CEMENT – SUPERPLASTICIZER INTERACTION:
LINK BETWEEN MACROSCOPIC PHENOMENA
AND MICROSTRUCTURAL DATA OF THE
EARLY CEMENT HYDRATION.

Anatol Zingg

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Cement-superplasticizer interaction: link between macroscopic phenomena and microstructural data of the early cement hydration.

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Anatol Zingg
Dipl. Natw. ETH

born July 1, 1976
citizen of Rapperswil, BE (Switzerland)

accepted on the recommendation of

Prof. Dr. L. Gauckler, examiner
Prof. Dr. H. van Damme, co-examiner
Dr. F. Winnefeld, co-examiner
Dr. L. Holzer, co-examiner

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This thesis is dedicated to my parents

Lore Zingg-Dubach and Hans Jürg Zingg

for their love and patience,
encouragement and support
throughout my life.
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Abstract

Superplasticizers are commonly used for industrial high performance concrete applications such as self compacting concrete, high strength concrete and prefabricated concrete elements. They are added in order to control the workability of concretes, mortars and cement suspensions. Enhanced workability properties are associated with undesired delay of hardening.

This study aims to investigate the influence of a polycarboxylate-ether based superplasticizer (PCE) with different architectures on the rheological properties of cement suspensions. Thereby, a special emphasize is used on the investigation of the microstructures in the cement suspension.

The thesis contains three main foci:

i) Investigation of various PCE architectures on the workability properties of cement suspensions.

ii) Application of a non-destructive sample preparation technique for (cement) suspensions, qualitative and quantitative microscopic characterization of particulate structures in cement suspensions.

iii) Experiments on the interaction of pure mineral phases of cementitious materials with PCEs with different architecture.

The study on the PCE influence on plain cement suspensions shows that in terms of workability, the charge density of the PCE is of major importance. In general, higher charged PCE has a stronger adsorption ability and results in enhanced workability properties. However, the stronger the PCE-cement interaction, the stronger is the setting and hardening of cement suspensions delayed. This delay is an undesired side effect, which can induce serious problems on a construction site. Thus, for an optimization of the PCE architecture, both effects, fluidization and retardation have to be taken into account.

Enhanced workability and associated rheological properties are closely related to the microstructural evolution of cement suspensions. However, due to the lack of suitable sample preparation, microscopic investigations on long range particle structures were not possible up to date. Therefore, in this study a major aim has been the modification of cryo sample preparation from life sciences to cement suspensions. High-pressure freezing as used in this study enables the preservation of long range particle arrangements in cement suspensions. Additionally, the FIB nanotomography (focused ion beam) has been modified for cryo-experiments. The successfully implemented cryo-fixation and cryo-FIB enables qualitative descriptions of microstructural phenomena and their quantification.

Cryo-FIB cross sections illustrate the microstructural difference of a non-dispersed and a dispersed cement suspension containing PCE for the first time. Furthermore, this study demonstrates that in plain cement suspensions the hydrate phases tend to deposit on clinker surfaces, whereas in presence of PCE the hydrate particles remain dispersed in the pore solution. Additionally, high resolution cryo-SEM images enables to investigate
microstructural features below 100 nm such as e.g. early C-S-H crystals and diffuse structures such as C-S-H gels and PCE networks.

However, the cement-water system is very complex. For the development of new generations of superplasticizers, it is important to understand the mechanism of interaction between superplasticizer molecules and the major mineral components in cement suspensions. Therefore, tricalciumsilicate, calcium silicate hydrate and ettringite has been synthesized and their PCE adsorption ability, rheological behaviour and change of zeta potentials in presence of PCE has been recorded in an synthetic pore solution environment (as preset in real cement pore solutions). This study demonstrates that the ettringite is the major mineral phase which strongly controls the overall surface properties and associated particle interactions and thus also the workability of cement suspensions. The production of ettringite during early hydration is governed by the tricalciumaluminate content and the availability of sulfate.

This thesis shows the importance of the link between macroscopic data and the microstructural development of cement suspensions in order to get a more complete picture about the mechanisms of PCE-cement interaction. Furthermore, the thesis points out the importance of high-pressure freezing and the power of cryo-microscopy concerning qualitative and quantitative descriptions of particulate structures. The latter is just about to commence.
Zusammenfassung


Im Fokus dieser Arbeit sind folgende Themen:

i) Auswirkung verschiedener PCE Architekturen auf die Eigenschaften der Verarbeitbarkeit von Zementsuspensionen bezüglich des Adsorptionsverhaltens von PCE, Einfluss auf die interpartikularen Kräfte und die rheologischen Eigenschaften.

ii) Applizieren einer zerstörungsfreien Probenpräparation von Suspensionen für elektronenmikroskopische Untersuchungen.

iii) Einfluss verschiedener PCE Architekturen und Dosierungen auf vereinfachte Zweiphasensysteme (eine synthetisierte Zementmineralphase in synthetischer Porenlösung).

Diese Studie zeigt, dass sich mit steigender Ladungsdichte des PCEs auch die Fließeigenschaft verbessert da die Moleküle besser adsorbieren. Jedoch ist mit höherer Ladungsdichte auch eine sehr starke Verzögerung des Erhärtens messbar. Für die Optimierung von Fliessmitteln, müssen sowohl die Verflüssigung als auch die Verzögerung berücksichtigt werden.


Mit Hilfe des Kryo-FIB an hochdruckgekühlten Zementsuspensionen wird gezeigt, dass in Proben ohne Fliessmittel, die Partikel verstärkt zur Bildung von Agglomeraten tendieren. Im Weiteren kann beobachtet werden, dass sich die Ettringite bevorzugt an Oberflächen von Klinkerpartikeln anlagern. Im Gegensatz dazu führt die Zugabe von Fliessmittel zu einer

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# Nomenclature and abbreviations

## Cement nomenclature

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<th>oxides</th>
<th>CaO</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>SO$_3$</th>
<th>K$_2$O</th>
<th>Na$_2$O</th>
<th>MgO</th>
<th>H$_2$O</th>
<th>CO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>cement notation</td>
<td>C</td>
<td>S</td>
<td>A</td>
<td>F</td>
<td>s</td>
<td>K</td>
<td>N</td>
<td>M</td>
<td>H</td>
<td>c</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>mineral name</th>
<th>chemical formula</th>
<th>cement notation</th>
</tr>
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<tbody>
<tr>
<td>calcite</td>
<td>CaCO$_3$</td>
<td>Cc</td>
</tr>
<tr>
<td>calcium silicate hydrate</td>
<td>CaO$_4$(SiO$_2$)$_y$ • zH$_2$O</td>
<td>C-S-H</td>
</tr>
<tr>
<td>dicalcium silicate (belite)</td>
<td>Ca$_2$SiO$_4$</td>
<td>C$_2$S</td>
</tr>
<tr>
<td>ettringite</td>
<td>Ca$_6$Al$_2$(SO$_4$)$<em>3$(OH)$</em>{12}$ • 26H$_2$O</td>
<td>C$_6$As$<em>3$H$</em>{32}$</td>
</tr>
<tr>
<td>gypsum</td>
<td>CaSO$_4$ • 2H$_2$O</td>
<td>CsH$_2$</td>
</tr>
<tr>
<td>monosulfate</td>
<td>Ca$_4$Al$_2$(SO$<em>4$)(OH)$</em>{12}$ • 6H$_2$O</td>
<td>C$<em>4$AsH$</em>{12}$</td>
</tr>
<tr>
<td>portlandite</td>
<td>Ca(OH)$_2$</td>
<td>CH</td>
</tr>
<tr>
<td>tetracalciumaluminateferrite</td>
<td>Ca$_4$Al$_2$Fe$<em>2$O$</em>{10}$</td>
<td>C$_4$AF</td>
</tr>
<tr>
<td>tricalciumaluminate</td>
<td>Ca$_3$Al$_2$O$_6$</td>
<td>C$_3$A</td>
</tr>
<tr>
<td>tricalciumsilicate (alite)</td>
<td>Ca$_3$SiO$_5$</td>
<td>C$_3$S</td>
</tr>
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</table>
### Most important abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E)SEM</td>
<td>(Environmental) Scanning Electron Microscope</td>
</tr>
<tr>
<td>(P)NS</td>
<td>(Poly-)Naphthalene-Sulphonate</td>
</tr>
<tr>
<td>BAF</td>
<td>fracturing, etching and coating apparatus (BAL-TEC)</td>
</tr>
<tr>
<td>BSE</td>
<td>BackScattered Electron (image)</td>
</tr>
<tr>
<td>DTA</td>
<td>Differential Thermal Analysis</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive X-ray analysis</td>
</tr>
<tr>
<td>FEG</td>
<td>Field Emission Gun</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused Ion Beam</td>
</tr>
<tr>
<td>HPM</td>
<td>High-Pressure freezing Machine</td>
</tr>
<tr>
<td>LEO</td>
<td>Zeiss Leo Gemini 1530</td>
</tr>
<tr>
<td>LG</td>
<td>LaserGranulometry</td>
</tr>
<tr>
<td>LS</td>
<td>Lignin-Sulphonate</td>
</tr>
<tr>
<td>OPC</td>
<td>Ordinary Portland Cement</td>
</tr>
<tr>
<td>PCE</td>
<td>PolyCarboxyl-Ether</td>
</tr>
<tr>
<td>PEO</td>
<td>PolyEthylene-Oxide</td>
</tr>
<tr>
<td>PSD</td>
<td>Particle Size Distribution</td>
</tr>
<tr>
<td>SCC</td>
<td>Self Compacting Concrete</td>
</tr>
<tr>
<td>SE</td>
<td>Secondary Electron (image)</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscope</td>
</tr>
<tr>
<td>TGA</td>
<td>ThermoGravimetric Analysis</td>
</tr>
<tr>
<td>TOC</td>
<td>Total Organic Compounds</td>
</tr>
<tr>
<td>w/c</td>
<td>water/cement (weight) ratio</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray powder Diffraction</td>
</tr>
<tr>
<td>XRF</td>
<td>X-Ray Fluorescence</td>
</tr>
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1 Introduction

Concrete is defined as a mixture of cement (µm), sand (mm), gravel (cm) and water, where the cement acts as the binding material. Therefore, cement properties and cement hydration behaviour are one of the major key factors which govern the properties of concrete systems. Special concretes for industrial applications such as for high performance concrete, ultra high performance concrete and self compacting concrete demand for specific technical design. Therefore, properties and time frame of the workability of cementitious materials are of major importance.

The addition of superplasticizers as an organic additive enhances the workability properties of cementitious materials. On one hand, superplasticizers act as fluidizing agents, but on the other hand, they can lead to strong undesired delay of cement setting. The time frame in which cementitious material can be processed (workability) as well as the onset time of setting and hardening are of major importance on a construction site. However, modern cementitious materials with superplasticizers represents very complex multiparameter systems which are sensitive to changes of their parameters such as for example water to cement ratio, chemical composition of the cements, architecture and concentration of superplasticizers.

The present study is focusing on the cement-superplasticizer interactions and the corresponding relationship between micro- and macroscopic phenomena.

1.1 Basics of cement hydration

1.1.1 Main clinker phases of ordinary Portland cements

The cement powder is a multimineral system and its chemical composition is strongly depending on the chemical composition of the raw meal, from which the clinker is sintered in a kiln at ~1450ºC. Beside this mineralogical variation, the sintering and the subsequent cooling process, the co-grinding of the clinker with calcium sulfates as set regulator and the use of grinding aids are also varying.

In general, there is a wide variation in the amount of the main clinker phases in ordinary Portland cements from different plants. The most important clinker phases and their range of weight fractions are mainly as follows [1]:

- Alite (tricalciumsilicate): 40-80%
- Belite (dicalciumsilicate): 2-30%
- Tricalciumaluminate: 3-15%
- Tetraalciumaluminateferrite: 4-15%
1.1.2 Hydration of cements

The term “hydration” includes all ongoing chemical and physical processes in the cement-water system. This includes e.g. dissolution of clinker phases, formation of hydrate phases and diffusion processes at later hydration times. The hydration of cementitious systems is strongly time dependent and can be divided in four major periods [2]:

i) initial hydration (minutes): mainly dissolution of aluminate-rich clinker phases (e.g. C_3A) and precipitation of calciumaluminate sulfate hydrates (e.g. ettringite, monosulfate)

ii) dormant period (up to 2-4 hours): the hydration reactions are slowed

iii) main hydration (up to 24-48 hours): accelerated dissolution of clinker phases, mainly tricalciumsilicate and increased precipitation of calcium silicate hydrates (C-S-H) and calciumhydroxides (portlandite) leads to hardening of the cement-water system

iv) continuous hydration (days to years): hardening and ageing of cementitious materials

In terms of workability, initial and dormant periods are of major importance. The beginning of the main hydration period determines the end of the workability. During early hydration, mainly aluminate-rich clinker phases and calcium sulfates dissolve and lead to formation of first hydrate phases. Between these initial reactions and the hydration of the onset of the main hydration period all processes are slower. Thus, the hydration process can be simplified and divided in two systems, first the hydrating aluminate system (e.g. C_3A, which has a strong influence on the workability and second, the hydrating silicate system (e.g. C_3S), which determines the end of workability and governs the final strength.

1.1.3 Aluminate system:

The hydration of aluminate-rich phases in systems with sufficient availability of sulfates leads to the formation of ettringite (C_6A_3S_3H_32) as shown in equation 1. If a sufficient amount of sulfate is not available, monosulfate (eq. 2) or calciumaluminate hydrates are formed instead of ettringite. Undersulfatisation leads to the undesired phenomenon of flash set (within minutes) and is usually compensated by the manufacturers by the addition of a calcium sulfate as set regulator (mostly mixtures of gypsum and anhydrite) during the grinding process.

\[
C_3A + 3(CsH_2) + 26H \rightarrow C_6A_3S_3H_{32} \quad (eq. 1)
\]

\[
C_3A + CsH_2 + 10H \rightarrow C_4AsH_{12} \quad (eq. 2)
\]
1.1.4 Silicate system:

The hydration of the calcium silicate phases leads to the formation of C-S-H and, due to lower Ca/Si ratio in C-S-H than in C₃S, portlandite is additionally formed (eq. 3).

\[ \text{C}_3\text{S} + (y+z)\text{H}_2 \rightarrow \text{C}_x\text{SH}_y + z\text{CH} \quad (\text{eq. 3}) \]

C-S-H is the main mineral phase of hardened cements and is responsible for the final strength.

1.2 Cement-superplasticizer interaction (state of the art)

Superplasticizers (SP) are used to improve the workability of cement suspensions. Newer generation products are mainly comb-shaped types of superplasticizers, providing enhanced fluidizing abilities. The superplasticizers are anionic polyelectrolytes with molecular weights between $10^3$-$10^5$ g/mol. However, they can lead to undesired delay of the main hydration [3-5] and the associated hardening of the cement suspensions. In addition, certain cement-superplasticizer combinations can cause incompatibilities [6-8] such as e.g. drastic slump loss or strong retardation.

In the present study, the interaction of superplasticizers with the relevant mineral phases of Portland cements will be investigated in order to improve our understandings of the associated mechanism. As a model one can think of three different superplasticizer reservoirs in the cement suspension. The molecules can either be adsorbed on clinker or hydrate surfaces, be intercalated by coprecipitation with early hydrate phases or remain dispersed in the solution (fig. 1).

![Fig. 1: Three reservoirs of superplasticizers in cement-water system: i) intercalation of SP, ii) adsorption of SP or iii) SP remaining in solution. (OMP = organomineral phase)](image-url)
1.2.1 Adsorbed superplasticizer molecules

The adsorption of SP molecules influences the electrostatic potential [9-19] of the particles in the cement suspension. The low zeta potentials (-3 to -7 mV) of ordinary Portland cement suspensions can be stabilized electrostatically by the addition of anionic polyelectrolytes. Although the addition of polycarboxylate-based SPs (PCE) shifts the zeta potential towards the IEP (isoelectric point) and thus, should lead to strong flocculation, the degree of dispersion of the cement suspensions with PCE is increased. This is due to steric forces, evoked by the polyethylene-oxide side chains of PCE. The influence of PCE on the rheology and PCE adsorption has been investigated extensively on ordinary Portland cement suspensions [20-28]. For comb-shaped SP a mushroom-like or conformation is suggested by [10], whereas [29] assumes a conformation with side chains protruding straight into the solution. However, independent on the conformation, the side chains induce steric repulsive forces.

The mechanisms of SP adsorption on pure clinker and hydrate phases as well as the SP influence on the retardation of the hydration process have been increasingly investigated in the last years. A study shows that e.g. the presence of PCE in the cement suspension lowers the hydration activation energies of the main clinker phase (C₃S) during the initial period whereas the at later hydration times, more energy is needed to activate the hydration (acceleration of main hydration) [30-32]. This findings would indicate, that the amounts of hydrates after initial period is higher in presence of SP, and the retardation results from the higher demand of energy for the main hydration.

1.2.2 Intercalation of superplasticizer molecules

Coprecipitation of SP molecules with hydrate phases is suggested as a possible sink for SP molecules [10]. Thus, the concentration of the SP which is able to adsorb and stabilize the suspension is reduced. It is assumed, that delayed addition (after initial hydration) prevents the formation of intercalates. The lower demand of SP in delayed addition mode compared to direct addition mode is suggested as possible explanation.

Intercalates have been studied by XRD, where the basal distance between layered double hydroxides (LDH) such as e.g. monosulfate is measured [33-35]. The intercalation on silicate-rich hydrate phases are discussed more controversially. Intercalation of SP in C-S-H has been found in C-S-H [36, 37], whereas in other studies [38, 39], no intercalation of SP have been found. Instead of intercalation within a single crystal, those studies have suggested that the superplasticizers are adsorbed on individual crystals which form layered assemblages of C-S-H.
1.2.3 Superplasticizer molecules remaining in the pore solution

The third reservoir is the pore solution. SP in the pore solution is thought to influence nucleation and growth of hydrate phases [8, 23, 40-42]. Furthermore, it is known that polycarboxylate-based superplasticizers (PCE) can be involved in Ca complexation [43-44]. However, the stability of these complexes is found to be quite low. A role may play intermediate hydrate phases, where the ionic sites of the PCE act as seeds for temporary formation of small hydrate crystals which may dissolve and reprecipitate as larger particles at later times [45].

In addition, superplasticizers influence not only the nucleation but also the growth and crystal shape of hydrate phases. Studies on C-S-H formation have shown that its type of nucleation, minimum number of atoms, growth and zeta potential are influenced by the chemistry of the solvent and the presence of SP [40-42, 46, 47].

Fig. 2: The fluidizing effect and the delay of setting is illustrated by the evolution of the viscosity of a cement suspension without (black) and with superplasticizer (red). The corresponding evolution of the microstructures is schematically illustrated in the lower part of the figure.
1.2.4 Influence of superplasticizers on the particulate structure in cement suspensions

Hydration permanently changes the microstructures of cement suspensions. The presence of SP enhances the workability and influences the associated microstructures. In terms of cement-water systems, the microstructures range over several length scales. Particle networks (long range particle structure) and their strength can be related to the yield stress of cement suspensions. Bridged agglomerates and particles are assumed to be the basis for network structures. Agglomerates consist of individual crystals. Crystal shape and the surface potentials are strongly related to interparticle forces and rheological phenomena.

Mechanisms of nucleation and growth as well as the different crystal shapes have been investigated also with microscopic tools. In the context with the workability, the shape and size of ettringite (among the first hydrate phases) in presence of SP has been described controversially. The ettringite shapes reported low degree of hydration (up to setting) range from short prismatic and nearly prismatic [8] to long prismatic and needle-like [48].

The formation of early hydrate phases (during the initial period) leads to changes in particle size distribution, specific surface area and number of particles per unit volume compared to the unhydrated cement powder. These microstructural parameters are changing with evolving hydration time. The changes in the particle size distribution have been found to be small with a tendency of larger particles being formed with evolving hydration [49] due to agglomeration.

Rheological properties (e.g. viscosity, yield stress) are closely associated with the interparticle forces of suspended materials. Superplasticizers show a strong impact on rheological properties, interparticle potentials (zeta potential) of cement suspensions and thus, inevitably lead to changes in their particulate structure. Although many microstructural studies have been carried out in the past in the context of cement-superplasticizers, no experimental data about long range particle structures of cement suspensions during early hydration is available. This is due to the lack of suitable, non-destructive sample preparation methods in terms of preservation of the original 3D particle structure of cement suspensions. In this work, the high-pressure freezing technique was modified from life sciences. This cryo-technique enables to preserve original particle arrangements. The basic principles are described in the following subchapter.

1.3 Principles of high-pressure freezing and modification for cement suspensions

Sample preparation by cryo-fixation of e.g. emulsions and biological for SEM analysis is well established in the life sciences. The aim of cryo-fixation is the preservation of original 3D microstructures by vitrifying the solvent. The simplest cryo-fixation method is the shock/plunge freezing where the sample is put into liquid nitrogen. For samples in aqueous solutions, the heat transfer in water and associated cooling rates are not sufficient to overcome the high heat capacity of water and to assure the preservation of the original microstructures. With simple plunge freezing, in most cases artefacts are produced by formation of large ice
crystals instead of vitrification and thus, related dislocation of nanoparticles. In special cases (e.g. life sciences), the aqueous phase can be substituted by solvents with low heat capacities. However, the latter can not be applied in the field of cement suspensions because on one hand, the aqueous pore solution is an important parameter of the cement-water (-admixture) system and on the other hand, substitution could hardly be performed without significant dislocations of the suspended particles.

In addition to the high heat capacity, also the low viscosity, the fast diffusion processes and the high mobility of ions in aqueous solutions require higher cooling rates \[50, 51\] in order to avoid ice crystal formation. An alternative to plunge freezing is high-pressure freezing (HPF). By applying 2 kbar isostatic pressure, the solid-liquid phase transition is shifted to -20°C (fig. 1) \[52, 53\]. Thus, viscosity increases, diffusion processes and mobility are slowed and vitrification can be achieved also at lower cooling rates. With a pressurized jet of liquid nitrogen (supplying sufficient cooling rate) followed by a sudden pressure release vitrifies the aqueous suspensions without the destruction of original 3D particulate structures is enabled. Below -140°C the samples are stable; storage or experimental temperatures above can lead to recrystallization or sublimation phenomena. Studies on high-pressure frozen samples could confirm the preservation of original particle arrangements \[54-56\] to a satisfactory degree of vitrification which means that the ice segregation patterns are below microscopic resolution.

For the present study, the high-pressure freezing preparation procedure was modified for cement suspension samples concerning specimen carrier, storage for hydration experiments, fracturing and coating.
1.4 Aim and structure of this study

This PhD-thesis aims to investigate the influence of polycarboxylate-based superplasticizers (hereinafter called PCE) on the macroscopic properties during early hydration of cement-suspensions (chapter 2 [57]). PCE architecture and dosage will be varied in order to find an optimized architecture of side chain density and side chain length combination with maximum fluidization and minimum retardation of the cement setting.

The gap of non-destructive sample preparation for microscopic investigations will be closed by the modification of cryo sample preparation techniques from life sciences. Additionally, the cryo-technique will be introduced to FIB-nanotomography (chapter 4 [58]). The cryo-methods will enable investigations of original long range particle structures in young cement suspensions.

The influence of PCE on the microstructural evolution of early cement hydration will be investigated by qualitative cryo-microscopy (chapters 3 [59]). Thereby the crystal shape and distribution of ettringite will be investigated. Cryo-microscopic images will give an insight to the long range particle structures of a cement suspension without and with PCE. At later time, the study will focus on the evolution of hydration layers and the formation of agglomerates (chapter 6 [60]) Further, quantitative analysis of particle size distributions will be performed with cryo-FIB nanotomography. The data will be linked to macroscopic properties of cement suspensions.

Due to the complexity of the cement-water-PCE system, single phases such as C₃S, C-S-H and ettringite in synthetic pore solution shall be studied regarding PCE adsorption, the impact on rheological properties and the zeta potentials on each phase (chapter 5 [61]). This part of the study aims to deepen the knowledge of single phase-PCE interaction. The result of adsorption and zeta potentials will be compared with the values and mechanisms in the bulk cement suspensions. The comparison will be supported by microstructural data of bulk systems obtained by cryo-microscopy.

References


Chapter 2

Interaction of polycarboxylate-based superplasticizers with cements containing different C₃A amounts

Anatol Zingg, Frank Winnefeld, Lorenz Holzer,
Joachim Pakusch, Stefan Becker, Renato Figi, Ludwig Gauckler

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2 Interaction of polycarboxylate-based superplasticizers with cements containing different C₃A amounts

Anatol Zingg a,* , Frank Winnefeld a, Lorenz Holzer a, Joachim Pakusch b, Stefan Becker b, Renato Figi a, Ludwig Gauckler c

a Empa, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Concrete/Construction Chemistry, Ueberlandstrasse 129, 8600 Duebendorf, Switzerland
b BASF AG, GKD/C-B1, Carl-Bosch-Strasse 38, 67056 Ludwigshafen, Germany
c ETH, Swiss Federal Institute of Technology Zurich, Institute of Nonmetallic Inorganic Materials, Department Materials, Wolfgang-Pauli-Strasse 10, 8093 Zurich, Switzerland

Abstract

This parametric study links the molecular structure of a carboxylate-type of superplasticizer with their performance in cement pastes with different C₃A-contents. Beside the variation of the C₃A-content, the experimental synthesized superplasticizers have been varied by polyethylene-oxide side chain density and length. The connection between the superplasticizers, their effect on workability properties and retardation phenomenon and the dependency of C₃A-content in the cement paste has been investigated.

The characteristic interaction phenomenons between different PCE-architectures and different C₃A-contents have been examined by calorimetric, rheological, adsorption and zeta potential measurements. This study shows that with decreasing side chain density the PCE molecules adsorb stronger and thus, lower the yield stress of a cement paste by steric stabilization. It is also shown that PCE molecules with long side chains delaying the setting of the cement paste to less extend than PCE molecules with shorter side chains. Consequently, in terms of optimization of the molecular architecture, good workability can be achieved by addition of highly charged PCE with long side chains. The latter minimizes undesired retardation phenomena.

Keywords: superplasticizers, zeta potential, adsorption, rheology, cement, C₃A-content

* Corresponding author
E-mail address: azingg@postmail.ch (A. Zingg)
2.1 Introduction

Superplasticizers are frequently used in concrete technology in order to improve the workability of mortar and concrete systems for demanding applications. The addition of superplasticizers is aiming at two objectives: first, the addition of superplasticizers allows controlling 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 while maintaining workability in order to reach high strength and durability.

The properties of cement-water systems are depending on various chemical and physical parameters. The precipitation of hydrate phases during early hydration (up to three hours until setting) and thus workability are affected on one hand by the chemical composition of the clinker, essentially its C$_3$A-content, the availability of soluble sulphates and the chemical composition of the pore solution. On the other hand, physical properties such as particle size distribution, packing density, surface area and the interparticle forces govern the rheological behaviour of cement pastes.

The cement-water system is highly sensitive to the addition of superplasticizers. Already small amounts of superplasticizers enhance the workability properties efficiently, but are often associated with strong, undesired retardation phenomena of the setting of the cement paste.

Newer superplasticizer generations are based on comb-shaped polycarboxylates (as used in this study, hereinafter called PCE). Their dispersing effect is due to the adsorption of polymers on particle surfaces and evocation of electrostatic and/or steric repulsive forces [1, 2]. Those mechanisms can be derived from theories of colloidal sciences [3-5].

The addition of superplasticizers impacts the interface between particle surface and the pore solution and influences physical properties such as viscosity and yield stress of the paste. The adsorption behaviour depends on the PCE architectures. The molecules are comb-shaped, consisting of an adsorptive backbone unit and a hydrophilic polyethylene-oxide (PEO) side chain [6]. Both parameters, side chain length and side chain density, can be varied in order to take control of the adsorption behaviour and dispersion ability.

By changing PCE architecture and dosage, workability properties and prolongation of the dormant period can be controlled [7-11]. Despite numerous research project have been carried out on the subject cement-superplasticizer interaction, many questions remain unsolved. Certain cement-superplasticizer combinations are incompatible [12-14] exhibiting poor flow behaviour, early slump loss, strong retardation or flash set.

The study presented here is part of a project where macroscopic phenomena of cementitious suspensions containing superplasticizers [15, 16] are linked to their microstructural evolution [17, 18] during early hydration up to setting.

It aims to contribute to a better understanding of fresh cement pastes containing PCE. The mechanism of PCE interaction with cement as a function of C$_3$A-content, PCE architecture
and dosage will be investigated. It is a parametric study, on one hand by a systematic variation of the PCE-architecture (side chain density, side chain length) and on the other hand, by variation of the C₃A-content of cement by using three different CEM I 42.5 N.

The interaction between cement and superplasticizers is investigated with various methods. Adsorption data are gained in order to quantify the amount of the molecules that are involved in the process. The impact of adsorbed PCE on the interparticle forces is followed by recording the zeta-potential of the cement pastes. The macroscopic consequence is investigated by rheological measurements. In order to examine the hydration evolution and the undesirable delay of the acceleration period in presence of PCE, calorimetric measurements are carried out.

2.2 Materials

2.2.1 Superplasticizers

For this study, three comb-shaped polycarboxylate-type superplasticizers (PCE) were synthesized. Methylpolyethyleneglycole 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 figure 1.

The PCEs were synthesized as follows: preformation of mono unsaturated “teeth” and linking of (meth)acrylic acid units with alkyl-polyethylene glycols followed by radical
copolymerization with additional (meth)acrylic acids as described in [15]. In order to ensure the same reaction kinetics, the molar concentrations of all monomers were kept constant during the polymerization, which lead to different final solid contents of the products. This circumstance was compensated in all paste and mortar tests by referring to the dry matter of the admixture and correcting the water/cement ratio by the water content of the polymer solution. However, for certain data comparisons of the different polymer architectures, it is useful to refer to the charge density (mol carboxylic acid groups per gram cement). The used PCE architectures and their molecular characteristics as well as their calculated (theoretical) charge densities are listed in table 1. All superplasticizers were applied as sodium salts.

2.2.2 Portland cements

Three ordinary Portland cements (CEM I 42.5 N) according to European Standard EN 197-1 have been used for this study (tab. 2). According to Bogue calculations (tab. 3), these cements exhibit C₃A-contents of 1% (L-OPC), 8% (M-OPC) and 10% (H-OPC) respectively. The cements also differ in their Al₂O₃/SO₃ ratio (1.9, 1.7 and 2.1 respectively). Their specific surfaces (Blaine values) range within 3000-3600 cm²/g.

2.3 Sample preparations and methods

In order to compare the results obtained from different measurement methods, water to cement ratio of 0.35, hydration times and PCE concentrations were kept constant. Variations will be mentioned in the relevant section. For all measurements except for the zeta-potential titration experiments, simultaneous addition of PCE was applied. The PCE solutions and water were premixed, whereas for the zeta-potential measurements the PCE was titrated after mixing the cements with water.

<table>
<thead>
<tr>
<th>Tab. 2: Chemical composition and calculated properties of the used ordinary Portland cements CEM I 42.5 N</th>
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<td>CaO</td>
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*loss of ignition

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<th>Tab. 3: Mineral composition after Bogue, calculated from XRF-data</th>
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2.3.1 Conduction calorimetry

All experiments were carried out using an isothermal heat flow calorimeter (Thermometric TAM Air) at a measurement temperature of 20°C. For each sample, 6.00 grams of cement were weighted into a flask, and 2.10 ml of water or water-admixture solution (0.10%, 0.20%, 0.30% of cement weight) were added. The cement paste was then mixed with a small stirrer for 2 minutes. Afterwards, the flask was capped and placed into the calorimeter. Note that the initial heat peak is not recorded due to external mixing. The heat flow was recorded for 72 hours.

The onset of the acceleration period was derived from the calorimetric curve in two steps: first, determination of minimum heat flow during the dormant period, second, addition of 0.25 J/(g·h) to the determined minimum value. The corresponding hydration time was then defined as the start of the acceleration period. The starting time of the acceleration period (as described above) determined from the heat flow curve roughly corresponds to the “initial setting” determined by the Vicat needle test (according to European Standard EN 196-3) given in table 2. Hereinafter, the term “setting time” is used for the determined start of the acceleration period from the heat flux curve.

2.3.2 Rheology

A kitchen blender (Brown Multiquick 5550 M CA) was used for mixing. All cement pastes were prepared by weighting 300 grams of cement into the mixing bowl and by adding 105 grams of water or water-admixture solution (0.05%, 0.10%, 0.15%, 0.20% of cement weight). The mixing procedure was set to 60 seconds of mixing at stage 6, 30 seconds scraping the paste off the walls of the bowl by hand and then again 60 seconds of mixing at the same stage.

A Paar Physica MCR 300 rheometer with concentric cylindrical geometry was used for these experiments. The rotating bob was serrated with 100 µm 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 of 1.08. The temperature of the cement paste was controlled by a water bath and kept at 20°C.

After blending, the cement paste was transferred into the measurement beaker by a spoon. Then, the measuring system with a rotating bob was lowered to measuring position and the beaker was covered with a solvent trap to protect the sample from water evaporation. The measurements were taken 5, 30 and 60 minutes after blending performing 1 minute pre-shearing at a shear rate of 100 s⁻¹ in order to break particle agglomerates. Afterwards, a flow curve with shear rates between 100 and 0.1 s⁻¹ was recorded using a ramp time of 5 s in the shear rate range of 100-1 s⁻¹ and of 10 s for shear rates below 1 s⁻¹. Apparent yield stress and plastic viscosity were calculated using the Bingham model.
2.3.3 Adsorption isotherms

To determine the superplasticizer adsorption isotherms, the same blending procedure as for the rheology samples was used. 5, 30 and 60 minutes after mixing, the alkaline pore solution was removed through a 0.45 \( \mu \text{m} \) Nylon filter by air pressure filtration. 1 ml of the solid free pore solution was then stabilized by adding 9 ml of 0.1 mol/l HCl. The total organic content (TOC) of the pore solution samples were then determined by using a Shimadzu TOC-Analyzer 5000A. The consumed amount of PCE was calculated from reference TOC measurements of aqueous polymer solutions.

In order to correct the adsorption measurements for the organic content of the Portland cements due to e.g. grinding agents, TOC of pore solutions of plain cement pastes were taken as well. In addition, the TOC content of the used deionized water was measured. Both background values were taken into account when calculating the consumed amounts of PCE.

2.3.4 Zeta potential

All zeta potential data were collected with the ZetaProbe (Colloidal Dynamics Inc.), which works on the basis of the electroacoustic method. A high frequency alternating electric field is applied and causes charged particles to oscillate. The motion of the particles generates a sound wave which is recorded and delivers the dynamic mobility of the suspended particles. The software calculates the zeta potential from the dynamic mobility.

Foregoing the sample measurements, pH-meter (4.01, 7.01 and 10.01) and zeta dip probe (KSiW-standard, provided by Colloidal Dynamics Inc.) were calibrated. All samples were measured in a beaker and stirred (400 rpm) in order to prevent segregation. The syringe-unit (titration unit) was washed prior to the use with the titrant to insure its purity.

All cement pastes were blended using same procedure as for the TOC and rheology experiments. Approximately 270 ml of cement paste (beaker weighted empty and filled with cement paste for later corrections) was then transferred into the beaker. In a preliminary test series, all cement pastes used for this study were found to yield a stable zeta potential after 15 minutes of hydration.

For the investigation of the impact of PCEs with different architectures on the zeta potential of the cement paste, concentration series with constant titration increments of diluted PCE solution of 0.025 weight percentages referring to cement were measured. Note, that this experimental setup measures the impact of delayed PCE addition.

The obtained raw data of for the zeta potential are strongly affected by the fact that the pore solutions of cement pastes are highly charged with various ionic species and charged polymer. Therefore, background measurements were carried out using the following procedure: first, pore solutions of each cement paste was extracted by air pressure filtration and then diluted until the conductivity of the cement paste after 15 minutes (~15 to 25 mS/cm) was reached. Second, background measurements of different conductivity levels from 15 to 25 mS/cm (increment of 1 mS/cm) were measured, because the conductivity of cement
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Third, PCE was titrated to a 18 mS/cm pore solution. After each titration step a background measurement was taken. Subsequent to each experiment, the raw data was recalculated by applying the corresponding background files.

2.4 Results and discussion

2.4.1 Conduction calorimetry

The heat evolution of cement pastes depends on one hand on the mineralogical composition and on the other hand on physical parameters such as fineness and particle size distribution of the cement. At this early stage of hydration, the C3A-content and the availability of sulphates which determines type and amount of hydration products, is a key factor. The total hydration reactions can be followed by recording the heat flow of the cement paste.

Directly after addition of water to the cement, a part of the C3A dissolves quickly. This leads to formation of ettringite, if sufficient sulphate ions are provided [19]. Otherwise, flash setting of the cement paste could occur. It has to be kept in mind that this study uses commercial available cements and therefore, their sulphate contents had been adjusted in order to prevent flash setting. Furthermore, the setting times for all three cements ranges from 185 (H-OPC) to 235 (L-OPC) minutes (tab. 3) and are within the requirements of European standard EN 197-1.

The heat flow curves of the three cement pastes exhibiting different C3A-contents are shown in figure 2. Higher C3A-contents result in higher heat release during the dormant period. This higher heat flow indicates an exothermic process, which may be related to increased formation of ettringite. The main hydration peak of H-OPC is broader and the peak height is lower than for L-OPC and M-OPC. Due to the high amount of Al2O3 in the cement, in H-OPC cement pastes the sulphate is probably earlier exhausted than in L-OPC and M-OPC cement pastes. According to the literature [20-23], the right part of the peak can be

Fig. 2. Conduction calorimetry curves: heat flows of L-OPC, M-OPC and H-OPC cement pastes with w/c 0.35 measured for 72 hours are shown in this figure. The noted setting times are set equal to the start of the acceleration period.
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assigned probably to the so-called sulphate depletion peak. The presence of PCE generally shows some retarding effect on the start of the acceleration period of cement pastes. The higher the charge density of a PCE (fig. 3, left column) and the higher the PCE dosage (fig. 3, right column), the stronger the setting is delayed. With increasing contents of C3A in the cement pastes, the retardation effect of the PCEs decreases.
independent of their architecture and dosage (fig. 3, increasing C₃A-content from top to bottom).

Generally, PCE 102-2 shows the smallest influence on the cement pastes concerning the delay of the onset of the acceleration period (fig. 3, left column). Even at higher concentrations, PCE 102-2 does hardly retard the onset of the acceleration period and does not influence the main hydration peak shape. This indicates no or only little interaction between the PCE molecules and the mineral phases of the cement paste (i.e. adsorption), because i) the charge density is low (high side chain density) and ii) the high side chain length allows only poor accessibility to the anionic sites of PCE 102-2 and thus, adsorption is hindered.

Generally, the presence of higher charged PCE (23-6 and 102-6) lead to a shift of the main hydration peak to the right and thus delays the acceleration period of the cement paste (L-OPC and M-OPC). 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. Similar results are reported by other authors [8, 10]. Generally it is assumed, that PCE molecules preferably adsorb on C₃A, C₄AF and their hydration products. However, they

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**Fig. 4.** Differential thermogravimetric analysis of medium C3A-content OPC pastes (M-OPC) with w/c 0.35 after 0, 4, 18 hours and 28 days of hydration time. The M-OPC paste without superplasticizer (a) contains portlandite after 18 hours whereas the M-OPC paste containing 0.2% of PCE 23-6 (b) no portlandite can be observed at this time.
mainly retard C$_3$S hydration [16, 24, 25], thus delaying the formation of C-S-H and portlandite. These findings are supported by TGA data taken from Winnefeld et al. [16] in figure 4 where the formation of portlandite starts after 4 hours in a M-OPC paste (w/c = 0.35) without PCE (start of acceleration period) whereas with 0.2 wt.-% PCE 23-6 (system still in dormant period) no portlandite is formed at this time. The formation of portlandite in the paste (w/c = 0.35) with PCE starts after 18 hours (start of acceleration period). No significant difference between the amounts of portlandite in the two pastes could be observed after 28 days. In addition, no delay of ettringite formation nor significant differences in the amount of ettringite precipitated was observed.

The presence of highly charged PCE (23-6 and 102-6) not only shift the main hydration peak of H-OPC cement pastes (fig. 3, right figure bottom row) 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. However, even at low concentrations of PCE 102-6 (almost no retardation) the shape of the main hydration peak is narrower and its intensity higher.

One mechanism could be a simple peak shift in presence of PCE, where the C$_3$S hydration peak and the sulphate depletion peak completely overlap. A shift of the sulphate depletion peak to the left would imply earlier exhaust of sulphate and thus implies that in presence of PCE 23-6 and PCE 102-6, the renewal of C$_3$A hydration would occur earlier and roughly at the same time as the C$_3$S hydration. Consequently, in presence of high charged PCE, the consumption of sulphate...
must be increased. Other studies have measured increased amount of monosulphate and suggest a so-called organomineral phase in presence of PCE [26, 27]. However, it is not clear, how and to what extend the available amount and concentration of sulphate ions are influenced by the formation of such organomineral phases or vice versa. Another study by Peng [28] has shown, that PCE molecules can be adsorbed on gypsum surfaces as well. One could hypothesize, that the early formation of monosulphate phases are not due to intercalation of organomineral phases but due to hindrance of dissolution of sulphate of PCE-coated sulphate phases and thus, decreased availability of sulphate.

Another mechanism could be a shift of the sulphate depletion in presence of PCE 23-6 and PCE 102-6 to the right, indicated by the shoulder after the main hydration peak. This could be due to competitive adsorption between sulphate ions and the carboxylic groups of the PCE molecules during initial hydration [29, 30]. Partial (or total) replacement of sulphate by PCE molecules in the double layer leads to less sulphate consumption and thus would ensure a sufficient supply of sulphate ions during the acceleration period and main hydration later on. This hypothesis fits well the presented result obtained from calorimetry where the shoulder after the main hydration peak may indicate the remnant of the sulphate depletion peak.

2.4.2 Rheology

In this study, apparent yield stresses of cement pastes after 5, 30 and 60 minutes of hydration were measured. This paper reports only the 5 min data because it was found, that all samples show only slight increases of yield stress within the first 60 minutes.

The apparent yield stresses of plain L-OPC and M-OPC pastes are about 30 Pa whereas for the H-OPC a significantly higher (55 Pa) yield stress was measured (fig. 5, C$_3$A-content increases from top to bottom). Due to its C$_3$A-content [31], the latter cement system produces higher amounts of ettringite. The formation of ettringite consumes a reasonable amount of water and thus, the volume of free pore solution is reduced, while the solid content increases.

Independent of the C$_3$A-content of the cement it turned out, that a low charge density PCE (high side chain density and long side chains) hardly affects the yield stress of the cement paste. Despite long polyethylene-oxide side chains are thought to increase the paste fluidity by steric repulsive forces [1, 8, 32], the combination with a high side chain density seem to
prevents PCE adsorption and thus, steric stabilization of the paste. With increasing charge densities, the fluidization ability of the PCE improves significantly. Above a certain side chain density (around 4:1), the influence of the side chain length was found to be negligible in a previous study [15, 16]. Both, PCE 23-6 and PCE 102-6 are capable to lower apparent yield stress already at low concentrations (fig. 5). However, an increased PCE 102-6 concentration leads to bleeding phenomenon at lower concentrations than PCE 23-6 does. This observation is supported by slump flow measurements on mortars (unpublished results), where PCE 102-6 shows better flow behaviour than PCE 23-6 does. In addition, figure 6 shows that with same charge density, PCE 102-6 decreases the yield stress more efficiently than PCE 23-6. Remember, that in this study the backbones of all PCEs were kept roughly at constant lengths. Therefore, in terms of charge densities, the comparison of the yield stress values referred to mol anionic sites of the PCE (mol anionic sites / g cement) is much more reasonable. After Plank et al. [30], the carbon bonds of the side chains of polycarboxylates have high rotational degrees of freedom. Therefore, it can be assumed, that PCE 23-6 and PCE 102-6 molecules have the same adsorption abilities but differ in their potential for steric repulsion, where PCE 102-6 with longer side chains is more efficient.

### 2.4.3 Adsorption of PCE

No significant differences in the adsorption isotherms after 5, 30, and 60 minutes have been found. This indicates a rapid PCE adsorption process shortly after contact of the cement powder with water. Assuming that polyethylene-oxide side chains are very adsorb on cement and hydrate particles. PCE 23-6 and PCE 102-2 show similar adsorption behaviour; with increasing C₃A-content, higher PCE dosages are required in order to reach saturation concentration.

![Graph showing adsorption isotherms](image)
flexible, the backbone charge density should be the decisive parameter which mainly determines the adsorption ability of a PCE molecule. In addition, a previous study on similar cement-water-superplasticizers systems revealed, that the PCE fraction with the higher molecular weight is adsorbed preferably [15, 33].

Increasing C₃A-content of the cement leads to higher PCE adsorption (fig. 7, C₃A-content increases from top to bottom) and requires higher PCE concentrations in order to reach saturation. This may be an indication of preferred PCE adsorption on aluminate phases, which is supported by a study of Yoshioka [34]. They carried out their investigation on pure clinker phases and could show a preferred PCE adsorption on C₃A and C₄AF and their hydration products.

Independent of the C₃A content of the cement paste, PCE 102-2 (high side chain density and high side chain length, low charge density) does hardly adsorb. This result fits well the obtained yield stresses of the same cement pastes, where PCE 102-2 shows only minor influence on paste rheology. It can be concluded, that despite the very flexible carbon bonds of the PEO side chains [30], the accessibility of the carboxyl-groups for PCE with high side chain density is hindered and thus, strong adsorption such as ionic binding is not possible. Note, that with increasing side chain length and density, the carboxyl equivalents (mol carboxyl groups / g PCE) increase and thus, lead to lower the charge densities.

Generally, the PCE adsorb increasingly with decreasing side chain density. Above a ratio of 4 backbone units to 1 side chain unit [15], the influence of side chain length seems to be negligible (fig. 7) as shown in e previous study. The graph of PCE 23-6 is congruent with the one of PCE 102-6. However, if the charge densities are compared, PCE 102-6 reaches saturation at a lower adsorbed carboxyl groups. This might be due to the fact, that the steric action radii of the longer side chains of PCE 102-6 are larger than PCE 23-6 and thus, less molecules are needed in order to reach the same fluidization state. Despite lower saturation concentrations, the efficiency of the larger PEO side chains seems to have stronger influences on the workability of a cement paste. This can be attributed to higher steric repulsive forces of the longer PEO side chains.

However, by TOC analysis of the pore solution, the amount of PCE adsorbed on cement and hydrate particles is measured indirectly and may not represent the actual amount of PCE adsorbed. According to Flatt and Houst [27], the term “consumption” should be used rather than “adsorption” because adsorbed PCE and intercalated PCE can not be distinguished. However, PCE coprecipitation with mineral phases (e.g. monosulfate, monocarbonate) and thus the formation of organomineral-phases, may act as a chemical sink for PCE molecules. According to Plank et al. [26], PCE with short side chain length shows higher affinity for intercalation and thus, formation of organomineral phases. Intercalation counteracts the dispersion ability of the PCE. This is especially the case for cements where a high level of C₃A is combined with insufficient supply of sulphate (high Al₂O₃/SO₃ ratios) during early hydration.
Dealing with cement-superplasticizer interaction phenomena, the question about the relevant interparticle forces is of major importance. Surface charges and the availability of ionic species (counter-ions) and thus the constitution of the diffuse double layer determine the behaviour of two approaching particles. The zeta potential represents the potential at the slip surface where a particle in motion separates from the surrounding liquid phase. It is the potential that an approaching particle “feels”.

After (initial period) 15 minutes, all cement pastes reach an “apparent” steady state with zeta potentials between -5 and -7 mV (fig. 8, C$_3$A-content increases from top to bottom). Those zeta potentials are in good agreement with values reported in literature [5, 35]. The negative zeta potentials are probably due to negative zeta potential of C$_3$S and C$_2$S [34] as the major components in the cement. But this is discussed controversially in literature where for the C$_3$S also positive zeta potentials [36-38] are given. Other studies report positive zeta potentials [39, 40] or both, negative and positive zeta potentials [3, 41] for cement pastes.

However, the cements used in those papers differ in their mineralogical composition, the reactivity of their components and thus, in composition of their pore solutions. Note that often publications lack precise information about the experimental setup and sample parameters used and thus, direct comparisons of the data are difficult.

In this study, the zeta potentials for the plain cement pastes are found to be stable between 15 and 60 minutes of hydration, independent of the C$_3$A-content. After 60 minutes a slight increase of around 2-4 mV could be observed. This may result in a stronger flocculation of the cement paste which is in agreement with the slight increase of its yield stress and viscosity. The slow but still ongoing formation of ettringite during the dormant period could be an explanation for this behaviour.

In contrast to the stable zeta potential of cement pastes, their conductivity increases with evolving hydration time and is mainly influenced by dissolution, formation of hydrate phases and thus, evolution of solid content. Throughout preliminary titration studies, cement pastes consistently showed lower increase of conductivity with increasing PCE contents (fig. 8). This fact may indicate either complexiation of cations by anionic PCE molecules or slowed
dissolution caused by adsorption and coverage of PCE molecules on clinker surfaces. The latter may act as diffusion barriers and lowering the surface area of C₃A directly connected with the pore solution. Other investigations have found the complexation to be negligible as the chemical composition of the pore solution evolves independent of PCE presence [24] or have found complexes with calcium ions exhibiting only low stability constants [42]. Therefore, the mechanism of PCE adsorption and formation of diffusion barriers is favoured.

The titration of cement pastes with higher charged PCE 23-6 and PCE 102-6 leads to a zeta potential shift close to zero charge (fig. 9) and reach saturation concentrations below 0.1 wt.-%. Despite similar adsorption isotherms (fig. 7), the impact of side chain length on the zeta potential shows some C₃A-content dependency. PCE 102-6 reaches its saturation concentration in the L-OPC system faster than PCE 23-6. In the cement paste with medium C₃A-content (M-OPC) both PCE reach saturation at the same concentration whereas in the H-OPC, PCE 102-6 shows higher saturation concentration than PCE 23-6 does. This difference in C₃A-content dependency might be due to different adsorption rate which probably depends on the PCE architecture where on one hand the long side chained PCEs adsorb slower and on the other hand, the amount and dissolution rate of the C₃A may play a key role. In other words, the higher the amount of C₃A and the higher its reactivity, the more the interaction seems to be governed by the PCE adsorption rate. Another difference can be observed in the ability to shift the zeta potentials: both are close to zero, but PCE 23-6 stays negative whereas PCE 102-6 shows positive potentials. This is in agreement with findings of Plank et al. [5], where very long...
side chained PCE’s are proved to change the negative into positive zeta potentials. This could be due to the fact that at same weight concentration, much more carboxylic groups are available with PCE 23-6. Furthermore, the amount of PCE 23-6 molecules is around four times higher than PCE 102-6 molecules for the same dosage by weight. Therefore, at same weight concentrations, PCE 23-6 covers a larger surface area and thus, a larger area is occupied with negative charged carboxyl groups.

PCE 102-2 reaches saturation concentration around 0.5 wt.-% in L-OPC and M-OPC cement pastes. At high C₃A-contents (H-OPC), saturation concentration is not yet reached at 0.5 wt.-%. However, according to TOC experiments, the molecules do hardly absorb 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 latter seem to be of major importance with increased molecular weight and dosage. In a cryo-microscopic study with the methods described in [17, 43] could be observed that a large part of PCE 102-2 remains in the pore solution (unpublished results) and also strongly impacts the fracturing behaviour of the frozen sample. Up to now, the impact of PCE on the physical properties of the pore solution is not very well investigated in the field of cement and concrete sciences.

2.5 Conclusions

In this parametric study, conduction calorimetry, rheology, adsorption isotherms and zeta-potential measurements were carried out in order to investigate the influence of PCE architecture and PCE dosage on cements containing different C₃A-contents.

Generally, the qualitative phenomenon of the impact of PCE addition to fresh cement pastes is independent of the C₃A-content of the cement and the availability of sulphates. On a quantitative level, the demand of PCE for a given workability increases with increasing C₃A-content in the cement paste. Higher C₃A-contents require larger amounts of PCE in order to reach saturation concentration. Also, with increasing C₃A higher amounts of PCE are required to reach zero yield stress.

The calorimetry data shows that PCE with long side chains lead to significant smaller retardation times than PCE with short side chains. Consequently, the side chain length is the key parameter concerning the retardation effect of PCEs. Note that at same weight concentration, approximately four times more PCE 23-6 molecules than PCE 102-2 and PCE 102-6 are added to the paste and are able to cover more surface area and thus, may act as a diffusion barrier.

This study shows that workability is mainly influenced by the ionic charge density of the PCE used. Therefore, the side chain density is the key parameter which controls the adsorption behaviour and thus the strength of electrostatic and steric stabilization. The latter
governs the flow behaviour of the fresh cement pastes. It could be demonstrated, that the role of side chain length is of minor influence if PCE weight concentrations are compared. However, if the charge densities are taken in account, the PCE with higher PEO numbers in its side chains shows enhanced dispersion ability, which is due to its stronger steric repulsive forces. Despite the influence on the zeta potential of cement pastes, the very dense and long side chained PCE shows only minor impact on the paste rheology, which is supported by adsorption data.

From the obtained results and discussion, following hypothesis arise:

1. If not sufficient sulphate (or sulphate phases with lower dissolution rates) is available, anionic PCE molecules are alternatively adsorbed (competitive adsorption) in the diffuse double layer at the particle pore solution interface.

2. During the first hour of hydration, the increase of conductivity is lowered in presence of PCE. This indicates (weak) complexation, hindered dissolution by adsorbed PCE (acting as a diffusion barrier) or increased precipitation of hydrates. The latter might be a reason for early slump loss induced by some PCE-cement combinations.

3. A PCE with high side chain density and length (PCE 102-2) is weakly adsorbed onto surfaces by London forces or ion-dipole bonds. The weak PCE adsorption and its impact on the zeta potential can be measured. However, these bonds are too weak and the PCE molecules are removed with the pore solution during sample preparation for TOC analysis.

4. PCE molecules which remain in the pore solution have a significant impact on the physical properties of the pore solution such as water cluster structure, viscosity and surface tension. This might be of major importance for methods where those parameters significantly influence the measured data (e.g. zeta potential measurements).

These hypotheses require further studies of the superplasticizer interaction with pure clinker phases, hydrate phases and the pore solution. Furthermore, in terms of interparticle forces and associated rheological phenomena, the links to the microstructural evolution of a cement paste concerning particle size distribution, surface area and particle packing has to be investigated.

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References


Chapter 3

The microstructure of dispersed and non-dispersed fresh cement pastes – new in-sight by cryo-microscopy

Anatol Zingg, Lorenz Holzer, Andres Kaech, Frank Winnefeld,
Joachim Pakusch, Stefan Becker, Ludwig Gauckler

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3 The microstructure of dispersed and non-dispersed fresh cement pastes – new in-sight by cryo-microscopy

Anatol Zingg\textsuperscript{a,*}, Lorenz Holzer \textsuperscript{a}, Andres Kaech \textsuperscript{b}, Frank Winnefeld \textsuperscript{a}, Joachim Pakusch \textsuperscript{c}, Stefan Becker \textsuperscript{c}, Ludwig Gauckler \textsuperscript{d}

\textsuperscript{a} Laboratory for Concrete/Construction Chemistry, Swiss Federal Laboratories for Materials Testing and Research (EMPA), Ueberlandstrasse 129, 8600 Dübendorf, Switzerland
\textsuperscript{b} Electrom Microscopy Centre Zurich (EMEZ), Swiss Federal Institute of Technology (ETH) Zurich, Schafmattstrasse 18, Zurich, Switzerland
\textsuperscript{c} GKD/C-B1, BASF AG, Carl-Bosch-Strasse 38, 67056 Ludwigshafen, Germany
\textsuperscript{d} Institute of Nonmetallic Inorganic Materials, Department Materials, Swiss Federal Institute of Technology (ETH) Zurich, Wolfgang-Pauli-Strasse 10, 8093 Zurich, Switzerland

Abstract

This study aims to give new insights to the microstructural development of fresh cement pastes without and with polycarboxylate-type (PCE) of superplasticizers. Qualitative comparisons of the particulate structure of such cementitious systems were carried out by using cryo-FIB and cryo-SEM techniques. The natural structure of fresh cement pastes were preserved by high pressure freezing.

It is illustrated that non-dispersed cement systems tend to form hydration rims on the surface of the clinker grains immediately after mixing. This leads to an interlocking of the particles. In contrast, in the dispersed systems the early hydrates precipitate in the pore solution and thus, agglomeration is prevented. These microstructural observations are important aspects of the fluidization effect of superplasticizers.

Keywords: microstructure; cryo-SEM; cryo-FIB; superplasticizer; cement paste

\footnotesize* Corresponding author.
E-mail address: azingg@postmail.ch (A. Zingg)
3.1 Introduction

In order to enhance the workability of cements, mortars and concrete, superplasticizers are widely used. It is assumed, that the molecules of the superplasticizers adsorb onto particles surfaces and evoke mainly electrostatic (e.g. polynaphthalin-sulphonate type of superplasticizers) or electrostatic and steric (polycarboxylic-ether type of superplasticizers) repulsive forces [1-4]. As shown in figure 1, the addition of superplasticizers has two main rheological effects: fluidization and retardation. The viscosity is decreased due to electrostatic and steric stabilization of the cement paste [5-8]. In addition to this fluidization-effect, superplasticizers also often interfere with the hydration process, which usually leads to a retardation of the setting (stiffening of the material).

These superplasticizer-effects depend on numerous parameters such as chemical composition of cement and pore solution, type of hydrate-phases, particle size distribution and water-to-cement ratio. It is assumed that these parameters also have a strong influence on the microstructure of the fresh cement paste. As illustrated schematically in figure 2, the addition of superplasticizers can influence the microstructure of hydrating cement systems on different scale levels: presence of polymers can strongly affect shape and size of nuclei and growing hydrates. The latter is usually far below the µm-scale. Also the spatial distribution of hydrates can be affected by addition of superplasticizers. Agglomeration process can take place at smaller and at larger scales, whereby clinker particles and hydrates start to flocculate. Close to the setting time, these particle interactions may lead to the formation of long range particle network structures. The understanding of the microstructural processes is still limited due to a lack of suitable microscopic methods. New methods for the microstructural

![Complex Viscosity of a Fine Cement](image_url)

Fig. 1. Temporal evolution of the complex viscosity (obtained by rheological oscillation experiments) of fresh cement pastes (fine fraction of OPC, d50 = 5 µm) without and with PCE. The figure illustrates the effects of fluidization and retardation [7, 8] due to the addition of PCE.
investigation of fresh cement pastes have to be developed in order to improve the understanding of the effects of superplasticizers.

Most microstructural investigations on fresh cement pastes have been carried out on filter residues after removal of the pore solution. BSE-imaging with ESEM and SEM are well suited for morphological studies and size measurements of individual particles [9-15] or for microstructural characterization of hardened cement pastes. However, by applying conventional SEM sample preparation techniques the original particle arrangements of fresh cement pastes are destroyed by removing the pore solution. Investigations on filter residues for instance, should take into account that fine particles which were originally floating in the pore solution are deposited in a compacted sediment. Therefore, microstructural investigations on hydration rims and particle deposition of filter residues and polished epoxy-fixed samples should be treated with caution. The original particle arrangements of bulky hydrated, fresh cement pastes can only be preserved by high-pressure freezing[16-18]. Under high pressure condition (2 kbar) the melting point for ice is shifted to -20°C which gives the benefit of increased viscosity and decreased diffusion rates. As a consequence, homogeneous nucleation of ice is favoured whereas the mobility of ice nuclei is decreased. This prevents formation of artefacts. In contrast, conventional freezing techniques such as plunge freezing may lead to severe ice crystal damage by fast growing, large ice crystals in specimens thicker than 10 μm and hence to an artificial rearrangement of the microstructure [19-22]. High pressure freezing is essential for the preservation of the ultra-structure of soft condensed and hydrated matter. This technique was developed and well established in life sciences [23-26].

Recently, high pressure freezing has been combined with FIB-nt (Focused-Ion-Beam Nanotomography) [27, 28]. Cryo-FIB-nt is based on a serial sectioning procedure using a dual-beam FIB. From each section, a BSE image is taken with the electron beam. The dimensions of such data volumes commonly measures around 20x20x20 μm and each section has a thickness of 40 nm. For the first time, a tomography method enables high resolution 3D-

Fig. 2. Schematic illustration of the three major microstructural effects due to addition of PCE: i) change of shape and size of hydrates, ii) change of interfaces and distribution of hydrates and iii) change of the long range particle structures.
The microstructure of dispersed and non-dispersed fresh cement pastes – new in-sight by cryo-microscopy

even small nuclei in the 100 nm range can be identified reliably. This opens new possibilities for quantification of particle size distribution and corresponding surface area in fresh cement pastes as described by Holzer [29]. The particle size distribution shown in figure 3 illustrates a remarkable shift to smaller grain sizes within the first 6 minutes of hydration due to nucleation and precipitation of hydrates (10% of the solids volume smaller than 500 nm). Simultaneously the formation of small crystals leads to an increase of the specific surface area by a factor of three.

analysis of particles in fresh cement pastes whereby even small nuclei in the 100 nm range can be identified reliably. This opens new possibilities for quantification of particle size distribution and corresponding surface area in fresh cement pastes as described by Holzer [29]. The particle size distribution shown in figure 3 illustrates a remarkable shift to smaller grain sizes within the first 6 minutes of hydration due to nucleation and precipitation of hydrates (10% of the solids volume smaller than 500 nm). Simultaneously the formation of small crystals leads to an increase of the specific surface area by a factor of three.

The gain of 3D-data by serial sectioning with cryo-FIB-nt is very time consuming and this puts strong limitations to the application of this 3D-technique for extended investigations of the cementitious multi-parameter system. In addition, the data processing of such huge image stacks requires considerable computing power. The computing time for the extraction of parameters like particle size distribution, number of particles, surface area and possible particle contacts is in the range of several days. However, for quantitative characterization of 3D structures, this procedure is inevitable. Instead of excavating a cube with the ion beam and subsequent serial sectioning for 3D analysis, only a vertical cross section can be cut into the sample. The performance of single cryo-FIB cross sections as a shortened procedure is less time consuming and, on a qualitative level, this 2D-technique gives comparable insight to the particle structure of fresh cement pastes. Nevertheless, the magnification of cryo-FIB cross sectioning is limited to a voxel resolution of approximately 20-40 nm mainly due to charging-problems. For more detailed investigations of fine structures at very high resolution, cryo-SEM (pixel resolution 2-4 nm) is a powerful tool which gives complementary information to
cryo-FIB(nt). The data is acquired from fractured surfaces of high pressure frozen samples. High resolution cryo-SEM enables to investigate detailed surface morphologies, grain textures of hydrate layers, structural interfaces between particles and shape and size of precipitates far below 100 nm.

In this paper, cryo-FIB and cryo-SEM are used to visualize the difference of a non-dispersed and a well dispersed cement-water system for the first time. The investigations concentrate on qualitative descriptions of early hydration products, their spatial distribution, interfaces and surface morphologies. This microstructural information gives new insight into the principle mechanisms of superplasticizers.

### 3.2 Materials and Methods

FIB cross-sections are limited to an approximate image-size of 50x50 µm due to the time consuming erosion procedure. In order to obtain statistically reasonable results (i.e. analysis of a representative volume), fine grained Portland cements with a high specific surface area (prepared by grinding or by air separation) have been used.

#### 3.2.1 Raw materials

Cement I is a fine fraction of a CEM I 42.5 N, air separated, with $d_{10} = 1.0$ µm, $d_{50} = 3.2$ µm and $d_{90} = 5.8$ µm. Due to the separation method, cement I is enriched with alkaline-sulphates, gypsum and calcite as indicated by chemical analysis in table 1.

Cement II is also a sample of a CEM I 42.5 N (same as for cement I), which was ground with a laboratory disc mill (Siebtechnik GmbH, Germany), with $d_{10} = 0.6$ µm, $d_{50} = 9.0$ µm and $d_{90} = 37.6$ µm. In order to avoid undersulfatisation, gypsum was added to a total of 4 weight-percent $SO_3$ (tab. 1).

In this study, a superplasticizer based on anionic, comb-shaped polycarboxylic-ethers (hereinafter called PCE) with low density of short, grafted polyethylene-oxide (PEO) units with methyl (Me) end groups has been used. This PCE has a molecular weight of 19'000 g/mol. It is characterized by strong adsorption and retardation behaviour on both cement types (unpublished results).

### Tab. 1: Chemical composition of the fine cements used

<table>
<thead>
<tr>
<th></th>
<th>CaO wt.-%</th>
<th>MgO wt.-%</th>
<th>SiO$_2$ wt.-%</th>
<th>Al$_2$O$_3$ wt.-%</th>
<th>Fe$_2$O$_3$ wt.-%</th>
<th>Na$_2$O wt.-%</th>
<th>K$_2$O wt.-%</th>
<th>SO$_3$ wt.-%</th>
<th>CO$_2$ wt.-%</th>
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<tr>
<td>Cement I</td>
<td>58.0</td>
<td>1.6</td>
<td>15.8</td>
<td>4.2</td>
<td>2.2</td>
<td>0.2</td>
<td>2.1</td>
<td>7.3</td>
<td>6.8</td>
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<tr>
<td>(air separated)</td>
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<tr>
<td>Cement II</td>
<td>63.4</td>
<td>1.8</td>
<td>20.0</td>
<td>4.8</td>
<td>2.5</td>
<td>0.1</td>
<td>0.9</td>
<td>4</td>
<td>1.9</td>
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<td>(disc mill)</td>
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</table>
3.2.2  **Samples**

The following cement pastes were investigated with cryo-microscopy:

1. Unhydrated cement I, dispersed in a glycolic matrix, with a glycol/cement weight ratio of 0.55 which is equivalent to a volumetric proportion of a water/cement weight ratio of 0.5
2. Cement I, w/c = 0.50, hydrated for 24 min
3. Cement I, w/c = 0.50, PCE addition of 0.2 wt-% of cement I, hydrated for 6 min
4. Cement II, w/c = 0.55, PCE addition of 0.7 wt-% of cement II, hydrated for 6 min

3.2.3  **Methods**

3.2.3.1  **High pressure freezing**

For this study, high pressure freezing was performed with a HPM 010 apparatus (BAL-TEC AG, Balzers, Liechtenstein). Kinetic and thermodynamic aspects of high pressure freezing and associated vitrification of water are discussed extensively in Bachmann [25] and Moor [26]. The complete preparation process from “paste” into the “cryo-SEM/FIB chamber” can be schematically followed in figure 4. Because of the high alkalinity of the cement pastes (pH > 13), inert brass specimen carriers (TedPella Inc.) were used. A droplet of a cement paste was mounted on a “bottom” planchet (type A) with a cylindrical cavity depth of 100 µm and then covered with a flat “top” planchet (type B). The brass sandwich was then high-pressure frozen with pressurized, supercritical nitrogen at 2100 bar.

Note that different PCE-architecture, PCE-concentrations and different hydration times result in different freezing behaviour and morphology of the pore solution. Therefore, fracturing, etching (sublimation of water), coating and imaging-techniques vary strongly, depending on the sample and microscopy technique. The different sample treatments are described in the following subchapters (cryo-SEM and cryo-FIB cross sections).

3.2.3.2  **Cryo-SEM**

In a liquid nitrogen bath, the high pressure frozen specimen carrier sandwich was vertically mounted on a cold specimen holder (Bal-Tec). The sandwich was then notched with a cooled saw blade. Afterwards the top planchet was pushed off and the specimen holder was transferred onto the cold stage of a freeze-fracturing/etching/coating device BAF060 (Bal- tec). Subsequently, the sample was fractured by bending the sample planchet with the BAF microtome. The fractured surface was etched at -105°C for 5 minutes. By using electron beam evaporation, the revealed surface was coated with 2 nm of Pt/C at an angle of 45° (~65 mA) and with an additional 1 nm of Pt/C by moving the gun between an angle of 45° and 90°. The specimen was then transferred onto the cold stage (-115°C to -120°C, vacuum 2.5*10^-7 mbar) of a LEO Gemini 1530 SEM. All transfers were performed using the high vacuum cryo-transfer system VCT 100 (Bal-tec) [30, 31].
3.2.3.3 Cryo-FIB cross sections

The cryo-FIB cross sections were obtained with a dual beam FIB-SEM microscope (FEI Strata DB 235). The cryo-extensions and accessory units are similar to those described for cryo-SEM.

The fractured samples were sputtered with Pt in a MED 020 (Bal-Tec.) for several minutes at 65 mA. After transfer to the FIB, a metallorganic layer of several hundreds of nanometre thickness were deposited on the surface of the fractured sample. Subsequently vertical cuts with cross-sectional areas of around 10 μm x 20 μm have been eroded with the ion beam. After erosion, backscattered electron images were taken from these cross-sections. In order to avoid charging low beam voltage (3 kV), spot size (2) and relatively fast scan times (30 sec) have been used.

3.3 Results

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 figures 5-7 the spatial distribution of large unhydrated clinker particles and small hydration phases are demonstrated for three different samples: an unhydrated, a non-dispersed (without PCE) and a well dispersed (with PCE) cement paste. Figures 5 and 6 are taken from two 3D-FIB-nt stacks. The curves in figure 3 are calculated from those two stacks. Complementary to cryo-FIB, high resolution cryo-SEM allows insights to fine structures of surfaces, hydration rims and interfaces between fractured clinker particles and pore solution. Figures 8 and 9 illustrate the high degree of microstructural details that can be resolved with this technique.
Fig. 5. Cryo-FIB cross-section (image width: 18 μm) of the unhydrated sample 1: fine fraction of an OPC (cement I), embedded in frozen glycol-matrix, volumetric proportions equivalent to w/c ~0.50. The sample has been high-pressure frozen and coated with Pt.

Fig. 6. Cryo-FIB cross-section (image width: 18 μm) of a non-dispersed, strong agglomerating cement paste (sample 2, hydrated for 24 min): the paste has been high-pressure frozen and coated. Note the numerous small particles (<1 μm) which are not present in the unhydrated sample (fig. 5).

Fig. 7. Cryo-FIB cross-section (image width: 18 μm) of dispersed sample 3: fine fraction of OPC with PCE hydrated for 6 min. Note that the population of fine particles (<0.5 μm) is well dispersed in the interstitial pore space.
It has to be mentioned that the two systems compared in figures 6 and 7 are characterized by different reaction kinetics. The setting times are 140 minutes for sample 2 (fig. 6) and 400 minutes for sample 3 containing PCE (fig. 7). However, it was observed in our investigations that the microstructures of both systems are hardly changing during the first hours of hydration after the initial reactions of the initial period (< 5 minutes).

Figure 5 shows the particle structure of sample 1 (cement I dispersed in a glycolic matrix), which represents the microstructure of the unhydrated cement paste at hydration time 0. The particles of the unhydrated cement are irregularly shaped, but they show clean and sharp boundaries. The glycolic matrix seems to be free of very fine particles. As shown in figure 3 the particle size distribution determined from 3D-data volume (cryo-FIB-nt) of the unhydrated cement is quite broad, ranging from several microns down to the submicron-scale. However, the volume fraction of particles at the submicron-scale is less than 10% and the fraction smaller than 500 nm is close to 0%.

In the non-dispersed cement paste (hydrated for 24 minutes), two populations of particles can be distinguished (figure 6) 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 hydration products. Note, that these small particles are not present in the unhydrated sample (fig. 5). The small particles are not dispersed in the interstitial space (as in fig. 7) 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. 7, 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 figure 6), 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 as shown in figure 3. Up to 10% of the total solids volume is represented by particles smaller than 500 nm, which are not present in the unhydrated cement sample. The small particles in the interstitial pore space are interpreted as fresh precipitates that have formed within the first 6 minutes (compare fig. 5).
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 (fig. 7). This additional information is illustrated for the dispersed system, hydrated for 6 minutes, in figures 8 and 9.

Besides the large, fractured clinker particle in the top right corner, two different types of hydration products can be distinguished in figure 8. 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) that are agglomerated and partially intergrown with ettringite crystals. As indicated in figure 8 with arrows, both euhedral ettringite and the fine fibres are forming together a dense rim of hydration products on the surface of the clinker particle. This rim varies in thickness between almost 0 to 200 nm.

At higher magnification (fig. 9) 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.

3.4 Discussion

Once the initial hydration peak (after around 5 minutes) is over, no significant changes in the particle structures could be observed within the first hour of hydration (dormant phase). This circumstance could be observed throughout all cryo-investigations and thus, allows qualitative comparison of samples with slightly different hydration times within the early stage of the dormant phase (5-30 minutes).

The unhydrated cement I contains a low percentage of the particle size fraction below 1 µm (fig. 3). The clinker particles show relatively clean surfaces (fig. 5). During the initial hydration phase, nucleation and precipitation of numerous small crystals (mainly ettringite) takes place which results in an increase of the specific surface area. These initial hydration reactions can be observed in both, non-dispersed and dispersed cement pastes. The cryo-methods presented in this study, for the first time enable a direct comparison of the microstructures of fresh cement pastes with and without PCE. According to figure 3, in a fresh cement paste with PCE, the size fraction of particles in the submicron range and the corresponding specific surface area increase significantly during the first 6 minutes. The corresponding cryo-FIB cross section (fig. 7) shows that the hydrate crystals (mainly ettringites) are well dispersed in the interstitial pore space. This can be attributed to electrostatic and steric repulsive forces evoked by the adsorption of PCE molecules on the surfaces of clinker and hydrate particles. Those forces hinder the particles from precipitating onto clinker surfaces and prevent the system from agglomeration. Nevertheless, at high resolutions, cryo-SEM images of high-pressure frozen fresh cement pastes with PCE locally also show fine hydration rims (fig. 8). Some minor agglomerates of ettringite in the range of few hundreds of nm in diameter can be observed (fig. 9). The surfaces of these agglomerates are covered with a very thin layer of small fibrous crystals that are embedded in a gel-like mass and result in an increase of surface roughness. The chemical nature of these fibrous crystals and the gel can not be analysed by the microscopic methods used but can be interpreted as very early C-S-H phases. However, in contrast to the numerous ettringite precipitates (100-500 nm) the small C-S-H needles (<50 nm) do not form individual particles.
With quantitative microscopic methods (cryo-FIB-nt) only particles larger than 50-100 nm can be measured. The surface roughness of C-S-H is below this resolution and hence C-S-H hardly contributes to the measured surface in figure 3.

The cryo-FIB cross section of the non-dispersed cement paste (fig. 6) documents that irregularly shaped hydration rims form around the clinker particles within the initial period during the first few minutes. Different from well dispersed cement pastes, only few submicron particles can be observed in the interstitial pore space. Thus, in systems without PCE, early hydrates are instantaneously precipitating onto clinker surfaces and form agglomerates of a few microns in diameter. Those agglomerates represent flocculated bridges between the larger clinker particles which lead to the formation of an interconnected particle network. This microstructural observation can be correlated with the relatively high yield stress of fresh cement pastes without PCE compared to a cement paste containing PCE. A similar microstructural phenomena has been described for cement pastes at later hydration times close to the setting, where small interstitial grains (so-called SIGs) of approximately 2 µm form rigid bridges between the larger clinker grains [32]. The formation of a flocculated particle network based on the SIGs is associated with the physical transition at the time of setting. The observed agglomerates in the non-dispersed cement paste may represent precursors for these SIGs. The addition of PCE prevents the formation of such agglomerates (fig. 7). Therefore the gyration radii of the particles are much smaller, which reduces the particle flocculation and leads to a decreased viscosity.

### 3.5 Conclusion

High-pressure freezing enables the preservation of internal 3D structures of fresh cement pastes. Combined with cryo-FIB sectioning and high-resolution cryo-SEM, the cryo-method provides a powerful tool for microstructural investigations of original particle structures in fresh cement pastes. For the first time, spatial distribution of suspended cement particles and hydrates can be investigated time resolved. Nevertheless, the cryo-methods are very time consuming and the present study only represents preliminary observations.

Cryo-FIB cross sectioning opens new possibilities for investigations on long range particle structures (networks), development of hydration rims, spatial distribution of hydrates (in our example mainly ettringites) and formation of agglomerates. Cryo-FIB cross section covers a representative area, whereas high resolution cryo-SEM investigations are more suitable for detailed morphological investigation of very fine structures on specific locations such as interfaces or particle surfaces.

This advanced microscopy technique has been applied for investigations on the impact of PCE on the microstructural development of fresh cement pastes. The following hypotheses can be formulated from the preliminary study on high-pressure frozen cement pastes after few minutes of hydration:
1. In absence of PCE, early hydrates (ettringites) tend to precipitate on clinker surfaces (hydration rims) and tend to form agglomerates (SIGs), which will lead to interlocking bridges and thus, to higher yield stresses at later hydration times (setting).

2. Hydration rims around clinker particles in cement pastes without PCE are relatively thick compared to those in cement pastes with PCE. In both cases, at early hydration times, the rims do not cover the particle surfaces homogeneously and their thickness is not constant.

3. The interstitial pore space in cement pastes without PCE is almost free of smallest hydrate particles. In contrast, in presence of PCE, the hydrates (mainly ettringites) are well dispersed in the interstitial pore space and only minor amounts are attached on the clinker surfaces. With PCE, almost no agglomerates are formed during the first minutes of hydration. Yield stress and viscosity of such cement pastes are lower than in cement pastes without PCE.

4. The addition of PCE influences the volume of hydration phases and their spatial distribution (fig.5, 6). This effect leads to changes of the particle size distribution, specific surface area and numbers of particle and thus, changes the rheological behaviour of fresh cement pastes.

The cryo-techniques presented in this study open new possibilities for the investigation of the formation of hydrates, their spatial distribution, the development of particle agglomeration and the formation of long range particle networks. Further cryo-studies shall be performed with different cement-PCE-systems and for different hydration times. This information is needed for a more profound understanding of the rheological effects of PCE.

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References


Chapter 4

Cryo-FIB-nanotomography for quantitative analysis of particle structures in cement suspensions

L. Holzer, Ph. Gasser, A. Kaech, M. Wegmann, A. Zingg, R. Wepf, B. Muench

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4 Cryo-FIB-nanotomography for quantitative analysis of particle structures in cement suspensions

L. Holzer¹, Ph. Gasser¹, A. Kaech², M. Wegmann¹, A. Zingg¹, R. Wept², B. Muench¹

1: EMPA, Materials Science and Technology, 3D-Mat group, Ueberlandstr. 129, CH-8600 Dübendorf
2: Electron Microscopy Centre Zürich (EMEZ), ETH Zürich, Schafmattstr. 18, CH-8093 Zürich

Abstract

Cryo-FIB-nanotomography is a novel high resolution 3D-microscopy technique which opens new possibilities for the quantitative microstructural analysis of complex suspensions. In this paper we describe the microstructural changes associated with dissolution and precipitation processes occurring in a fresh cement paste which has high alumina and sulphate contents. During the first 6 minutes, precipitation of ettringite leads to a general decrease of the particle size distribution. In the unhydrated cement paste almost no particles smaller than 500 nm are present, whereas after 6 minutes this size class already represents 9 vol%. The precipitation of ettringite also leads to a significant increase of the particle number density from $0.294 \times 10^9$/mm$^3$ at $t_{0\text{min}}$ to $20.55 \times 10^9$/mm$^3$ at $t_{6\text{min}}$. Correspondingly the surface area increases from $0.75$ m$^2$/g at $t_{0\text{min}}$ to $2.13$ m$^2$/g at $t_{6\text{min}}$. The small ettringite particles tend to form agglomerates which strongly influence the rheological properties. The particular strength of cryo-FIB-nt is the potential to describe higher-order topological features such as the number of contacts and the surface area of particle-interfaces, which are important for the study of agglomeration processes.
4.1 Introduction

The relationship between the microstructure and rheological properties of suspensions with high solids loading (>30 vol%) is of major interest for process optimization in various industrial applications, e.g. for concrete technology (Flatt 1999), or for DCC processing of ceramic pastes (Lewis 2000). Conventional characterisation methods such as light scattering, small angle neutron and/or X-ray scattering (SANS, SAXS) work well for suspensions with low solid contents (Goodwin 2004), however, in concentrated systems, multiple scattering strongly disturbs the analysis process when these methods are used. Consequently, for concentrated suspensions there is a need to develop suitable microscopy methods.

In this paper we present the first application of cryo-FIB nanotomography as a new microscopic tool for the quantification of particle structures in dense suspensions with highly disordered and complex microstructures, namely to the analysis of fresh cement pastes. In these suspensions, agglomeration of the finest components on the sub-µm scale tends to reduce flow properties and associated workability. Due to the addition of superplasticisers, the workability can be improved considerably (Uchikawa et al., 1992; Uchikawa et al., 1996; Flatt and Houst, 2001). However, the influence of additives on the particle structure in cement pastes and on the associated rheological properties is still not fully understood, mainly because suitable quantitative analysis techniques for such complex systems are hardly available. In this work, cryo-FIB nanotomography in combination with image based modelling is shown to be a potent quantitative technique to apply to just such problems.

There are several very challenging problems to overcome when studying fresh cement pastes with microscopy techniques: First, the particle size distributions range over many orders of magnitude from 100µm down to the 10nm-scale. Since the smallest particles in such systems represent the most reactive components, it is important to develop microscopy methods with a spatial resolution in the lower nm range. In addition, the image window should be large enough to also acquire the coarser components in a representative way. Second, the particle structure in the cementitious system is time-dependent, being affected by physical particle interactions as well as by chemical hydration reactions. Thus, for electron microscopy a sample preparation method needs to be found, which permits the particle structures at specific reaction stages to be fixed without introducing artefacts. Third, the particle structure is heterogeneous and disordered and, therefore, two dimensional microscopy can not reveal the relevant microstructural features which dominate the rheological properties. The most critical parameters in this context are the coordination number, the number of particle-particle contacts and the geometry of the particle-particle interfaces. These parameters can only be described quantitatively with high resolution 3D-microscopy in combination with advanced image-based modelling.

At present, 3D methods that operate in the range between the nm- and µm-scales are rare. Objects with dimensions below the µm-scale can hardly be resolved with X-ray absorption tomography (for discussions of the method see Ito et al., 2003; Kaestner et al., 2003; Sutton et
Cryo-FIB-nanotomography for quantitative analysis of particle structures in cement suspensions

Yamauchi et al., 2003). Higher resolution down to the molecular level in 3D can be achieved with transmission electron microscopy (TEM-tomography) (Yamauchi et al., 2003). However, the sample thickness for TEM-tomography is very small (<100nm) and therefore, for disordered microstructures with a wide particle size distribution (PSD), no representative volume can be analysed with this technique.

In the past few years a new 3D-microscopy method based on serial sectioning with a focused ion beam (FIB) (Inkson et al., 2001) has emerged, which has the potential to overcome many of the problems hampering these techniques. As a refinement of the standard commercial 3D-FIB procedures, we have recently developed the so-called FIB-nanotomography (FIB-nt) technique (Holzer et al., 2004). The refinements applied include automated drift and focus corrections, and now FIB-nt is capable of precise serial sectioning at resolutions below 20nm (see fig. 1). In contrast to TEM-tomography, the samples can be relatively thick and larger volumes can be analysed (50*50*50µm). Consequently, FIB-nt closes the gap in 3D-microscopy between TEM-tomography at the molecular level and classical X-ray absorption tomography on the µm-scale and thus opens new possibilities for the study of complex granular microstructures.

FIB-nt has been used for the statistical particle shape analysis and topological characterisation of granular textures in unhydrated cement (Holzer et al., 2006). There it was demonstrated that even in complex microstructures with dense agglomerates, it is possible to identify the individual sub-grains, which is the basis for precise statistical analysis. As an example, moments of inertia have been determined for cement powder. The smallest grain size fraction that was analysed had a 50% fractile of 0.7µm. This unique data can be used as structural input for object-oriented modelling of rheological processes (e.g. dissipative particle dynamics (Martys, 2005)).

For statistical analysis of the data volumes from FIB-nt, specifically designed computational procedures have been developed for object recognition and for stereological correction of truncation effects at the sample volume boundary (Münch et al., 2006). In combination with the high-resolving power of FIB-nt, the algorithms developed enable...
Precise statistical characterization of complex microstructures such as particle size distributions (PSD) and particle shape analysis from fine cement fractions where the smallest objects have diameters under 100nm.

For microscopy analysis of suspensions with SEM, TEM and also with FIB-nt, aqueous samples need to be solidified. This can be done by cryo-fixation (Bachmann and Mayer, 1987). Conventional shock freezing has been applied to fresh cement pastes for cryo-SEM investigations (Bachmann and Mayer, 1987), however, simple shock-freezing leads to the formation of relatively large ice crystals which may disturb the particle structure considerably. By using the high-pressure freezing (HPF) technique as developed in the life sciences (Moor, 1987), growth of ice crystals can be reduced and the water vitrified (Shimoni and Müller, 1998). HPF has already been applied to concentrated ceramic suspensions (Wyss et al., 2002; Wyss et al., 2004). In these investigations the particle structure of monosized silica-particles in the electrostatically-stabilized and in the flocculated state was characterised by means of pair correlation functions based on stereo-cryo-SEM. To date, the HPF technique has not been applied to fresh cement pastes, nor has it been combined with FIB-nt.

In this paper we present first results from the new cryo-FIB-nanotomography method. The technique has been used for the quantitative characterisation of particle structures in high-pressure-frozen cement pastes. Before presenting the details of the method and the results from the cryo-FIB-nt analysis, the basic questions relating to the microstructure of fresh cement pastes are briefly discussed in the next section.

4.2 Principles of the relationship between particle structure and rheological properties

The yield stress ($\tau_0$) of concentrated colloidal dispersions is dependent on two basic factors: interparticle forces and microstructure. With respect to the microstructure, the most relevant parameters are the number of interparticle contact points and the geometry of these contacts. The latter parameter is related to the contact curvature and the surface area of the
particle-particle interfaces, and to date, no suitable microscopy method is available that can resolve these structural details in real cement pastes.

Under the assumption of spherical particle shape, the number of contacts can be determined indirectly based on geometrical considerations including the solid volume fraction ($\phi$), the mean particle size ($D_v$) and the particle size distribution (PSD) (Suzuki and Oshima 1983). These relationships have been incorporated into the following expression for the yield stress (Flatt, 2004):

$$\tau_0 = \frac{1.8 \ G \ F_{PSD} \ \phi^2}{\pi^4 \ D_v \ \phi_m (\phi_m - \phi)}$$

Here $G$ is the interparticle force parameter, $F_{PSD}$ is the particle size distribution function and $\phi_m$ is the volume fraction at maximum packing. It has been shown, that this expression fits well the volume fraction dependence of independent sets of yield stresses (Flatt, 2004).

While this analysis appears to hold in nonreactive particle systems, in cement the yield stress is affected by distinct chemical and physical processes associated with the early cement hydration. The effects of these processes in reactive systems are difficult to quantify. Qualitatively they can be described as follows:

4.2.1 Chemical effects:

During the first minutes of hydration, dissolution of Ca-aluminate phases and alkali-sulfates are predominant. Almost simultaneously, nucleation and precipitation of ettringite and other sulfo-aluminate phases also occurs. As a consequence of dissolution and precipitation, the PSD of the particles in suspension is expected to change. Dynamic measurements of the PSD by means of laser granulometry (LG) (see eg. Stark et al., 2005) are affected by agglomeration and hence, reliable statistical size information is difficult to obtain with LG in reactive systems. In addition, the solid volume fraction will also undergo changes due to hydration. The net reaction volume during the early stages is in the range of only a few vol. %, and conventional analytical methods such as XRD, TGA and SEM are generally not precise enough to reliably quantify the small volumetric changes which occur.

In summary, the chemical effects lead to a change of solid volume fraction ($\phi$), mean particle size ($D_v$) and particle size distribution (PSD) as a function of hydration time. The lack of suitable methods for precise quantification of hydration imposes major limitations on the theoretical prediction of the rheological properties of fresh cement paste.

4.2.2 Physical effects:

The state of dispersion/agglomeration depends strongly on the nature of the interparticle forces (attractive or repulsive). Fig. 2 illustrates three stages of dispersion/agglomeration for a simplified system with two distinct size classes (blue > 0.5µm / black < 0.5µm). The solid volume fraction and the PSD are constant for all three stages and the microstructural changes are only due to the clustering and rearrangement of the small particles (< 0.5µm). The
location of the larger particles (> 0.5µm) remains nearly unchanged. As a consequence of clustering, the effective particle size increases in the sense that the clusters effectively act as single objects consisting of numerous subgrains (fig. 2b). Based on ESEM investigations of fresh cement pastes, clusters with a typical size of 2 µm have been described as a very common feature during the early hydration of portland cement (Holzer et al., 2003). These clusters are termed "small interstitial grains" (SIG) and are found to form bridges between the larger particles at longer hydration times (setting time, 3-5 hrs). This agglomeration process leads to the formation of a long-range particle network (fig. 2c), which can be correlated with a significant increase in yield stress and associated solidification. For a detailed understanding of the relationships between the microstructure and the rheological properties, a quantitative description of the time dependent agglomeration is necessary, and obtaining this remains a challenging problem which has not yet been solved.

The aim of this paper is to demonstrate the capability of cryo-FIB-nt for obtaining a quantitative description of the relevant microstructural parameters in cement pastes. Specifically the effects of the early hydration on the PSD, particle density and surface area are addressed. In addition, the potential of cryo-FIB-nt for the topological description of particle-particle interfaces in agglomerates is illustrated.

4.3 Experimental: Materials and Methods

4.3.1 Materials and paste mixture

The raw material for this work was ordinary portland cement (OPC) CEM I 42.5R (Normo4: www.holcim.ch). A fine particle fraction was separated from this cement using air classification (Hosokowa Alpine 1000 MZR: www.alpinehosokawa.com). The fine fraction was chosen so that the data volume obtained with FIB-nt (14.6 * 17.1 * 9.2µm) would encompass a statistically representative number of particles. The particle size distribution (PSD) of the cement fine fraction was determined by laser granulometry (ZetaSizer, Malvern Instruments, Malvern, Worchester, UK) of a suspension in ethanol (5 min ultrasonic treatment). The resulting PSD is shown in fig. 5. The 50% fractile is 3.16 µm.

Fresh cement pastes were produced with a water-to-cement ratio (w/c) of 0.5 (g/g) and contained a polycarboxylate superplasticiser (0.5% solid matter). For cryo-FIB-nt, a sample was prepared by stopping the hydration after 6 minutes with high-pressure freezing (Sample C6).

4.3.2 High-pressure freezing (HPF)

In order to maintain the true particle structure in the frozen suspension, growth and formation of ice crystals should be avoided. Due to the thermal properties of water and ice (Bachmann and Mayer, 1987), vitrification can only be achieved with very small samples. With high-pressure freezing (HPF), 2100 bars are applied rapidly to the sample prior to the
cooling process with liquid N$_2$ (Moor, 1987; Monaghan et al., 1998). Under these conditions, formation of ice crystals is suppressed.

Simulation of the temperature evolution during HPF and the associated cooling rates along a profile through the sample has been performed for flat and cylindrical samples (thickness/diameter 200µm) (Shimoni and Müller, 1998). These simulations indicate fast cooling rates at the boundary, where temperatures drop from ambient to -100°C within 30 msec during HPF. In the center of the samples (100µm distance to the sample wall), cooling rates are at least a factor 3 to 4 slower. Hence the degree of vitrification is strongly dependent on sample geometry, sample size and location within the sample.

In the current study, HPF was performed with the high-pressure freezer HPM 010 (Bal-Tec, Liechtenstein: www.bal-tec.com) at ETH Zürich. For each sample, two brass specimen carriers were used with a cavity depth of 200 µm of each carrier (TedPella Inc, Redding, CA: www.tedpella.com). After freezing and fracturing under liquid nitrogen, the carriers were

Fig. 3. Various stages of the cryo-FIB-nt data obtained: a) 3D reconstruction of the particle structure from sample C6 (fresh cement paste, hydrated for 6 minutes, high-pressure frozen); b) Binary particle mask of the region in (a) encompassing 47'284 objects, 3.75% of which are truncated at the boundary. The effects of truncation on the PSD (see figs 4 and 5 and tables 2 and 3) are corrected for according to the stereological procedures described previously (Münch et al., 2006). For the segmentation procedures applied (I), see references in text.; c) and d) Binary masks for separation (II) of particles >0.5µm and < 0.5µm, respectively. 97% of all objects are smaller than 0.5 µm, but their volume represents only 9 %; e) and f) Semitransparent visualization (III) of c and d, respectively.
transferred into a high-vacuum sputter coater MED-020 (Bal-Tec). The transfer was performed in a tube-like container filled with nitrogen gas in order to avoid ice formation on the sample surface. For cryo-FIB-nt, a relatively thick Pt-coating was applied (> 20nm) without freeze etching.

4.3.3 Cryo-SEM

A high-pressure-frozen specimen sandwich was transferred onto the cold stage of a freeze-fracturing/etching/coating device BAF060 (Bal-tec). The specimen was fractured at -115°C by pushing away the top carrier of the sandwich using a hard metal knife. Subsequently, the specimen was etched (sublimation of water) at -105°C for 4 minutes, rotary shadowed (40rpm) with 3nm of Pt/C at 45° using electron beam evaporation, and transferred onto the cold stage (-115°C) of a LEO Gemini 1530 SEM. The sample transfer for cryo-SEM was performed using the high-vacuum cryo-transfer system VCT100 (Bal-tec). (See Fig. 4c)

4.3.4 Cryo-FIB-nanotomography

In this study, the serial sectioning procedure of FIB-nt was adapted for the cryo application. For this purpose, a dual-beam FIB (Strata DB 235 from FEI, Hilsboro, USA: www.feicompany.com) was used. Details of our FIB-nt method (without cryo) have been published recently (Holzer et al., 2004; Holzer et al., 2006). Similar 3D-FIB techniques have also been described by others (Inkson et al., 2001; Inkson et al., 2001; Kubis et al., 2004).

Charging effects are a major problem when using FIB-nt under cryo-conditions, and careful optimisation is needed to obtain suitable image quality. The procedure can briefly be described as follows: The sample is transferred to the FIB under N₂-gas in order to avoid condensation. Once in the FIB, the sample temperature is stabilised at < -140°C on a N₂-cooled cryo-stage (Bal-Tec). Subsequently, a thick (~1 µm) metalorganic layer is deposited for protection of the surface during milling. In the conventional mode, the metalorganic gas molecules (i.e. trimethyl-methylcyclopentadienyl-platinum; (CH₃)₃CH₂C₅H₅Pt)) are decomposed in the ion beam and a conductive metal deposit is thus formed. In cryo-mode, the gas condenses on the cold sample surface without metallisation, and without metallisation of the protective layer, charging effects become very strong during the subsequent FIB-milling and imaging processes. However, at least the surface of the metalorganic condensation can be metallised after deposition by controlled exposure to the ion beam. In order to minimise the charging effects during serial sectioning, the electron beam voltage and spot size were decreased (3 kV and spot 3, respectively) and the backscattered detection mode (TLD-B) was chosen. While charging is minimized, these settings result in rather low image contrast.

A further problem in the cryo-mode is caused by the inhomogeneity of the condensed protective layer. This layer tends to have numerous pores which results in irregular milling rates and consequently stripes form on the FIB-milled planes (the so-called waterfall effect). These stripes and the low contrast level currently represent the most problematical factors for segmentation, object recognition and quantification of microstructures from cryo-FIB-nt data.
Quantitative analysis of 3D data volume

Fig. 3a illustrates the 3D-reconstruction of the image stack shown above in fig. 1 (230 images from sample C6, paste with fine fraction of OPC, hydration stopped after 6 minutes with HPF). The voxel resolution is 19.8 x 25.1 x 40.0 nm and the cube dimensions are 17.1 x 14.6 x 9.2 µm.

In order to obtain reproducible and accurate microstructural results, the subsequent segmentation step is of major importance. For this purpose special algorithms have been developed for particle recognition and for stereological correction of the boundary truncation effects (Münch et al., 2006). For the present study, these methods were extended in order to correct for the image defects that are specific to cryo-FIB-nt imaging. The vertical stripes (waterfall effect) are corrected with a procedure incorporating fast Fourier transform (FFT)-filtering. In addition, edge detection algorithms have been developed to replace the grey-scale thresholds used previously. In this way, problems that arise from varying grey-scale values across the stack of images (z-direction) and also from low contrast and from brightness gradients within the images (x-y-directions) can be compensated for. A detailed description of the computational correction procedures applied is beyond the scope of this article and will be the issue of a forthcoming article (Münch et al., in prep.).

The resulting binary particle mask after object recognition is shown in fig 3b. The volume contains 48'000 particles. From this data statistical information (PSD, specific surface area, nr. of particles per volume) can be gained by applying procedures that have been described previously elsewhere (Münch et al., 2006). The quantitative data for sample C6 is discussed below.
4.4 Results: particle size distribution, number of particles and surface area

In the following sections, qualitative and quantitative results from the cryo-FIB-nt analysis are presented for the particle structure in the cryo-stabilized cement suspension that was hydrated for 6 minutes ($t_{6\text{min}}$) (Sample C6). The quantitative results are compared with reference data from the unhydrated cement powder at $t_{0\text{min}}$ obtained with laser granulometry (LG). It was shown for different grain size fractions of a cement powder that FIB-nt and laser-granulometry give nearly identical size distributions for the size range above 1 µm (Münch et al., 2006). From a comparison of three methods (FIB-nt, LG and SEM), it becomes obvious that laser granulometry tends to overestimate the amount of particles smaller than 1 µm, whereas FIB-nt gives reliable results for this size range (unpubl. results, Holzer et al, in prep.). This has to be kept in mind for the following comparison of data from FIB-nt and LG.

The theoretical volume fraction of the solid content in the initial paste mixture at $t_{0\text{min}}$ is 39.4%. The latter value was calculated for a water-to-cement ratio of 0.5 and a density of 3.077 g/cm$^3$. The solid volume fraction obtained with cryo-FIB-nt for the cement suspension

Table 1: particle size distribution (see fig. 5)

<table>
<thead>
<tr>
<th>size distribution</th>
<th>volume fraction [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LG $t_{0\text{min}}$</td>
</tr>
<tr>
<td>particles with a diameter $&gt; 1$ µm</td>
<td>90.00</td>
</tr>
<tr>
<td>$&lt; 1$ µm</td>
<td>10.00</td>
</tr>
<tr>
<td>$&lt; 0.5$ µm</td>
<td>0.20</td>
</tr>
<tr>
<td>$&lt; 0.2$ µm</td>
<td>0.00</td>
</tr>
<tr>
<td>$&lt; 0.1$ µm</td>
<td>0.00</td>
</tr>
<tr>
<td>solid volume fraction in suspension</td>
<td>39.39</td>
</tr>
</tbody>
</table>

*1 LG = Laser Granulometry data from unhydrated cement powder ($t_{0\text{min}}$)
*2 Cryo FIB-nt analysis of cement suspension C6 after 6 min hydration ($t_{6\text{min}}$)
*3 total solid=100%
*4 total solid and liquid=100%
*5 calculated for water-to-cement ratio=0.5 and density of cement=3.08 g/cm$^3$
Cryo-FIB-nanotomography for quantitative analysis of particle structures in cement suspensions

The small difference of 1.8 vol% is in the same range as the analytical uncertainty, which indicates that no detectable segregation or sedimentation occurred during the cryo-sample preparation procedure (Assumption: The absolute value of the reaction volumes from dissolution and precipitation are equal).

Although in the first six minutes the total volume of solids thus remains constant (or the changes are beyond the detection limit), significant changes are observed in the particle size distribution (PSD) as a consequence of the ongoing hydration reactions (dissolution and precipitation). This effect can be observed qualitatively by comparing two FIB-cross-sections of cryo-stabilised samples in the unhydrated and hydrated states (fig. 4). The unhydrated sample (t₀min, dispersed in ethylene glycol) contains only very few particles with diameters in the sub-µm range (fig. 4a). In contrast, the hydrated sample (t₆min) is characterised by numerous small particles, that are well dispersed in the interstitial space (fig. 4b). As observed in high-resolution cryo-SEM (fig. 4c), most of the small, interstitial precipitates are characterised by hexagonal, short prismatic crystal shapes, which is typical for ettringite (Ca₆[Al(OH)₁₂](SO₄)₃)*26H₂O) (Moore and Taylor, 1968). These qualitative observations correlate well with the PSD curves at t₀min (from LG) and at t₆min (from cryo FIB-nt), as shown in Fig. 6. Specific particle density (i.e. nr of objects per volume) as a function of particle size in sample C6. Red curve: Unhydrated cement / LG. Blue curve: Cement paste hydrated for 6 minutes / cryo-FIB-nt. See also table 2.

<table>
<thead>
<tr>
<th>Particle density (Nr of particles per volume suspension)</th>
<th>from cryo FIB-nt analysis of suspension C6</th>
<th>from LG at t₀min*³</th>
</tr>
</thead>
<tbody>
<tr>
<td>in FIB-cube C6*¹</td>
<td>per mm³</td>
<td>in %</td>
</tr>
<tr>
<td>all particles</td>
<td>47284</td>
<td>2.055E+10</td>
</tr>
<tr>
<td>truncated*²</td>
<td>1773</td>
<td>7.71E+08</td>
</tr>
<tr>
<td>&gt; 1 µm</td>
<td>364</td>
<td>1.58E+08</td>
</tr>
<tr>
<td>&lt; 1 µm</td>
<td>46920</td>
<td>2.04E+10</td>
</tr>
<tr>
<td>&lt; 0.5 µm</td>
<td>46149</td>
<td>2.01E+10</td>
</tr>
<tr>
<td>&lt; 0.2 µm</td>
<td>37638</td>
<td>1.64E+10</td>
</tr>
<tr>
<td>&lt; 0.1 µm</td>
<td>10733</td>
<td>4.66E+09</td>
</tr>
</tbody>
</table>

*¹ cube volume of sample C6 = 14.6*17.1*9.2 µm = 2301 µm³

*² particles affected by truncation at the cube boundary

*³ calculated from PSD for w/c ratio=0.5, density=3.08 g/cm³. Assumption: spherical particles

C6 (t₀min) is 41.2%. The small difference of 1.8 vol% is in the same range as the analytical uncertainty, which indicates that no detectable segregation or sedimentation occurred during the cryo-sample preparation procedure (Assumption: The absolute value of the reaction volumes from dissolution and precipitation are equal).
Cryo-FIB-nanotomography for quantitative analysis of particle structures in cement suspensions

in fig. 5. The entire PSD curve for \( t_{6\text{min}} \) is shifted towards smaller particle sizes due to the early hydration reactions, and the 50% fractile is reduced from 3.1µm at \( t_{0\text{min}} \) to 2.1µm at \( t_{6\text{min}} \). Since LG tends to overestimate the volume of particles in the sub-µm range, the difference between the two samples might be even larger in reality. The difference of the two curves is attributed mainly to the precipitation of small crystal seeds in the sub-µm range, as illustrated qualitatively in fig. 4a-4c. In addition, particles with small fractures may become fragmented into distinct subgrains due to dissolution processes, which are triggered along the initial cracks, and hence dissolution-fragmentation also contributes to the observed shift in the PSD towards smaller diameters. As a consequence of these processes, the volume fraction of particles with diameters smaller than 500 nm increases from 0% to 9% during the first 6 minutes (see table 1). This increase occurs at the expense of the larger particles, whereas the total solid volume remains nearly constant.

The difference between \( t_{0\text{min}} \) and \( t_{6\text{min}} \) is even more significant when looking at the number of particles and the corresponding size distributions (see table 2). In total, there are 47'284 particles detected in the FIB-nt cube (C6) at \( t_{6\text{min}} \). The specific particle number density (i.e. number of particles per mm\(^3\) of suspension) is plotted as a cumulative function of the particle

Table 3: Data for surface area (see fig. 7)

<table>
<thead>
<tr>
<th>Surface area</th>
<th>\textbf{from FIB-nt analysis} of suspension C6 after 6min hydration</th>
<th>\textbf{from LG(^4)} at ( t_{6\text{min}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \mu m^3 ) in FIB-cube C6(^1)</td>
<td>( \text{mm}^2 ) per mm(^3)</td>
</tr>
<tr>
<td>all particles</td>
<td>6655</td>
<td>3951</td>
</tr>
<tr>
<td>&gt; 1 µm</td>
<td>2628.7</td>
<td>1560.6</td>
</tr>
<tr>
<td>&lt; 1 µm</td>
<td>4026.3</td>
<td>2390.4</td>
</tr>
<tr>
<td>&lt; 0.5 µm</td>
<td>3114.5</td>
<td>1849.1</td>
</tr>
<tr>
<td>&lt; 0.2 µm</td>
<td>1657.1</td>
<td>983.8</td>
</tr>
<tr>
<td>&lt; 0.1 µm</td>
<td>247.6</td>
<td>147.0</td>
</tr>
</tbody>
</table>

\(^1\) cube volume of sample C6 = 2301 \( \mu m^3 \)

\(^2\) per g of suspension (w/c ratio=0.5)

\(^3\) per g of dry powder (particles)

\(^4\) LG=Lasergranulometry data from dry cement powder

![Fig. 7. Specific surface area (mm2 per mm3) as a function of particle size in sample C6. Red curve: Unhydrated cement / LG. Blue curve: Cement paste hydrated for 6 minutes / cryo FIB-nt. See also table 3.](image)
size in fig. 6. The total particle number density is 0.294 billion particles per mm$^3$ at $t_{0\text{min}}$ and 20.55 billion particles per mm$^3$ at $t_{6\text{min}}$ (Table 2). Thus, for the unhydrated cement at $t_{0\text{min}}$, the calculated particle number density is two orders of magnitudes smaller and the particles are much coarser (see table 2 and fig. 6, red curve). In contrast, at $t_{6\text{min}}$, more than 97% of the particles have a diameter under 0.5µm, but they represent only 9% of the total solid volume. It is obvious that the small particles <500nm dominate the particle density at $t_{6\text{min}}$, as can be seen in the 3D-structure of the particle classes >500nm and <500nm depicted in fig. 3e and 3f, respectively. Thus, during the first 6 minutes of hydration an enormous amount of very small particles (<500nm) are precipitated.

Particle interactions and associated rheological processes are strongly influenced by the amount of surface area in a given solid/liquid mixture which is contributed by the particles present. For sample C6, the specific surface area was calculated based on the PSD and particle density data. As shown in table 3, the total surface area at $t_{0\text{min}}$ is 0.75 m$^2$ per g of suspension and 1.12 m$^2$ per g of dry solid content. In contrast, the surface area in the hydrated cement paste at $t_{6\text{min}}$ is three times higher (i.e. 2.13 m$^2$/g suspension and 3.17 m$^2$/g dry powder). In the unhydrated cement, 70% of the surface can be attributed to the particles >1µm. In the hydrated sample, the particles <500nm represent a surface area fraction of >45 %, although their volume fraction is only 9 vol%. This corresponds with the fact, that these size classes represent 97% of the total number of objects in the suspension. The precipitates <200nm still contribute 25% of the total surface. The comparison of hydrated and unhydrated samples (see above) indicates that the particles <500nm at $t_{6\text{min}}$ mostly represent new precipitates, since they can not be detected at $t_0$.

Thus, the formation of hydration products during the first 6 minutes leads to an increase of the specific surface area by a factor of 3. This increase can be attributed to the numerous small ettringite crystals, which precipitate during the first minutes of cement hydration. As

Fig. 8. Visualisation of 3D particle structure obtained with cryo-FIB-nt for 6-minute-old cement paste (compare with fig. 3): a) Particle-particle interfaces in red; b) Overlay of particle interfaces with large, and mostly unhydrated, clinker particles (blue, >500nm) and with small particles, mostly ettringite precipitates (yellow, <500nm); c) Same as b), but blue particles are rendered semitransparent.
mentioned earlier, dissolution-fragmentation of larger particles also contributes to an increase in the specific surface and a decrease in the average particle size.

4.5 Discussion

In the present study FIB-nt is combined for the first time with cryo-techniques in order to analyse quantitatively the microstructural changes that occur during the first minutes of cement hydration. Since the fresh cement paste is a highly-loaded and structurally-complex suspension, no other technique can reveal equivalent microstructural data. Nevertheless, since Cryo-FIB-nt is a new technique, many critical points require further improvement. The most critical points for the investigation of cement suspensions are a) sample preparation, b) representativity and c) the link of microstructural data with rheological properties: These issues are discussed in turn below.

4.5.1 Sample preparation: Stopping hydration and preservation of the particle structure

With the high-pressure freezing technique, the cement suspension can be solidified and the hydration stopped at specific hydration times. Because of the low thermal conductivity of water, only very small samples can be vitrified with HPF. For the present investigation we used brass specimen carriers with a cavity depth of 200μm. The handling of such small amounts of suspension is a delicate task which represents a potential source of error that is difficult to quantify. The small change of the solid volume fraction (t_{min} 39.4%; t_{6min} 41.2%) and the absence of visually detectable freezing artefacts (e.g. ice crystals or a freezing-front) indicate that the original particle structure of the cement suspension can be preserved with this technique. Nevertheless, in order to prove the accuracy of the cryo-FIB-nt method, more quantitative work needs to be done, and this should include the analysis of suspensions containing inert reference particles.
4.5.2 Representativity

Ordinary Portland cement has a relatively wide particle size distribution ranging from sub-μm- up to 100 μm-scales. For a reliable quantification of the entire particle system, the current size of the imaging window (i.e. the edge length of the analysed FIB-cube) is a limiting factor which is directly related to the magnification. The higher the magnification, the smaller the window size is. In systems with a wide particle size distribution, the relatively small window size of the FIB-nt technique causes problems for the representative analysis of the coarser system components. In our example the window size is 15 μm, and this is clearly not sufficient for a representative analysis of normal portland cement, which is typically characterised by a 50% fractile of approximately 20 to 30 μm. Therefore, for purposes of the present study, we separated and used a fine fraction of the cement with a $d_{50}$ of 3.2 μm. However, the separation of the fine fraction results in an enrichment of sulphate (gypsum) and aluminate-clinker. This chemical fractionation leads to an unusually high production of ettringite during the first few minutes of cement hydration. In a normal portland cement, the amount of ettringite is expected to be less than 9 vol % after 6 minutes. For future cryo-FIB-nt studies with cement fine fractions, chemical fractionation can be avoided by complete grinding of the entire cement batch. But even if mineralogical fractionation during grinding is avoided, the reduction of the particle size will still effect the hydration kinetics. Thus in order to study the microstructure of cement paste with the full grain size distribution, a multi-scale microscopy approach is required. Technically it is possible already today to analyse the coarse system components by Cryo-X-ray tomography and the fine components with cryo-FIB-nt. However, the integration of 3D-data from different methods into a consistent microstructural model will require extensive computational analysis.

4.5.3 Link of microstructural data with rheological properties

As discussed previously, the influence of the microstructure on the yield stress ($\tau_0$) of concentrated suspensions can be described theoretically by relatively simple parameters such as particle size distribution (PSD), mean particle size ($D_v$) and solid volume fraction ($\phi$) (see equation 1, (Flatt, 2004). These microstructural parameters can be determined experimentally for the raw material (ie. dry cement powder). Based on such measurements the rheological properties can be predicted for inert systems with different solid loadings. However, cementitious suspensions are affected by chemical reactions and by agglomeration processes which lead to a time-dependent change of yield stress and viscosity and finally to solidification (setting and hardening). Up to now, the effects of chemical hydration and physical agglomeration could not be distinguished or quantified, because no suitable method was available. Cryo-FIB-nt for the first time allows us to quantify the time-dependent microstructural changes directly from the reactive suspensions. For example, the mean particle size in sample C6 is decreasing from 3.1μm at $t_{0\text{min}}$ to 2.1μm at $t_{6\text{min}}$. Also an overall shift of the PSD-curve can be described during the first 6 minutes of hydration, as illustrated in fig. 5. Rheological measurements (unpubl. data) of the fresh cement paste C6 indicate that this PSD-shift is associated with a rapid increase of viscosity and yield stress. During the
same period, the solid volume fractions ($\phi$) are nearly unchanged (i.e. within the analytical error). This may explain the observation that equation 1 describes well the experimentally validated relationships between yield stress ($\tau_0$) and solid volume fraction ($\phi$) for different mixtures (Flatt, 2004). However, the time dependent influence of chemical hydration on rheological properties is still not validated experimentally. For this purpose a more systematic study is currently performed including more extensive cryo-FIB-analyses at different hydration times and combining this data with rheological measurements.

4.5.4 Perspectives: higher order topological parameters

The simple parameters such as PSD, mean particle size ($D_v$) and volume fraction ($\phi$) represent only a very indirect and thus rudimentary microstructural description of complex suspension. Especially the microstructural changes resulting from agglomeration cannot be described with these simple parameters. Fig. 2 schematically illustrates the clustering process (2b) and the formation of a long-range particle structure (2c) that leads to an increase of viscosity and finally to solidification. For a microstructural description of these processes, higher order topological information is required such as the number of interparticle contacts and the geometry (curvature and surface area) of the associated particle interfaces. As illustrated qualitatively in figs. 8 and 9, it is the specific strength of cryo-FIB-nt to reveal such higher-order topological features from complex suspensions at fixed points in time during processing. At the moment, a quantitative description of the particle contacts and interfaces is beyond the scope of this paper, however for future investigations this kind of parametrisation opens new perspectives, because it enables a more direct description of the critical microstructural parameters that dominate the visco-mechanical properties of complex and reactive suspensions.

4.6 Conclusions

In conclusion, this work demonstrates, that cryo-FIB-nt is a powerful technique which opens new ways to describe the critical microstructural features in highly-loaded and structurally-complex suspensions. When applying this technique, artefact-free sample preparation represents a major challenge, and it has been successfully shown that high-pressure freezing is a suitable sample preparation method. The combination of techniques used in this work lays the foundations for future studies on the complex relationships between particle structures in suspensions and the corresponding mechanical and rheological properties where direct parameterisation of features related to the particle interactions such as the area of interfaces and the number of contacts will be of major importance.
References


Chapter 5

Adsorption of polyelectrolytes and its influence on the rheology, zeta potential and microstructure of various cement and hydrate phases

Anatol Zingg, Frank Winnefeld, Lorenz Holzer, Joachim Pakusch, Stefan Becker, Ludwig Gauckler

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5 Adsorption of polyelectrolytes and its influence on the rheology, zeta potential and microstructure of various cement and hydrate phases

Anatol Zingg a,*, Frank Winnefeld a, Lorenz Holzer a, Joachim Pakusch b, Stefan Becker b, Ludwig Gauckler c

a Empa, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Concrete/Construction Chemistry, Ueberlandstrasse 129, 8600 Dübendorf, Switzerland
b BASF AG, GKDC-B1, Carl-Bosch-Strasse 38, 67056 Ludwigshafen, Germany
c ETH, Swiss Federal Institute of Technology Zurich, Institute of Nonmetallic Inorganic Materials, Department Materials, Wolfgang-Pauli-Strasse 10, 8093 Zurich, Switzerland

Abstract

In cement suspensions many chemical and physical processes occur at the same time. Therefore, the complex cement-water system was simplified for this study with experiments carried out on synthesized individual clinker and hydrate phases. Thereby, the interaction of each mineral phase with superplasticizers (polycarboxylate-ether) was investigated by zeta potential experiments, rheology measurements and adsorption analysis. Cryo-microscopic results of cement suspensions will link the macroscopic mineral-superplasticizer interaction with the bulk cement-water (-PCE) system.

It will be shown, that the zeta potential of calciumaluminatesulfates (ettringite, hydrate phase) governs the zeta potential of the bulk cement. In addition, the particle interaction behaviour between tricalciumsilicate (clinker), calciumsilicatehydrate and ettringite (hydrate phases) will be shown as they are the major constituents during early hydration times of cement suspensions. Furthermore, the influence of superplasticizers on these major constituents will be demonstrated and the consequence for the workability of cement suspensions shall be discussed. The macroscopic findings will be confirmed by cryo-microscopic data.

Keywords: polyelectrolytes; superplasticizers; cement suspensions; hydrate phases; clinker phases; zeta potential; adsorption; cryo-microscopy

* Corresponding author
E-mail address: azingg@postmail.ch (A. Zingg)
5.1 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 loosing the workability in order to reach high concrete strength and durability.

In this study we focus on the interaction of specific clinker and hydrate phases with superplasticizers. The study of specific defined phases aims to improve the understandings about the influence of polycarboxylate-ether based superplasticizers (hereinafter called PCE) on the microstructural evolution of cement suspensions during the early hydration and its link to macroscopic data like rheology or setting behaviour. The microstructures are the result of precipitation reactions and interparticle forces. The latter determine whether the system tends to agglomerate or remains dispersed. In order to link macroscopic phenomena with microstructural data, the influence of PCE on the main clinker and hydrate phases has to be known.

The hydration of Portland cement, mainly composed by calciumsilicates and calciumaluminates interground with gypsum, is a time dependent process and four major hydration periods [1] can be distinguished:

i) Initial hydration (minutes): dissolution of mainly aluminium-rich clinker phases and precipitation of calciumaluminate-sulfate hydrates.

ii) Dormant period (minutes to several hours): hydration rates decrease significantly.

iii) Main hydration (hours to days): acceleration of dissolution of dominating silicate-rich phases and precipitation of calcium silicate hydrates and calciumhydroxide lead to setting and early strength development of the cement suspension.

iv) Continuous hydration (days to years): strength development is continued.

In terms of workability and cement-superplasticizer interaction, the initial hydration up to the start of the main hydration is of major importance. During this early hydration, tricalciumsilicate (C₃S), tricalciumaluminate (C₃A), gypsum (Cs•2H), ettringite (C₃A•3Cs•32H) and calcium silicate hydrates (C-S-H) are the main mineral compounds¹ which are involved in a cement suspension.

¹ C = CaO, A = Al₂O₃, S = SiO₂, H = H₂O and  s = SO₃
Adsorption of polyelectrolytes and its influence on the rheology, zeta potential, and microstructure of various cement and hydrate phases

<table>
<thead>
<tr>
<th>Reference</th>
<th>Solvent</th>
<th>C₂S</th>
<th>C₂S</th>
<th>C₂A</th>
<th>C₂AF</th>
<th>C₃H₁</th>
<th>-</th>
<th>CH</th>
<th>ettringite</th>
<th>M₂S</th>
<th>Additional information</th>
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</thead>
<tbody>
<tr>
<td>Singh and Ojha [14]</td>
<td>10 mmol/L Ca(OH)₂</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<td>0.3 g in 100 ml</td>
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<tr>
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<td>10 mmol/L Ca(OH)₂</td>
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<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
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<td></td>
<td>2 h equil. time</td>
</tr>
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<td>Chen and Mehta [16]</td>
<td>dest H₂O, 1 mmol/L Ca(OH)₂</td>
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<td>Nachbaur et al. [17]</td>
<td>NaOH as f(CaO) KCl as f(CaO) K₂SO₄ as f(CaO)</td>
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<td></td>
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<tr>
<td>Viallis-Terisse et al. [18]</td>
<td>&gt; 2 mmol/L CaO</td>
<td></td>
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<td>IEP: 2 mmol/L Ca</td>
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<tr>
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<td>500 mmol/L NaOH</td>
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<td></td>
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<tr>
<td>Divret et al. [20]</td>
<td>1500x dilution dest. H₂O</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>negative</td>
</tr>
<tr>
<td>Peng et al. [21]</td>
<td>water / gypsum = 0.53</td>
<td></td>
<td></td>
<td></td>
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<td>IEP: 2 mmol/L Ca</td>
</tr>
<tr>
<td>Labbe et al. [22]</td>
<td>CaCl₂ + Ca(OH)₂ &lt; (10 mmol/L Ca)</td>
<td></td>
<td></td>
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<td></td>
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<td></td>
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</tr>
<tr>
<td>Pointeau et al. [23]</td>
<td>Equilibrated waterionic strength: -1-50 mmol/L</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Hirsch [24]</td>
<td>different solid loads, diluted</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

Zeta potential [mV] and chemical composition of the solvents [mmol/L] reported from literature. N indicates negative, P positive zeta potentials. C₂S=tetracalcium silicate, C₂S=dicalcium silicate, C₂A=tricalcium aluminate, C₂AF=tetracalcium aluminate f的安全, gypsum, C₃H₁=calcium silicate hydrate, CH=portlandite, M₂S=monosulfate.
Although the influence of PCE on cementitious systems has been extensively investigated [2-8], 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) over the last decades. However, the possibility of simplification is limited if one wants to obtain relevant results, because of the complex chemical processes involved in cement suspensions. Such limitations will be discussed e.g. by comparing the zeta potential data of this study with zeta potentials reported in the literature (tab. 1) which are strongly related to the chosen chemical compositions of the solutions.

Unfortunately, zeta potentials strongly depend on the chemical composition of the solution. Ionic strength, ionic species and their valence are important parameters. The more defined the solution properties, the more precise and unambiguous are the zeta potential data. However, the pore solution of cement pastes presists certain parameters such as pH, conductivity and composition of ionic species. In general, pore solutions of CEM I 42.5 N after one hour of hydration are dominated by K⁺, SO₄²⁻ and OH⁻ ions (200-500 mmol/l) as major and Na⁺, Ca²⁺, Si⁴⁺ as minor (> 1 mmol/l) ionic species [9]. The concentration of additional ionic species such as Fe³⁺, Al³⁺, Mg²⁺, etc. is much lower and therefore, the influence of these species on the zeta potential measurement is negligible. Consequently, in this study a synthetic pore solution was used as main solution which has a chemical composition that is very similar compared with a real pore solution of a CEM I 42.5 N suspension. The results will be discussed and compared with the zeta potentials reported in the literature, taking into account the different chemical properties of the corresponding solution.

Long range particulate structures of dispersed and agglomerated systems are closely associated with interparticle forces between the different mineral particles [10-13]. Measurements of the zeta potential are commonly used to determine the interparticle forces. To our best knowledge, all reported data of zeta potential measurements in the literature (SCI, SCIE) on pure clinker and hydrate phases, are listed in table 1 [14-24]. At a first glance, the scattering of the zeta potentials is broad and the data contradictory (negative and positive values for the same mineral compound). However, the experiments reported in the literature have been carried out with various solutions, which differ considerably with respect to their chemical composition and ionic strength.
Tab. 2. Characterization of the polycarboxylate ether superplasticizers

<table>
<thead>
<tr>
<th>polymer</th>
<th>length of side chain p</th>
<th>density of side chains n:m</th>
<th>$M_n^1$ g/mol</th>
<th>$M_w^2$ g/mol</th>
<th>PDI $^3$</th>
<th>solid content mass.-%</th>
<th>mmol anionic Sites $^4$ / g solid</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCE 23-6</td>
<td>23</td>
<td>6:1</td>
<td>7600</td>
<td>18900</td>
<td>2.5</td>
<td>13.8</td>
<td>3.4x10$^{-3}$</td>
</tr>
<tr>
<td>PCE 102-2</td>
<td>102</td>
<td>2:1</td>
<td>16800</td>
<td>78000</td>
<td>4.7</td>
<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>

$^1 M_n$ = number-average molecular weight

$^2 M_w$ = mass-average molecular weight

$^3$ PDI = $M_n/M_w$ = polydispersity index

$^4$ calculated values, corresponds also to minimum mmol/l Na which is added to the solid-solvent system by titration, direct addition

This work focuses mainly on C$_3$S, C-S-H and ettringite because these minerals represent the key phases during early hydration period. The investigation includes zeta potential measurements, rheological experiments and PCE adsorption analyses. Finally, cryo-microscopic data from high-pressure frozen cement suspensions are presented in order to illustrate the link between the findings of interparticle behaviour of C$_3$S, C-S-H and ettringite phase with specific microstructural phenomena.

5.2 Materials

5.2.1 Superplasticizers

Three comb-shaped polycarboxylate-ether type superplasticizers (PCE) consisting of methacrylic acid copolymer (backbone) with grafted methylpolyethyleneglycole copolymers (side chains) were synthesized [25]. The architecture was varied by using different side chain densities and lengths. The basic chemical structure is shown in figure 1.

The used PCE architectures and their molecular characteristics are listed in table 2. All superplasticizers were applied as sodium salts.

5.2.2 Synthesis of hydrate phases and C$_3$A

C$_3$S and gypsum (Fluka) were purchased commercially. C$_3$A, ettringite and C-S-H were synthesized. Prior to the synthesis of ettringite and C-S-H, Ca(OH)$_2$ (Fluka) was burned at 1000°C for 12 hours to CaO and then ground (< 63 µm).

5.2.2.1 Synthesis of C3A

C$_3$A was synthesized by mixing stoichiometric portions of CaCO$_3$ (Merck, purified) and Al$_2$O$_3$ (Sigma-Aldrich, purified).

$$3\text{CaCO}_3 (s) + \text{Al}_2\text{O}_3 (s) \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 (s) + 3\text{CO}_2 (g) \quad (1)$$
The mixture was homogenized for 24 hours with ceramic bullets of 5 mm diameter. Afterwards the powder was granulated with purified water to pellets of about 3 mm diameter. The pellets were fired in platinum crucibles in a furnace at 1425°C for 12 hours. After cooling, the C₃A was ground to a grain size below 20 microns and then stored in a desiccator. The synthesized C₃A was controlled for its free lime content (<1%) and confirmed by SRD for phase purity.

5.2.2.2 Synthesis of ettringite

Ettringite was obtained by precipitation from solutions containing stoichiometric contents of burned CaO (for 12 hours at 1000°C) and Al₂(SO₄)₃•16H₂O (Fluka) in excess of deionized water.

\[
6\text{CaO (aq)} + \text{Al}_2\text{(SO}_4)_3\text{•16H}_2\text{O (aq)} + 16\text{H}_2\text{O} \rightarrow 3\text{CaO•Al}_2\text{O}_3\text{•3CaSO}_4\text{•32H}_2\text{O (s)}
\] (2)

After 14 days, the precipitate was filtered, dried at 37°C and afterwards ground below 45 microns. XRD and TGA analysis confirms the product to be ettringite.

5.2.2.3 Synthesis of C-S-H

The C-S-H phase was obtained by precipitation from solutions containing stoichiometric contents of burned CaO (for 12 hours at 1000°C) and SiO₂ (Aerosil 200, Degussa) in excess of deionized water.

\[
\text{CaO (aq)} + 1.3\text{SiO}_2\text{(aq)} + 1.4\text{H}_2\text{O} \rightarrow \text{CaO•1.3SiO}_2\text{•1.4H}_2\text{O (s)}
\] (3)

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 proofs the precipitated material to be C-S-H.

5.2.3 Portland cement

For the cryo-microscopic investigations, an ordinary Portland cement (CEM I 42.5 N) was ground with a laboratory disc mill (Siebtechnik GmbH, Germany) to \(d_{50} = 9\) μm. In order to avoid undersulphatisation, gypsum was added to a total amount of 3.9 wt.-% SO₃ of the cement powder (tab. 3).

<table>
<thead>
<tr>
<th>Tab. 3. Chemical composition of the fine Portland cement used</th>
</tr>
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<tbody>
<tr>
<td></td>
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<tr>
<td>fine cement</td>
</tr>
</tbody>
</table>
5.3 Sample preparations and methods

Due to the different experimental setups, different water to solid ratios were used. Except for the zeta potential titration experiments, the PCE was added to the solution prior to the experiments. The zeta potential, the rheology and the adsorption measurements were done on pure mineral phases. For the cryo-microscopy experiments the fine ground Portland cement was used.

5.3.1 Zeta potential

The investigations were carried out using the ZetaProbe (Colloidal Dynamics Inc.), which works on the basis of the electroacoustic method. An alternating high frequency electric field is applied and causes charged particles to oscillate. The motion of the particles generates a sound wave which is monitored and delivers the dynamic mobility of the suspended particles. The zeta potential is calculated from the dynamic mobility with the standard software.

Prior the sample measurements, pH-meter (4.01, 7.01 and 10.01) and zeta flow-through cell (KSiW-standard, provided by Colloidal Dynamics Inc.) were calibrated. The syringe-unit (titration unit) was washed prior to the use with the titrant to insure its purity.

PCE titration experiments were carried out on suspensions with solid volume fractions around 2%. The PCE concentrations refer to the weight of the solid content. They ranged from 0.01 to 0.20 wt.-% with titration increments of 0.01 wt.-%. The increase of sample volume is considered by the ZetaProbe machine.

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 (such as pore solutions of cementitious suspensions) evoke strong background signals which can not be neglected. Consequently, background measurements were carried out for the different solutions. In order to work in the conductivity range of cement pastes, the solutions were adjusted with deionised water to a conductivity of around 18 mS/cm. Furthermore, the titration of PCE also increases the background signal. Therefore, for each PCE architecture and concentration level a background measurement was performed. Subsequent to each

<table>
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<tr>
<th>solvent</th>
<th>K⁺</th>
<th>Na⁺ (1)</th>
<th>Ca²⁺</th>
<th>OH</th>
<th>SO₄²⁻</th>
<th>conductivity</th>
</tr>
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<tr>
<td>KOH 0.1M</td>
<td>100</td>
<td></td>
<td></td>
<td>100</td>
<td></td>
<td>18</td>
</tr>
<tr>
<td>Ca(OH)₂ 0.1M</td>
<td>100</td>
<td>200</td>
<td></td>
<td></td>
<td></td>
<td>8</td>
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<td>100</td>
<td>100</td>
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<td>18</td>
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<td>444</td>
<td>40</td>
<td>10</td>
<td>104</td>
<td>200</td>
<td>48</td>
</tr>
<tr>
<td>Synt.PS (diluted)</td>
<td>164</td>
<td>15</td>
<td>4</td>
<td>38</td>
<td>74</td>
<td>18</td>
</tr>
</tbody>
</table>

(1) PCE titration: Na⁺ addition in mmol Na/g solid to titration of the Na-PCE salt
experiment, the zeta potentials were recalculated with the corresponding background files.

5.3.2  **Rheology**

For the rheology experiments a Paar Physica MCR 300 rheometer with plate-plate geometry was used. The rotating plate exhibits a rough surface (100 µm). The gap between the plates was 1 mm. The temperature of the samples was controlled by a water bath and kept at 20°C. A solution trap kept the humidity of the sample constant.

All samples were mixed for 2 minutes by hand. The measurements were taken 10 minutes after mixing performing 1 minute pre-shearing at a shear rate of 100 s⁻¹ in order to break particle agglomerates. Afterwards, a flow curve with shear rates from 100 down to 40 s⁻¹ was recorded using a ramp time of 5 s. Plastic viscosity was calculated from the slope of the flow curve.

5.3.3  **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 then determined by a Sievers 5310 C apparatus (GE Water & Process Technologies). For each sample, a reference solution (same concentration, same ionic composition) was measured. In addition, the TOC content of the used deionized water was also measured. The background values and the standards were taken into account when calculating the adsorbed amounts of PCE.

5.3.4  **Cryo-microscopy**

All cement suspensions exhibit a water/cement ratio of 0.5 and were mixed by hand for 2 minutes. Three different types of cement suspensions were produced: without PCE, with 0.7 wt.-% of PCE 23-6 or with 0.7% wt.-% PCE 102-2. 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. The chosen hydration times of the samples is ranging from 5 minutes up to 2.5 hours. All hydration times lie 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 [26, 27] 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 the cited references [28, 29].

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).
5.4 Results

5.4.1 Zeta potential

Most of the zeta potentials obtained in this study are very low and within the range of -15 to 15 mV. Systems with zeta potentials in this range tend to flocculate. However, the measured systems were quite diluted, and no macroscopic flocculation could be observed except for the C₃A phase in synthetic pore solution.

5.4.1.1 Zeta potentials of clinker phases C₃S, C₃A and gypsum

C₃S, C₃A and gypsum show positive zeta potentials (fig. 2) in a 0.1 M KOH. The zeta potentials of C₃S and C₃A are close to +10 mV whereas gypsum shows a zeta potential around 1 mV. In synthetic pore solution, the zeta potentials of C₃S and gypsum remain positive. However, the presence of SO₄²⁻ instantaneously leads to a strong flocculation and...

For the investigations on cryo-FIB cross-sections [30], 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).
Adsorption of polyelectrolytes and its influence on the rheology, zeta potential and microstructure of various cement and hydrate phases

The sedimentation of C₃A and thus, the suspension could not be measured. The C₃A suspension could be stericly stabilized by the addition of 1 wt.-% of PCE 23-6 to the solution prior to the addition of the solid. Consequently, no macroscopic floculation or sedimentation could be observed and the suspension could be measured. The strong floculation in this highly diluted suspension implies a zeta potential around zero. Clearly, the measured negative zeta potential of C₃A in synthetic pore solution does not reflect the electrostatic potential of a non-dispersed experiment due to the presence of PCE 23-6.

5.4.1.2 Zeta potentials of the hydrate phases ettringite and C-S-H

In 0.1 M KOH, the zeta potentials of both hydrate phases are slightly positive (fig. 3). If double charged cations are available, the electrostatic potential of the ettringite suspension increases. The presence of SO₄²⁻ ions, leads to a charge inversion for the ettringite phase. If a real pore solution (solution removed from a suspension of an ordinary Portland cement) or a synthetic pore solution (chemical composition given in table 4), based on the analysis of real pore solutions [9]) is chosen, the zeta potential of ettringite shifts towards higher negative zeta potentials. In contrast to the ettringite, the zeta potential of the C-S-H phase remains slightly positive in synthetic pore solutions.

5.4.1.3 Impact of PCE on the zeta potentials of C₃S, C-S-H and ettringite

Independently from the solution, the zeta potentials of C₃S and C-S-H in synthetic pore solutions (fig. 4) are not significantly influenced by the addition of PCEs. With increasing PCE concentration, the zeta potential of the suspension remains constant and positive. In further experiments with KOH as solutions, the zeta potentials of the ettringite phase decrease and turn to negative values with increasing PCE concentration (unpublished data). In synthetic pore solution, the zeta potential of ettringite shifts towards -4 to -2 mV with increasing PCE concentration. The influence of PCE

Fig. 4. PCE titration experiments to C₃S, gypsum, C-S-H and ettringite suspensions in synthetic pore solutions. C₃S, gypsum and C-S-H are not significantly influenced by the presence of PCE. The ettringite phase is influenced by all three PCE architectures.
molecules on the zeta potential of ettringite shows only minor dependency of the PCE architecture – all PCE types reached their saturation concentrations around 0.1 wt.-% PCE referred to the solid material. This is in contrast to the adsorption data, where PCE 102-2 does hardly adsorb.

5.4.2 Rheology

The viscosities of C₃S (solution/C₃S wt.-ratio = 0.4), C-S-H (solution/C₃S wt.-ratio = 0.95) and ettringite (solution/ettringite wt.-ratio = 1.3) are shown in figure 5. In all three phases, the addition of PCE 102-2 with high side chain density and length shows low impacts on the plastic viscosity whereas PCE 23-6 and PCE 102-6 very efficiently fluidize the suspensions. At higher PCE concentrations (1 mg PCE/g C₃S, 3 mg PCE/g ettringite), the viscosities of C₃S and ettringite phase are below 0.1 Pa•s. This is not the case for the C-S-H phase, where at higher PCE concentrations (above 3 mg PCE/g C-S-H) the viscosity remains at 0.5 Pa•s.

However, the viscosities of the three phases are not directly comparable to each other because of the different experimental set-ups. In addition, the behaviour of the materials differs strongly.

5.4.3 Adsorption of PCE

Adsorption isotherms of PCE on C₃S (top left), C-S-H (bottom left) and ettringite (bottom, right) are shown in figure 6. It can be observed, that the PCE 102-2 with high side chain density and length do hardly adsorb on any of the three phases (fig. 6, top right). The higher charged PCE 23-6 and PCE 102-6 show similar adsorption isotherms. PCE molecules with similar side chain to back bone ratio but different side chain length do not exhibit significantly different adsorption behaviour.

Fig. 5. The viscosities as a function of PCE concentration (wt.-% solid) is shown for C₃S, C-S-H and ettringite. PCE 102-2 shows minor effects on the viscosity for all phases. PCE 23-6 and PCE 102-6 show similar fluidizing abilities and with increasing dosage, lead to low viscosity for C₃S and ettringite. C-S-H seem to reach a plateau at around 0.4 Pa•s.
Fig. 6. This figure shows the adsorption isotherms for $\text{C}_3\text{S}$, C-S-H and ettringite. The adsorption of PCE 102-2 is almost zero for all three phases. PCE 23-6 and PCE 102-6 show similar adsorption isotherms in all three phases. The silicate phases $\text{C}_3\text{S}$ and C-S-H show similar adsorption behaviour whereas ettringite is able to adsorb high amounts of PCE.

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 silicate phases show saturation concentration at 0.1 wt.-% whereas ettringite has not reached saturation concentration at 0.4 wt.-%.

5.4.4 Cryo-microscopy of cement suspensions before hardening

During early hydration up to the hardening state, $\text{C}_3\text{S}$ (main clinker phase), ettringite and C-S-H (hydrate phase) are the dominant mineral compounds in an ordinary Portland cement paste, which control mechanisms of PCE adsorption, rheology and particle interactions. The cryo-microscopy images give insight to morphological and particulate phenomena which are the direct consequence of the macroscopic findings on pure $\text{C}_3\text{S}$, C-S-H and ettringite systems.
Adsorption of polyelectrolytes and its influence on the rheology
zeta potential and microstructure of various cement and hydrate phases

Despite of the strong time dependency of cement suspensions, the presented structures have been found to be typical for the morphological phenomena in cement-water and cement-water-PCE systems before setting.

5.4.4.1 Hydrate phases on the surface of Portland clinker particles

Particle interactions are strongly controlled by the surface properties. Thereby, thin layers of hydrates can control the surface properties of large particles. With the ion beam of a FIB, flat cross sections can be produced from high-pressure frozen samples. As shown in figure 7 (right column), this allows to identify the thickness of the hydration layer (dark grey) on the yet unhydrated clinker particle (bright grey). Some parts of clinker particles show clean surfaces whereas layers of compacted hydrates with uneven thickness can be observed locally (fig. 7, bottom right). However, due to the limited resolution, cryo-FIB cross sections (> 100 nm) can not resolve very fine hydration products such as C-S-H needles.

Fig.7. The top left cryo-SEM image (cement suspension containing 0.7% of PCE 102-2, after 5 minutes of hydration) show a C₃S surface (clinker, dark grey) with attached hexagonal short prismatic ettringite. Very fine C-S-H needles cover both, C₃S and ettringite. Such individually deposited ettringite can also be observed in the cryo-FIB cross-section (top right), marked by arrows (cement suspension containing 0.7% of PCE 23-6, after 2 hours of hydration). As shown in cryo-SEM image (bottom left) mixtures of ettringite and C-S-H form dense hydration layer around a clinker particle (cement suspension after 2.5 hours of hydration) which can also be observed by cryo-FIB cross-sections (bottom right) where the arrows indicate the discontinuous hydration layer (cement suspension containing 0.2% of PCE 23-6, after 24 minutes of hydration).
For higher resolutions, cryo-SEM investigations on freeze-fractured samples were performed. The precipitates of the blocky, irregular hydration layer that was observed with cryo-FIB can now be identified as hexagonal shaped ettringite intergrown with fine needle-like C-S-H, which are deposited on the clinker surface (fig. 7, top left). The ettringite crystals are deposited either as individual crystals or as a compacted and agglomerated mass where the individual crystals can hardly be distinguished (fig. 7, bottom left). The fine C-S-H needles cover the clinker particle as well as ettringite surfaces.

5.4.4.2 Formation of agglomerates

The rheological properties are strongly influenced by the state of dispersion. Therefore, the mechanisms of particle agglomeration are of major interest. Figure 8 (right) shows a cryo-FIB cross section in a cement suspension where the particles have formed a network structure. Thereby, the larger clinker particles are bridged by smaller hydration products and agglomerates of hydrates. Details of such agglomerated hydrates are shown in figure 8 (left) from cryo-SEM. Mixtures of ettringite and C-S-H crystals form small agglomerates of a few hundred nanometres in diameter. Such small agglomerates can be observed on clinker surfaces (fig. 7, top left) or in the interstitial pore space. Several small agglomerates can also form larger agglomerates (fig. 8, right).

5.5 Discussion

The results of PCE adsorption behaviour, its impact on rheological properties and influence on the colloidal behaviour of different clinker and hydrate phases were shown in the previous section. In addition, cryo-microscopic data about the deposition, formation of
hydrate layers and agglomeration phenomena of cement suspensions during the early hydration period were presented.

In this section, the adsorption behaviour, associated changes of zeta potentials and the consequence for rheology shall be linked with cryo-microscopic observations from the cement suspensions. Throughout the discussion, the interaction phenomena will be exemplary shown with PCE 102-6, which shows similar adsorption and fluidizing behaviour as PCE 23-6.

It is important to note, that the solution to solid ratios differ for zeta potential experiments (~50) on the one hand, and for rheology and adsorption experiments (~1) on the other hand. The solid content in the cement suspensions is 0.5.

5.5.1 Influence of the chemical composition of the solution on the zeta potentials

As mentioned in the introduction, the zeta potential is controlled by the chemical and physical properties of the suspended particles and the ionic composition of the (aqueous) solution. The ionic composition of the solutions is strongly variable for the zeta potential studies reported in the literature. That is the reason, why reported zeta potentials show broad scattering and seem to be very contradictory. Results from literature (tab. 1) and results obtained in this study (tab. 4) in different solutions show that the ionic species and their charge as well as the ionic strength are very important factors. Consequently, when discussing and comparing the results from the different studies, the chemical compositions of the solutions have to be taken into account. Common for all zeta potential measurements on pure hydrate phases are the low solid loads. The description of experimental setups can be divided in three groups: i) hydrate phase is measured in the (diluted) solution in which the phase was synthesized, ii) hydrate phase is added to deionised water and equilibrated up to several days and iii) hydrate phase is added to a solution of a defined ionic composition. The advantage of the latter group is the controlled measurement conditions.

In basic theories it is assumed that the surfaces of silicate phases (C₃S and C-S-H) and of CH are negatively charged, whereas the surfaces of the aluminate phases (C₃A, ettringite, monosulfate) are positively charged. Unfortunately the zeta potential measurements of these phases show a much more puzzling picture, whereby charge inversions at the Stern layer can be induced depending on the chemical environment of the solutions [18].

No charge inversion is observed for silicate phases in very dilute systems. Negative zeta potentials were measured in systems with low ionic strength and for pH>11 [14, 16, 19, 24]. However, in chemical environments which have more similar compositions as the pore solutions of cement suspensions (i.e. at pH >12 and at higher ionic strength with concentrations of Ca²⁺, K⁺ and Na⁺ >1-20 mmol/l) charge inversion occurs and positive zeta potentials are reported for silicate phases.
Fig. 9. This scheme illustrates a model interface between C₃S, C-S-H (top) and ettringite (bottom) with synthetic pore solution without PCE (left column) and with PCE (right column). The carboxylate-groups of PCE in a synthetic pore solution adsorbed at the slip surface of C₃S, C-S-H particles. In ettringite suspensions (synthetic pore solution), the carboxylate-groups adsorb directly on the ettringite surface.
A puzzling picture is reported for silicates in Na-rich solutions (together with sulphate), where even at high concentrations (up to 500 mmol/l) no charge inversion occurs and negative zeta potentials are measured for C-S-H [20].

However, these findings are supported by [22] where for C-S-H in 1 mmol/l Ca\textsuperscript{2+} and high loads of Na\textsuperscript{+} the zeta potential remains negative. This indicates that Na\textsuperscript{+} is not that efficient in inducing a charge inversion compared to K\textsuperscript{+} and Ca\textsuperscript{2+}. The latter can be explained with the stronger charge. It is unclear, why the Na\textsuperscript{+} is not able to lead to a charge inversion whereas K\textsuperscript{+} leads to a positive zeta potential even though it has the same valence but the larger ion diameter. Maybe this is due to the fact that K\textsuperscript{+} ions are easier to polarize. For the present study, the irregularities related to Na\textsuperscript{+} are not of further importance because the concentrations of K\textsuperscript{+} [100 mmol/l] in our experiments are significantly higher than the concentrations of Na\textsuperscript{+}. In addition, the aluminate phases tend to undergo charge inversions at
high ionic strength and pH. Positive zeta potentials (+10 mV) are observed at low ionic strength [19] or in solutions with low concentrations of sulphate. At high SO$_4^{2-}$ concentrations (similar to real pore solution of cement suspensions) the zeta potential turns to negative values. It is remarkable that in one experiment positive zeta potentials are measured for pH between 11 and 12.9 [23]. Below and above this pH, negative zeta potentials are reported.

5.5.2 Influence of PCE on the interparticle behaviour of C$_3$S and C-S-H

C$_3$S and C-S-H exhibit negatively charged surfaces. In synthetic pore solutions, both mineral phases show slightly positive potentials at the slip surface. This charge inversion is due to the high Ca$^{2+}$ concentration in the pore solution. Therefore, the ionic composition of Stern and diffuse double layer is most likely to be dominated by Ca$^{2+}$ ions (fig. 9, top left).

Figure 10 (top) shows that the presence of PCE molecules has hardly an influence on the zeta potentials of C$_3$S and C-S-H. In contrast to the zeta potential data, adsorption isotherms clearly show an adsorption of PCE molecules by C$_3$S and C-S-H particles. Additionally, a fluidizing effect of PCE molecules on C$_3$S and C-S-H suspensions can be observed.

Taken in account, that in solutions with high ionic strength (such as the used synthetic pore solution) the double layers are thin, it can be assumed that the slip surface is at very close distance to the Stern layer. The negatively charged carboxylate-groups mainly adsorbed at the slip surface (fig. 9, top right) and consequently, can not be detected by zeta potential measurements.

The steric forces of PEO side chains of the PCE are responsible for the fluidizing effect of C$_3$S and C-S-H suspensions.

5.5.3 Influence of PCE on the interparticle behaviour of ettringite

The high concentration of SO$_4^{2-}$ ions in synthetic pore solutions lead to a charge inversion of the positively charged surface of ettringite (fig. 9, bottom left) which is indicated by the negative potential at its slip surface.

In contrast to C$_3$S and C-S-H, the zeta potential of ettringite is influenced by the presence of PCE molecules (fig. 10, bottom). The addition of PCE shifts the zeta potential from -12 mV to a constant zeta potential of -3 mV for concentrations higher than 6 mg PCE/g solid. This change of the zeta potential indicates adsorption of PCE molecules, which is confirmed by PCE adsorption measurements. The viscosity is much influenced by the presence of PCE molecules. Note that a concentration below saturation is sufficient to obtain low viscosities of ettringite suspensions.

In contrast to C$_3$S and C-S-H, the carboxylate-groups are adsorbed directly at the ettringate surface (fig. 9, bottom right). A competitive adsorption between anionic PCE and sulphate ions is assumed. Thus, the PCE molecules are the dominating “anionic” species between ettringite and slip surface. The decrease of the zeta potential is probably due to the low charge densities of PCE molecules compared to sulphate. In addition, the larger volume of PCE
molecules shifts the slip surface towards the solution. The distance of this displacement depends on the conformation of the side chains (protruding in the solution [31] or mushroom like [32]).

5.5.4 Relationship of zeta potentials of pure clinker and hydrate phases with the microstructures of Portland cement suspensions

On the one hand, the silicate phases and gypsum in synthetic pore solution show slightly positive zeta potentials which, according to the common understandings of colloidal systems, should lead to agglomeration. On the other hand, ettringite shows a negative zeta potential with values within the transition from an agglomerating to an electrostatically stabilized system.

As a consequence, after the initial formation of ettringite (within the first minutes of cement hydration) in a fresh cement suspension, the negatively charged ettringite (size <500 nm) tends to precipitate on the positively charged C₃S surfaces (size of several microns). Thus, the ettringite crystals might be able to electrostatically stabilize the C₃S phase by coating its surface. This is probably the reason why the bulk zeta potential of ordinary Portland cement suspensions is slightly negative. However, during ongoing hydration, C-S-H needles start to cover both, C₃S and ettringite surfaces (fig. 7, top left). It is assumed that local differences of the C₃S-clinker surfaces and the pore solution may control the deposition behaviour of ettringite and C-S-H. In addition, these chemical inhomogeneities determine not only the location but also the density and thickness of hydration layers formed as observed with cryo-microscopy (fig. 7, bottom right). Homogeneous precipitation of ettringite and C-S-H in the pore solution will lead to formation of small agglomerates (submicron range) because the hydrate phases attach to each other due to their opposite zeta potentials (fig. 8, left).

By the addition of PCE, probably the ettringite surfaces will be saturated with PCE molecules first (due to higher affinity). The remaining PCE molecules adsorb on the other phases such as C₃S and C-S-H. Thus, the particles in the cement suspension are sterically stabilized. However, the PCE molecules preferably adsorb on ettringite surfaces and prevent them from precipitating on C₃S surfaces. Consequently, in a dispersed system the ettringite is present as individual crystals in the interstitial pore solution and thus, the size fractions in the ettringite range (< 500 nm) increase significantly. This conclusion is confirmed by a cryo-microscopic study [29] of a cement suspension with PCE, where large amounts (qualitatively) of small ettringite crystals are well dispersed in the interstitial pore space, whereas in cement suspensions without PCE, almost no submicron particles can be observed in the interstitial pore space. Quantitative particle analysis based on cryo-FIB-nanotomography supports these qualitative observations [30].
5.6 Conclusions

The level of simplification for model experiments with pure phases of the Portland cement system is limited by the complex chemical processes in real cement suspensions. The effects of oversimplification are illustrated by the comparison of zeta potential data of this study with findings reported in the literature. This comparison reveals the importance of an appropriate and realistic choice of the ionic composition in the solution. Concerning the interparticle behaviour of clinker and hydrate phases during early hydration times and correlation with microscopic data of fresh cement suspensions, we propose to measure the zeta potentials of pure clinker and hydrate phases in synthetic or real pore solution environment.

The high ionic Ca\(^{2+}\) and SO\(_4^{2-}\) contents of pore solutions lead to inversion of the surface charges of the C\(_3\)S, C-S-H and ettringite. The latter is relatively strong (-13 mV) compared to C\(_3\)S (+7 mV) and C-S-H (+2 mV). Consequently, the interaction forces of ettringite with C\(_3\)S and C-S-H are attractive and thus, the coexisting minerals tend to coagulate. This is confirmed by cryo-microscopic data of cement suspensions, showing that the ettringite crystals are covering surfaces of C\(_3\)S particles. Therefore, despite the low volume fraction of ettringite, the zeta potential of early hydration of ordinary Portland cement suspensions is dominated by the negative zeta potential of the ettringite.

The presence of PCE prevents the ettringite from coagulation with C\(_3\)S and C-S-H by steric hindrance. As a consequence, the ettringite crystals are mainly present in the interstitial pore space as shown in a previous cryo-microscopic study [29]. Differently from systems without PCE, the ettringite governs the electroacoustic signal because the high number of dispersed ettringite particles dominates over all the other phases. This is supported by a cryo-FIB nanotomography study, where after 6 minutes of hydration 97% of the particles of a cement suspension containing 0.2 wt.-% PCE 23-6 are interpreted to be ettringite [30]. Consequently, also the negative zeta potentials of bulk cement suspension are dominated by the ettringite phase.

In the rheology literature, the time of PCE addition is often discussed. It is accepted that delayed addition requires lower PCE concentrations in order to reach the same flow ability of the cement suspension. Some studies propose the formation of organomineral phases, acting as a sink for PCE molecules, in systems where the PCE was added simultaneously [11, 33]. Thereby, intercalated PCE molecules do not contribute to the fluidization. However, another mechanism could explain the different demand of PCE without the formation of organomineral phases: In a dispersed system where the numerous ettringite particles are floating in the pore solution instead of being attached to the clinker surfaces the intrinsic surface area is significantly increased. Therefore, in order to saturate all available surfaces with PCE molecules, the demand of PCE is much higher. With delayed PCE addition, precipitated ettringite crystals on C\(_3\)S surfaces can not be redispersed and hence, the surface area and associated saturation of PCE are lower.
Adsorption of polyelectrolytes and its influence on the rheology
zeta potential and microstructure of various cement and hydrate phases

It can be hypothesized that PCE molecules are adsorbed at the slip surface of C₃S and C-S-H whereas on ettringite, the PCE molecules are adsorbed directly at the particle surface (fig. 9). This might be a reason for stronger PCE adsorption and bonding on ettringite than on silicate phases.

The conclusions drawn from the presented results and the rise of new hypothesis urge for more information about the interfacial (mineral-solution) processes at the molecular level. This also includes investigations on type and strength of PCE adsorption on cementitious materials.

Acknowledgments

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Chapter 6

Microstructural analysis of fresh cement suspensions and the link with macroscopic properties

Anatol Zingg, Lorenz Holzer, Frank Winnefeld, Beat Münch, Joachim Pakusch, Stefan Becker, Renato Figi, Ludwig Gauckler

To be submitted
6 Microstructural analysis of fresh cement suspensions and the link with macroscopic properties

Anatol Zingg \textsuperscript{a,}\textsuperscript{*}, Lorenz Holzer \textsuperscript{a}, Frank Winnefeld \textsuperscript{a}, Beat Münch \textsuperscript{a}
Joachim Pakusch \textsuperscript{b}, Stefan Becker \textsuperscript{b}, Renato Figi \textsuperscript{a}, Ludwig Gauckler \textsuperscript{c}

\textsuperscript{a} Empa, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Concrete/Construction Chemistry, Ueberlandstrasse 129, 8600 Duebendorf, Switzerland
\textsuperscript{b} BASF AG, GKDC-B1, Carl-Bosch-Strasse 38, 67056 Ludwigshafen, Germany
\textsuperscript{c} ETH, Swiss Federal Institute of Technology Zurich, Institute of Nonmetallic Inorganic Materials, Department Materials, Wolfgang-Pauli-Strasse 10, 8093 Zurich, Switzerland

Abstract

The particulate structures of cement suspensions change with evolving hydration time. The change of the microstructures is closely associated with dissolution and precipitation processes and can be related to the rheology of cement suspensions. Thus, deeper understandings of the microstructural evolution of cement suspensions help to improve the predictability of such complex systems. Up to now, most simulations and models for prediction of rheological properties are based on simplified assumptions such as e.g. spherical, monodispersed particles.

The application of cryo-FIB nanotomography combined with high-pressure freezing sample preparation enables the quantification of basic microstructural parameters. This study reveals that the particle sizes in the submicron range dominates the size distributions of number of particles densities and specific surface areas of cement suspensions without and with superplasticizers after initial hydration and close to setting time. It is also shown, that with evolving hydration the surface area and the number of particles density increase significantly although between initial hydration and setting time, the production of hydrates is assumed to be low. Although these cryo-FIB nanotomography first results prove the method to be a powerful tool, further improvements are needed.

Keywords: microstructures, quantification, cryo-microscopy, cement suspensions, superplasticizers

\textsuperscript{*} Corresponding author
E-mail address: azingga@postmail.ch (A. Zingg)
6.1 Introduction

Superplasticizers are commonly used for demanding applications in concrete technology. On one hand the addition of superplasticizers enables the control of the flow properties and on the other hand allows the reduction of the water content without the loss of workability.

In order for a better understanding of the complex cement-water (-superplasticizer) system, the interaction of its single mineral phases with superplasticizer molecules, research projects are carried out increasingly on pure clinker and hydrate phases. Investigations on simplified systems [1-4] and model suspensions [5, 6] 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. In terms of rheology, the interparticle forces play a decisive role [6-9]. 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 (between -15 and +15 mV) zeta potentials attract each other and tend to form agglomerates. Depending on the architecture and dosage, superplasticizers can have 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.

However, for investigations concerning rheological properties of fresh cement suspensions, experiments on simplified systems are not suitable because the evolution of both viscosity and yield stress are much depending on the chemistry of the cement-water system. Chemical composition and dissolution rates of the mineral compounds of the cements on one hand, nucleation and growth behaviour on the other hand govern the amount, type and size of hydrate phase formation. The latter processes lead to changes of the rheology and associated microstructural properties such as solid content, particle size distribution, surface areas and number of particles per unit volume changing. The link between the viscosities of cement suspensions without and with PCE, with the microstructures is schematically illustrated in figure 1.

Most of the microstructural investigations of cement suspensions at early hydration times have been carried out on filter residues or in-situ experiments in a ESEM [10, 11], wet cell (e.g. Quantomix WETSEM cell) [12] or on plunge frozen samples [13]. However, none of the method 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 [14-16]. 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 the quantification of particle size distributions.

A first qualitative cryo-microscopic study [16] of fresh cement pastes showed the strong influence of PCE on the long range particle arrangement in a fresh cement paste after induction period. Without the addition of PCE, the ettringite tends to deposit on clinker particles or forms agglomerates with other small clinker particles and C-S-H needles to so-called SIG (small interstitial grains) with diameters around 2 µm. In contrast, the cement-water-PCE system is well dispersed. Individual ettringite crystals (< 500 nm length) are well distributed over the interstitial pore space.

In this study, the basic microstructural parameters such as number of particle densities, volume fractions and specific surface areas shall be quantified from high-pressure frozen cement suspensions by means of cryo-FIB nanotomography. However, cryo-FIB limits the analysed sample volume (approximately 20*20*20 µm). In order to be statistically reasonable, an ordinary Portland cement CEM I 42.5 N was ground.

![Schematic figure of microstructures in cement suspensions during early hydration and the influence of PCE](image)

Fig. 1. Schematic figure of i) the link between viscosity with the microstructures in cement suspensions during early hydration and ii) the influence of PCE of microstructural parameters like particle size fractions, surface area, number of particles and on the long range particle structure.
Tab. 1. Chemical composition of the fine cements used

<table>
<thead>
<tr>
<th></th>
<th>CaO wt-%</th>
<th>MgO wt-%</th>
<th>SiO₂ wt-%</th>
<th>Al₂O₃ wt-%</th>
<th>Fe₂O₃ wt-%</th>
<th>Na₂O wt-%</th>
<th>K₂O wt-%</th>
<th>SO₃ wt-%</th>
<th>CO₂ wt-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>fine cement</td>
<td>64.0</td>
<td>1.8</td>
<td>21.0</td>
<td>5.1</td>
<td>2.5</td>
<td>0.04</td>
<td>0.8</td>
<td>3.9</td>
<td>1.9</td>
</tr>
</tbody>
</table>

The ground fine cement and its interaction with different PCE architectures and dosages will be characterized concerning the workability of the suspensions by PCE adsorption (TOC) analysis, viscosity and zeta potential measurements. Calorimetric data provides information about the delay of the main hydration period induced by the presence of PCE. Weight fractions of ettringite and portlandite after 6 and 24 hours respectively, will be provided thermogravimetric data.

The present cryo-microscopic investigation aims to differentiate microstructural phenomena at different size scales and the influence of PCE on the formation of hydration layers, shape and distribution of individual hydrate crystals, morphologies of unhydrated clinker surfaces, formation and constituents of small agglomerates, and structures in the interstitial pore space will be presented on a qualitative level.

Basic particulate parameters such as number of particles densities, volume fractions and specific surface areas will be quantified from high-pressure frozen cement suspensions by means of cryo-FIB nanotomography. Those data shall give the link between high resolved microstructures from cryo-SEM with PCE adsorption on cements and the associated change of zeta potential.

6.2 Materials

6.2.1 Fine cement

In order to obtain representative microstructure analysis with cryo-FIB, it is important to decrease the size of the largest particles. Therefore all experiments are performed with a fine cement. In order to avoid chemical and mineralogical fractioning, the fine cement was produced by grinding a bulk CEM I 42.5 N with a laboratory disc mill (Siebtechnick GmbH, Germany) to a medium diameter \( d_{50} \) of 9 µm (\( d_{10}=0.6 \) µm and \( d_{90}=37.6 \) µm). To avoid undersulfatisation, gypsum was added to a total SO₃ wt-% of 3.9 (tab. 1). The fine cement exhibits a specific density of 3.07 g/cm³ and a specific surface (Blaine value) of 5640 cm²/g.

6.2.2 Superplasticizers

For this study, three comb-shaped polycaboxylate-type superplasticizers (PCE) were synthesized (tab. 2). Methylpolyethyleneglycole

Fig. 2. 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.
copolymers (side chains) were grafted on a methacrylic acid copolymer (backbone) [17]. The polymer architecture is varied by using different side chain densities and lengths. The chemical structure is shown in figure 2.

### 6.2.3 Recipes of cement pastes for macro- and microscopic investigations

For all experiments the above mentioned ground fine cement was used (sample name fc0).

The samples for PCE adsorption, rheology, calorimetry and thermogravimetry measurements exhibit a water to cement ratio (w/c) of 0.35 and with PCE (23-6, 102-2, 102-6) concentrations up to 4 mg PCE/g cement.

Zeta potential measurements were carried out with a w/c of 0.5 and with PCE (23-6, 102-2, 102-6) concentrations up to 20 mg PCE/g cement.

The samples for cryo-microscopy exhibit a w/c of 0.5 and were high-pressure frozen after:

- 6 minutes of hydration (sample name: fc0.1, i.e suspension with Fine Cement after 0.1 hour)
- 2.5 hours of hydration (sample name: fc2.5)
- 2 hours of hydration, sample containing 6.5 mg PCE 23-6/g cement (sample name: fc2p, i.e. paste with Fine Cement after 2 hours of hydration, with Polymer-addition)
- 24 hours of hydration, sample containing 6.5 mg PCE 23-6/g cement (sample name: fc24p)

<table>
<thead>
<tr>
<th>polymer</th>
<th>length of side chain</th>
<th>density of side chains n:m</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>PDI $^3$</th>
<th>solid content mass.-%</th>
<th>mmol anionic Sites $^4$ / g solid</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCE 23-6</td>
<td>23</td>
<td>6:1</td>
<td>7600</td>
<td>18900</td>
<td>2.5</td>
<td>13.8</td>
<td>3.4x10^{-3}</td>
</tr>
<tr>
<td>PCE 102-2</td>
<td>102</td>
<td>2:1</td>
<td>16800</td>
<td>78000</td>
<td>4.7</td>
<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>

$^1 M_n =$ number-average molecular weight

$^2 M_w =$ mass-average molecular weight

$^3 PDI = M_n/M_w =$ polydispersity index

$^4$ calculated values, corresponds also to minimum mmol/l Na which is added to the solid-solvent system by titration, direct addition.
6.3 Sample preparation and methods

6.3.1 Measurements of rheology, adsorption and zeta potential of fine cement suspensions

For the rheology experiments, a Physica MCR 300 rheometer with concentric cylindrical geometry was used. The rotating bob was serrated with 100 μm 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. The temperature of the cement paste was controlled by a water bath and kept at 20°C. A solvent trap protected the sample from water evaporation. Yield stress and plastic viscosity were calculated using the Bingham model.

The superplasticizer adsorption isotherms were gained from the same cement pastes as used for the rheology experiments. The alkaline pore solution was removed by air pressure filtration through a 0.45 μm Nylon filter and acidified by the addition of 0.1 M HCl. The total organic content (TOC) of the pore solution samples were then determined by using a Shimadzu TOC-Analyzer 5000A. The consumed amount of PCE was calculated from reference TOC measurements of aqueous polymer solutions. In addition, the TOC of deionized water and of the plain cement paste was also taken in account.

All zeta potential data was collected with the electroacoustic ZetaProbe device from Colloidal Dynamics Inc.. Foregoing the sample measurements, pH-meter (4.01, 7.01 and 10.01) and zeta flow through cell were calibrated (KSiW-standard, provided by Colloidal Dynamics Inc.). All samples were stirred and pumped constantly in order to prevent segregation. The syringe-unit (titration unit) was washed prior to the experiments with the titrant to insure its purity. The raw data was then corrected by the corresponding background files as discussed in chapter 5.

The heat evolution during early hydration was measured using an isothermal heat flow calorimeter (Thermometric TAM Air) at a constant temperature of 20°C. All samples consist of 6 g of cement and 2.1 g of deionised water and were mixed outside the calorimeter with a small stirrer. For the samples containing 4 mg PCE/g cement, the PCE solution 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 flows were recorded for 48 hours.

The investigation of PCE influence on the formation of hydration products (ettringite, portlandite) were carried out on 10 mg samples by thermogravimetric analysis (Mettler-Toledo TGA/SDTA 851) in an N₂ (g) environment by heat rates of 20°C/minute up to 980°C. The samples were prepared by mixing 30 g of cement with 10.5 ml of deionised water or deionised water containing 4 mg PCE/g cement. The hydration was stopped after 6 and 24 hours respectively, by submersing the cement suspension in acetone. The cement-pore solution-acetone mixture was filtered and washed with acetone. Afterwards the filter residue was dried at 40°C for three days and then ground to < 63 μm. The weight fractions of ettringite (~80°C) and portlandite (~440°C) were calculated from the weight losses at the characteristic temperatures.
6.3.2 Cryo-microscopy

The cement suspensions (sample volume ~6.5 ml) for the cryo-microscopy exhibit a water to cement weight ratio of 0.5 and were mixed by hand for 2 minutes. A droplet of the cement suspensions was mounted on brass specimen carrier and then high-pressure frozen with a HPM 010 apparatus (BAL-TEC AG, Balzers, Liechtenstein).

For the cryo-SEM investigations, the sample was fractured (in a liquid nitrogen bath), etched by sublimation (5 minutes at -105°C) and Pt coated (~2 nm) in a BAF 060 apparatus (BAL-TEC) and then transferred with a VCT 100 (BAL-TEC) into the chamber of a LEO Gemini 1530 SEM (Zeiss).

For the cryo-FIB experiments, the sample was fractured (in a liquid nitrogen bath) and transferred into the chamber of a dual-beam FIB-SEM microscope (FEI Strata DB 235). The fractured surface was cleaned from precipitated ice crystals (~5 minutes at -105°C, scanning with ion-beam) and coated in-situ in the FIB with a metalorganic layer [14].

The objects of an image stack obtained by cryo-FIB-nt are extracted by several complex and time consuming data processing steps. Special algorithms have been developed [18] and implemented for cryo-FIB-nanotomography [14, 19]. The most important steps and their chronology are roughly described in the following paragraph.

After cropping and alignment of the image stack a background levelling procedure is performed. Subsequently the vertical stripes (waterfall effect) are corrected by a FFT filter (fast fourrier transformation). The particle segmentation is based on the perception of grey scale gradients at the particle edges by means of a canny filter and subsequent constrained region growing (fig. 3a). Afterwards, the agglomerated particles are split into their individual constituents based on the concavities that form at the contact of neighbouring particles. From the splitted volume each particle is then labelled with a specific colour (fig. 3b). Boundary

Fig. 3. The particle edges are marked by the red lines (a). Each separated object is labelled and randomly coloured (b).
Fig. 4. The left graph shows the viscosity of dispersed cement suspensions (w/c of 0.35) as function of PCE concentration. PCE adsorption isotherms are shown in the right graph. PCE 102-2 does hardly adsorb and has no strong influence on the viscosity.

6.4 Results

First, the influence of PCE addition on the macroscopic properties of the cement suspension will be shown by rheology, zeta potential, PCE adsorption and calorimetric measurements. Quantitative thermogravimetric data will lead over to qualitative results of high resolved microscopic structures of individual crystals, small agglomerates and clinker-hydrate interfaces, followed by quantitative cryo-microscopic data about particulate structures of fresh cement suspensions containing PCE.

6.4.1 Macroscopic analysis of bulk fine cement suspensions

Figure 4 shows the influence of PCE on the viscosity of fresh cement pastes. PCE 102-2 (low charge density) does hardly affect the viscosity whereas PCE 23-6 and PCE 102-6 (both PCEs exhibit higher charge densities) show similar ability to increase the viscosity of fresh cement pastes. Note, that the PCE solution was premixed with the mixing water prior to the addition of the cement. The slight increase of the viscosity at 1 mg PCE 102-6/g cement is probably due to different influence on the initial hydration compared to PCE 23-6.
The adsorption behaviour is compatible with the influence of PCE on viscosity. PCE 102-2 does hardly adsorb whereas PCE 23-6 and PCE 102-6 show strong adsorption. Above 4 mg PCE/g cement, the incremental increase of adsorption is reduced for both PCEs and they reach saturation concentration above 5 mg PCE/g cement.

Also the zeta potential data is in accordance with the adsorption isotherms (fig. 5) for the higher charged PCEs 23-6 and 102-6. Note, that for these experiments the PCE was added after blending the cement with water (delayed addition). In agreement with data from literature, the saturation concentration for delayed PCE addition is lower than for simultaneous PCE addition as determined by TOC measurements. In contrast, the influence of PCE 102-2 on the zeta potential measurements is not compatible with the corresponding viscosity and adsorption data. PCE 102-2 hardly shows an influence on the viscosity of the cement suspension. However, with increasing concentration the zeta potential changes significantly and in a similar way as for the higher charged PCEs.

Fig. 5. Influence of PCE titration on the zeta potential of cement suspensions with w/c ratio of 0.5. PCE 23-6 and PCE 102-6 have higher charge densities. This leads to constant zeta potentials at concentrations below 2 mg PCE/g cement. In contrast, PCE 102-2 with lower charge density reaches saturation only above 4 mg PCE/g cement. The small inset on top right qualitatively illustrates the zeta potential measurements from suspensions with ettringite or C₃S. A comparison of both graphs (top, bottom) indicates that the zeta potential of bulk cement suspensions are dominated by the zeta potential of ettringite.
The fluidizing effect of PCE is associated with undesired retardation of the hydration and associated delayed setting times. PCE 23-6 with higher charge densities (lower side chain density combined with shorter side chains) induce a stronger retardation of the setting. In figure 6 (top graph) the heat evolutions of a plain cement suspension and cement suspension containing 4 mg PCE/g cement 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 for 2 hours at least (PCE 102-2) and 4 hours the most (PCE 23-6). After 6 hours of hydration, the cement suspension containing PCE shows a lower hydration level than the plain cement suspension. This is supported by thermogravimetric data (fig. 6, bottom graph) after 6 hours of hydration. The presence of PCE has no significant influence on the amount of ettringite formed between 6 and 24 hours of hydration.

Fig. 6. Top graph shows the heat evolution of a plain cement paste and cement suspensions containing 4 mg PCE/g cement for PCE 23-6, PCE 102-6 and 102-6 respectively. The bottom graph shows thermogravimetric data of the same samples after 6 hours of hydration. The small insets show calculated ettringite and portlandite weight fractions from TGA measurements after 6 and 24 hours. PCE has no major influence on the amount of ettringite in the cement suspensions whereas in presence of PCE, the portlandite formation is delayed.
Fig. 7. This figure marks out the scale from long range particulate structures (µm) to high resolved morphologies of fine structures (nm): (a) shows a cryo-FIB cross-section of an agglomerated (full circle) and bridged (dashed oval) cement suspension in the mm-range. (b) BSE cryo-SEM image shows that agglomeration (agglomerated ettringite crystals, full circle) and bridging (by ettringite crystals, dashed oval) also takes place in the submicron range. (c) is a close-up to a small agglomerate of ettringite (hexagonal shaped crystals) and C-S-H (fine needle-like structures). (d) High resolved cryo-SEM image shows a 300 nm particle covered with fine C-S-H needles. (e) Fractured clinker particle with fine C-S-H needles on the surface.
Fig. 8. Orthoslice (b) is a close-up from a cryo-FIB nanotomography stack (a). The clinker particle (light grey) is surrounded by a hydration layer (medium grey). The reconstructed (c) 3D particle (red) is discontinuously covered by the hydration layer (green).
Fig. 9. The clinker particle (a1) and its hydration layer (a2) are three-dimensional reconstructions from a processed data stack. High resolved cryo-SEM image (b1) show a thin massy hydration layer as well as individually attached ettringite crystals. An additional close-up (b2) of a fractured clinker surface shows a less dense hydration layer where massy (green) is covered by small C-S-H needles at its outer surface. Ettringite crystals poke out of the massy hydration layer (c).
Fig. 10. A cryo-FIB nanotomography slice displays a clinker particle (a) with a roughness in the sub-micron range. The reconstruction of the ettringite crystal layer is displayed in (b) and the total 3D reconstruction is illustrated by (c). A cryo-SEM close-up shows that the attached ettringite crystals are smaller than < 500 nm (d)
Fig. 11. A cryo-SEM close-up shows attached ettringite crystals < 500 nm (a), which induce the surface roughness. (b) Shows a 3D reconstruction of a particle (red) and attached ettringite crystals (green).
The formation of portlandite has already started in the plain cement suspension after 6 hours, whereas in the cement suspension containing PCE, no portlandite is formed at this time. In spite of delayed portlandite formation, after 24 hours the cement suspension containing PCE do not significantly differ from the plain cement suspension in their amounts of portlandite, except for the cement suspension with PCE 23-6, which shows the strongest retardation effect.

6.4.2 Qualitative cryo-microscopy (cryo-SEM, cryo-FIBx)

In this section observations obtained from cryo-microscopy are presented. Thereby the following qualitative microstructural phenomena are described specifically: i) morphology of hydration layers, ii) individual small crystals attached to clinker surfaces, iii) “unhydrated” surfaces and iv) microstructural features in the interstitial pore space (frozen aqueous phase of suspension).

Fig. 12. Cryo-FIB cross section shows clean clinker particle surfaces (a). The interfaces (b) between the sliced particle and the interstitial pore space are very sharp, almost no attached hydrate particles at clinker surfaces (c). A hydrate particle (ettringite) is attached (bottom circle) to the clinker surface (d); small, individual attached particles can not always be separated from the clinker surface by image analysis.
An overview of microstructural features at different magnifications is displayed in figure 7. The most important microstructural phenomenon is the formation of long range particle arrangements such as agglomerates and the bridging of particles in (a) the micron and (b) in the submicron range. The cryo-FIB cross section (a) shows on one hand agglomerates in the range of 2 µm which consist of small clinker particles and/or hydrates (circle). On the other hand, several agglomerates can form bridges (dashed oval) between larger clinker particles (> 2 µm). A high resolution close-up BSE (back scattered electrons) cryo-SEM image (b) shows similar phenomena but at smaller length scales. Small agglomerates of ettringite crystals are connected like a string of beads, bridging small clinker particles together (dashed oval). At even higher magnification (c) agglomerates of 500 nm consist mainly of small ettringite crystals (100-300 nm). At longer hydration times, such agglomerates consist not only of ettringite but also of very fine, fibre-like C-S-H crystals. Those fibres are observed within the ettringite agglomerates (d) and as a coverage of the clinker surfaces (e). In order to resolve the fine C-S-H crystals, at least magnifications of 50kx are needed. Consequently, the C-S-H can not be resolved by cryo-FIB cross sections.

With respect to the hydration kinetics the particles show very different behaviour. Some particles show a strong dissolution and hydration phenomena (fig. 8 and 9), some are covered with individual crystals (fig. 10 and 11) and some particles are nearly unhydrated (fig. 12).

An overview of the particle structure at low magnification is shown in the BSE image from cryo-FIB (fig. 8a and 8b). The images show, besides the dark grey area (frozen pore solution), areas which is characterized by two different grey levels: i) medium grey for hydration products (such as ettringite and C-S-H) and ii) light grey for unhydrated clinker particles. This is due to the fact that hydrate products exhibit lower specific densities (ettringite ~1.8 g/cm³, C-S-H ~2.2 g/cm³) than an average clinker particle (~3.1 g/cm³). The initial hydration and associated precipitation of early hydrate phases (ettringite, C-S-H) can lead to formation of hydration layers around clinker particles. The 3D reconstruction of the clinker particle (fig. 9a1) shows a rough surface with concave dissolution pits. The hydration layer (fig. 9a2) does not continuously cover the particle surface (fig. 8c) and exhibits an inhomogeneous thickness. High resolved cryo-SEM images confirm those findings. A close-up from the same cement suspension (fig. 9b1) shows a massy hydration layer with irregular thickness. Individual ettringite crystals are attached directly to the clinker surface. Both, clinker and ettringite surfaces are covered by C-S-H fibres which cannot be resolved by cryo-FIB.

The massy hydration layer can be divided in two different morphological types: i) a dense (fig. 9b1) and a porous (fig. 9b2) hydration layer. The chemistry of such hydration layer remains unclear. A further close-up (fig. 9c) to the first type shows, that crystalline ettringite pokes out of an (amorphous?) mass of hydrate phase.

Besides the formation of rather continuous hydration layers, individual ettringite crystals attached (fig. 10a) to a clinker surface can also be observed frequently. At higher magnification (cryo-SEM) it can be observed that ettringite crystals and clinker surfaces are covered by fine C-S-H fibres (fig. 11a). The 3D reconstruction of individual ettringite crystals
attached on the surface of a clinker particle is displayed in figure 10b and 10c. The ettringite crystals measure less than 500 nm, are short prismatic to isometric (fig. 10d) and remain at this size over the first hours of hydration (dormant period). 2D cryo-SEM images (fig. 11a) and the cryo-FIB nanotomography 3D reconstruction (fig. 11b) show an inhomogeneous distribution of ettringite crystals on the clinker surfaces.

During early hydration (dormant period) of cement suspensions many clinker surfaces remain almost in an unhydrated state which is shown by the upper left cryo-FIB cross section (fig. 12). The difference of the grey level between the unhydrated clinker particle (a) to the surrounding interstitial pore space is very sharp. This implies that, within the resolution of cryo-FIB, no hydration layer was formed. High resolution cryo-SEM images (b) confirm this result. Between the clinker particle and the matrix almost no hydrate particles can be observed (red line). Also the 3D reconstruction of the clinker particle shows very smooth surfaces. With high resolution cryo-SEM individually attached ettringite crystals (d, circles) can be observed. However, it is not possible to separate the attached ettringite crystals from the clinker surface by means of image analysis.

Fig. 13. C-S-H gel in the interstitial pore space and embedding particles is shown in (a) by a BSE high resolved cryo-SEM image. Image (b) shows a PCE network structure in the interstitial pore space of a cement suspension before the formation of C-S-H gel. The combination of C-S-H gel and PCE-network is displayed in (c) where the gel is intergrown with the network structure. Embedded in this structure (circle in (c)), small nuclei of hydrate phases can be observed (d).
Not only the microstructures of suspended particles are important, but also the morphology of the matrix (figure 13). The fracture behaviour of the frozen aqueous phase is very different for samples with different types of PCE (23-6 and 102-2). After 2 hours, depending on the parameter settings (solvent to solid ratio, PCE architecture, PCE concentration, etc.) of the cement suspensions, the formation of C-S-H gel-like structures can be observed. This C-S-H gel-like structure is inhomogeneously distributed over the interstitial pore space. As shown in the BSE cryo-SEM image (a), small particles (lighter grey) can be embedded in the C-S-H gel-like structure which exhibits low specific density (darker grey). In cement suspensions containing PCE, network structures of the polymer pervade the interstitial pore space. Prior to the formation of C-S-H gel-like structures, the pure PCE network can be observed (b). During the experiments, under the electron-beam such PCE network structures thin out (loss of water bound by PCE molecules) whereas C-S-H gel network maintains its morphology. After the start of C-S-H gel formation in cement suspensions containing PCE, a combined structure can be observed where the PCE network (medium grey) is embedded into the C-S-H gel-like structure (darker grey). Particles can be embedded in this mixture of C-S-H gel and PCE (light grey). Furthermore, the C-S-H gel-like structure and PCE mixture in the interstitial pore space seem to act as seeds for nucleation of hydrate phases (d).

6.4.3 Particle size distributions obtained by cryo-FIB nanotomography

The modelling of rheological properties is generally based on various assumptions such as e.g. volume fractions of the particles, number of particles and particle shapes which can be determined from the unhydrated cement powder e.g. by means of laser granulometry. However, the rheological properties of cement suspensions are strongly related to the real particle structures which are affected by dissolution, precipitation and agglomeration. These effects cannot be characterized with conventional methods such as laser granulometry.

Cryo-FIB nanotomography is a powerful tool which enables to extract more realistic particle shapes, particle size distribution of particle number, volume fractions and specific surface areas directly from the hydrating suspensions. However, the process of data acquisition including cryo sample preparation, cryo microscopy and image analysis is very time consuming and lasts for one sample more than two weeks.

In the following sections quantitative results from cryo-FIB-nt are presented from different samples with a finely ground portland cement. Thereby the results from unhydrated cement (fc0, dispersed in glycol) are compared with hydrated suspensions without polymer (fc0.1, fc2.5) and with 0.65% PCE 23-6 (fc2p, fc24p) at different hydration times. Because of the retardation effect, which is documented by calorimetry (fig. 6), the samples fc0.1 (5min, no Polymer) and fc2p (2hours, with PCE) both have similar degrees of hydration despite the different hydration times, i.e. they represent the early dormant period. For similar reasons the samples fc2.5 (2.5h, no Polymer) and fc24p (24h, with PCE) represent similar degrees of hydration at the beginning of the acceleration period and close to setting.
Fig. 14. In this figure triplet, graphs of the number of particles as function of particle diameter are shown for the submicron range. In (a) is shown that the percentile fraction of particles < 400 nm are decreased for samples with hydration times close to setting compared to cement suspensions in the dormant period. After initial hydration the percentile fraction of those fine particles increases. In all samples the number of particle density is increased compared to the unhydrated sample (b). With evolving hydration time the presence of PCE seem to decrease the number of particle density. The forced particle size distribution (volume fraction of 0.5 for samples in dormant period, volume fraction of 0.6 for samples close to setting time) shown in (c) has no influence on the qualitative evidence of the curves.
The size distributions of these samples are presented as density functions (particle numbers, solid volume and surface area normalized per total volume) and also in terms of the corresponding %-functions. As will be discussed later, considerable uncertainties exist with respect to the measured total volume fractions. Therefore the density functions are also presented after normalization to forced volume fractions which were set to 0.4 for the unhydrated mix at, to 0.5 during the dormant period and to 0.6 during the setting).

In figure 14a the size distributions of particle numbers are presented as % of the total particle numbers. The particle numbers in all samples are dominated by objects in the sub-µm range. Compared to the unhydrated cement (cf0), the fresh pastes in the dormant period (cf0.1 and cf2p) have higher %-fractions of very small particles in the range of 100-400 nm. In contrast, the small particles (< 400 nm) in the older suspension close to the setting time (cf2.5 and cf24p) exhibit similar %-fractions as the unhydrated cement. These findings are the same for systems with and without polymer.

The differences between the samples are more pronounced when looking at the particle number densities, as shown in figure 14b and 14c. The particle number densities (i.e. particles per volume) are drastically increasing due to the hydration process. The particle numbers of all 4 hydrated suspensions are increasing relative to the unhydrated cement (fc0) by a factor of 4 to 8. Nevertheless, the relative changes between younger and older, and between dispersed and non-dispersed systems give a contradicting picture. Apparently processes of precipitation and agglomeration may lead to an increase (for the non-dispersed system) and to a decrease (for the dispersed system) with time. Nevertheless the particle numbers are very sensitive to the particle recognition process by means of image analysis. The numerous small precipitates that are attached to the surfaces of larger clinker particles (as shown in fig. 10 and 11) are very difficult to identify as individual particles by means of automated image analysis which may lead to large uncertainties with respect to the measured particle numbers in the range below 500 nm.

The size distributions related to the volume fractions are shown in figure 15. In general the hydration process leads to a shift towards smaller particles. This shift can either be attributed to the fact that the larger particles are not captured in a representative way within the small FIB volume. Alternatively the initial hydration process may lead to a splitting of a portion of the larger particles because the interstitial alkali-sulphates and other reactive phases are dissolved immediately after mixing. When comparing the differences due to hydration time or due to the addition of PCE again no systematic changes can be determined.

The differences of the size distributions related to the surfaces are shown in figure 16. Again there is a general shift towards smaller sizes in the hydrated samples compared to the unhydrated. However the differences among the hydrated samples are surprisingly small when plotted as %-fractions (fig. 16a). With respect to the density functions again the differences are small. Only the non-dispersed sample at longer hydration time (fc2.5) shows significantly higher surface area fractions compared to the other hydrated systems.
Fig. 15. In this figure triplet, graphs of the volume fractions as function of particle diameter are shown. In (a) is shown that the percentile volume fractions contain higher submicron particles with evolving hydration. In contrast, the presence of PCE leads to an increase of the > 3 µm fraction close to setting compared to samples in the dormant state. The increase of the solid volume fraction (b) with evolving time is consistent for all samples. At similar degrees of hydration, the volume fractions of cement suspensions containing PCE are lower. (c) shows the forced volume fractions if the volume fractions are set for a certain degree of hydration (0.5 after initial hydration, 0.6 close to setting times).
Fig. 16. In this figure triplet, graphs of the triangulated surface areas as function of particle diameter are shown. In (a) is shown that the percentile surface areas are increased for all hydrated samples. The differences between various degrees of hydration and presence of PCE are only minor. The specific surface area (b) increases with evolving time. This effect is higher for samples without PCE. If the volume fractions are forced (c), the qualitative evidences remain the same. There is only a small shift for sample fc0.1 to smaller a specific surface area.
Overall, there is a general increase of particle numbers due to the initial hydration reaction in all systems. However the differences among the systems are small and they show no correlation with hydration time or addition of polymer. Nevertheless, the data indicates that the system is dominated by particles in the submicron range. Furthermore, the volume fraction of the sample fc0.1 is very high compared to fc2p. At this early hydration times, both volume fractions are assumed to be only slightly above 0.4. Possible reasons for the overestimation will be discussed in the next subchapter.

6.5 Discussion

In terms of workability, the amount of PCE adsorbed is of major importance. The side chain density and thus, the charge density, is the key parameter which determines the adsorption behaviour of the PCE molecules as shown by the adsorption isotherms. Higher charged PCE molecules (PCE 23-6 and PCE 102-6) adsorb strongly on the particles in the cement suspension in contrast to PCE 102-2. The side chains of adsorbed PCE molecules evoke steric repulsion and prevent the formation of agglomeration of the cement and hydrate particles. As a consequence, the ettringite floats individually in the suspension as shown in [16]. Zeta potential measurements support the assumption, that the early cement-water system is dominated by the formation and the spatial distribution of ettringite. However, the impact of PCE 102-2 on the zeta potential might have a different origin. PCE 102-2 does hardly adsorb which means that almost the total amount of PCE added remains in the pore solution. It should be noted, that the viscosity and/or the dielectric properties of the pore solution are important parameters when calculating the zeta potentials. Therefore, the presence of PCE 102-2 in the pore solution and the influence on the zeta potential might be assigned more to the influence of the PCE on the properties of the pore solution than to adsorption and steric hindrance.

Based on the opposite zeta potentials of ettringite (negative) and tricalciumsilicate (positive), agglomeration can be expected. However, the size of an average clinker particle is at least one magnitude larger than the size of the ettringite crystals. Therefore, after precipitation of ettringite, one can expect that the crystals are deposited on clinker surfaces and start to form an ettringite-hydration layer [20]. This macroscopic conclusion, drawn from the zeta potential measurements, is supported by high resolution cryo-SEM analysis where it could be demonstrated, that the ettringite preferably attaches to clinker surfaces, forming a dense or porous hydration layer. The dense layer structure might originate from fast and heterogeneous nucleation on tricalciumaluminate rich surface domains of clinker particles. In contrast, the porous morphology might be the result of ettringite crystal deposition on clinker surfaces of ettringite formerly nucleated in the pore solution.

In presence of PCE does not show a significant influence on the amounts of ettringite production as revealed by thermogravimetric data. The results indicate, that in presence of PCE the state of dispersion is less due to change of chemical parameters (such as dissolution and precipitation behaviour) than to the influence of PCE on physical parameters (such as e.g.
interparticle forces, microstructures). The quantified microstructures support the assumption of low PCE influence on the amount of ettringite formed. In the unhydrated cements, the number of particle density of submicron particles is much lower compared to samples after initial hydration where the aluminate-rich clinker particles quickly dissolve, the precipitation of hydrates leads to a significant increase of the submicron particle fraction. However, the difference of number of particle density between the sample without to the sample with PCE is small and might be not even significant. But it underlines, that the presence of PCE has no major influence on the amount of ettringite formed.

With evolving hydration the particle density, the volume fraction and the specific surface area is controlled by the submicron particles. After initial hydration up to setting, low but continuous production of hydrate phases lead to a further increase of small particles. However, the high resolution cryo-SEM on high-pressure frozen cement suspensions after 6 minutes indicates that the early hydrate phases are dominated not only by the ettringite but also by the C-S-H. The latter are very fine fibrous crystals below the resolution of cryo-FIB. The C-S-H fraction (either weight or volume) is very small and thus, probably below the detection limit of the TGA instrument used or is overlapped by the strong ettringite and/or gypsum peaks.

As already mentioned, the presence of PCE primarily influences the state of agglomeration between ettringite on one side, C-S-H and triclaciumsilicate on the other side. However, the data processing is still not sufficiently developed to recognise whether an object is an agglomerate or a loose assemblage of particles. Therefore, the segmentation causes some semantic problems. Does an agglomerate should be considered as one object or should it be separated in its individual constituents? What is the definition of a particle?

A significant problem with high resolution microscopy of heterogeneous microstructures is the representativity. It could be observed that the volume fraction tends to be overestimated by cryo-FIB. A first explanation for this overestimation could be the obvious inhomogeneities of the particle distribution which can be observed even within the scale of single FIB images. However, the large clinker particles are homogeneously distributed in the investigated sample volumes. The inhomogeneities are observed mainly for the smaller hydrate particles (< 1 µm) in the interstitial pore space. A second explanation is, that the segmentation procedure probably captures dense colloidal domains as solid materials whereas in reality these domains contain significant amounts of water but with very fine suspended or dissolved components that are beyond microscopic resolution. These dense colloidal domains exhibit grey levels similar to those of hydrate phases. Such diffuse colloidal phases can be build of i) segregation patterns which contain significantly increased ionic concentrations, ii) diffuse C-S-H gel-like structures (> 2 hours of hydration) and iii) networked PCE structures in the interstitial pore space. The three types pervade the interstitial pore space and show very fine, network-like structures far below 100 nm. The third explanation is that the FIB BSE images of frozen suspensions are characterized by very low contrast. Additionally, artificial roughness of the sectioned surfaces may produce noisy images and thus, segmentation result in an overestimation of the solid phase.
As observed with high resolution cryo-SEM there are indeed colloidal domains in the cement suspension and thus, the second reason for overestimating the volume fractions with FIB is probably the most important. Furthermore, it is important to note, that C-S-H crystals are in the similar size range as the fine C-S-H gel-like structures, segregation patterns or networked PCE. Thus, for the quantitative analysis in this study a particle is defined as an object larger than 100 nm and thus, the C-S-H crystals and other fine structures are beyond the threshold level. Nevertheless, the fine particles in dense colloidal domains may be locally attributed to the solid phase as well.

6.6 Conclusion

The cryo-microscopic methods combined with specific image analysis techniques are powerful tools for the quantification of the particulate structure of cement suspensions. The cryo-FIB method enables to obtain highly reproducible and accurate particle size distributions of clinker and hydrate phases concerning particle densities, volume fractions and specific surface areas. The data sets from cryo-FIB nanotomography are considered as the basis for further characterization such as e.g. number of contacts and contact area. However, the results are sensitive to the quality of BSE cryo-FIB imaging, object recognition and definition of particles and agglomerates.

All size distributions are very similar for the different systems irrespective of their hydration age and PCE content. The influence of PCE on the particle size distributions are apparently very subtle and can not be resolved with cryo-FIB. In addition, the data processing is not yet sufficiently developed to recognise whether the object is an agglomerate or a loose assemblage of particles.

Nevertheless, it could be demonstrated, that the presence of PCE modifies the long range particle arrangement in cement suspensions. 97% of all particles are smaller than 1 micron and represent approximately 50% of the surface area. Thus, the submicron particles, mainly ettringite, are the dominating phase up to setting time for all investigated cement suspension independent of the presence of PCE. The ettringite crystals tend to be attached to clinker surfaces (C\textsubscript{3}S) whereas in presence of PCE, the ettringite crystals are floating in the pore solution.

The microstructural phenomena (agglomerates and surface morphologies) in the cement suspension are often independent of the presence of PCE as demonstrated by the high resolution cryo-SEM analysis. Furthermore, microstructural observations indicate that the non-adsorbed PCE molecules in the pore solution also influence nucleation, growth and immobilization of small precipitates and thereby also contribute to the stabilization of the cement suspension. PCE molecules remaining in the pore solution, form network-like structures and at later hydration times (> 2 hours) intergrow with the C-S-H gels. The carboxylate-groups possibly act as seeds for hydrate phases. However, the total amount of hydrate phases seems not to be influenced by the presence of PCE during the early cement hydration.
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References


Chapter 7

General Conclusions and Outlook
7 General conclusions and Outlook

7.1 General conclusion

In the following, the conclusions of the individual chapters of this thesis are put into a more general context.

The polycarboxylate-ether (PCE) adsorption and rheology measurements combined with heat evolution analysis of cement suspensions demonstrates 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 is needed. Low side chain density is correlated with high anionic charges which leads 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 was 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 was modified for cryo experiments on high-pressure frozen cement suspensions. Combined with extensive image analysis, cryo-technique was proven to be a powerful tool for 2D and 3D investigations of complex particulate structures.

Cryo-FIB investigations could 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. The quantification of number of particles densities, volume fractions and specific surface area demonstrates the importance of submicron particles for both, non-dispersed and dispersed systems. In unhydrated cements, the volume fraction of submicron particles is below 5% whereas shortly after initial hydration, the newly formed particles (mainly ettringite) dominate the number of particles and surface area.

It could be demonstrated that cryo-FIB is not sensitive enough to resolve very fine structures below 100 nm which is the range of C-S-H needles and network-like PCE structures. Therefore, high resolution cryo-SEM was applied. It enables to investigate these individual crystals, particle surfaces, morphologies of hydration layers and small
agglomerates on a qualitative level. It could be demonstrated that the small agglomerates mainly consist of ettringite with intergrown C-S-H needles. Furthermore it was shown, that 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. Therefore, investigations on pure clinker and hydrate phases were carried out. It could be revealed that the zeta potentials of the silicate phases (tricalciumsilicate, calcium silicate hydrate) are slightly positive, whereas the zeta potential of the aluminate phase (ettringite) was negative. These opposite potentials lead to attraction between C$_3$S and ettringite, C-S-H and ettringite particles which could be confirmed by cryo-microscopic analysis. Thereby it could be 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 C$_3$S 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 adsorbs at the positive charged shear plane and/or Stern layer of C$_3$S 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 (fig. 1). 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, dispersed ettringite is floating as individual crystals in the interstitial pore solution as demonstrated by cryo-FIB experiments.

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 represents to control a large part of the surface area which again dominates the zeta potential of the cement suspension.

As a closing remark it can be stated that throughout my studies, the importance of simplified systems got more accentuated. However, the boundary conditions of simplified system has to be chosen very carefully if the results shall be related to realistic bulk cement-water (-superplasticizer) systems. Some of the experiments described in the literature are of highly scientific interest, but should be treated with caution concerning their relevance for industrial applications.
7.2 Outlook

The modification of cryo-techniques, the application of cryo-FIB and the development of special algorithms for data processing is now on a methodical level, which enables its use for extended quantification of particulate structures. For future investigations the focus should be on further improvement of object recognition, reconstruction and calculation of higher order topologies such as e.g. number of particle contacts, contact surfaces, particle coordination and quantification of network structures.

PCE-particle interface and the associated surface properties remains a very interesting field for research. Zeta potential measurements provide important information about the colloidal behaviour of the different mineral phases and may indicate the constitution of the particle-solution interface. However, new methodological approaches have to be found in order to characterize the chemical nature and type of PCE bonding at this interface and the corresponding conformation of PCE molecules.

Throughout the work on the modification of the cryo-technique and the cryo-microscopic experiments, the importance of PCE on chemical and physical properties of the aqueous pore solution arose and got accentuated. PCEs are likely to exhibit some pore water retention abilities which may lead to changes of the ionic concentration of the free pore water and thus, changes of dissolution and precipitation rates accompanied by rheological changes of the cement suspension. Furthermore, the presence of PCE probably changes the surface tension and the fluidity of the pore solution. Therefore, the PCE-pore solution interaction and the resulting consequences should be more intensively investigated in the future.
Appendix

Cryo-microscopy for fresh cement pastes:
First results

By A. Zingg, P. Gasser, F. Winnefeld, A. Kaech,
J. Pakusch, S. Becker, L. Holzer

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Cryo-microscopy for fresh cement pastes: First results

By A. Zingg, P. Gasser, F. Winnefeld, A. Kaech, J. Pakusch, S. Becker, L. Holzer

Synopsis: For investigations on the microstructural development of fresh cement pastes, the high pressure freezing technique for aqueous samples has been adapted from life sciences. The vitrification of aqueous solutions and suspensions under high pressures and high cooling rates allows maintaining the particle structure within the sample. In this paper first high-resolution cryo-SEM and cryo-FIB images of fresh cement pastes will be presented. This paper gives qualitative information about microstructural features in fresh cement pastes and discusses shape and distribution of ettringite crystals, development of hydration layers, formation of particle networks and surface morphology of particles.

Keywords: freezing techniques, cryo-microscopy, cryo-SEM, cryo-FIB, fresh cement pastes, microstructures
Anatol Zingg is a PhD-Student at ETH Zurich (Dept. of Material Sciences) and Empa (Swiss Laboratory of Material Testing and Research, Duebendorf, Switzerland) under the guidance of Prof. Dr. L. Gauckler (ETH Zurich, Dept. of Material Sciences), Dr. L. Holzer and Dr. F. Winnefeld. The Project is supported by Dr. J. Pakusch und Dr. S. Becker from the BASF AG (Ludwigshafen, Germany).

Philippe Gasser is a technician at Empa's Concrete/Construction Chemistry Laboratory. He is in charge for the SEM, TEM, FIB and is involved in several project concerning microscopy.

Frank Winnefeld is a senior researcher at Empa's Concrete/Construction Chemistry Laboratory. His research has been focused on the chemistry, hydration, and rheology of cementitious systems.

Andreas Kaech is an Application Manager Life Sciences in Bal-Tec Inc.'s , working at the ETH (Center of Electron Microscopy) Zurich. He focuses on new methods in the field of cryo-SEM and on high-pressure freezing.

Joachim Pakusch is a senior R&D Manager in BASF's Research Technology Platform Polymers.

Stefan Becker is responsible for the global product development of HRWRA within BASF's Business Unit Functional Polymers.

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

**Introduction**

During the first hours of hydration, cement systems are changing from suspensions into rigid materials. While stiffening, macro- and microscopic properties such as viscosity, surface potentials, chemical composition of the pore solution (hereinafter called "continuous phase") and particle morphologies are changing significantly [1].

Cement suspensions are highly dynamic systems which tend to form artefacts during sample preparation. In conventional cement suspensions the solid volume fraction is ranging between 50% and 60%. The continuous phase is supersaturated with Ca(OH)$_2$ and has a
high ionic strength with a pH between 13 and 14. Simultaneous dissolution and precipitation processes during the first hours lead to a continuous change of the electrostatic surface potentials, of the particle size distributions, particle morphology and associated surface area. An important consequence of these processes is the tremendous increase of viscosity with setting time.

For specific applications, workability and setting behaviour can be influenced by addition of organic admixtures [2-5]. Organic admixtures influence the setting time (retarders) and the workability (superplasticizers, used in this study) of cements. The standard theory of the mechanisms behind the enhanced workability can be derived from colloid sciences.

A thorough understanding of the interaction between admixtures and hydrated/ unhydrated minerals and of the impact of admixtures on agglomeration and associated long range particle structures are considered as the basis for a controlled design of new admixtures and improvement of the corresponding formulations of cement pastes and concretes. Thus, the linkage between the development of microstructures, properties of workability and setting behaviour is of major importance.

In this study we are applying cryo-microscopy techniques (2D and 3D) for the investigation of particle microstructures in the liquid cement pastes. In life sciences, high-pressure freezing as an artefact free technique to solidify the aqueous phase of fragile biological systems has been well established. This sample preparation technique has been applied in only a few studies for the investigations of cementitious materials [6, 7]. Thus, especially for the investigation long range particle structures (3D) in cement pastes (suspensions) before setting, specific modifications of the cryo-techniques are required.

After a short introduction to the cryo freezing techniques used in this study and to Focused Ion Beam-nanotomography (hereinafter called FIB-nt), first high resolution cryo-SEM and cryo-FIB-nt results will be presented. On the basis of qualitative observations from the microstructure in cement suspensions, the potential of cryo-microscopy and cryo-sample preparation techniques for the study of superplasticizer-cement interactions will be discussed.
Principles of the cryo-technique

The principles of the cryo-technique are intimately related to the properties of H$_2$O. Due to the high mobility and large heat capacity of water molecules, freezing frontiers can induce strong displacements of suspended particles in the order of one micron. High cooling rates (above $10^4$ K/s) and high pressures (above 2 kbar) are required in order to avoid the growth of isolated large ice crystals [8]. The application of high pressures supercools the aqueous phase, and thus the mobility of the water molecules is dramatically reduced. It has been proofed that the original 3D structures can be maintained to a satisfactory degree due to the vitrification of water by high pressure freezing [9, 10].

The frozen aqueous phase is highly non-conductive which causes charging-effects under the electron beam. High-resolution microscopy requires a high vacuum mode and needs a sufficient thickness of coating material on top of the samples [11].

Based on Riehle’s dissertation “About vitrification of diluted aqueous solutions” in 1968 [12] various freezing techniques have been developed. In the field of cement research only a few studies have been performed by shock-freezing [10, 11]. Up to now high-pressure freezing has not been applied for the study of cement pastes. In the following sections the cryo-preparation steps for cement suspensions are described in chronological order.

Sample preparation of cement suspension

Freezing requires specimen carriers consisting of a material which is inert and has a high thermal conductivity capacity. The specimen carriers commonly have an outer diameter of 3 mm with a cylinder-shaped indentation with a diameter between 1 to 2 mm. Brass specimen carriers from TedPella Inc. have been used in this study.

A small droplet of a suspension is mounted between two specimen carriers. The sample “sandwich” is then ready for the freezing process.

Shockfreezing

A filled specimen carrier “sandwich” is dropped into liquid nitrogen at -196°C.

Only sample layers up to 10 µm thickness can be vitrified by shockfreezing [13]. By shockfreezing of water-rich samples, the formation of ice crystals can not be avoided and as the consequence, the original 3D structure can not be maintained. A broad distribution
and many variations (shape) of ice crystals and freeze frontiers can be observed.

High-pressure freezing

The sandwiched brass specimen carriers are mounted on a holder for the high-pressure freezing apparatus (HPM 010 BalTec, ETH Zürich). A pressure of 2100 bar is then applied within 50 to 100 msec and with nearly contemporaneous cooling with liquid nitrogen.

If the high-pressure technique is applied properly, the aqueous phase of a suspension is vitrified. The ice nuclei are far below the SEM resolution and form a homogeneous, isotropic phase.

Sublimation (=Freeze-Etching)

On the fractured surface, the object of interest (e.g. partially hydrated clinker particle, covered with ettringite) is embedded in the vitrified aqueous phase. The particles and precipitates within the pore solution can be brought to the surface by freeze etching, which is done by carefully sublimating the top layer of the vitrified aqueous phase before deposition of a metal layer in the coating apparatus (see below).

Common sublimation time and temperatures are ranging from 1 to 5 minutes and from -90°C to -110°C [14]. These sublimation conditions are strongly dependent on the state of vitrification.

Coating

Solidified aqueous phase and cement particles are both non-conductive materials. Coating of the sample surface is thus a prerequisite for imaging at reasonable resolutions (i.e. >10kx). For the MED 020 (Bal-Tec), a tungsten target turned out to coat reasonably well for cement samples. Other sputtering metals used in the literature are Cr [15] and Au/Pd [18].

FIB-nanotomography

Focused Ion Beam-nanotomography (hereinafter called FIB-nt) has been developed at Empa by the 3D-mat group [15]. This novel 3D microscopy method closes the gap between TEM tomography (nm) and X-ray tomography (μm) allowing microstructural analysis in the submicron range with a possible voxel resolution down to 12 nm.

The FIB-nt technique requires a dual-beam FIB and is based on slicing a well defined cube with the ion beam (fig. 1). From each slice a backscattered electron (BSE) image is taken. The stacked images
are then processed with special algorithms, developed by the 3D-mat group at Empa.

FIB-nt is a powerful technique for investigations on 3D microstructures. In combination with special data processing tools pore structures [16], particles size distributions and granular textures [17, 18] can be reconstructed and quantified.

Materials

For this study, a low aluminate content cement and a fine fraction of a CEM-I have been chosen. Differently architectured polycarboxylates (comb-shaped polymers, hereinafter called PCE) have been used as fluidizing agents, so-called superplasticizers. Two different cement suspensions have been prepared.

Sample 1

A water-PCE mixture was poured in a vessel with a low aluminate content cement (HS) at a w/c ratio of 0.25. Amount of PCE added was 0.2 percentages (solid matter) of the cement weight. The cement suspension was hydrating for 4 hours. The sample then was high-pressure frozen (HPM 010 apparatus, Bal-Tec Inc.), fractured and coated with platinum (BAF 060 apparatus, Bal-Tec Inc.) and transferred (VAC 100, Bal-Tec Inc.) into the chamber of a cryo-SEM (Gemini).

Sample 2

A water-PCE mixture was poured in a vessel with the finer grain size fraction (50% fractile around 3 microns a CEM I cement at a w/c ratio of 0.5. Amount of PCE added was 0.5 percentages of the cement weight. The cement suspension was hydrating for 6 minutes. The sample then was high-pressure frozen (HPM 010 apparatus, Bal-Tec Inc.), fractured and coated with platinum (MED 020 apparatus, Bal-Tec Inc.) and transferred into the chamber of a cryo-FIB (Quanta, Fei Company).
Results

In the following sections, first cryo-SEM and cryo-FIB-nt results from high pressure frozen cement pastes are presented in order to document the potential of the cryo-microscopy method and to discuss the limiting factors.

Cryo-SEM

For microstructural characterizations of early cement suspensions, where nuclei of hydration products such as ettringite are formed, high resolution imaging is essential. Therefore, the presented images start at high magnification, where single crystals are resolved (fig. 2). Subsequently images of lower magnification are presented in order to gain an impression of larger scaled two dimensional structures, Figure 2 displays hexagonal shaped ettringite crystals after 4 hours of hydration (sample 1). The length of the ettringite crystal typically is around 200 nm with a ratio length to thickness around 2. The vitrified pore solution forms the fine, smooth matrix. Very thin and light coloured short filaments and filament-clusters are observed most frequently on the surface of cement particles and ettringites.

Contact between precipitated hydrates and particle surface can be studied on fractured particles (fig. 3). Most of the fibres at the particle interface are perpendicular to the surface and form a layer of about 100 nm of thickness. This layer is discontinuous and not homogeneous in thickness. Many of those short filaments are curved.

In figure 4, conjunct filaments (network) and filament clusters (bright) are attached to or growing out of the particle surface (dark). Those clusters and small networks are more or less evenly distributed over the fractured particle surface.

Figure 5 implies that after 4 hours hydration time the ettringites are not evenly distributed in the pore solution and are locally enriched on the particle surfaces. It seems that the ettringites form clusters. But since we are looking at two dimensional image projections care must be taken with interpretations of the 3-D structure. The smooth shaped network like structure in the middle of the image is interpreted as eutectic structures which indicate formation of ice crystals during the cooling process instead of thorough vitrification.

Locally net-like structures as shown in fig. 6 can be observed on the particle surfaces. These structures might be adsorbed polymeric clusters. If those networks are exposed to the electron beam, the inherited water-content is evaporated. Interestingly, the structure of
the networks thins out (refining of the structural features) but does not collapse, and the mesh dimensions remain unchanged.

**Cryo-FIB-nanotomography analysis**

Based on FIB sectioning three dimensional aspects of the microstructure can be investigated, which is briefly shown in the following sections which starts with BSE-images of FIB-cross-sections at moderate magnifications (Fig. 7 and 8: 15kx). These images display the spatial distribution of clinker particles and hydrates in the continuous phase. When zooming to higher magnifications as shown in fig. 9, details of the hydration layer can be studied from cross-sections through the interface between particles and continuous phase.

The contrast of the FIB-images is similar to BSE-images of a conventional SEM. Three phases can be distinguished by their grey-level: i) continuous phase (dark) ii) hydrates (intermediate) and iii) unhydrated particles (bright).

In conjunction with the question how the PCE is distributed in the cement suspension, the question about the distribution of the smallest particles (hydrate phases) and thus the highest surface area fraction is of great interest. Fig. 7 shows the result of cryo-FIB-nt analysis from sample 2. The larger particles are clinker grains. After 6 minutes only very locally a discontinuous hydration layer has formed on the surface of the clinker grains (fig. 7 and 8). Many edges show concave-shaped features that are typical for dissolution phenomena (fig. 7 and 8).

Locally idiomorphous grains can be observed which are interpreted as monocrystalline C₃S. In dry cement such grains are typically embedded within an interstitial phase of C₃A. Since the C₃A is dissolving faster, the isolated C₃S grains (now embedded in pore solution) can be interpreted as remnants from previous polycrystalline clinker. Numerous very small crystals are well dispersed in the continuous phase (pore solution). These small particles of a few hundred nm in length are supposed to be ettringite. This result is consistent with the observation from cryo-SEM at much higher resolution (fig. 5) where small ettringites are “floating” in the continuous phase.

Figure 7 is a 3D-reconstruction of a FIB-nt cube. The analysis has been done on sample type 2 after 24 minutes of hydration. The very fine and coarse particle fractions have been removed by air calcification.

The particles do hardly have any precipitated hydration products on their surfaces. The two particles in the centre of fig. 8 start forming a bridge by a small particle, which is supposed to be a newly formed
hydration product (as indicated by a white circle). The smaller particles (<2 µm) tend to have more hydration products on their surface. This is shown in fig. 9 at higher magnifications for a particle with a discontinuous hydration layer which varies in its thickness. The hydration layer varies between a few tens to several hundreds of nanometers.

**Discussion and Conclusions**

The above presented first high-resolution cryo-SEM and cryo-FIB-nt images on cement suspensions give insight into the microstructural development of fresh cement pastes which is a prerequisite for the understanding of the corresponding rheological behaviour.

For the qualitative discussion, three scale frames are distinguished: a submicron frame (single crystals/ hydration products), a meso scale frame (single hydrated/ unhydrated clinker grains) and a micron frame for description of long range particle structures.

*Submicron scale frame – crystallization of hydrates (ettringite) and influence of organic admixtures*

The hexagonal short-prismatic ettringites (fig. 2, 5 and 7) with an average length of 200 nm show an aspect ratio of 2 (length/width). The crystals are very numerous (fig. 5) and well dispersed (fig. 7). However, both samples (cryo-SEM; cryo-FIB-nt) contain high concentrations of PCE. It is known that surfactants and polymers influence the geometry of the crystal shape either by adsorption on the surface and subsequent intercalation or by pure presence in the solution (without being intercalated). It is assumed that ionic polymers (such as the PCEs used in this study) adsorb onto crystal faces and thereby hinder crystal growth in that specific direction. The short prismatic shape and the consistently small size of the ettringite can be explained by the specific adsorption of PCE on the (001) crystal face which leads to a decrease of growth rates in general but specifically also along the crystallographic c-axis [6]. Hence, the system preferentially starts to form new nuclei whereas growth and formation of large ettringite crystals is hindered by the incorporation of the adsorbed PCE [19]. The nucleation process leads to a significant increase of the surface area fraction in the system. In dispersed systems it is important that there is enough dispersant in order to avoid agglomeration of the numerous small ettringite crystals. Thus, the combination of repulsive forces of the adsorbed PCE between the crystals (dispersibility) and the reduced growth rates in the presence of the polymer are considered as the primary factors which control the rheological properties of dispersed cement systems during the first
hours of hydration. Once the PCE is consumed, ettringite-growth may dominate over nucleation and consequently long-prismatic crystal shape with higher aspect ratios are expected. These needles are expected to form agglomerates which can be associated with the observed increase of viscosity in the paste. This hypothesis is supported by empirical data gained from experiments of superplasticizers-cement mixtures where delayed addition of superplasticizers shows larger effects at lower concentrations than for simultaneous addition [20].

Meso scale frame - Hydration layer on the surface of the clinker grains

This frame includes the consideration of the clinker grains and their surfaces. The hydration layer covering the individual grain is neither continuous nor homogeneous in its thickness (fig. 9). The inhomogeneous growth of hydrates on the clinker surface is attributed to the chemical and mineralogical inhomogeneity of the surface. It can be assumed that C3A domains on the surface will rapidly be covered by a thin (200 nm) hydrate layer. The layer thickness rarely exceeds 200 nm. Adsorbed PCE prevent precipitation and growth of hydrates on clinker surfaces, the repulsive forces prevent hydrates from the solution (ettringite) to attach on partially hydrated clinker grains. It is well known that C3S hydration during the first hours is very slow [21]. At this stage the C-S-H hydration layer on C3S is below the resolution of our cryo-SEM.

Micron scale frame – Long range particle structures in cement suspensions

On larger scales, particles may be either homogeneously distributed (well dispersed) or they start flocculating and forming particle networks. Once the reservoir of free PCE in the continuous phase is exhausted, newly crystallized hydrates will not be inhibited to grow by adsorbed PCE and the hydrate particles will tend to agglomerate. Agglomeration, either due to excess of attractive forces or through coalescence of growing hydration layer of two adjacent cement grains (fig. 8), leads to the formation of long range microstructures in the cement suspension. Networked clusters (fig. 6) are interpreted as polymer enrichment domains. Such polymeric networks may prevent particles from agglomerate.

At longer hydration times (close to the setting time) the agglomeration process becomes important. As stated by the SIG hypothesis (SIG=small interstitial grains [22]) small but reactive particles with high specific surface area tend to dominate the agglomeration process and therefore also the process of interconnecting between the larger particles. Thus, the SIG’s may contribute significantly to the stiffening
phenomena. It is supposed that the SIG’s represent clusters of early hydration products with various amounts of the smallest clinker particles. These hypotheses will be tested with further cryo-microscopy investigations.

*Potential of cryo-microscopy for the study of fresh cement pastes*

At the current stage it can be stated that the cryo-techniques allow the vitrification of the continuous phase in fresh cement pastes, thereby maintaining the original particle structure of the suspension.

Unlike in-situ measurements by an environmental-SEM which allows continuous screening, cryo-microscopy allows only static investigations. Therefore, investigations on different hydration stages require a separate sample for each time step and thus, make this method very time consuming.

The presented qualitative results document the power of cryo-microscopy techniques regarding microstructural investigations in the micron and submicron range. It could be insinuated that cryo-SEM (2D) and cryo-FIB-nt (3D) in combination with sophisticated image analysis is a powerful tool to link microstructural developments with rheological phenomena.

**References**


Fig. 1 — Schematic drawing of the FIB-Nanotomography method [19]

Fig. 2 — Hexagonal elongated (~200 nm) ettringites, aspect ratio ~ 2 (sample 1)
Fig. 3 — Fractured clinker particle in sample 1. Most fibres around the large grain are slightly bent, possibly consisting of “pure” adsorbed PCE or of an organo-mineral phase.

Fig. 4 — (Sample 1) Clusters of filaments attached onto the particle surface.
Fig. 5 — (Sample 1) Hexagonal, approx. 200 nm elongated ettringites are evenly distributed in the continuous phase.

Fig. 6 — (Sample 1) Polymeric networked clusters that are adsorbed onto particle surfaces and link different particles together.
Fig. 7 — FIB-Nanotomography slice sample 2 after 6 minutes of hydration. The very fine particles that are floating in the continuous phase are ettringites. The larger particles show partially hydrated surfaces.

Fig. 8 — FIB-Nanotomography 3D insight to sample 2 after 6 minutes of hydration. Smaller particle (hydrated or unhydrated) bridge larger particle together. Hydration layer can overlap (white circle in the figure) and thus lead to agglomeration.
Fig. 9 — FIB-Nanotomography slice of a sample-type 2 after 6 minutes of hydration. The large particle in the middle shows a hydration layer that is discontinuous and inhomogeneous in its thickness.
Curriculum Vitae

Anatol Zingg

Nationality: Swiss

Date of Birth:
1st of July 1976

EDUCATIONAL BACKGROUND
2004 Master of Science, ETH Zurich (Dipl. Natw. ETH)
2002 – 2004 Graduate student at the department of earth sciences at ETH Zurich
2001 – 2002 Graduate student at the geology department at Purdue University, IN, USA
(Student Exchange Program ETH-Purdue)
1998 – 2000 Undergraduate student at the department of earth sciences at ETH Zurich
1992 – 1998 High school student for law and economy at High School Bern-Kirchenfeld, CH

INTERNSHIP / TRAINEE
July/August 2002 Collaborator at the Geological Survey of Switzerland
Fall semester. 2001 Teaching assistant at Purdue University
March – July 2001 Trainee at the Geological Survey of Switzerland
April/March 2001 Trainee/scientific staff at Geotechnisches Institut AG

PROFESSIONAL BACKGROUND
2004 – 2008 PhD student at Empa Duebendorf
May-August 2004 eawag Duebendorf: scientific collaborator (arsenic removal project)

LANGUAGES
German – mother tongue
English – good knowledge
French – basic knowledge
ORAL PRESENTATIONS

27./28.09.2007  Bauchemie Tagung GDCh, Siegen, De
29.10. – 01.11.2006  8th Canmet Conference on Superplasticizers, Sorrento, It
05./06.10.2006  Bauchemie Tagung GDCh, Karlsruhe, De
29.09.2006  BASF AG, Abteilungssitzung, Ludwigshafen, De
29./30.09.2005  Bauchemie Tagung GDCh, Berlin, De

PUBLICATIONS (JOURNALS / PROCEEDINGS / TECHNICAL NOTES / THESIS)


