure 3 — Adsorption isotherm of PCE on fine cement (top) and influence of PCE concentration on the zeta potential of fine cement (below).
Figure 4 — Evolution of the heat of hydration of plain fine cement paste and fine cement pastes with 0.4 wt.-% PCE

Figure 5 — Thermogravimetric data (derivative weight change) of fine cement pastes hydrated for 6 hours (note that offsets of 0.03 %/K of the differential derivative weight were in the graph)
Figure 6 — Ettringite (left) and portlandite (right) contents in the fine cement pastes at various hydration times between 15 min and 24 hours.

Figure 7 — Plastic viscosity of ettringite (left) and C-S-H (right) suspensions with different PCE additions.
Figure 9 — Adsorption isotherms of PCE on ettringite (left) and C-S-H (right)

Figure 8 — Influence of PCE on the zeta potential of ettringite (left) and C-S-H (right) suspensions
Figure 10 — Cryo-FIB cross-sections of fine cement suspension hydrated without addition of PCE (left) and of fine cement suspension hydrated with addition of 0.2 wt.-% PCE 23-6.

Figure 11 — Cryo-SEM images of fine cement suspension hydrated with addition of PCE (left, top right) and of fine cement suspension hydrated without addition of PCE (bottom right), circles: ettringite crystals.